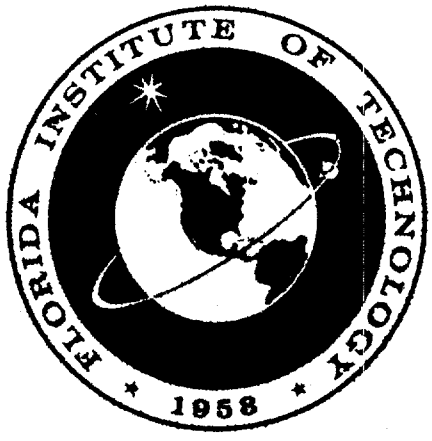
ECOLOGICAL STUDY OF LAGOONS AROUND JOHN F. KENNEDY SPACE CENTER

NGR 10-015-008



VOLUME 2

THESES AND PROJECT REPORTS

FLORIDA INSTITUTE OF TECHNOLOGY
MELBOURNE, FLORIDA

Final Report

to

John F. Kennedy Space Center

National Aeronautics and Space Administration

Kennedy Space Center, Florida

An Ecological Study of the Lagoons Surrounding the John F. Kennedy Space Center Brevard County, Florida

April 1972 to September, 1975

Volume II

Thesis and Project Reports

NGR 10-015-008

Florida Institute of Technology

Melbourne, Florida

INTRODUCTION

Many of the detailed studies done in connection with Ecological Study of the Lagoons surrounding the John F. Kennedy Space Port were performed as Master's Thesis investigations by various graduate students enrolled at F.I.T. during and subsequent to the report. The scope and purpose of what we came to call "the KSC Baseline Study" caught the imagination and interest of our student body. Many who were not financially or otherwise connected with the project found their inspiration in studies that were directly connected with project, and thus added materially to the totality of the knowledge gained. An example of one such study is the first article included in this Volume, A Master's Thesis study performed by Shen Phillip Chen, who chose the site for his investigation so that his results would correlate with and extend the results of others.

In addition to the Master's Theses contained in this Volume, six other graduate studies must be acknowledged here as contributing to this Report, although they have not reached the stage of final publication. Ms. Sandra Fettes has completed a study of the amounts of five trace metals in mangrove leaves from plants at various locations around the Kennedy Space Center. Mr. Bernard Cohenour has isolated and identified a number of oil consuming bacteria endemic in the waters of the Indian Rivers. Mr. Charles Waterhouse has analyzed historic data of tidal gauges in the lagoonal area and correlated it with wind field records. Mr. Renkert Meyer has measured the vertical and horizontal currents of the lagoons and is attempting an interpretation of them in terms of the wind field as a driving force. Mr. Richard Campbell has measured the rate of nitrogen fixation in both the water columns and the sediments under them in the lagoons. Mr. Craig Weiderhold has measured the annual variations in the populations of benthic invertebrates in the lagoons.

An integral part of the F.I.T. curriculum is a requirement that each undergraduate student perform an independent study during his Senior year and submit his results in the form and format of a professional scientific report. While none of these Senior Project Reports have been included in this Volume because of space limitations, many of them aided significantly in the overall study. Typical of these were: light and dark bottle studies of the blue-green algae respiration; writing and executing computer studies comparing the water chemistry data from various sites; detection and identification of nitrogen fixation bacteria in the Indian River; measurement of dissolved oils and greases in the river, photographically recording the benthic life-forms found in the river bottom; measuring the vertical structure of drift and slope currents in the lagoons; and measurement of water level variations along the long axis of a lagoon as a function of wind stress.

These articles are published as a part of this Final Report in an effort to make available for the record as much of the basic data as possible. The few articles published on the Indian River have in general not contained much detailed data, so that comparisons of current status to conditions of the past are difficult or impossible. A major effort of both the Oceanographic and Ecological communities for the past decade has been the retrieval and storage of basic data in order to permit determinations of trends or changes in baseline conditions. It is believed that the information compiled here will be of great value in any future investigations.

Index of Theses and Project Reports by Field of Study

Index of Theses and Project Reports by Author

Section 1, Article 1

A Study of the Decomposition Rate of Manatee Grass *Cymodoceum manatorum*

Shen Philip Chen

1974

A STUDY OF THE DECOMPOSITION RATE OF MANATEE GRASS (Cymodoceum manatorum)

by

Shen Philip Chen

B. S. in Oceanography, College of Chinese Culture, 1969

Submitted to the Graduate Faculty

in partial fulfillment of

the requirements for the degree

of

Master of Science

in

Oceanography

Florida Institute of Technology

1974

ABSTRACT

The rate and mode of decomposition of manatee grass (Cymodoceum manatorum) in the Indian River, Brevard County, Florida was measured in-situ and in the laboratory. Although there were variations in rates between the two methods, statistical analysis shows that they are not signigicant. Rates of change for seven parameters were measured. The rate of change of four parameters (chlorophyll, carbohydrate, caloric content and amino acid) correlated closely with the loss of dry weight through decomposition. The remaining two parameters (protein and total lipids) appear to reflect the growth of large bacterial, fungal and micro-invertebrate populations on the plant detritus.

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FOREWARD

This study was suggested by Dr. K. B. Clark, and had been done under the supervision of Dr. G. N. Wells and Dr. J. A. Lasater. Special acknowledgement is due Mr. Max Raymond Carey for his great help in correcting the writing of this report.

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I. INTRODUCTION

The Florida coastline extends over 3000 miles, and includes warm-temperate, sub-tropical and tropical zones. The Florida peninsula is surrounded by barrier islands, offshore Keys and wide shallow sandy bottoms. The barrier islands separate the moving waters of the Gulf Stream from the off-shore shallows, creating warm quiet saline lagoons, which are favorable habitats for submerged plants and extensive diverse populations of vertebrates and invertebrates. The submerged plants constitute one of the basic links in the food chain. The four most common and important of the Florida sea grasses, as determined by Phillips (1960) are Thalassia testudinum Konig, Syringodium filiforme Kutz, (or Cymodocea manatorum Aschers), Diplanthera wrightii Aschers (or Halodule wrightii Aschers) and Ruppia maritima L. In the north end of the Indian River, Brevard County, Florida, the area selected for this study, Cymodocea manatorum is the dominant species, therefore it was selected as the subject for this study of decomposition rates and products of decomposition.

Decomposition of plant materials by abiotic and biotic processes. The abiotic processes are primarily those of mechanical break-up and dispersal of the dead plant tissues. The biotic processes, accomplished primarily by bacteria and fungi, decompose plant materials into their component nutrients, feeding the bacteria and fungi and releasing other nutrient materials into the surrounding waters where they become the primary food source for other marine animals (Phillips, 1960). Because of the food

supply made available by decomposition, seagrass beds are nurseries and feeding grounds for young fish and shrimp, as well as for countless populations of small marine animals such as the Polychaeta, Holothuria, Amphipoda, and Mollusca which were found living inside the plastic milk-jugs that were used as decomposition chambers for this study. The nutrients released into the water when seagrass leaves decay help to support a large plankton population, which in turn supports an abundance of larger animals, and so on up the food chain (Phillips, 1960).

The principle source of primary production in the Indian River is the benthic seagrass beds. The nutrients locked up in the leaves are not available to other plants nor to most of the animals living in the river, because the animals are not able to digest directly the celluloses and lignins of the leaves. Even for those animals that eat the leaves, the utilization of lignin and cellulose by animals is largely mediated by symbionts, or involves passage through a detritic form (Margalef, 1968). The decaying leaves are broken up into many small pieces, called detritus, which are then further digested by bacteria until ultimately no part of the leaf is left intact. The bacteria and fungi are fed upon by larger zooplankton, or dying, release their nutrients into the water. Some detritus may sink to the bottom and become a part of the sediments, but even here, it is subject to attack and decomposition by both aerobic and anaerobic bacteria. The nutrients are not necessarily lost just because they are contained in the sediments:

"Since detritus refers to all the particulate organic matter involved in the decomposition of dead organisms, the sediments may act

as a nutrient storage bank (Patriquin, 1972)".

"..... rooted aquatic plants often recover nutrients from deep in the anaerobic sediments and thus provide a useful nutrient pump for the ecosystem (Odum, 1971)".

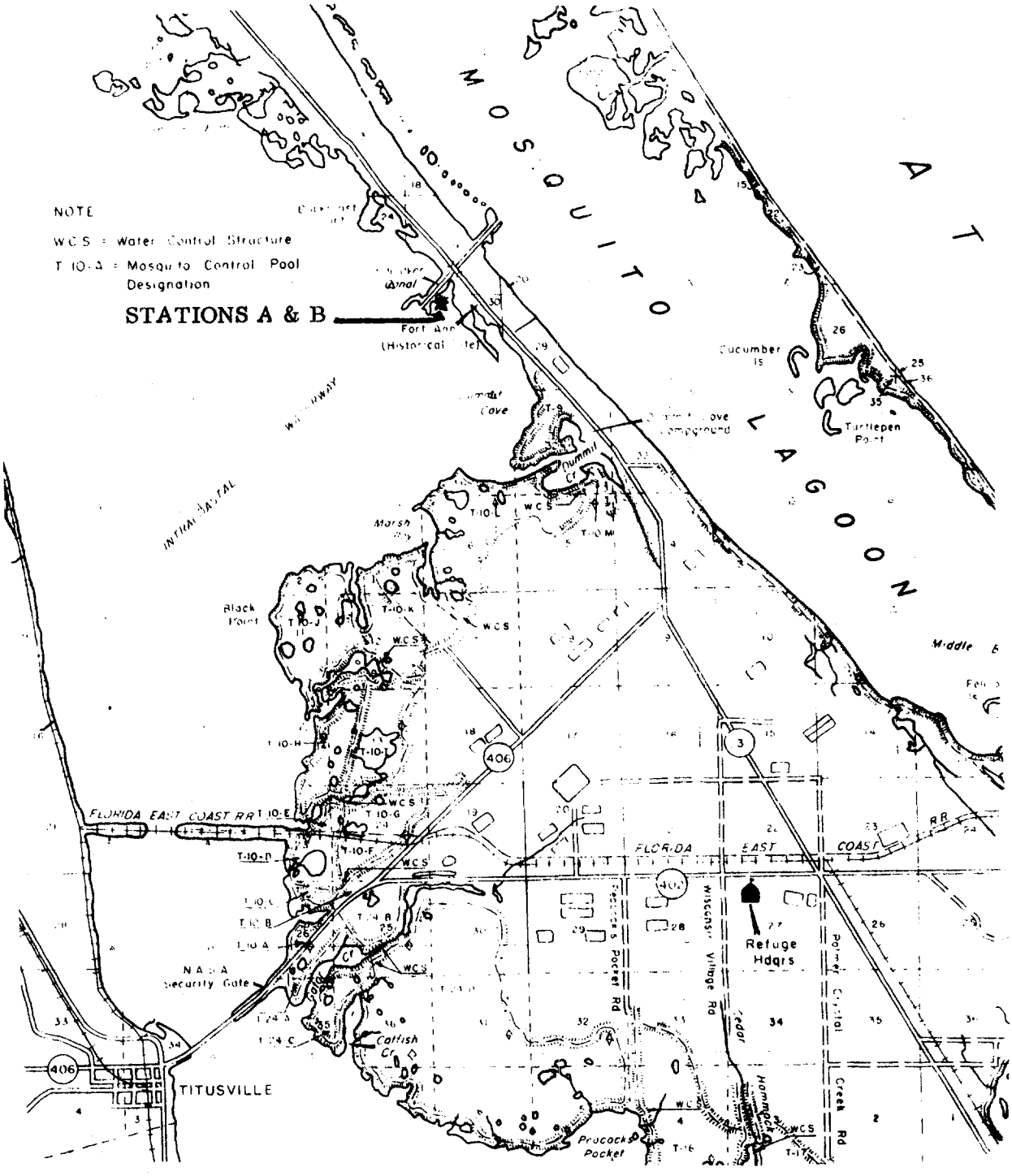

FIGURE 1. Station A and B - near the stations, there is the Haulover Canal connecting the Indian River and Mosquito Lagoon.

II. STATEMENT OF THE INVESTIGATION

This study of the decomposition rate of manatee grass (Cymodocea manatorum) was conducted in two modes, one in the laboratory and the other "in situ" in the Indian River. For each mode, a determination of rate of decomposition was made at two week intervals for a total span of ten weeks. Measurements of (1) total lipids, (2) protein content, (3) carbohydrate content, (4) chlorophyll, (5) amino acid content and (6) caloric content were also made at two week intervals. The data derived is examined statistically for correlation between the two modes as well as for comparability between the two parallel simple groups established for each mode.

III. METHODS AND MATERIALS

A. Indian River Site

1) For the "in-situ" investigation, a sample site near the Haulover Canal, at the north end of the Indian River, in Brevard County, Florida was selected. The geographic coordinates of the site are 28°43' 30" north latitude and 80°45'30" west longitude (Nautical Chart 843-SC, Intracoastal Waterway, U.S. Department of Commerce).

The site is an extensive manatee grass bed in three to four feet of warm, quiet water. The site is protected from violent water movement or disturbance by surrounding small islands and land masses. Existing water movement is wind-driven in character, with no tidal component measurable. The salinity of the water is determined by local rainfall and evaporation, and varies from 27 °/oo to 30 °/oo (see figure 1).

2) Two stations (A & B) were established about six feet apart in the grass bed. For each station, a group of five sample containers was prepared, lashed together, tied to a concrete block and sunk into the grass bed. Sample containers were made from one-gallon plastic milk jugs. Large oval holes were cut into each of the four sides of the jugs to assure adequate water flow around the mass of decomposing grass. After a 50 gram sample of freshly-pulled manatee grass leaves was placed in the jug, each jug was closely wrapped with fibre-glass screen cloth. At two week intervals, the site was revisited and one sample jug from each station was taken back to the laboratory for analysis (see figure 2).

B. Laboratory Investigation

1) Two groups of five each glass culture bottles were set up to parallel the in-situ study. Fresh, live manatee grass was pulled at the in-situ site returned to the laboratory, cut into lengths of approximately one centimeter and weighed into the bottles. Group 1 bottles received 20 grams of chopped grass while group 2 bottles received 50 grams each. Each bottle was then filled with two liters of river water taken in-situ. An aquarium air pump and distribution manifold was used to bubble air through each jar to maintain the dissolved oxygen level at or near saturation throughout the study, so that the decomposition would be under aerobic conditions similar to those in the river. The room temperature around the jars was maintained between 23°C and 25°C during this study. Available light in the laboratory was arranged with fluorescent lamps, which were turned on from 8:00 am to 5:00 pm daily during week days only (Figure 3).

C. Analytical Methods

1) Rate of decomposition

Each sample of live green leaves of manatee grass was weighed and the weight recorded before placing it in its container. Once each two weeks, one container was withdrawn from each sample group. The remaining grassy material was removed and weighed wet. A small portion was removed, weighed and oven dried at 60°C for twenty four hours, then weighed to determine the dry weight of material remaining. This dried sample was then ignited at 600°C for six hours and reweighed to determine the ash weight. The ratios of wet weight to dry weight and of wet weight to ash weight were then compared to similar ratios determined from wet

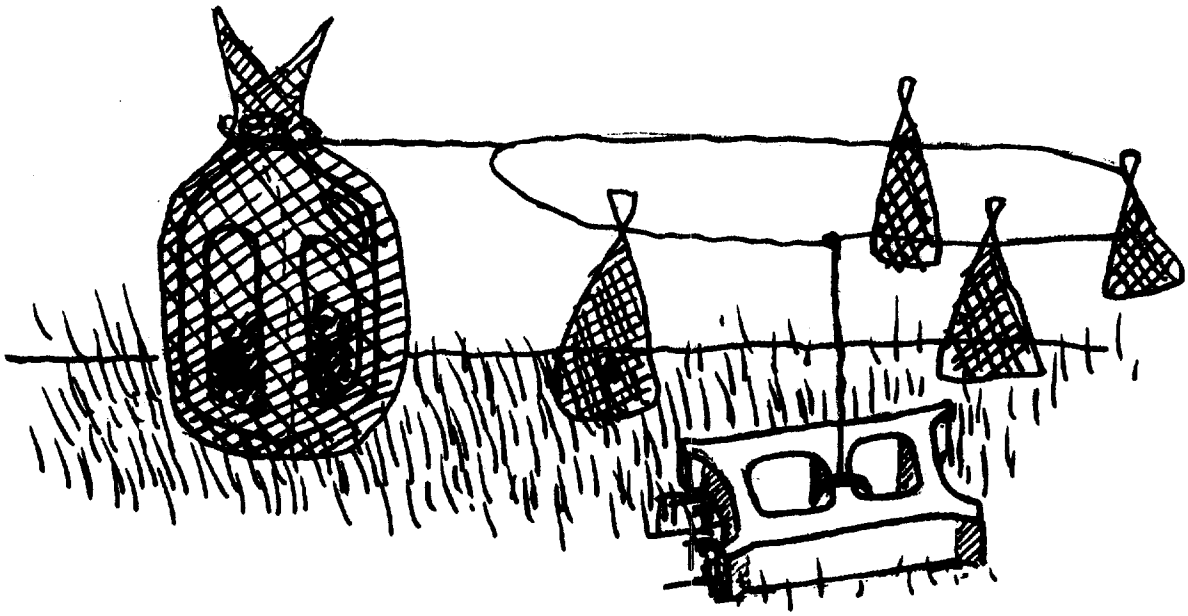

FIGURE 2. Sample Container Design and Station Lay-out

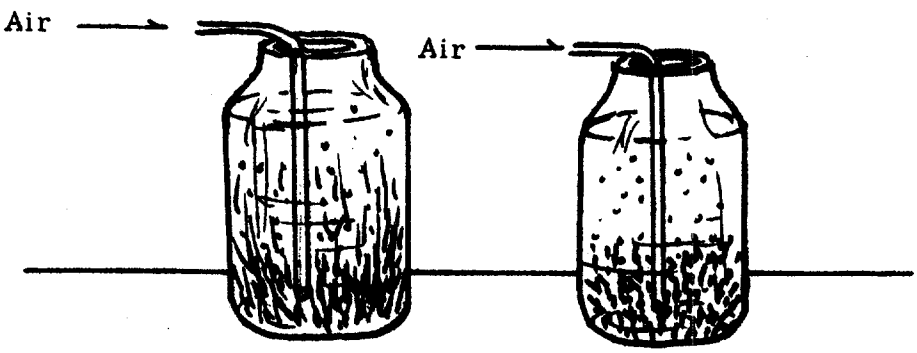

FIGURE 3. Bottles in Laboratory

samples of green leaves at the start of the study.

2) Caloric content

The heat of combustion, in Kcal/gram, was determined for each dried sample, using a Parr 1141 Calorimeter.

3) Biochemical Analyses

A sample aliquot (3 to 5 grams estimated) of moist sample material was ground in a Waring Blender in 25ml of hot ethanol for 5 minutes, the plant material allowed to separate and the ethanol carefully poured off. A second grinding was done with an additional 25ml of hot ethanol, then the two extracts were combined and centrifuged to separate the insoluble materials. The ethanol extract was collected and used for chlorophyll, amino acid and carbohydrate analyses. The insoluble material was further treated and used for total lipid and protein determinations.

a) Total chlorophyll was determined spectrophotometrically, reading optical densities at 665nm and 645nm.

b) Amino acids were estimated based on glycine, as determined by the Ninhydrin method.

c) Carbohydrates were determined by Anthrone method, (Wilson, 1965 & Ingle, 1965).

d) The insoluble portion was treated with tri-chloro acetic acid and the total lipid content measured by the sulfo-phosphovanillin colorimetric method described in the Harleco Products' manual.

e) The remaining residue was digested with potassium hydroxide overnight, then analyzed for protein content by the Lowry Protein Assay (Lowry, 1951).

D. Sample Handling

During the study, it was found that the manatee grass in the screened plastic jugs in the river became heavily covered with macro-invertebrates as well as with bacteria and fungi.

It was necessary to separate the manatee grass to be analyzed from its covering of macro-invertebrates. For analysis, a small aliquot of from 3 to 5 grams of grass was taken from the plastic jug and returned to the laboratory for separation of the invertebrates. If the sample lost moisture during the transfer to the laboratory, the invertebrates lost their moisture also and became glued to the grass making the separation very difficult. It was necessary to keep the sample aliquots wet during the transfer and until the separation had been completed.

IV. RESULTS

A. General

Samples were analyzed at two week intervals over a ten week period. These data are reported both in terms of actual amounts found and in per cent of amount found relative to the initial set of analyses. The data are reported in tables and graphs accompanying the descriptions of results below. A statistical analysis of the data is detailed in Appendices 1 through 8.

B. Dry Weight Remaining

Gross decomposition, as measured by the dry weight of material remaining, proceeded rapidly during the first two weeks, with losses of from 19% to 43%, then increased even more rapidly during the second period, with only 6 to 17% of the material remaining. Thereafter, weight loss continued, but at a much slower rate. Table 1 and Figure 4 show clearly the precipitous loss during the first four weeks, and show further that the decomposition was not so rapid for the laboratory cultures as for the in-situ river samples, nor did decomposition proceed as far for the laboratory cultures. Statistical analysis, using the Analyses of Variance tests, shows that there is no significant difference in the results between in-situ stations or laboratory cultures, but the difference between successive samples of both in-situ cultures and the laboratory cultures is significant at the 1% level. This suggests that laboratory culture is an adequate procedure for measuring in-situ decomposition. The rate of change between time periods is highly significant.

C. Total Lipids

The data from the total lipids analyses showed highly significant differences between the laboratory culture and the in-situ samples. The laboratory cultures showed an increase in total lipids during the first two-week period, then an abrupt drop during the next two weeks. After six weeks, the lipid content began to rise steadily again and by the end of the project had risen to levels greater than in the original sample, (see Table 2 and Figure 5). The in-situ samples declined steadily during the first four weeks, then rose abruptly between the fourth and sixth weeks. Between the sixth and eighth weeks, the lipid values recovered at the same rate as the laboratory cultures, but then began to level off at values slightly below the original samples (87% and 96% respectively). The statistical analysis showed no significant difference in behavior between the two laboratory cultures or between the in-situ samples.

D. Protein

At the in-situ river sites, the amount of protein in the samples decreased slowly but steadily through the sixth week, rose rapidly between the sixth and eighth week, then rose abruptly during the last period to values of 200% of the original samples (Table 3 and Figure 6). The differences between the two sites are not statistically significant. The laboratory cultures displayed a marked increase in protein level during the first two weeks to 170% and 230% of the original samples. From the second through the eighth weeks, the level rose slightly then dropped slightly, but remaining at a high level. Between the eighth and tenth weeks, the level rose abruptly in the

SITE	DATE 3-16	4-2	4-16	4-30	5-13	5-26
STATION A	39.640g	28.065g	2.659g	2.508g	2.09g	1.0539g
	(100%)	(70.78%)	(6.71%)	(6.33%)	(5.27%)	(2.66%)
STATION B	39.640g	22.589g	2.800g	2.453g	1.978g	1.224g
	(100%)	(56.98%)	(7.07%)	(6.19%)	(4.99%)	(3.09%)
GROUP 1	15.856g	12.270g	2.515g	2.379g	1.755g	1.6224g
	(100%)	(71.08%)	(15.86%)	(14.77%)	(11.07%)	(10.23%)
GROUP 2	39.64g	32.102g	7.098g	6.501g	5.759g	4.0264g
	(100%)	(80.98%)	(17.91%)	(16.37%)	(14.53%)	(10.16%)

TABLE 1. Dry Weight of Original Manatee Grass Remaining in Gram and Percent of Original Sample

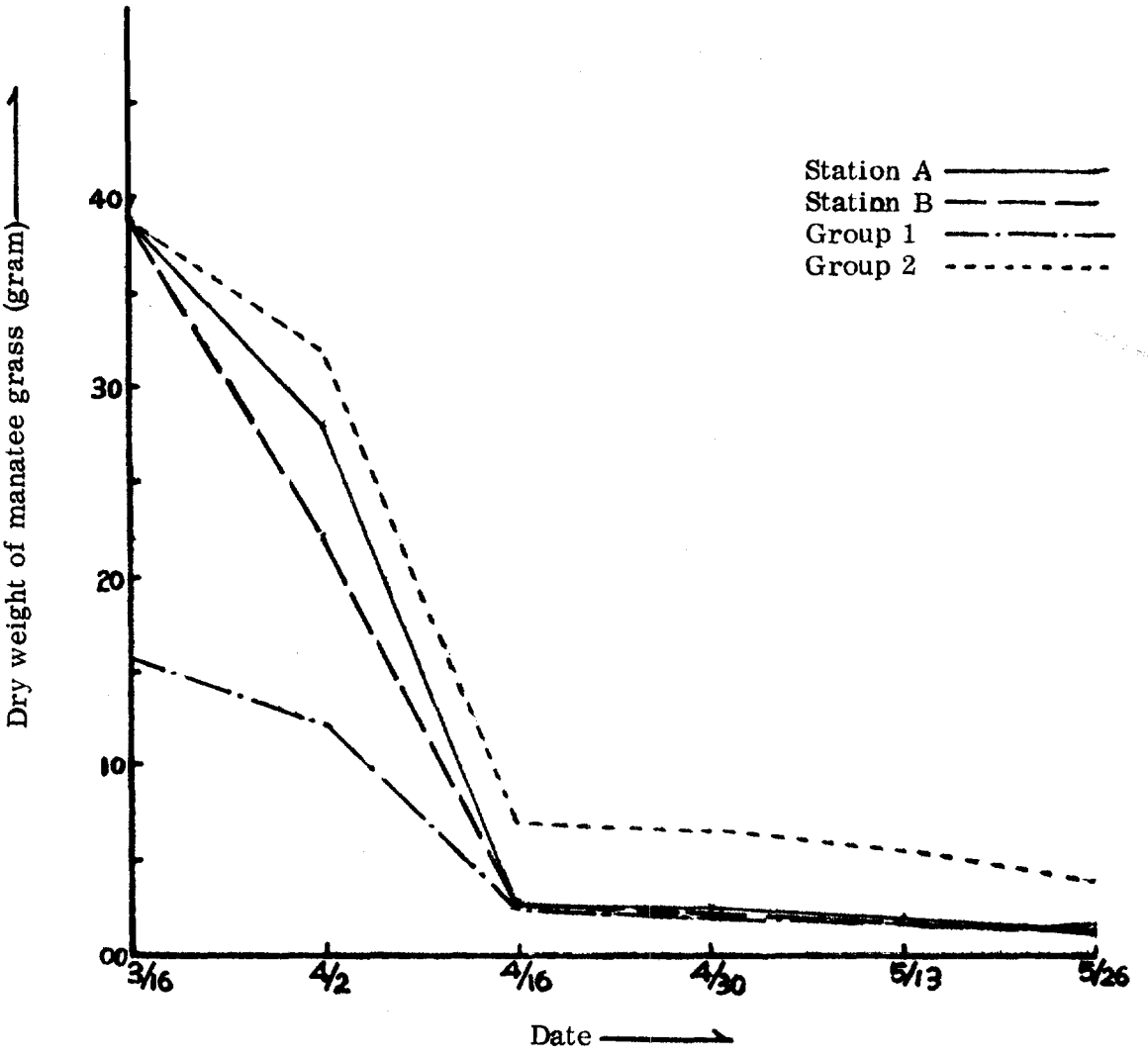

FIGURE 4A. Dry Weight of Original Organic Matter Remaining

SITE	DATE 3-16	4-2	4-16	4-30	5-13	5-26
STATION A	0.5439	0.4464	0.3782	0.1841	0.5118	0.5260
	(100%)	(82.07%)	(69.54%)	(33.85%)	(94.10%)	(96.71%)
STATION B	0.5439	0.4898	0.4550	0.1682	0.4143	0.4755
	(100%)	(90.05%)	(83.66%)	(30.93%)	(76.17%)	(87.42%)
GROUP 1	0.5439	0.6071	0.1496	0.1605	0.5484	0.7336
	(100%)	(111.62%)	(27.51%)	(29.51%)	(100.83%)	(134.88%)
GROUP 2	0.5439	0.5517	0.1328	0.1429	0.3886	0.6089
	(100%)	(101.43%)	(24.42%)	(26.27%)	(71.45%)	(111.95%)

TABLE 2. Total Lipid Content (mg total lipids/g of dry tissue)

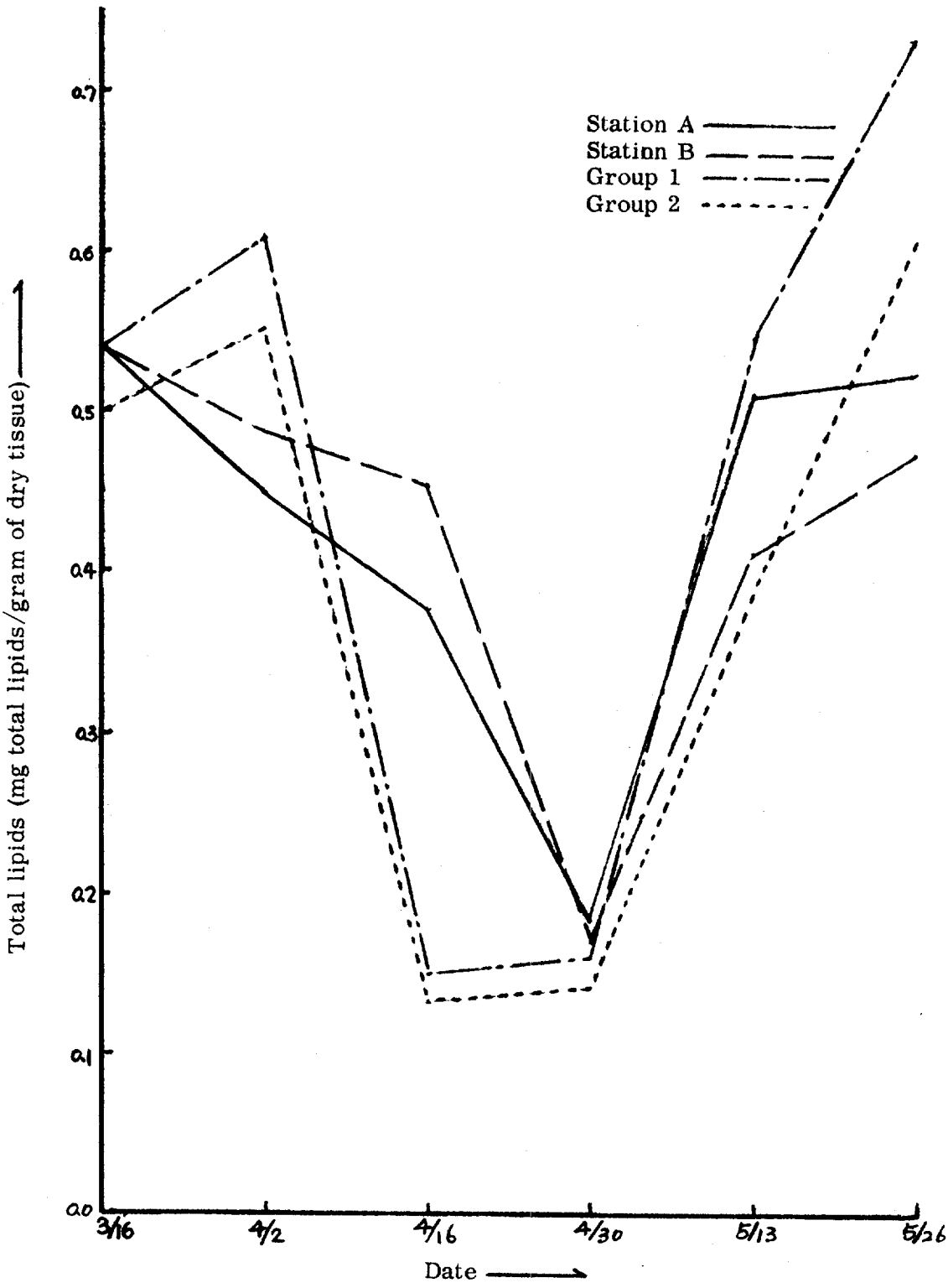

FIGURE 5. Total Lipid Content (per gram of dry tissue)

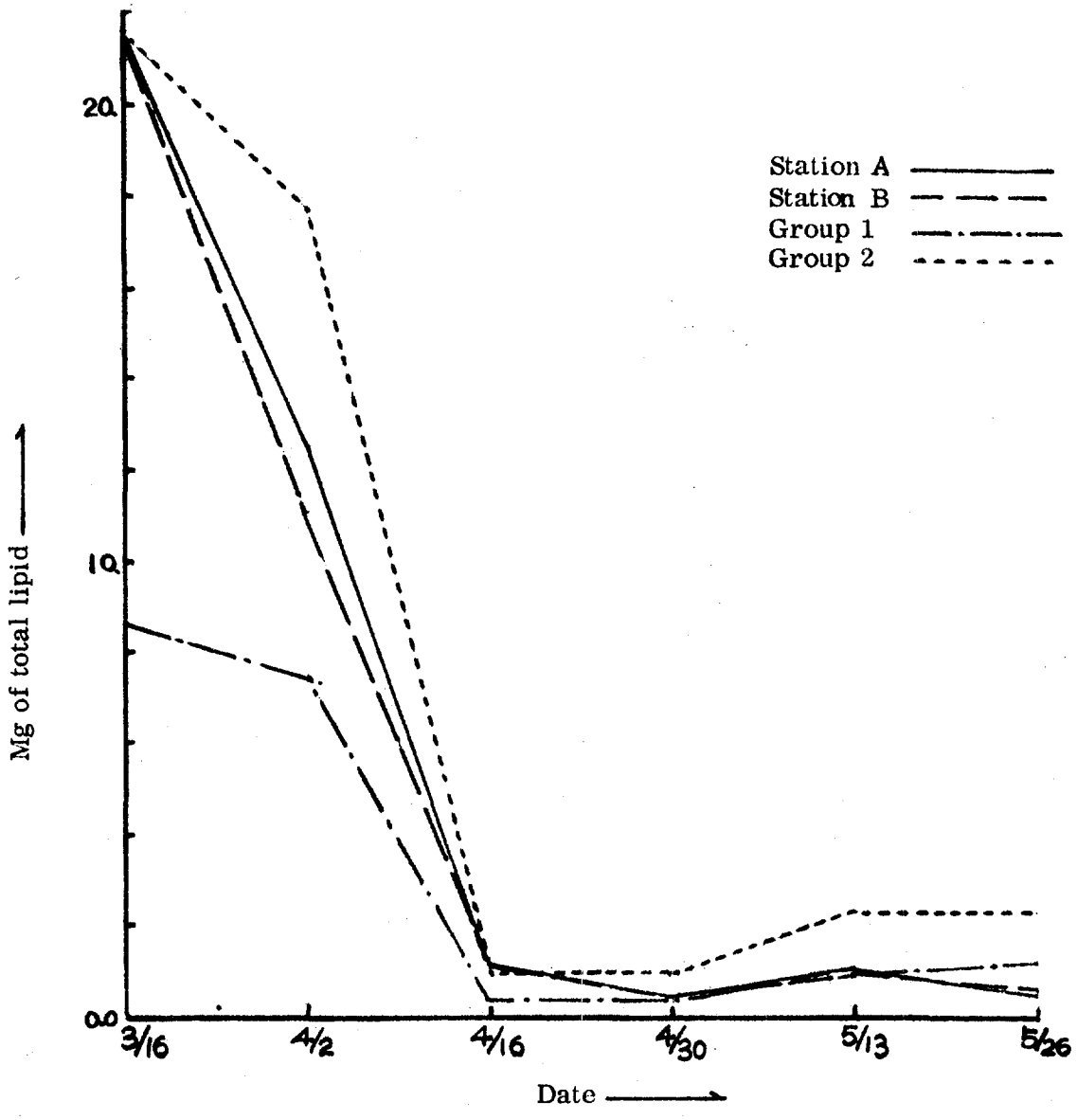

FIGURE 5A. Total Lipid Content (mg)

SITE	DATE 3-16	4-2	4-16	4-30	5-13	5-26
STATION A	47.8	47.5	44.2	41.6	53.7	95.9
	(100%)	(99.37%)	(92.47%)	(87.03%)	(112.34%)	(200.63%)
STATION B	47.8	36.2	32.2	27.5	35.3	107.0
	(100%)	(75.73%)	(67.36%)	(57.53%)	(73.85%)	(223.85%)
GROUP 1	47.8	81.9	85.2	78.7	72.1	142.6
	(100%)	(171.34%)	(178.24%)	(164.64%)	(150.84%)	(298.33%)
GROUP 2	47.8	111.9	113.4	111.1	99.9	103.9
	(100%)	(234.10%)	(237.24%)	(232.43%)	(209.00%)	(217.36%)

TABLE 3. Protein Content (mg protein/g of dry tissue)

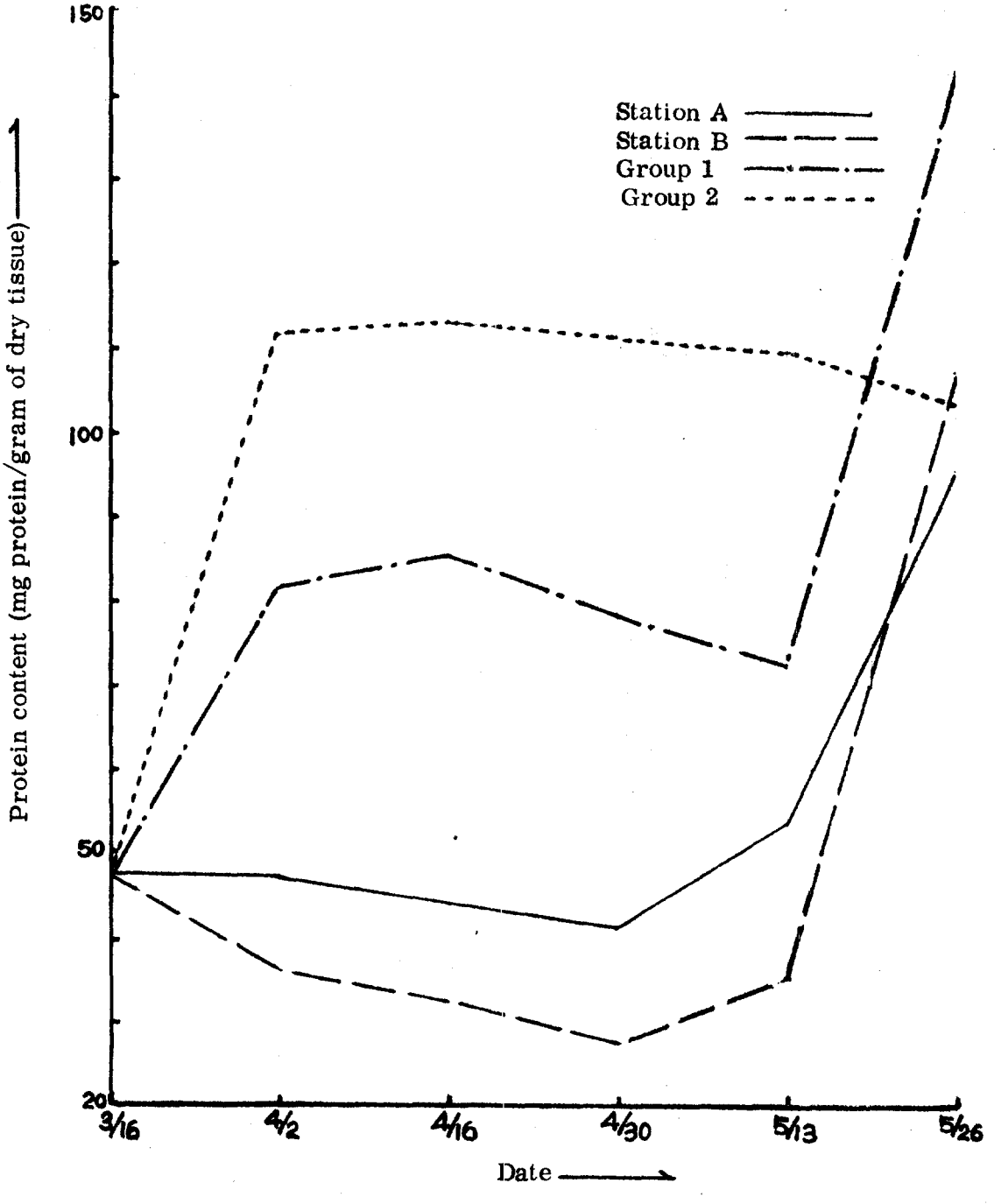

FIGURE 6. Protein Content (mg protein/g of dry tissue)

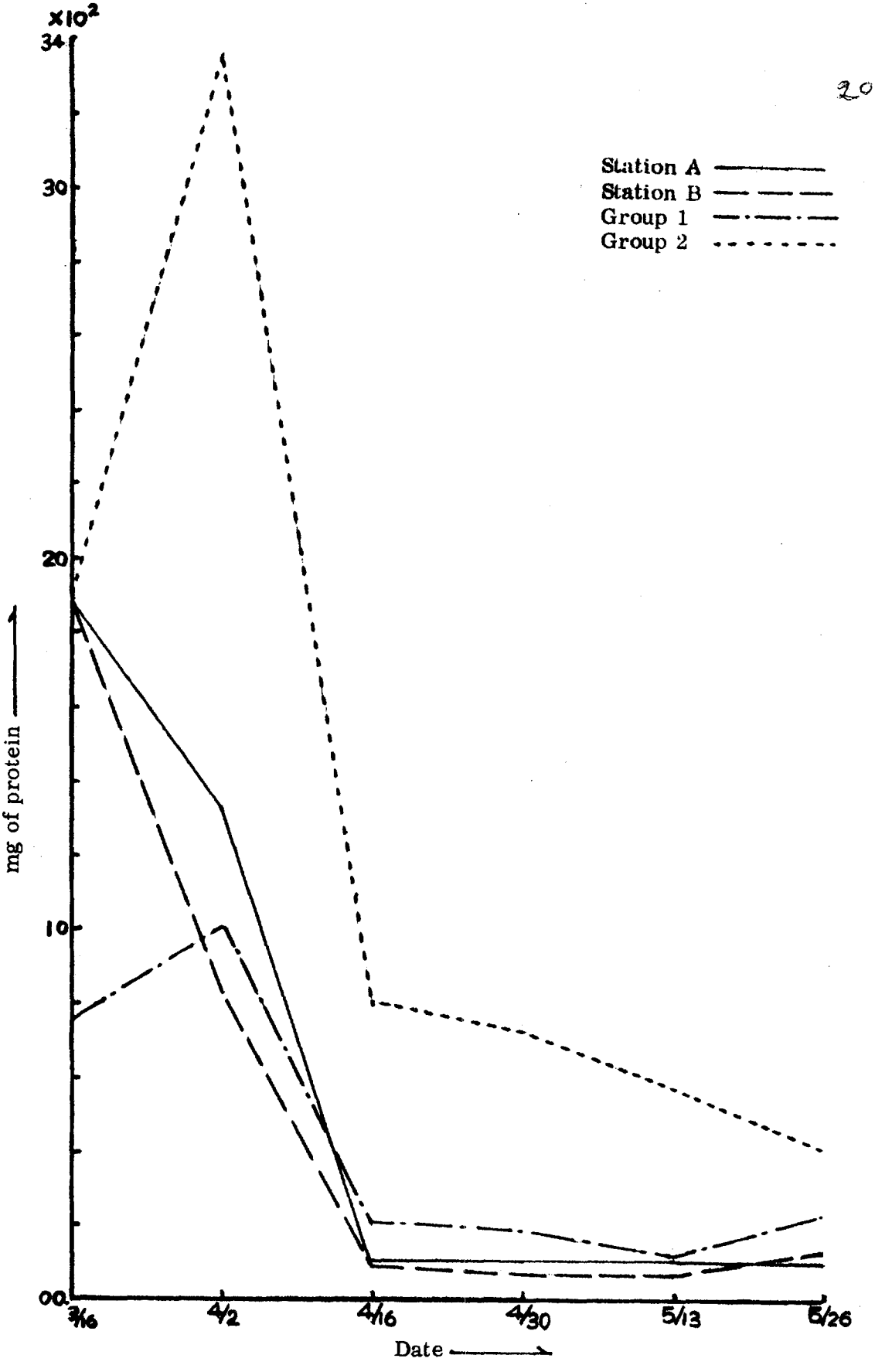

FIGURE 6A. Total Protein Content (mg)

group 1 culture, paralleling the rise demonstrated at the river in-situ sites. The cultures in group 2 rose very slightly. The differences between the two groups are found to be significant. The differences between the river sites and the laboratory cultures are found to be highly significant at the 1% level.

E. Carbohydrates

The carbohydrates decreased steadily during the first six weeks to values less than 10% of the original sample. From the sixth week to the end of the study, the values remained essentially static. The differences between the four sets of samples were not significant, whereas the change with respect to time was highly significant.

F. Chlorophylls

Both the in-situ sites and the laboratory cultures showed large decreases in the amount of chlorophyll during the first two weeks, with the laboratory cultures showing the greatest loss. Thereafter, the laboratory cultures showed very little loss until the tenth week, when a further slight decline was noted (see Table 5 and Figure 8). The river stations continued to decrease slowly throughout the time of the study. The differences between the two river stations and between the two laboratory cultures were not significant, nor was the difference between the stations and cultures. The rate of change of loss was highly significant.

G. Amino Acids

The amount of amino acid measured rose sharply to a level of 140% of the original sample during the first two weeks, then dropped steadily from the second through the sixth week to approximately 30%. The river stations showed a rise from the sixth to the eighth week and a loss again from

the eighth to the tenth week. The differences between stations and cultures was found not significant, although the change of rate with time was significant at the 1% level for the river stations and at the 0.1% level for the laboratory cultures (see Table 6 and Figure 9).

H. Caloric Contents

All samples showed a loss of caloric content during the first two weeks, with the laboratory cultures losing the most. For the rest of the study period, the river stations showed a steadily increasing caloric content. At the end of the study, the analysis showed 119% of the original sample. The laboratory cultures also showed an increase from the second week through the sixth week, a decrease at the eighth week and a small increase at the tenth week (see Table 7 and Figure 10). Statistical tests showed that the difference between the station sites or between the laboratory cultures were not significant. The rate change with time was highly significant. For the laboratory cultures, the rate of change was significant at the 5% level.

In another way, the authors also calculated the total amount left after each time period for these seven parameters by the way of using each value in Table 2 - 7 of specific period to multiply the relative specific value in Table 1 to figure out the total value left, not the value left per gram of dry tissue (see Fig. 4A, 5A, 6A, 7A, 8A, 9A and 10A).

DATE					
3-16	4-2	4-16	4-30	5-13	5-26
135.98	127.8	22.8	7.4	9.3	11.9
(100%)	(94.04%)	(16.78%)	(5.45%)	(6.84%)	(8.76%)
135.98	93.3	41.1	11.2	8.8	10.5
(100%)	(68.65%)	(30.24%)	(8.24%)	(6.48%)	(7.73%)
135.98	113.9	15.0	4.9	12.1	12.9
(100%)	(83.81%)	(11.04%)	(3.61%)	(8.90%)	(9.49%)
135.9	133.9	11.1	4.5	7.7	11.5
(100%)	(98.53%)	(8.17%)	(3.31%)	(5.67%)	(8.46%)

›hydrate Content (mg D-glucose/g of dry tissue)

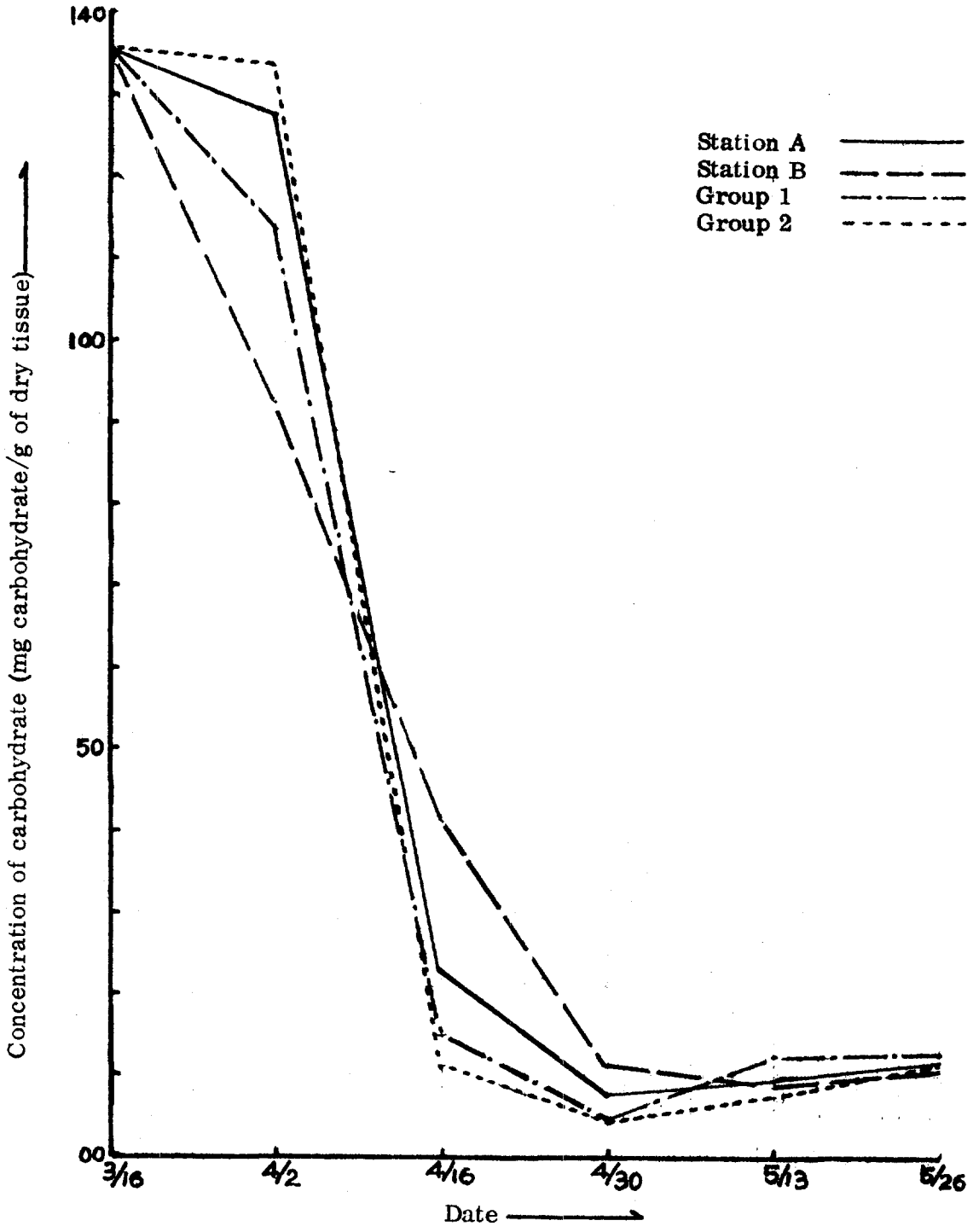

FIGURE 7. Total Carbohydrate Content

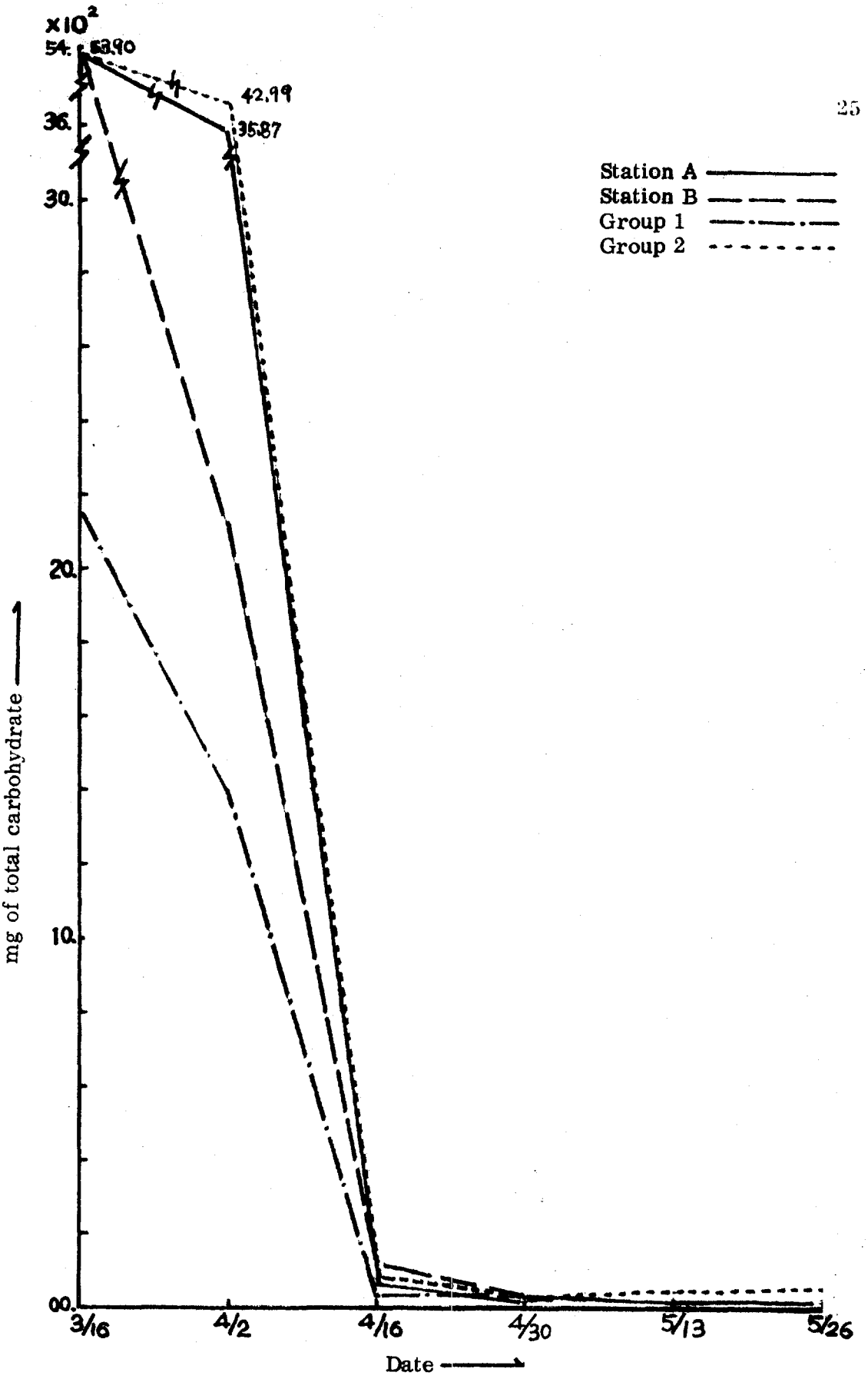

FIGURE 7A. Total Carbohydrate Content (mg)

SITE	DATE 3-16	4-2	4-16	4-30	5-13	5-26
STATION A	2.085	1.15	0.946	0.786	0.56	0.52
	(100%)	(55.16%)	(45.37%)	(37.70%)	(26.86%)	(24.94%)
STATION B	2.085	1.166	0.932	0.663	0.566	0.533
	(100%)	(55.92%)	(44.70%)	(31.80%)	(27.15%)	(25.56%)
GROUP 1	2.085	0.73	0.723	0.714	0.68	0.515
	(100%)	(35.61%)	(34.68%)	(34.25%)	(32.61%)	(24.70%)
GROUP 2	2.085	0.844	0.668	0.63	0.503	0.489
	(100%)	(40.48%)	(32.04%)	(30.22%)	(24.13%)	(23.45%)

TABLE 5. Total Chlorophyll (mg total Chlorophyll/ g of dry tissue)

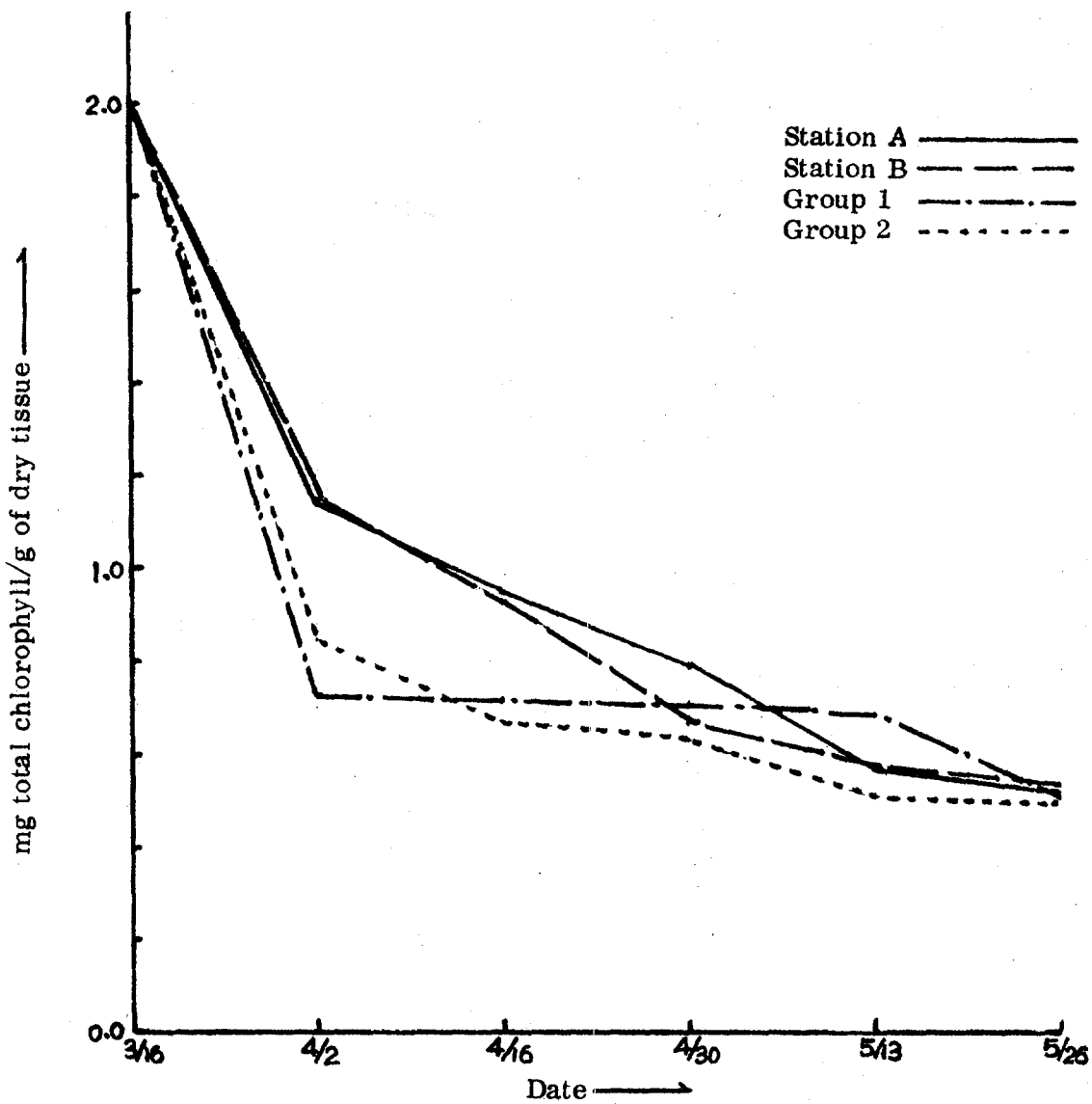

FIGURE 8. Total Chlorophyll Content.

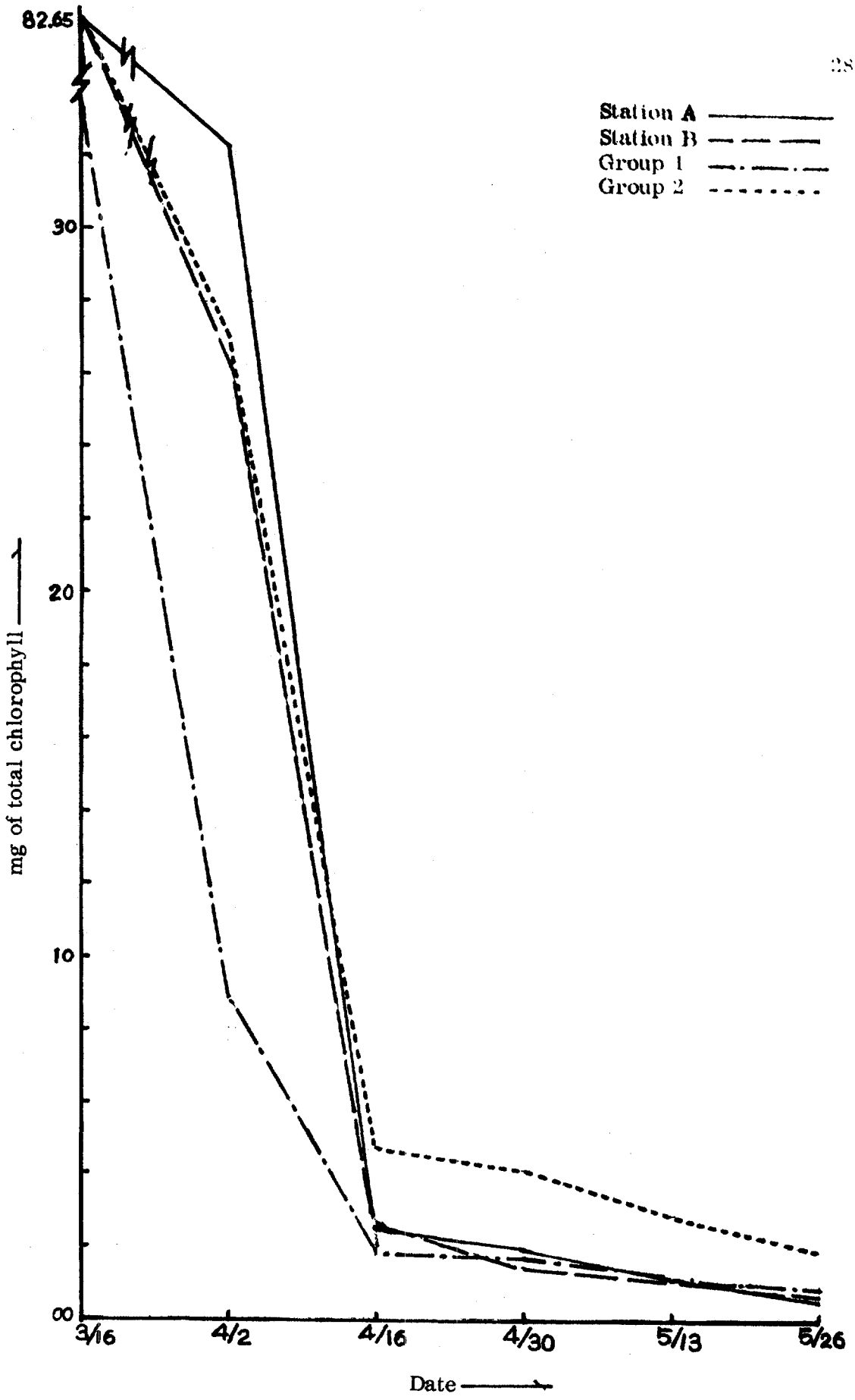

FIGURE 8A. Total Chlorophyll Content (mg)

SITE	DATE 3-16	4-2	4-16	4-30	5-13	5-26
STATION A	23.65	33.71	20.71	7.60	14.77	5.19
	(100%)	(142.53%)	(87.56%)	(32.13%)	(62.44%)	(21.95%)
STATION B	23.65	34.35	27.87	6.31	19.10	12.89
	(100%)	(145.25%)	(117.87%)	(26.70%)	(80.77%)	(54.53%)
GROUP 1	23.65	21.94	29.37	5.73	8.13	2.25
	(100%)	(92.76%)	(124.21%)	(24.21%)	(34.39%)	(9.50%)
GROUP 2	23.65	30.28	29.64	6.26	4.87	2.41
	(100%)	(128.05%)	(125.34%)	(26.47%)	(20.59%)	(10.18%)

TABLE 6. Amino Acid (mg Amino Nitrogen/g of dry tissue)

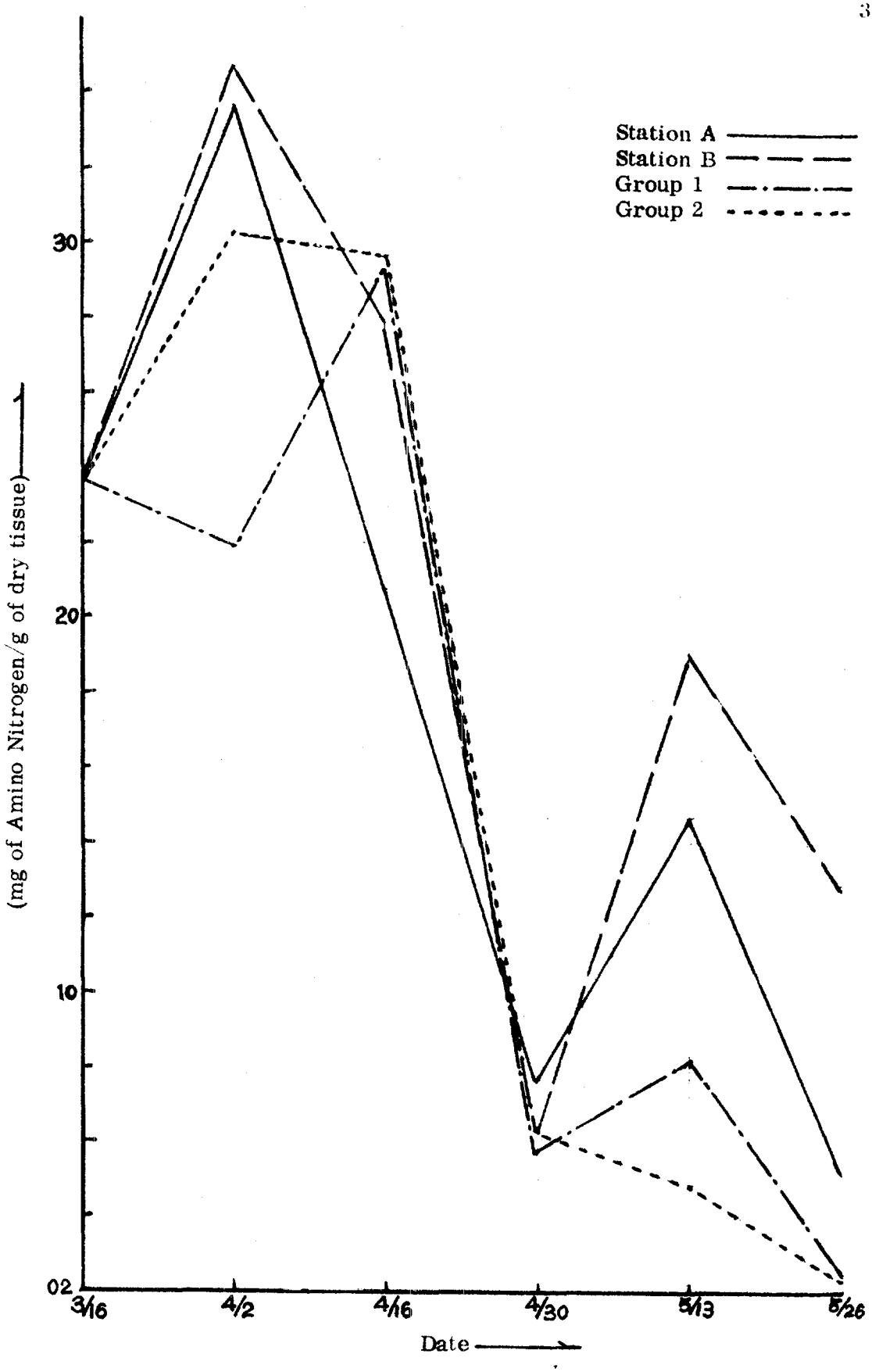

FIGURE 9. Total Content of Amino Nitrogen

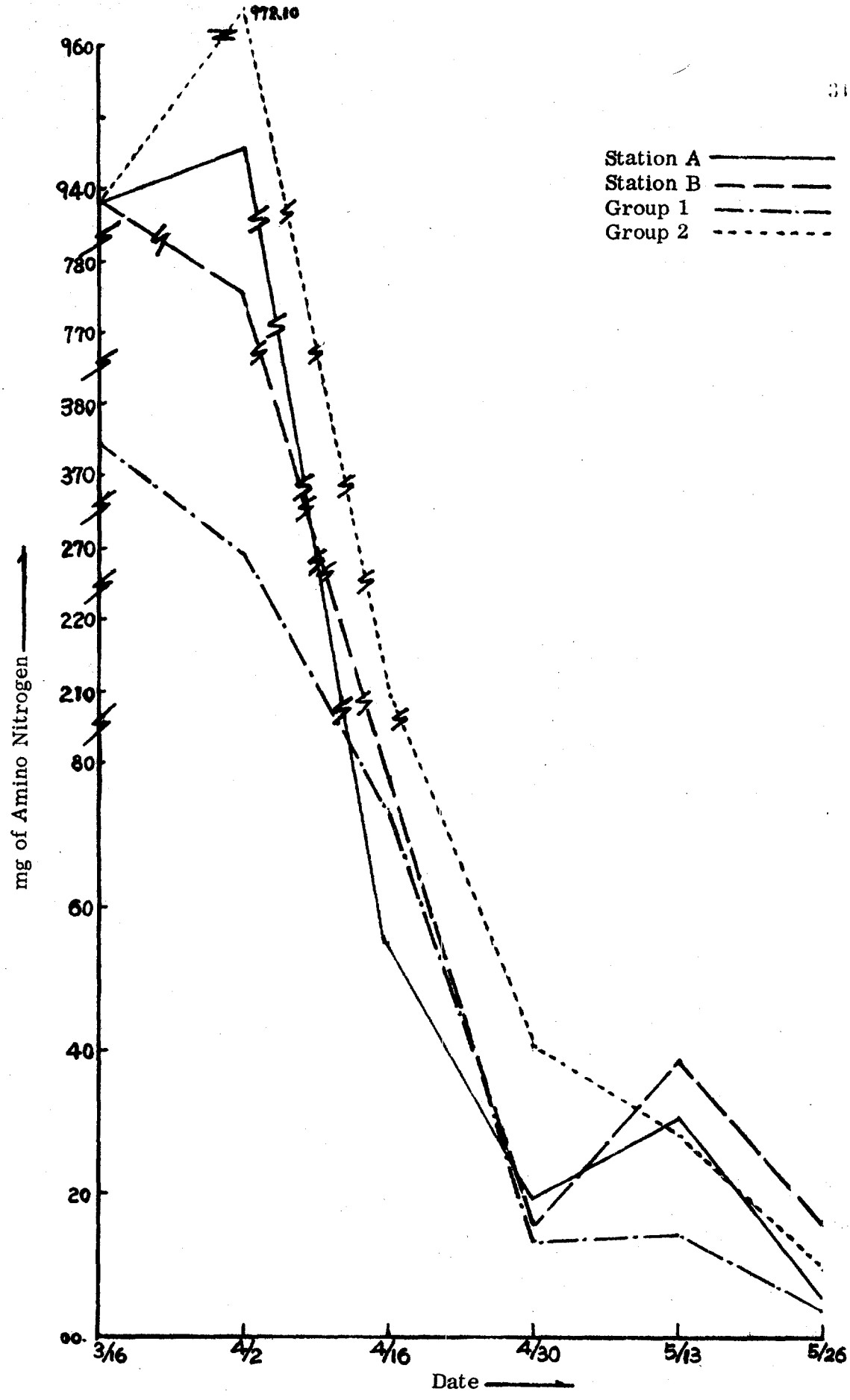

FIGURE 9A. Total Content of Amino Nitrogen

SITE	DATE 3-16	4-2	4-16	4-30	5-13	5-26
STATION A	4.30	3.27	3.67	4.47	5.07	5.14
	(100%)	(76.05%)	(85.35%)	(103.95%)	(117.91%)	(119.53%)
STATION B	4.30	3.01	3.44	3.90	4.70	5.12
	(100%)	(70.00%)	(80.00%)	(90.70%)	(109.30%)	(119.07%)
GROUP 1	4.30	2.34	3.44	4.13	3.94	4.24
	(100%)	(54.42%)	(80.00%)	(96.05%)	(91.63%)	(98.61%)
GROUP 2	4.30	2.77	3.31	4.62	3.40	3.88
	(100%)	(64.42%)	(76.98%)	(107.44%)	(79.07%)	(90.23%)

TABLE 7. Caloric Content in K cal/gram and Percent of Original Sample

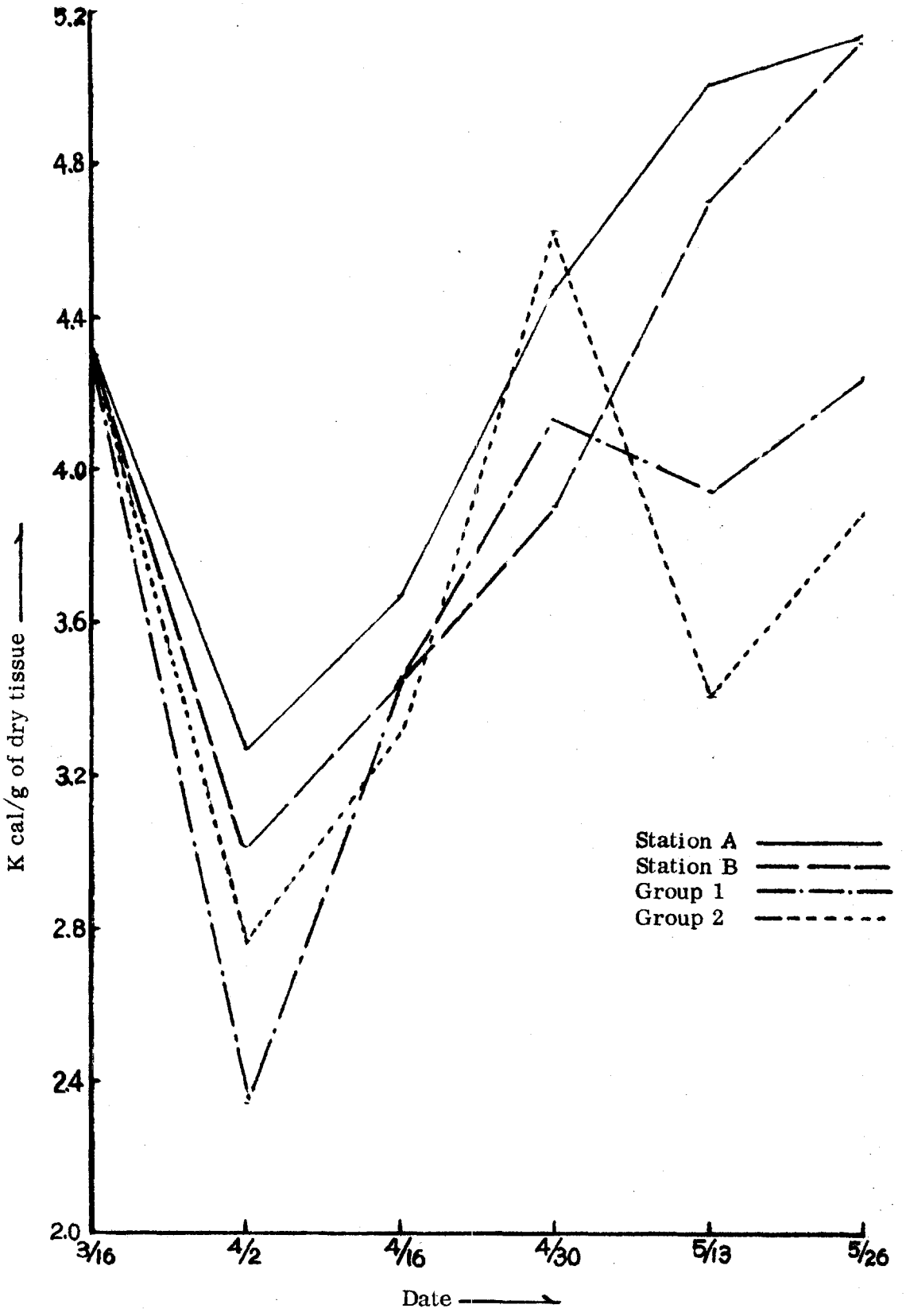

FIGURE 10. Total Caloric Content

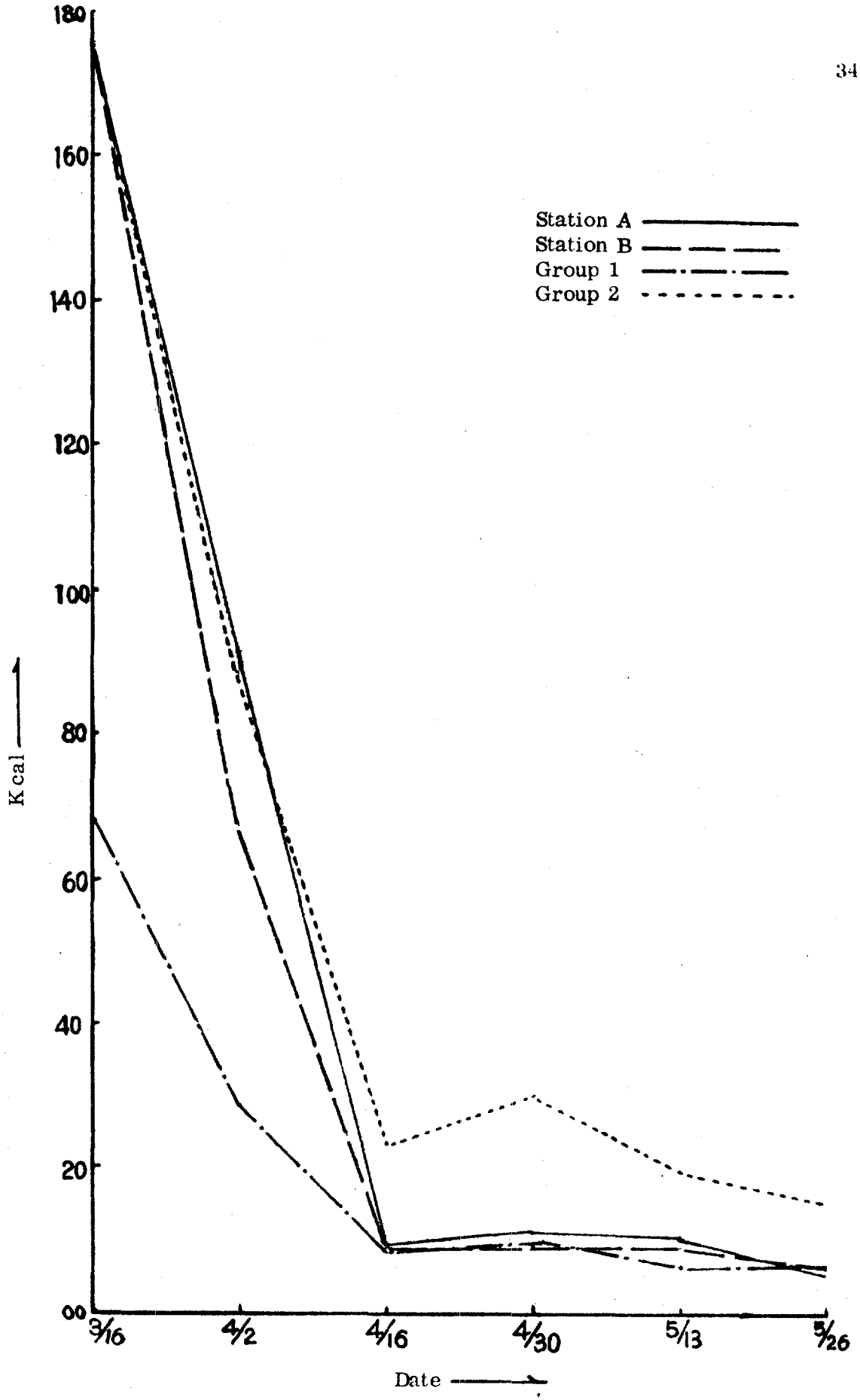

FIGURE 10A. Total Caloric Content (Kcal)

V. DISCUSSION

Because the number of samples in this study was necessarily small, even small errors in analysis might result in serious distortions of data and of final conclusions. Each test was therefore repeated three times, and the results were averaged for this report. The statistical analyses performed were the "two-way analysis of variance (ANOVA) without replication" and the "significance tests in correlations" as described by Sokal and Rohlf (1969).

At the beginning of this study, the larger animals that graze on manatee grass were excluded from the plastic sample bottles by the window screen that was wrapped closely around them, so that the test conditions might be identical between the river stations and the laboratory cultures. In practice, the laboratory room temperature could not be modified to parallel the changes in the river temperature, nor could the light levels of the open river be duplicated in the laboratory. Further, the volume of water in the laboratory culture bottles varied from evaporation, thus varying the salinity of the water also. Whether the increased salinity reduced or altered the activity of the bacteria in the water is not known. Such bacteria studies were outside the scope of this study.

As the grasses in the laboratory culture bottles decomposed, the products of decomposition caused a change in pH, which might also have caused a change in the activity of the bacteria. From Table 8, it can be seen that the pH in both groups first decreased to low values (6.1 and 6.9)

by the fourth week, then increased steadily to high values (8.1 and 7.7) during the eighth week.

A statistical analysis of variance (ANOVA) test was applied to all the data derived from the various analyses performed during this study. The purpose of the ANOVA test was to determine whether the differences between the two river stations or the two laboratory cultures were significant, and if so, to what level were they significant. ANOVA tests were also applied to the differences between the river stations and the laboratory cultures. Correlation coefficients were computed for each possible pair of parameters, to determine whether they were interrelated and if so, to what degree. If the statistical correlation is not strong, it is frequently easier to detect congruencies in patterns by plotting the data on charts or graphs. This has been recognized by ecologists, who use graphs extensively, but rarely use statistical correlations (R. Margalef, 1968). In this study, both charts and statistical correlations have been prepared in parallel.

The ANOVA tests showed that the differences between the river station and the laboratory cultures were not significant for the values found for total lipids, carbohydrates, total chlorophylls, amino acids and caloric content.

Most of the manatee grass was decomposed during the first four weeks, with approximately 7% by weight remaining in the river samples and 16% in the laboratory cultures. An abundant population of small invertebrates was found inside the screened plastic jugs in the river stations. In addition, the river stations were subjected to water movements which could wash away

small suspended particles and sediments. The laboratory cultures were not subjected to such losses, and showed a slightly lower rate of decomposition than the river stations as a result.

Micro-organisms are very important in the formation of the natural organic detritus through both aerobic and anaerobic processes (Schultz and Quinn, 1973). Bacteria attack the grass substances and convert a portion into bacterial protoplasm (Teal, 1962). The role of fungi in the degradation of plant material in fresh water was studied by Kashick and Hynes (1971), who stated that fungi were more important than bacteria in the initial stages of the degradation process. This study showed that the bacteria and fungi not only account for the increases noted for total lipids, but also account for the increase in protein concentration, which was double the original concentration after ten weeks of decomposition.

The photosynthesis systems of plants are not limited to one pigment, but usually involve many pigments, so many that the phrase "pigment diversity" is used to characterize the complexity of the photosynthetic system. The amounts of different pigments present at any one time are not independent of conditions around the plant. Chlorophyll will be abundant during conditions favorable to photosynthesis. On the other hand, when conditions are not favorable to growth, carotenoids are more resistant to destruction than other pigments and will be relatively more abundant. From an ecological point of view, the quality of the pigments is as important as the quantity of one of the pigments. In fact, the diversity of pigments is an important indicator of the history and activity of the

ecosystem (R. Margalef, 1968). In this study, only chlorophyll a and b were measured, but their value was taken as representative of the total chlorophyll present. The concentration of chlorophyll decreased rapidly during the first two weeks, to about 55% of the original value, then continued to decrease slowly but steadily to the end of the study. It is probable that all of the chlorophyll was decomposed during the first four weeks, and that the amounts indicated as remaining thereafter were phaeophitins and pheophorbides, which are the first stage decomposition products of chlorophyll. It was noted that the grass in the river samples retained their green color longer than the laboratory cultures did, which accounts for the higher amount of chlorophyll remaining at the end of the first two week period.

The amino acid concentrations determined in this study showed a pattern unique to this substance. The concentration rose sharply during the first two weeks to 140% of the initial value, decreased steadily over the next four weeks to 32% of initial value, increased to about 60% of initial value during the sixth week, then decreased again at the end of the study to about 20%. The differences between the various samples appear to be large when the data is graphed, but they were not significant by statistical analysis.

The caloric content of all the samples decreased during the first two weeks, then began a steady increase from the second through the sixth week. The two river stations continued to show an increase throughout the study, but the two laboratory cultures decreased from the sixth week through the eighth week, then increased slightly by the tenth week. At the end of the study, the river stations had a slightly higher caloric content (120% of initial value) than the laboratory cultures (100% and 90%). The higher caloric

content is probably the result of greatly increased populations of bacteria, fungi and small invertebrates that were feeding on the decomposition products of the manatee grass. The proteins and lipids manufactured by the bacteria and zooplankton have a higher caloric content than do the cellulose and lignins of the original plant material. Comparison of Figure 10, caloric content, with Figure 5 and 6, averaged values of protein and total lipids concentrations, appear to show that the general behavior for all three substances was the same, however the statistical correlation of caloric content with either protein or lipid content is not strong.

Correlation coefficients were computed for all pairs of the seven parameters. Significance tests of correlation were computed only for data from station A. Among the twenty one combinations of parameters, only four showed significant correlation. As shown in appendix 1, the highest degree of correlation was found between the dry weight remaining and the carbohydrate content, which was significant to the 1% level. Next in order of significance, at the 5% level, were correlations between dry weight remaining and chlorophyll content; between carbohydrate content and chlorophyll content; and between carbohydrate content and amino acid content. The data for these four parameters are plotted in Figure 12 for ease of comparison (Station A data only).

If one is concerned with the total amount left after each time period of these seven parameters, from Figure 4A, 5A, 6A, 7A, 8A, 9A and 10A, these show that most of the total amount of these seven parameters were lost during the time between April 2 (second week) and April 16 (fourth

week), and then remain essentially constant. After the first four weeks, at least, 93% of the original total lipid content, 58% of the original total protein content, 98% of the original total carbohydrate, 94% of the original total chlorophyll, 78% of the original amino acid content, and 88% of the caloric content were lost. Then, after that time, all seven parameters just stayed pretty stable.

But, even the quantities of the seven parameters at its own original sample weight were tremendously decreased after the first four weeks, the quality of the samples left at each time period were varied and showed that the relative concentration of total lipids, protein and caloric content were increased over the original value after ten weeks.

SITE	DATE 3-16	4-2	4-16	4-30	5-13	5-26
GROUP 1	7.2	...	6.9	8.0	8.1	7.6
GROUP 2	7.2	...	6.1	7.4	7.7	7.8

TABLE 8. pH Values

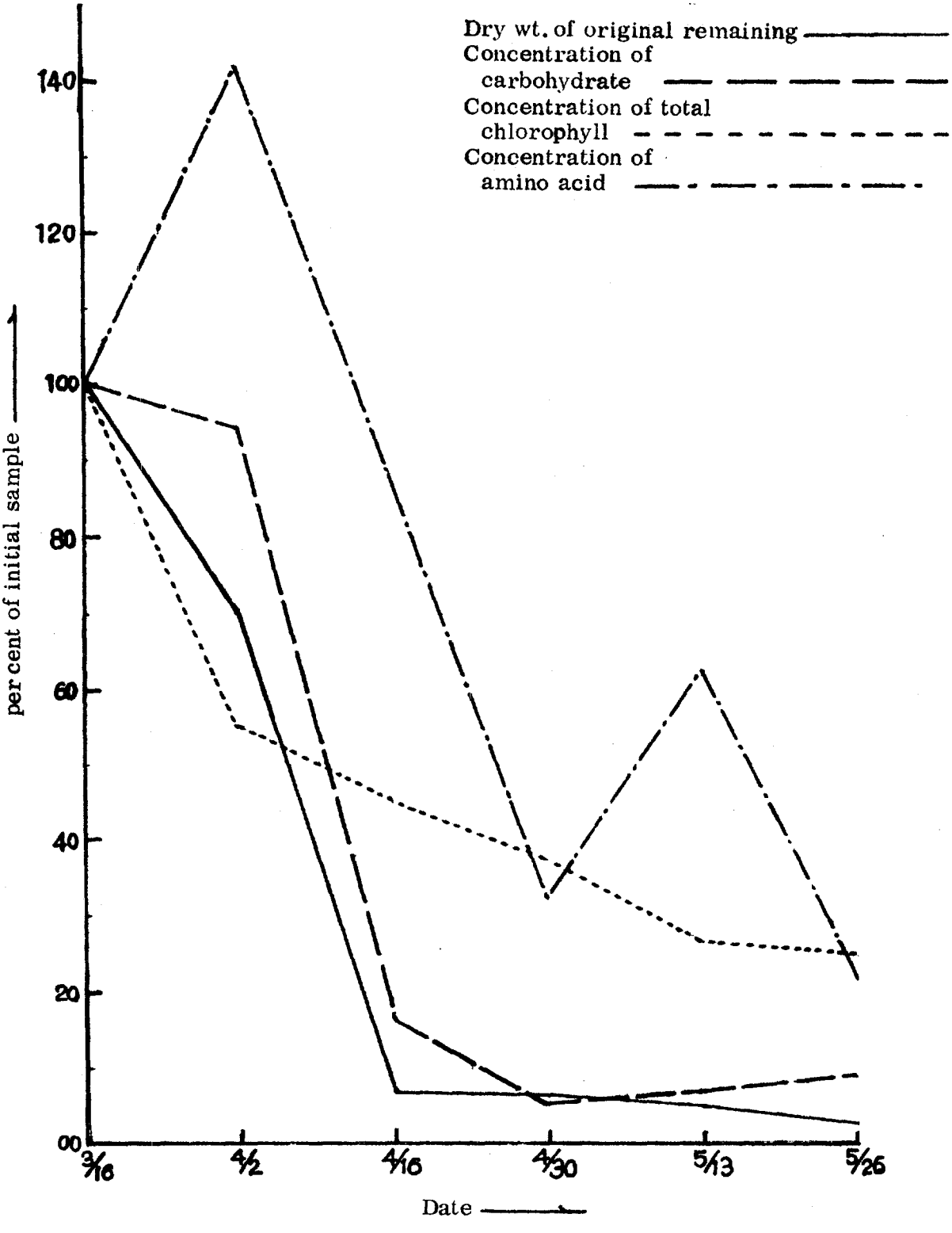

FIGURE 11. Comparison of the four curves of original organic matter remaining, carbohydrate content, total chlorophyll content and amino acid content in Station A.

VI. CONCLUSIONS

A. Most of the manatee grass, especially the softer parts, is decomposed during the first four weeks, as indicated by the loss in dry weight, loss of caloric content, loss of carbohydrate and loss of chlorophyll. Heavier cellulose parts, containing more lignin, continued to decompose, but at a very much slower rate with some still remaining after ten weeks. And the fastest rate of decomposition happens between the second week and fourth (i.e. April 2 to April 16 in 1974).

B. Two parameters measured, protein content and total lipid content, seemed to reflect the growth of large populations of bacteria, fungi and micro-invertebrates that were feeding on the plant detritus.

C. Although there were some variations in decomposition rates between the in-situ river stations and the laboratory culture groups, these variations were not statistically significant over the span of time of this study. It is concluded that laboratory methods can be used in lieu of more laborious in-situ studies with some degree of validity.

APPENDIX 1.

Codes: y_1 = original organic matter remaining dry wt. y_2 = total lipids y_3 = protein

y_4 = carbohydrate y_5 = total chlorophyll y_6 = amino acid y_7 = caloric content

Tested samples	Product-moment correlation coeff.	Tests of significance for correlation coeff. (test the null hypothesis $H_o : P = 0$)	Coefficient of determination
$y_1 - y_2$	-0.268	true to the null hypothesis	0.15
$y_1 - y_3$	0.38	true to null hypothesis	0.094
$y_1 - y_6$	0.732	true to null hypothesis	0.536
$y_1 - y_4$	0.981	reject it at 1% level	0.962
$y_1 - y_5$	0.915	reject at 5% level	0.837
$y_1 - y_7$	-0.465	true to null hypothesis	0.216

$y_2 - y_3$	0.486	true to null hypothesis	0.24
$y_2 - y_4$	0.38	true to null hypothesis	0.1442
$y_2 - y_5$	0.25	true to null hypothesis	0.0625
$y_2 - y_6$	0.254	true to null hypothesis	0.064
$y_2 - y_7$	0.22	true to null hypothesis	0.048
$y_3 - y_4$	-0.293	true to null hypothesis	0.086
$y_3 - y_5$	-0.420	true to null hypothesis	0.176
$y_3 - y_6$	-0.523	true to null hypothesis	0.273
$y_3 - y_7$	0.599	true to null hypothesis	0.359
$y_4 - y_5$	0.849	reject at 5% level	0.721
$y_4 - y_6$	0.822	reject at 5% level	0.675

$y_4 - y_7$	-0.581	true to null hypothesis	0.338
$y_5 - y_6$	0.589	true to null hypothesis	0.347
$y_5 - y_7$	-0.417	true to null hypothesis	0.174
$y_6 - y_7$	-0.827	true to null hypothesis	0.684

APPENDIX 1. Computation of the Product-moment Correlation coefficient and Significance Tests in Correlation.

APPENDIX-2 : Two-way ANOVA without replication for " dry weight of original organic matter remaining".

A) STATION-A to STATION-B:

site \ date	3/16	4/ 2	4/16	4/30	5/13	5/26	TOTAL
STATION-A	100.00	70.78	6.71	6.33	5.27	2.66	191.75
STATION-B	100.00	56.98	7.07	6.19	4.99	3.09	178.32
TOTAL	200.00	127.76	13.78	12.52	10.26	5.75	370.07

Source of Variance :	df	SS	MS	Fs
STATIONS	1	15.03	15.03	0.565 ns
TIME	5	16938.51	3387.702	127.33 ***
ERROR	5	133.03	26.606	
TOTAL	11	17086.57		

B) GROUP-1 to GROUP-2 :

site \ date	3/16	4/ 2	4/16	4/30	5/13	5/26	TOTAL.
GROUP-1	100.00	71.08	15.86	14.77	11.07	10.23	223.01
GROUP-2	100.00	80.98	17.91	16.37	14.53	10.16	239.95
TOTAL	200.00	152.06	33.77	31.14	25.60	20.39	462.96

Source of Variance:	df	SS	MS	Fs
GROUPS	1	23.91	23.91	3.47 ns
TIME	5	15290.73	3058.15	443.21***
ERROR	5	34.48	6.90	
TOTAL	11	15349.12		

C) STATION-A to GROUP-2 :

site \ date	3/16	4/ 2	4/16	4/30	5/13	5/26	TOTAL.
STATION-A	100.00	70.78	6.71	6.33	5.27	2.66	191.75
GROUP- 2	100.00	80.98	17.91	16.37	14.53	10.16	239.95
TOTAL	200;00	151.76	24.62	22.70	19.80	12.82	431.70

Source of Variance:	df	SS	MS	Fs
STATION-A & GROUP-2	1	193.60	193.60	22.75**
TIME	5	16824.05	3364.81	395.40***
ERROR	5	42.55	8.51	
TOTAL	11	17060.20		

APPENDIX-3 : Two-way ANOVA without replication for " Total lipid content".

A) STATION-A to STATION-B:

site \ date:	3/16	4/ 2	4/16	4/30	5/13	5/26	TOTAL
STATION-A	100.00	82.07	69.54	33.85	94.10	96.71	476.27
STATION-B	100.00	90.05	83.66	30.93	76.17	87.42	468.23
TOTAL	200.00	172.12	153.20	64.78	170.27	184.13	994.45

Source of Variance:	df	SS	MS	Fs
STATIONS	1	5.39	5.39	0.08^{ns}
TIME	5	5753.84	1150.77	17.21**
ERROR	5	334.30	66.86	
TOTAL	11	6093.53		

B) GROUP-1 to GROUP-2 :

site \ date:	3/16	4/ 2	4/16	4/30	5/13	5/26	TOTAL.
GROUP-1	100.00	116.62	27.51	29.51	100.83	134.88	509.35
GROUP-2	100.00	101.43	24.42	26.27	71.45	111.95	435.52
TOTAL	200.00	218.05	51.93	55.78	172.28	246.83	944.87

Source of Variance:	df	SS	MS	Fs
GROUPS	1	454.24	454.24	6.21^{ns}
TIME	5	17581.42	3516.28	48.09***
ERROR	5	365.61	73.12	
TOTAL	11	18401.27		

C) STATION-A to GROUP-2 :

site \ date:	3/16	4/ 2	4/16	4/30	5/13	5/26	TOTAL.
STATION-A	100.00	82.07	69.54	33.85	94.10	96.71	476.27
GROUP-2	100;00	101.43	24.42	26.27	71.45	111.95	435.52
TOTAL	200.00	183.50	93.96	60.12	165.55	208.66	911.79

Source of Variance:	df	SS	MS	Fs
STATION-A & GROUP-2	1	138.38	138.38	0.47^{ns}
TIME	5	9250.39	1850.08	6.30*
ERROR	5	1468.29	239.66	
TOTAL	11	10857.06		

APPENDIX-4: Two-way ANOVA without replication for " Protein content".

A) STATION-A to STATION-B:

site \ date:	3/16	4/ 2	4/16	4/30	5/13	5/26	TOTAL.
STATION-A	100.00	99.37	92.47	87.03	112.34	200.63	691.84
STATION-B	100.00	75.73	67.36	57.53	73.85	223.85	598.32
TOTAL	200.00	175.10	159.83	144.56	186.19	424.48	1290.16

Source of Variance:	df	SS	MS	Fs
STATIONS	1	728.83	728.83	0.111^{ns}
TIME	5	27267.21	5453.44	0.832^{ns}
ERROR	5	1311.30	6556.50	
TOTAL	11	2907.34		

B) GROUP-1 to GROUP-2:

site \ date:	3/16	4/ 2	4/16	4/30	5/13	5/26	TOTAL.
GROUP-1	100.00	171.34	178.24	164.64	150.84	298.33	1063.39
GROUP-2	100.00	234.10	237.24	232.43	209.00	217.36	1230.13
TOTAL	200.00	405.44	415.48	397.07	359.84	515.69	2293.52

Source of Variance:	df	SS	MS	Fs
GROUPS	1	2316.84	2316.84	1.326^{ns}
TIME	5	26692.57	133462.85	76.366^{***}
ERROR	5	8738.41	1747.68	
TOTAL	11	37747.82		

C) STATION-A to GROUP-2:

site \ date:	3/16	4/ 2	4/16	4/30	5/13	5/26	TOTAL.
STATION-A	100.00	99.37	92.47	87.03	112.34	200.63	691.84
GROUP-2	100.00	234.10	237.24	232.43	209.00	217.36	1230.13
TOTAL	200.00	333.47	329.71	319.46	321.34	417.99	1921.97

Source of Variance:	df	SS	MS	Fs
STATION-A & GROUP-2	1	24146.34	24146.34	17.778^{**}
TIME	5	12139.61	2427.92	1.788^{ns}
ERROR	5	6791.04	1358.21	
TOTAL	11	43076.99		

APPENDIX-5: Two-way ANOVA without replication for " Carbohydrate content ".

A) STATION-A to STATION-B:

site \ date:	3/16	4/ 2	4/16	4/30	5/13	5/26	TOTAL.
STATION-A	100.00	94.04	16.78	5.45	6.84	8.76	231.87
STATION-B	100.00	68.65	30.24	8.24	6.48	7.73	221.34
TOTAL	200.00	162.69	47.02	13.69	13.32	16.49	453.21

Source of Variance:	df	SS	MS	Fs
STATIONS	1	9.24	9.24	0.113^{ns}
TIME	5	17541.23	3508.25	42.978***
ERROR	5	408.16	81.63	
TOTAL	11	17958.63		

B) GROUP-1 to GROUP-2:

site \ date:	3/16	4/ 2	4/16	4/30	5/13	5/26	TOTAL.
GROUP-1	100.00	83.81	11.04	3.61	8.90	9.49	216.85
GROUP-2	100.00	98.53	8.17	3.31	5.67	8.46	224.14
TOTAL	200.00	182.34	19.21	6.92	14.57	17.95	440.99

Source of Variance:	df	SS	MS	Fs
GROUPS	1	4.42	4.42	0.194^{ns}
TIME	5	20893.62	4178.72	183.551***
ERROR	5	113.83	22.766	
TOTAL	11	21011.87		

C) STATION-A to GROUP-2:

site \ date:	3/16	4/ 2	4/16	4/30	5/13	5/26	TOTAL.
STATION-A	100.00	94.04	16.78	5.45	6.84	8.76	231.87
GROUP-2	100.00	98.53	8.17	3.31	5.67	8.46	224.14
TOTAL	200.00	192.57	24.97	8.76	12.51	17.22	456.01

Source of Variance:	df	SS	MS	Fs
STATION-A & GROUP-2	1	4.98	4.98	0.50^{ns}
TIME	5	21788.98	4357.80	434.48***
ERROR	5	50.17	10.03	
TOTAL	11	21839.15		

APPENDIX-6: Two-way ANOVA without replication for " Total Chlorophyll Content ".

A) STATION-A to STATION-B:

site \ date:	3/16	4/ 2	4/16	4/30	5/13	5/26	TOTAL.
STATION-A	100.00	55.16	45.37	37.70	26.86	24.94	290.03
STATION-B	100.00	55.92	44.70	31.80	27.15	25.56	285.13
TOTAL	200.00	111.08	90.07	69.50	54.01	50.50	575.16

Source of Variance:	df	SS	MS	Fs
STATIONS	1	2.00	2.00	0.619^{ns}
TIME	5	7807.06	1561.41	483.409***
ERROR	5	16.15	3.23	
TOTAL	11	7825.21		

B) GROUP-1 to GROUP-2:

site \ date:	3/16	4/ 2	4/16	4/30	5/13	5/26	TOTAL;
GROUP-1	100.00	35.01	34.68	34.25	32.61	24.70	261.25
GROUP-2	100.00	40.48	32.04	30.22	24.13	23,45	250.32
TOTAL	200.00	75.49	66.72	64.47	56.74	48.15	511.57

Source of Variance:	df	SS	MS	Fs
GROUPS	1	9.95	9.95	0.933^{Ns}
TIME	5	8113.61	1622.72	152.111***
ERROR	5	53.34	10.668	
TOTAL	11	8176.90		

C) STATION-A to GROUP-2:

site \ date:	3/16	4/ 2	4/16	4/30	5/13	5/26	TOTAL.
STATION-A	100.00	55.16	45.37	37.70	26.86	24.94	290.03
GROUP-2	100.00	40.48	32.04	30.22	24.13	23.45	250.32
TOTAL	200.00	95.64	77.41	67.92	50.99	48.39	540.35

Source of Variance :	df	SS	MS	Fs
STATION-A & GROUP-2	1	131.41	131.41	0.041^{ns}
TIME	5	8015.50	1603.10	0.4953^{ns}
ERROR	5	16184.60	3236.92	
TOTAL	11	24331.51		

APPENDIX- 7: Two-way ANOVA without replication for " Amino Acid concentration ".

A) STATION-A to STATION-B:

site \ date:	3/16	4/ 2	4/16	4/30	5/13	5/26	TOTAL.
STATION-A	100.00	142.53	87.56	32.13	62.44	21.95	446.61
STATION-B	100.00	145.25	117.87	26.70	80.77	54.53	525.12
TOTAL	200.00	287.78	205.43	58.83	143.21	76.48	971.73

Source of Variance:	df	SS	MS	Fs
STATIONS	1	513.65	513.65	3.875^{ns}
TIME	5	18730.77	3746.15	28.258^{**}
ERROR	5	662.85	132.57	
TOTAL	11	19907.27		

B) GROUP-1 to GROUP-2:

site \ date:	3/16	4/ 2	4/16	4/30	5/13	5/26	TOTAL.
GROUP-1	100.00	92.76	124.21	24.21	34.39	9.50	385.07
GROUP-2	100.00	128.05	125.34	26.47	20.59	10.18	410.63
TOTAL	200.00	220.81	249.55	50.68	54.98	19.68	795.70

Source of Variance:	df	SS	MS	Fs
GROUPS	1	54.44	54.44	0.408^{ns}
TIME	5	25743.87	5148.77	38.603^{***}
ERROR	5	666.89	133.378	
TOTAL	11	26465.20		

C) STATION-A to GROUP-2:

site \ date:	3/16	4/ 2	4/16	4/30	5/13	5/26	TOTAL.
STATION-A	100.00	142.53	87.56	32.13	62.44	21.95	446.61
GROUP-2	100.00	128.05	125.34	26.47	20.59	10.18	410.63
TOTAL	200.00	270.58	212.90	58.60	83.03	32.13	857.24

Source of Variance:	df	SS	MS	Fs
STATION-A & GROUP-2	1	107.88	107.88	0.303^{ns}
TIME	5	23711.75	4742.35	13.325^{**}
ERROR	5	1779.48	355.896	
TOTAL	11	25491.23		

APPENDIX- 8: Two-way ANOVA without replication for " Caloric Content ".

A) STATION-A to STATION-B:

site \ date:	3/16	4/ 2	4/16	4/30	5/13	5/26	TOTAL.
STATION-A	100.00	76.05	85.35	103.95	117.91	119.53	602.79
STATION-B	100.00	70.00	80.00	90.70	109.30	119.07	569.07
TOTAL	200.00	146.05	165.35	194.65	227.21	238.60	1171.86

Source of Variance:	df	SS	MS	Fs
STATIONS	1	94.76	94.76	7.545^{ns}
TIME	5	3119.11	623.82	49.667***
ERROR	5	62.80	12.56	
TOTAL	11	3276.67		

B) GROUP-1 to GROUP-2:

site \ date:	3/16	4/ 2	4/16	4/30	5/13	5/26	TOTAL.
GROUP-1	100.00	54.42	80.00	96.05	91.63	98.61	520.71
GROUP-2	100.00	64.42	76.98	107.44	79.07	90.23	518.14
TOTAL	200.00	118.84	156.98	203.49	170.70	188.84	1038.85

Source of Variance:	df	SS	MS	Fs
GROUPS	1	0.55	0.55	0.012^{ns}
TIME	5	2552.335	510.47	10.961*
ERROR	5	232.86	46.57	
TOTAL	11	2785.75		

C) STATION-A to GROUP-2:

site \ date:	3/16	4/ 2	4/16	4/30	5/13	5/26	TOTAL.
STATION-A	100.00	76.05	85.35	103.95	117.91	119.53	602.79
GROUP-2	100.00	64.42	76.98	107.44	79.07	90.23	518.14
TOTAL	200.00	140.47	162.33	211.33	196.98	209.76	1120.93

Source of Variance:	df	SS	MS	Fs
STATION-A & GROUP-2	1	597.13	597.13	4.295^{ns}
TIME	5	2077.48	415.50	2.989^{ns}
ERROR	5	695.13	139.03	
TOTAL	11	3369.74		

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Section 1, Article 2

A Study of the Thermal Effects on the Growth of Manatee Grass *Cymodoceum manatorum*

Jeff Robert Salituri

1975

A STUDY OF THE THERMAL EFFECTS ON THE GROWTH OF MANATEE GRASS (*Cymodocea manatorum*)

by

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B.S. in Oceanography, Florida Institute of Technology, 1973

Submitted to the Graduate Faculty
in partial fulfillment of
the requirements for the degree of
Master of Science
in
Oceanography

Florida Institute of Technology
1975

Jeff Salituri
(Signature)

ABSTRACT

Growth of the sea grass, Cymodocea manatorum, was studied in the Indian River, Brevard County, Florida, where the thermal effects of the effluent cooling water of a utilities plant were a factor. Chemical and physical parameters of the water and substrate were measured, along with growth, between February and May, 1975. A parallel study was carried out in a control site, where artificial thermal effects were absent.

Growth of the sea grass was observed to increase with temperature up to 29°C in all areas. At this temperature, a brown alga bloom occurred. The smothering effects of this alga caused a decrease in the growth of the sea grass. It was also observed that the sea grass, which was not covered with alga, continued to show an increase in growth with temperature, up to the maximum temperature reached during the study, of 34.1°C. From the data collected during the investigation and other factors affected by increasing temperatures, it was concluded that the net annual effect of increasing temperatures on manatee grass in the area of the power plant jetty was to reduce the net productivity of the grass.

The harvesting of the grass was accomplished by digging with a shovel, a measured area, at each site. By this method, both leaves and sub-substrate growth were measured, without hindering the leaf production for future growth and measurement.

ACKNOWLEDGMENTS

I would like to extend my thanks to certain individuals who have aided me in both studies and research. Dr. J.A. Lasater, my committee chairman and advisor, was extremely helpful in assisting me in my selection of this topic and throughout my research and investigation process. I would also like to thank Dr. K.B. Clark and Dr. O.von Zweck for their assistance and suggestions which smoothed out some of the problems which came up from time to time. Mr. Jim Gallatin also deserves a note of thanks for his patience and helpful cooperation along with the others at the Orlando Utilities Commission.

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I. INTRODUCTION

Along much of the coastline bordering temperate and tropical seas extend vast marine seagrass beds. These beds have long been recognized for their importance as nursery and breeding grounds for many species of fish and invertebrates, including some of the most important commercial species (Hoese, 1960; Wood, 1959). In spite of this, little work has been done on the basic ecology of the beds.

The Florida coastline extends over 3,000 miles, and includes warm-temperature, sub-tropical zones. Portions of the Florida peninsula are bordered by barrier islands, offshore keys and a wide shallow sandy continental shelf. The barrier islands shelter the waters of the near-shore shallows from the affects of the Florida Current, creating warm quiet saline lagoons, which are favorable habitats for submerged plants and extensive diverse populations of vertebrates and invertebrates.

Numerous authors have recorded animals feeding on the live grass. Randall (1965, 1967) stated the most important fishes feeding on sea grasses are members of the Scaridae, Sparidae, Monocanthidae, and several surgeonfishes (Acanthuridae) of the genus Acanthurus. Biotic processes, accomplished primarily by bacteria and fungi, decompose plant materials into their component nutrients, feeding the bacteria and fungi and releasing other nutrient

materials into the surrounding waters where they become the primary food source for other marine animals (Phillips, 1960). Because of the food supply made available by decomposition, seagrass beds are nurseries and feeding grounds for young fish and shrimp, as well as for countless populations of small marine animals such as the Polychaeta, Holothuria, Amphipoda, and Mollusca. The nutrients released into the water by decaying seagrass support a large plankton population, which in turn supports an abundance of larger animals, and so on up the food chain. If the food producer is eliminated, the absence affects organisms progressively up the pyramid until the pinnacle, man in this instance, is reached (Phillips, 1960).

A problem in the evaluation of the effects of grazing on seagrasses arises in that many animals graze on the epiphytic algae and leave the grass untouched. Some of these animals will occasionally eat the grass also, but the extent of this ingestion is unknown. This problem is further complicated because little is known about the ability of these animals to assimilate the fresh seagrass. Still, despite some grazing by animals, the majority of the blades remain untouched until they die or are torn from the plant by the movement of the water (Zieman, 1968). These loose leaves eventually decay and are thereby converted into detritus.

The four most common and important of the Florida seagrasses, as determined by Phillips (1960), are Thalassia testudinum Konig, Cymodocea manatorum Aschers (or Syringodium filiforme Kutz), Diplanthera wrightii Aschers (or Halodule wrightii Aschers), and Ruppia maritima L. Cymodocea manatorum is the dominant species in the study area.

Cymodocea manatorum has characteristically rather robust rhizomes, with two to four slightly branched or unbranched roots and short erect stem bearing two to three leaves at each node (figure 1). Internodes are one to five centimeters. Leaf sheaths are wide and two and a half to six centimeters long. Leaf blades are 10 to 30 centimeters long, one half to two millimeters wide and narrowed at the base (den Hartog, 1970). In areas of high salinity Cymodocea is usually seen interspersed with Thalassia testudinum. Cymodocea occurs in polyhaline and euryhaline coastal waters. It is completely restricted to the sublittoral belt, as its stiff, brittle leaves cannot resist desiccation. Cymodocea manatorum forms closed vegetation from mean low water springs down to at least six meters in depth. Feldmann (1936) reported growth of this grass at a depth of 25 meters. The depth to which the closed Cymodocea beds descend is largely dependent on the clarity of the water. In Florida, the lagoonal Cymodocea beds obtain their greatest density at a depth between two thirds and one and one half meters (Phillips, 1960). This species shows no

Figure 1. Cymodocea manatorum (Manatee grass) (Phillips, 1960)

preference for a particular substrate, as it is found in substrates of soft black mud to hard-packed sand. The growth is most luxuriant on the soft and mixed bottoms.

It is of importance to determine the effects of temperature increases on the growth of manatee grass (Cymodocea manatorum) because of the growing number of electric power stations that are adding heat to estuaries. It has been estimated that the demand for power station cooling water is doubling every ten years and by the year 1980 about 32 per cent of all existing power stations will be located adjacent to estuaries (Picton, 1960).

Thermal effects on the growth of Cymodocea manatorum will be investigated in this study in an attempt to establish a relationship between increased water temperatures and grass growth.

II. STATEMENT AND AREA OF INVESTIGATION

The purpose of this thesis is to study how the growth of manatee grass is affected by increasing water temperature. According to Phillips (1960), the possible adverse effects of very warm water on leaves of manatee grass are unknown.

Chemical and physical parameters, such as temperature, dissolved oxygen, pH, nutrients, turbidity, salinity, soil analysis, as well as growth of the grass were measured in two areas, with one area serving as a control. Except for temperature, these measurements were taken monthly, for four months, between February 8, 1975 and May 31, 1975. Temperature was recorded on a daily basis.

The area selected for primary sampling was the area just southeast of the effluent canal of the Orlando Utilities Commission Plant on the Indian River in Titusville, Florida (figure 2). It is located at 28°9'10" north latitude and 80°46'30" west longitude. This particular site was selected because manatee grass beds are abundant within this area and the water temperature ranges above the average temperature of the lagoon due to the utility plant's coolant water discharge. Manatee grass, which grows primarily along the shallow portions of the Indian River, is found abundantly adjacent to the jetty located just southeast of the utility plant's discharge canal. Five sample sites were selected along the

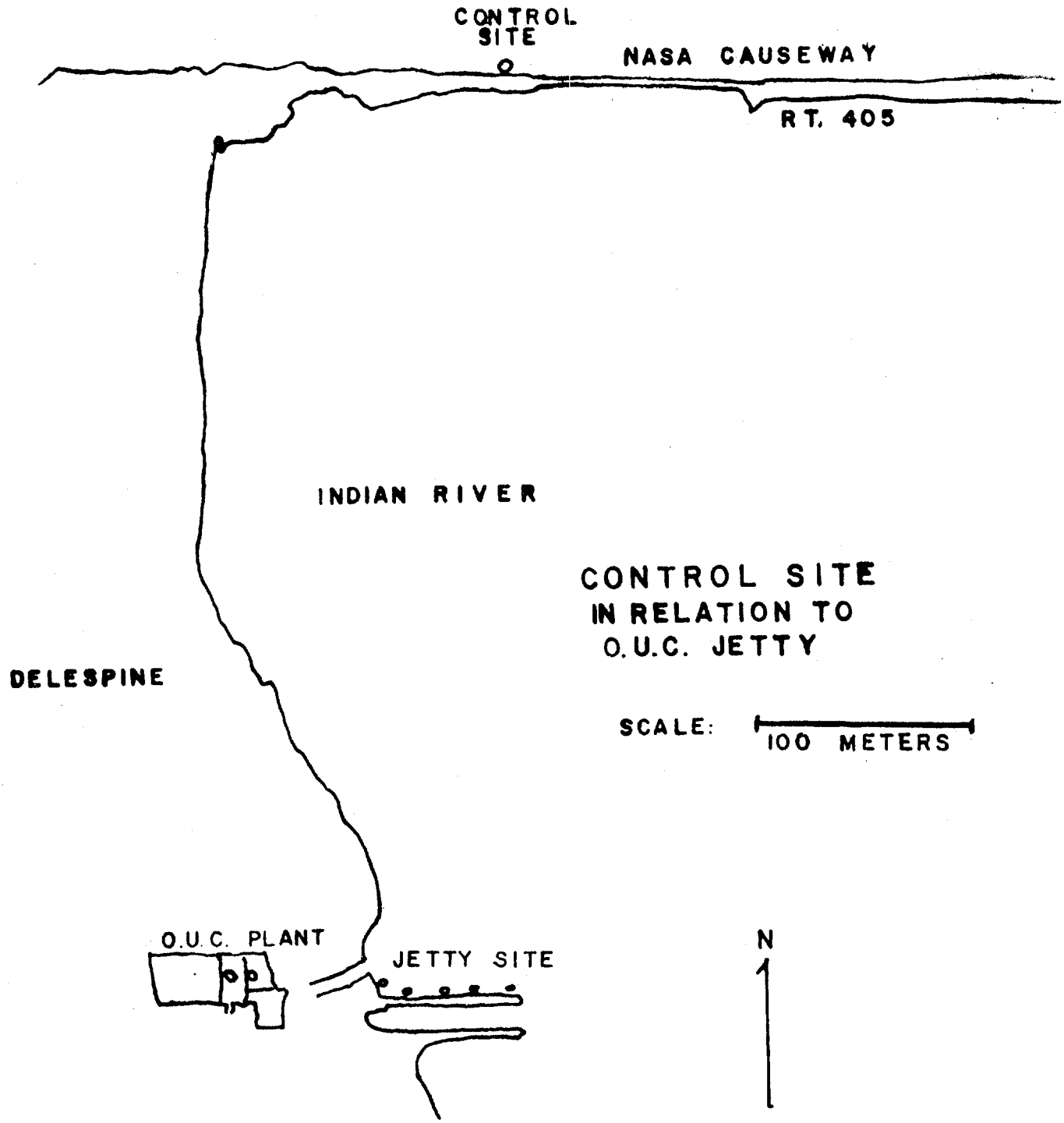


Figure 2. Total Investigation Area Showing Jetty and Control Sites

north side of the jetty from the western to the eastern end approximately 15 meters apart (figure 3). The mean water depth in the area of sampling during the period of sampling, February to May, 1975, was 27.5 centimeters.

The area selected as the control site was an area on the northwest side of the NASA Causeway (Route 405), three miles north of the jetty (figure 2). It is located at 28°31'40" north latitude and 80°46'20" west longitude. This area was selected because of the abundant manatee grass beds found and the absence of artificially heated water affecting the grass. Sampling was carried out at this site to measure the growth of Cymodocea in the natural temperatures of the water. Three sample sites were selected in this area approximately 12 meters apart. Their mean water depth was 28 centimeters.

Both sites are protected from violent water movement or disturbance by surrounding small islands and land masses. Existing water movement is wind-driven in character and of an insignificant amount, as shown by dye testing. There was no measurable tidal component.

Because of the somewhat "heated" water that flows through the canal at the utility plant, it was hoped to obtain an optimum temperature range where growth of this grass reaches its maximum in this area. If the nutrients and other measured parameters are changed little by the power plant operation, as compared to the control site, but an

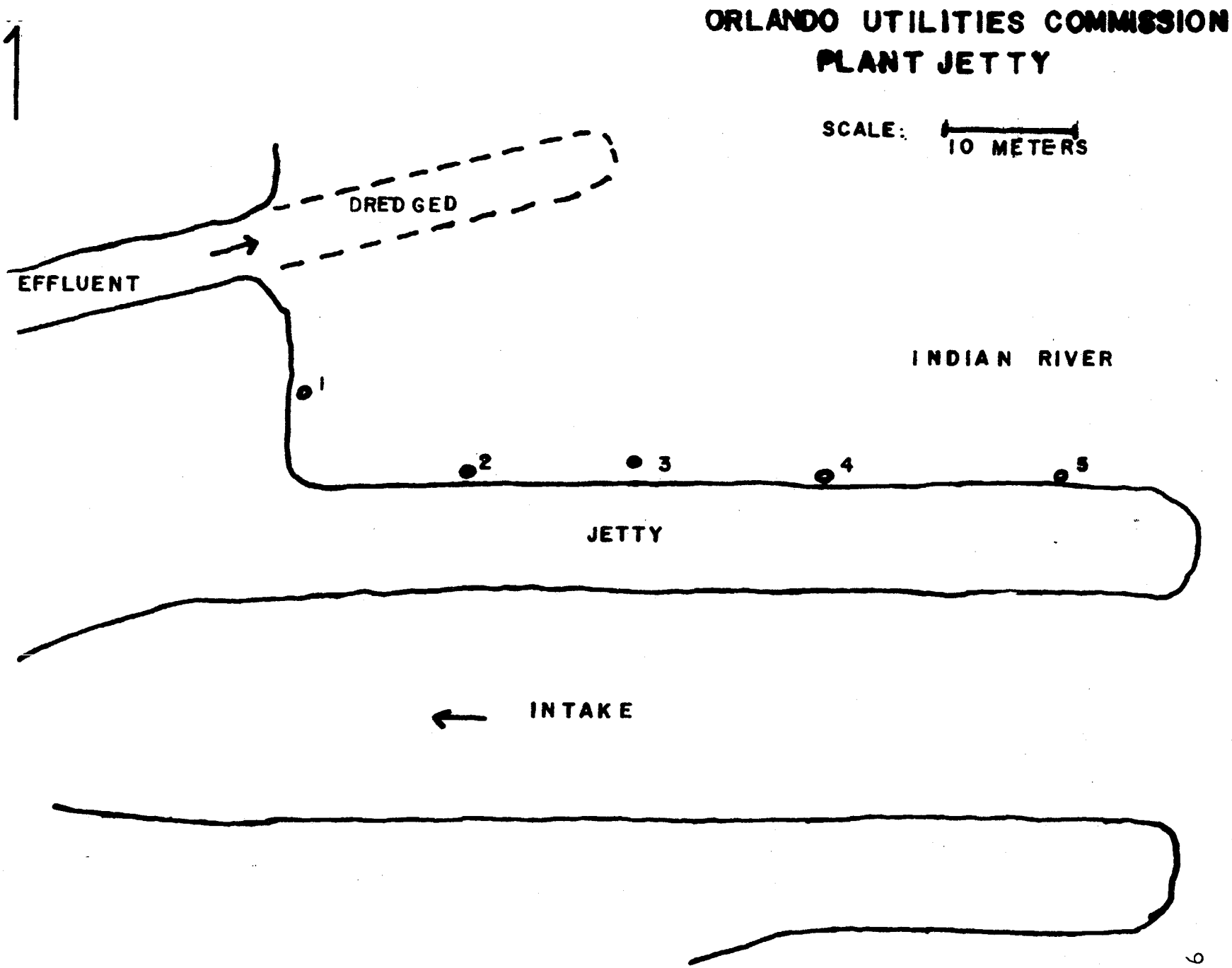


Figure 3. Five Sample Sites Along the Jetty

increase in temperature is shown, then the effect of a temperature increase on the growth of the grass may be defined.

The data derived from the measurements of the parameters at each site are examined statistically for correlation and comparability between the two sampling areas.

Sample Date	Jetty	Control
Feb. 8	27.5	28
Mar. 8	27.5	28
April 5	27.5	28
May 3	27.5	28
May 31	27.5	28

Table 1. Average Depth - centimeters

III. METHODS AND MATERIALS

A. Harvesting and Weighing

Grass was harvested at each sample site using a shovel to collect a sample of 26 centimeters by 22 centimeters. This method allows the harvesting and measurement of subsurface growth as well as leaf growth and eliminates the problem of fluctuating sediment depth. This method of harvest is more efficient than blade clipping because, as shown in Phillips' (1960) paper, blade clipping for growth measurements inhibits the growth in leaf reproduction.

The harvesting method employed during this investigation allows for comparison of dry weight of the total plants from uniform grass beds on each sampling date. This comparison shows the amount of grass growth which has taken place between respective sampling dates.

Samples were washed of all soil, algae and epiphytes, and their wet weights were recorded prior to being dried in an oven at 105°C. The dry weight per square meter was then recorded. The time from harvesting to drying was kept to three to four hours, so little or no weight would be lost due to decomposition and chemical change.

Weighing was carried out to thousandths of a gram but rounded off to tenths of a gram in the final tabulations. The average weight calculated from the weights measured at

each site was recorded for the jetty site and the control site.

B. Temperature

Temperatures at the jetty site were recorded on a continuous basis by the Orlando Utilities Commission at the point where the effluent canal discharges into the river. This temperature was also measured along the jetty and was consistently the same. The temperature data received from the Commission were on a daily maximum-minimum basis, from which average daily temperatures and average monthly temperatures were calculated.

Temperatures at the control site were measured with a stem thermometer, in situ, on each sampling date. The average temperature between each sampling date was assumed to be the average temperature of the two consecutive dates measured.

C. Dissolved Oxygen

Dissolved oxygen was measured for each sample site on each sampling date. Water samples were taken in sunlight, about three hours after sunrise, on respective sampling dates. Dissolved oxygen was measured in the lab within two hours of the sampling. The samples were shielded from sunlight to minimize any change in the actual dissolved oxygen that was present at the sample sites. Measurement was in accordance with the modified Winkler titration, as described in Standard Methods For Water and Wastewater Analysis, 13th

Edition.

Dissolved oxygen was measured in parts per million (ppm). The average dissolved oxygen was calculated for the jetty site and the control site for each sampling date.

Measurement of dissolved oxygen was taken primarily to establish the similarity of conditions, except for temperature, at the jetty and control sites.

D. pH

pH was measured for each sample site on each sampling date. pH was measured in the lab using a glass electrode and a standard buffer solution of 7.0. The average pH was calculated for the jetty site and the control site for each sampling date. pH measurement was taken primarily to establish the similarity of conditions, except for temperature, at the jetty and control sites.

E. Nutrients

Orthophosphate and nitrate nitrogen of the water were measured for each sample site on each sampling date. These nutrients were measured in the lab using Hach chemicals and the Spectrometer 20. For orthophosphates, the Phos Ver III method was used. This method is a modification of Murphy and Riley (1962) as given in Analytical Chimica Acta (1962). For nitrate nitrogen, the Nitra Ver IV, Cadmium

reduction method was employed, using no dilution as referred to in Standard Methods. Nitrite nitrogen was not detectable. Both the orthophosphate and nitrate nitrogen were measured in parts per million (ppm). The average for each of these nutrients was calculated for the jetty site and the control site for each sampling date. These measurements were taken primarily to establish the similarity of conditions at the jetty and control sites.

F. Turbidity

Turbidity was measured for each sample site on each sampling date. Turbidity was measured in the lab using the Spectrometer 20 and following the Formazin Standard method, as referred to in Standard Methods. Turbidity was measured in Jackson units. The average turbidity was calculated for the jetty site and the control site for each sampling date. Turbidity, along with depth, plays a part in determining both the quality and quantity of available light needed for photosynthesis. This measurement was taken primarily to establish the similarity of conditions at the jetty and control sites.

G. Salinity

Salinity was measured at each sample site on each sampling date. Salinity was measured with an optical

salinometer. The optical salinometer has been found accurate to plus or minus one part per thousand, (‰), in daily use (Lasater and Carey, 1974). This accuracy is quite adequate for brackish water such as we are dealing with, with a salinity of approximately 23‰. It has been found that the sea grass Zostera marina shows a high tolerance to different salinity and temperature (Biebl, 1971). The average salinity was calculated for the jetty site and the control site for each sampling date. This measurement was taken primarily to establish the closeness in the conditions of the jetty site and the control site.

H. Sieve Analysis

A grain size sieve analysis was done on 800.0 grams of soil from both the jetty and the control sites on May 20, 1975. This grain size analysis was used in an attempt to determine the relative proportions of the different grain sizes which make up the given soil mass. A sieve analysis consists of shaking a soil sample through a stack of wire screens with openings of known size. The particle diameter is defined as the dimension of the size of the screen hole upon which the particle is retained. The apparatus needed were a set of sieves (numbers 20, 40, 60, 80, 100 and 200), a sieve shaker, brush, balance, and drying oven. This analysis was done primarily to establish the closeness in

the substrate conditions of the jetty site and the control site.

IV. RESULTS

A. Effects of Temperature on Growth

At the beginning of this investigation, the temperature of the water at the jetty site was 10°C warmer than the water temperature measured at the control site. The average weight of the grass samples harvested was approximately 35 per cent heavier at the jetty site. By March 8, 1975, the second sampling date, the average temperature at the control was 19°C and the average temperature at the jetty site was 26.5°C, a difference of 7.5°C. The weight of grass harvested increased at both sites, but showed a considerably greater increase at the control site, where the temperature increase was also greater (tables 2 and 3). By April 5, 1975, the third sampling date, the average temperature at the jetty continued to increase, but the average temperature measured at the control site showed a decrease of 3°C. This temperature decrease to 16°C apparently caused a decrease in the growth of the grass at the control site. The growth at the jetty site was highest during this period, where the average temperature was 28.4°C (tables 2 and 3 and figures 3 and 4). By May 5, 1975, the fourth sampling date, the average at the jetty site continued to increase steadily to 30.3°C, but the average temperature at the control increased by 11 degrees, to 27.0°C, by far the largest increase shown between any sampling dates. At the control site, the harvest

Sampling Date	Jetty	Control
Feb. 8	24	14
Mar. 8	26.5	19
April 5	28.4	16
May 3	30.3	27
May 31	34.1	29

Table 2. Average Temperature - °C

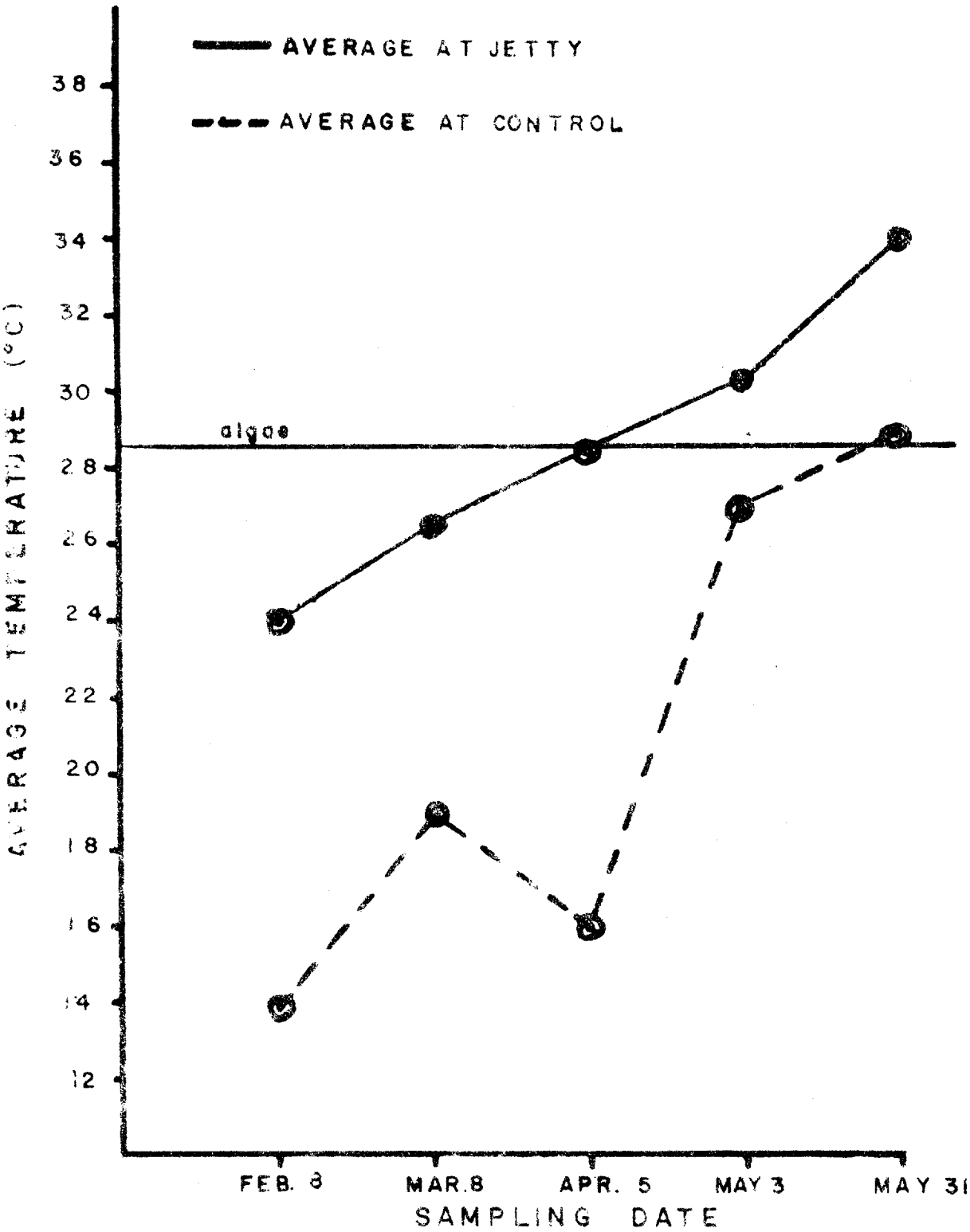


Figure 4. Average Monthly Temperature

Sampling Date	Jetty		Control	
	A	B	A	B
Feb. 8	96.9	---	61.4	---
Mar. 8	133.9	+38.3	157.3	+156.3
April 5	249.3	+86.1	188.8	+ 20.0
May 3	215.0*	-14.0*	381.1	+101.8
May 31	176.1*	-18.1*	367.1*	- 3.7

* algal growth present

Table 3. A. Average dry weight of Cymodocea harvest - gm/m^2

B. Per cent growth since previous harvest

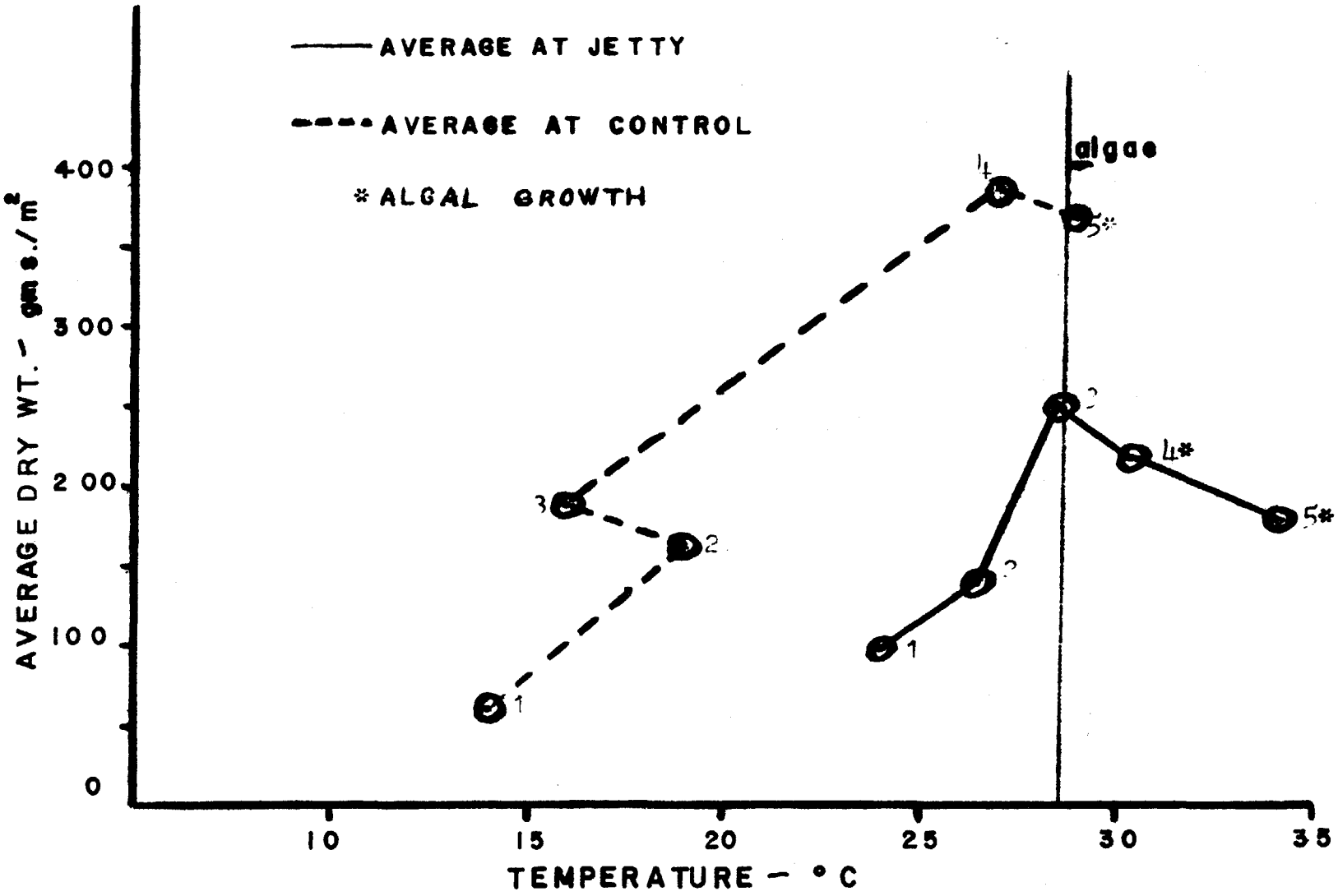


Figure 5. Average Dry Wt. vs. Average Temperature on Each Sample Date (numbered)

of grass showed its highest increase in growth, showing a 101.8 per cent increase in growth since the previous harvest (figure 5). The growth at the jetty site, although an increase in temperature was recorded, decreased 14.0 per cent.

A reddish-brown algae growth was seen covering much of the grass beds at all sample sites at the jetty on the fourth sampling date. This alga was identified as Hypnea cervicornis of the family Hypneaceae (Taylor, 1972). Hypnea are bushy with lateral, terete branches. These plants are small to moderate in size and form tangled tufts and extensive, rather fragile, reddish or bleached mats. The chief axes grow 2 to 15 centimeters long. Hypnea cervicornis is common to quite shallow water and occurs redder and more compact in relatively exposed places. Hypnea has been found in Bermuda, Florida, Texas, Mexico, Cuba, Cayman Islands, St. Barthelemy, Guadeloupe, Martinique, British Honduras, Panama, Columbia, Netherlands Antilles, Venezuela, and Brazil (Taylor, 1972).

By May 31, the fifth and last sampling date, the average temperature increased to 34.1°C at the jetty site and 29.0°C at the control site. The alga growth continued to increase and the grass growth continued to decrease by 18.1 per cent at the jetty site. The same alga, Hypnea cervicornis was, for the first time, seen growing on the grass at the control site. As a result, although an increase in temperature was recorded, the growth of the grass decreased 3.7 per cent (figures 4 and 5, tables 2 and 3).

Throughout the sampling, no flowering or fruiting of the Cymodocea occurred at either site. It has been suspected that a decline in the number of new blades is a result of the transfer into flower and fruit production of the energy normally used to produce new blades (Zieman, 1968). This was not the case during this investigation.

B. Dissolved Oxygen

Dissolved oxygen was measured to parts per million (ppm). From February 8 to April 5, the first three samplings, the dissolved oxygen content at the jetty sites and the control sites remained close to each other and at a constant per cent supersation level of 8.0 to 9.2 parts per million (figure 6 and table 4). The normal saturation level for water of salinity and temperature encountered during this investigation is approximately five to six parts per million. On May 3 and May 31, the measured dissolved oxygen was below the saturation level, at approximately 4.3 ppm. This is assumed to be due to the introduction of the reddish-brown alga present and the increased temperature. This alga, while producing a small amount of oxygen itself, shields the sunlight from the grasses, resulting in a net decrease in photosynthetic oxygen production. The dissolved oxygen content decreased, although to a lesser degree, at the control site as well. Here on May 3 the average dissolved oxygen content was 5.9 ppm, still above the saturation level. On May 31

Sampling Date	Jetty	Control
Feb. 8	8.10	8.50
Mar. 8	8.10	8.00
April 5	8.92	9.20
May 3	4.38	5.90
May 31	4.30	5.60

Table 4. Average Dissolved Oxygen - ppm

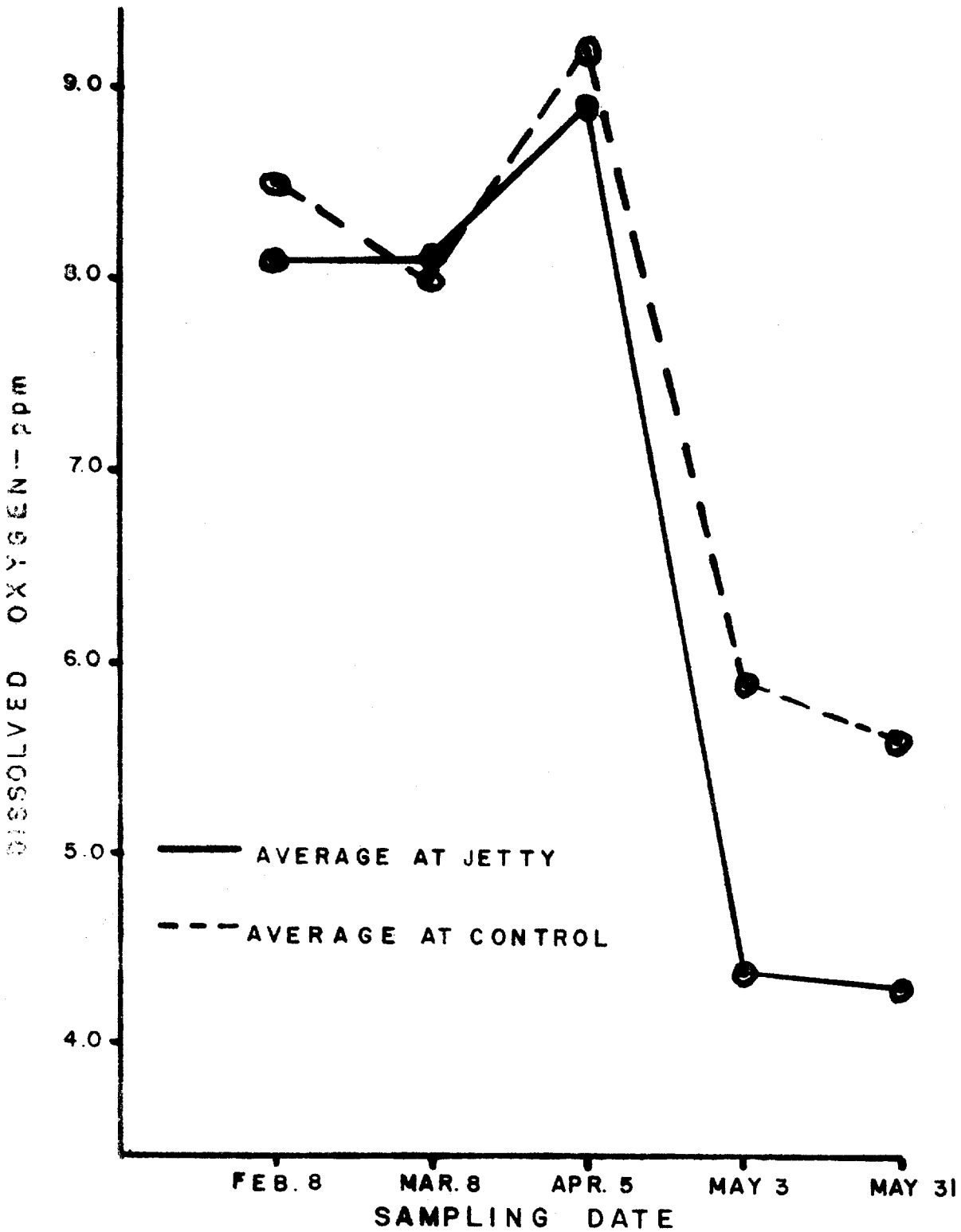


Figure 6. Monthly Changes in Dissolved Oxygen

the average dissolved oxygen level showed a continued decrease to 5.6 ppm. This smaller decrease in dissolved oxygen seen at the control site, as compared to that at the jetty site, seems to be due to the cooler water and thus the later introduction of the algae growing in this area.

C. pH

The mean values for pH were 9.6 in February, 8.8 in March, 8.9 in April, 7.2 in May at the jetty site. The values for pH at the control site were within two tenths of those measured at the jetty site at each date (figure 7 and table 5).

Sampling Date	Jetty	Control
Feb. 8	8.0	8.0
Mar. 8	9.6	9.5
April 5	8.8	8.8
May 3	8.9	9.1
May 31	7.2	7.2

Table 5. Average pH

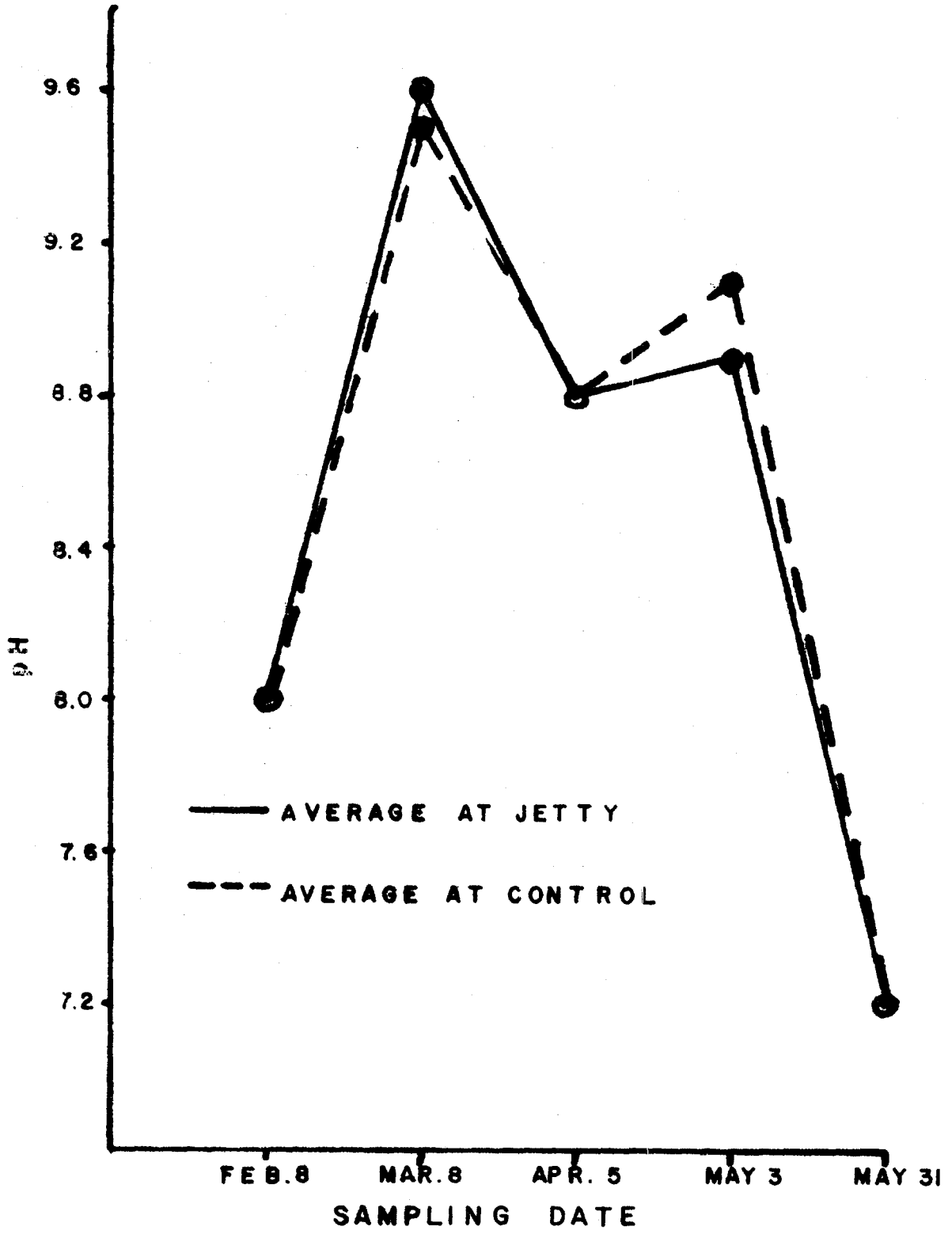


Figure 7. Monthly Changes in pH

D. Nutrients

The mean values of orthophosphate concentration at the jetty site were 0.12 ppm in February, 0.06 ppm in March, 0.09 ppm in April, and 0.11 ppm in May. The values of orthophosphate at the control sites were within one one hundredth of a part per million of those measured at the jetty site on the respective dates (figure 8 and table 6).

On the sampling dates of February 8 and March 8, nitrate nitrogen was not detectable at the jetty site or the control site. In the month of March, the mean value of nitrate nitrogen was 0.07 ppm at the jetty site and 0.10 at the control site. The mean values for April were 0.06 and 0.04 ppm at the jetty and control sites respectively, and for May, 0.09 and 0.10 ppm (figure 9 and table 7). These nutrient concentrations, combined with favorable dissolved oxygen levels and increasing temperatures and sunlight, are conditions suitable for the growth of those algae which have the ability to fix nitrogen as they require it (Lasater and Carey, 1974).

E. Turbidity

The turbidity of the water at the sample sites was exceptionally low throughout the investigation. The range at the jetty sites was from 20.8 to 34 Jackson Units. The mean values at the control site were within 4.8 Jackson

Sampling Date	Jetty	Control
Feb. 8	0.10	0.12
Mar. 8	0.12	0.12
April 5	0.06	0.06
May 3	0.09	0.10
May 31	0.11	0.12

Table 6. Average Phosphate - ppm

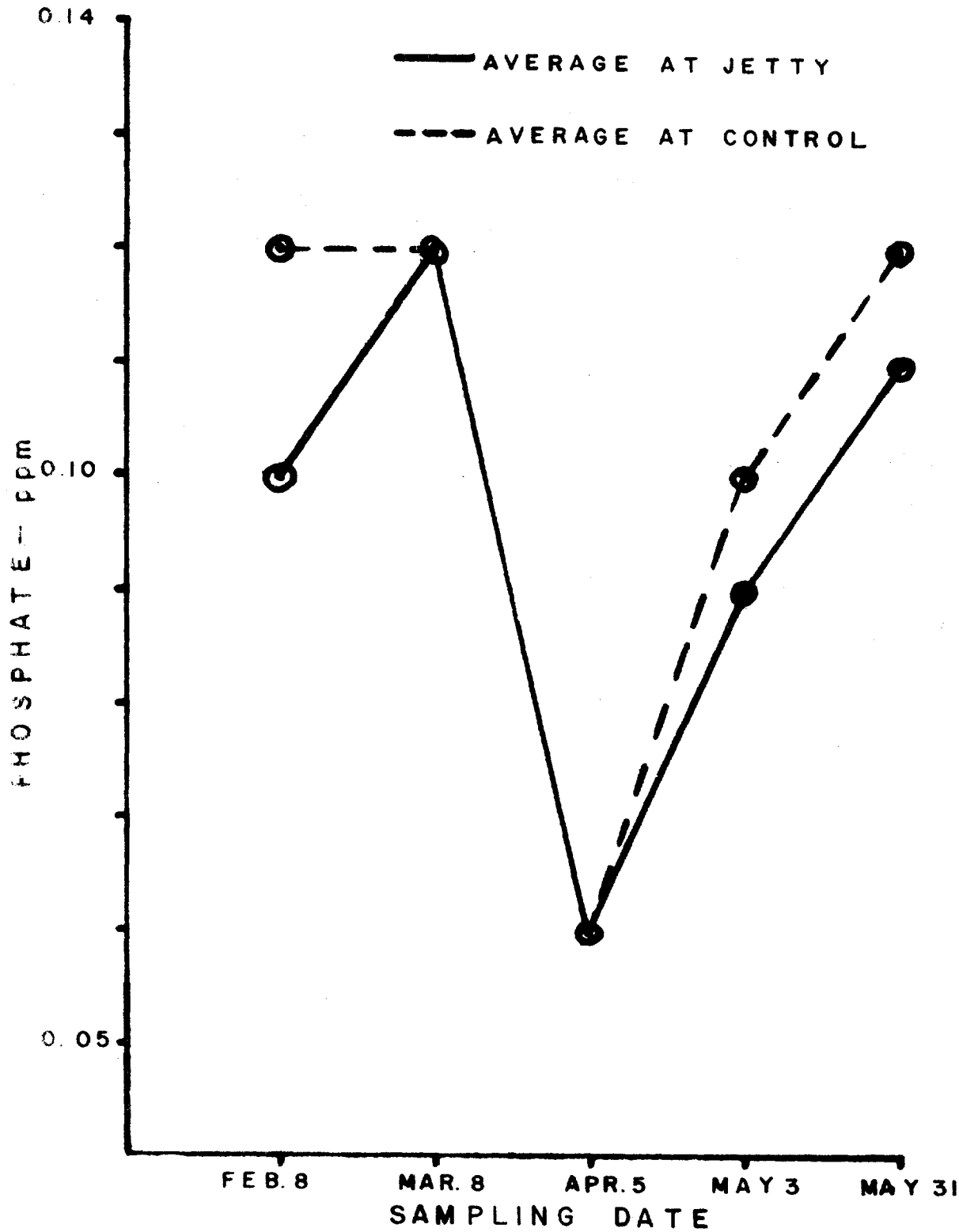


Figure 8. Monthly Changes in Phosphate

Sampling Date	Jetty	Control
Feb. 8	*	*
Mar. 8	*	*
April 5	0.07	0.10
May 3	0.06	0.04
May 31	0.09	0.10

* not detectable

Table 7. Average Nitrate Nitrogen - ppm

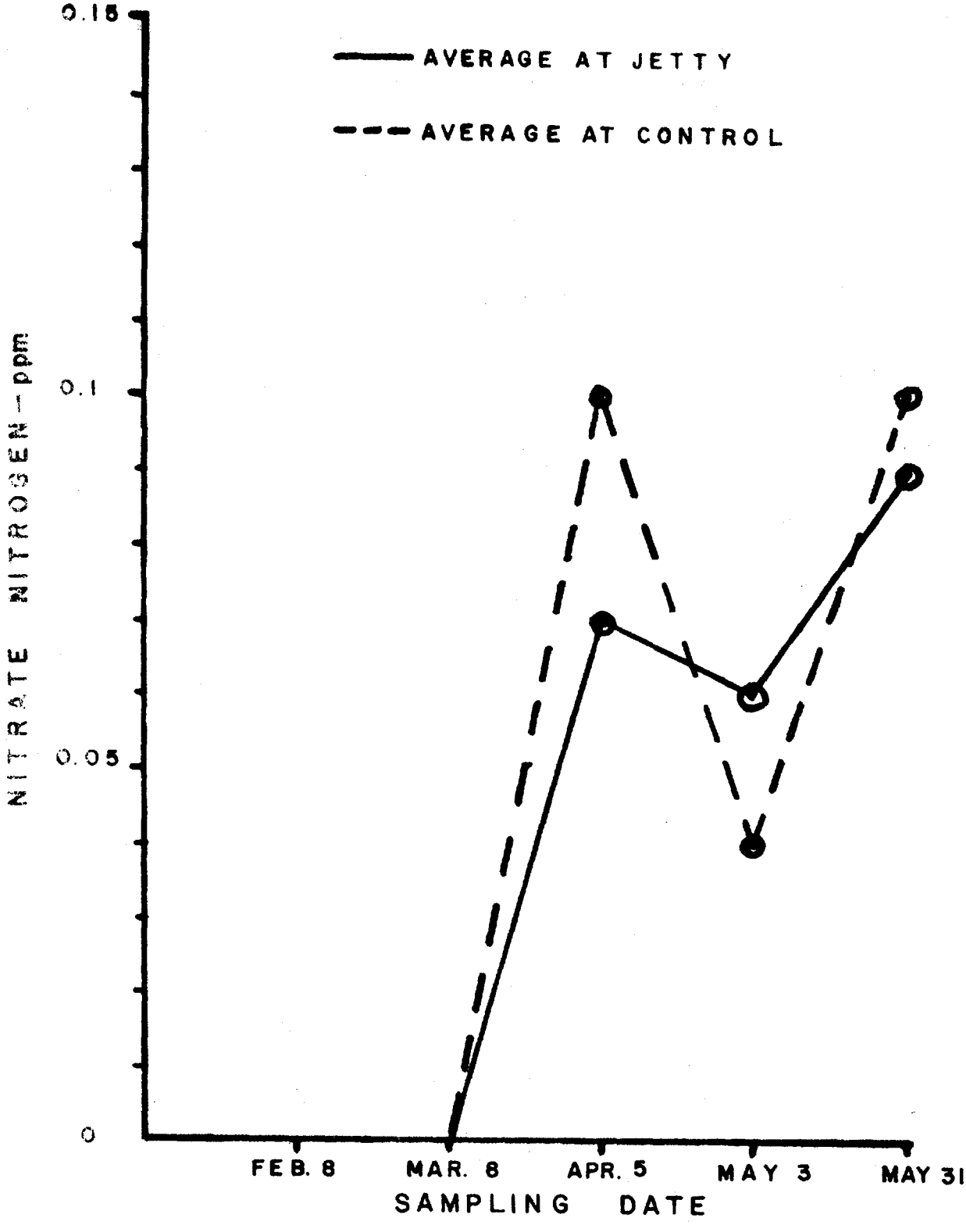


Figure 9. Monthly Changes in Nitrate Nitrogen

Units of those measured at the jetty site on respective sampling dates (table 8 and figure 10). Because of the clarity and the shallow depth of the water, sufficient light penetration was possible for the normal photosynthesis of the grass.

F. Salinity

The range of salinity was quite narrow throughout the investigation at both the jetty and control sites. The range at the jetty sites was from 22.0 to 24.6 ‰. The means at the control site were within 1.6 ‰ of those at the jetty site on respective sampling dates (figure 11 and table 9).

G. Sieve Analysis

For each soil sample, per cent finer by weight was ultimately calculated (tables 10 and 11). The percentage finer than any sieve size is equal to 100 per cent minus the cumulative percentage retained. These values were then plotted on a per cent finer by weight versus grain size (U.S. standard sieve size) graph, where curve A represented the soil at the control site and curve B represented the soil at the jetty site (figure 12). From this graph, the uniformity coefficient is an indication of the spread (or range) of grain sizes. The mean diameters, median diameters and effective

Sampling Date	Jetty	Control
Feb. 8	34	30
Mar. 8	20.8	20
April 5	20.8	16
May 3	25	26
May 31	27	28

Table 8. Average Turbidity - Jackson Units

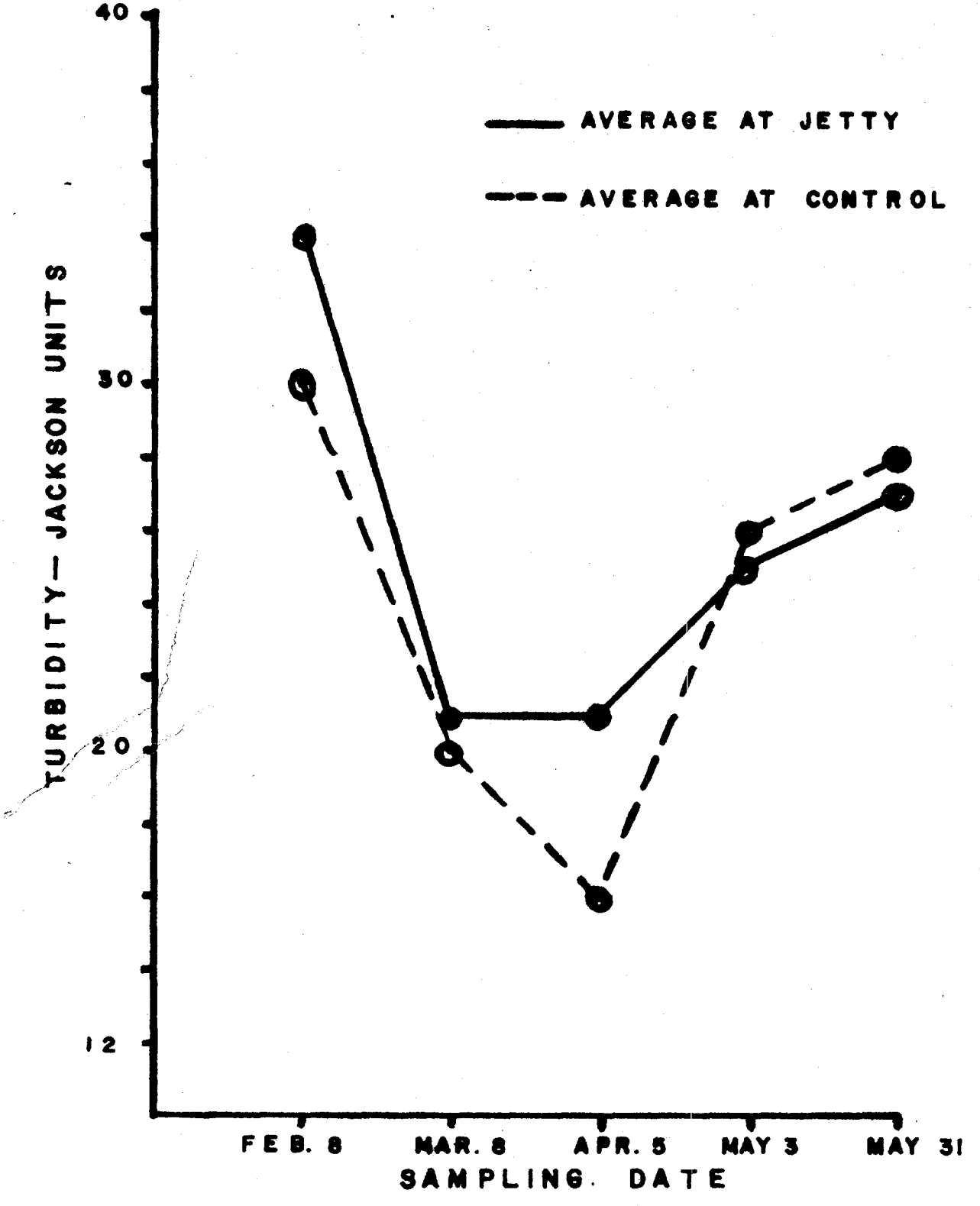


Figure 10. Monthly Changes in Turbidity

Sampling Date	Jetty	Control
Feb. 8	22.0	22.0
Mar. 8	23.4	25.0
April 5	24.6	25.0
May 3	24.3	24.0
May 31	23.5	24.0

Table 9. Average Salinity - ‰

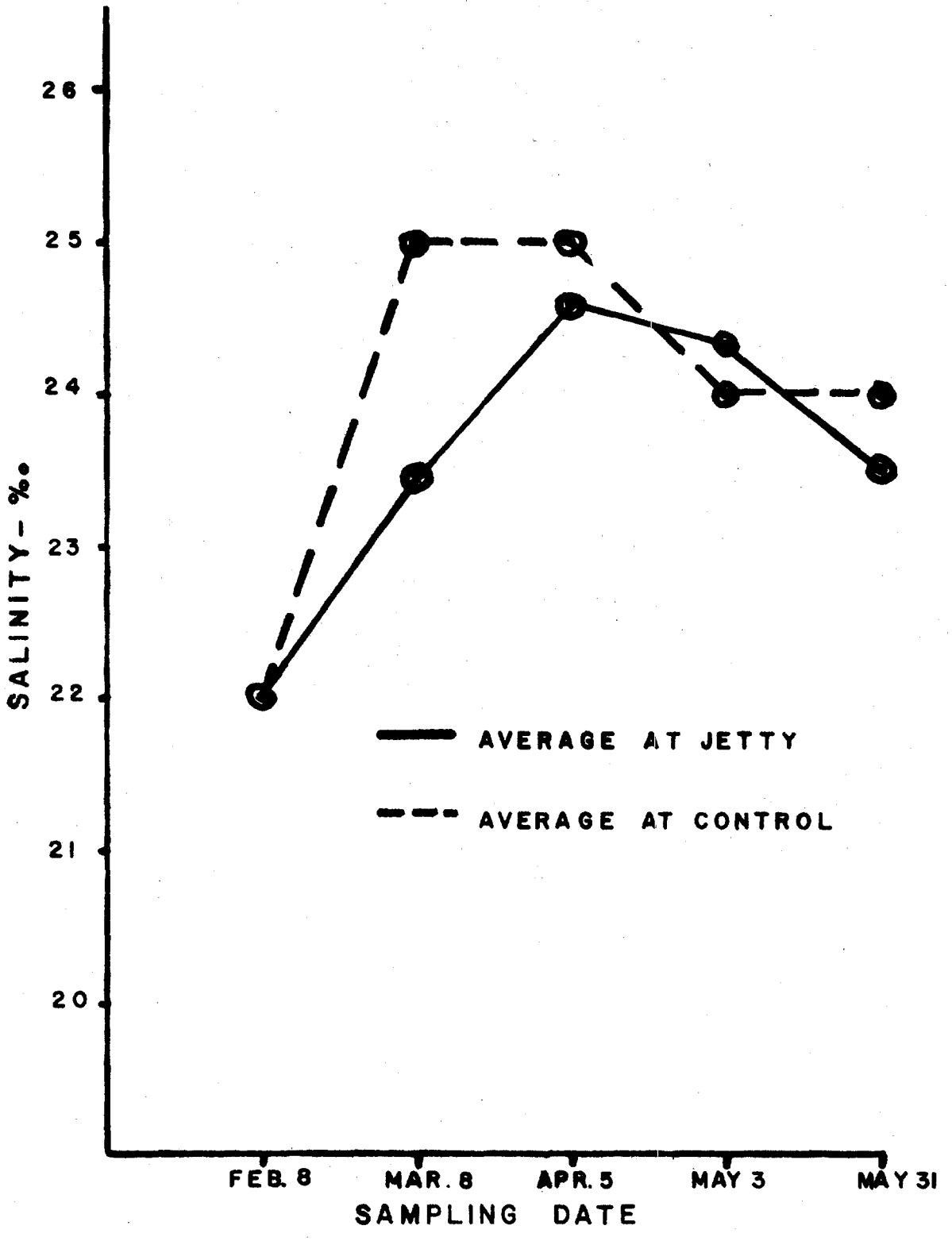


Figure 11. Monthly Changes in Salinity

SOIL MECHANICS LABORATORY

SIEVE ANALYSIS

SOIL SAMPLE

VISUAL CLASSIFICATION AND DESCRIPTION: Fine Sand --

LOCATION: Orlando Util. Comm. Plant Jetty

BORING NO.: -- SAMPLE DEPTH: 27.5 cm

SAMPLE NO.: --

SPECIFIC GRAVITY, G_s: --

SOIL SAMPLE WEIGHT

CONTAINER NO.: --

WT. CONTAINER + DRY SOIL IN g: 847.0

WT. CONTAINER IN g: 47.0

WT. DRY SOIL W_s, IN g: 800.0

TEST NO. 1

DATE: May 20, 1975

TESTED BY: J. Salituri

SIEVE NO.	SIEVE OPENING IN mm	WT. SIEVE IN g	WT. SIEVE + SOIL IN g	WT. SOIL RETAINED IN g	PERCENT RETAINED	ACCUMULATIVE PERCENT RETAINED	PERCENT FINER
20	.850	415.5	445.0	29.5	3.69	3.69	96.31
40	.425	377.0	413.5	36.5	4.56	8.25	91.75
60	.250	356.0	446.0	90.0	11.25	19.50	80.50
80	.180	358.0	504.0	146.0	18.25	37.75	62.25
100	.150	353.0	519.0	166.0	20.75	58.50	41.50
200	.075	332.0	656.0	324.0	40.50	99.00	1.00
PAN	---	480.0	488.0	8.0	1.00	100.00	---
				800.0			

REMARKS

Table 10. Jetty Site

SOIL MECHANICS LABORATORY

SIEVE ANALYSIS

SOIL SAMPLE

VISUAL CLASSIFICATION Fine Sand
AND DESCRIPTION ---
LOCATION N.W. side of NASA Causeway
BORING NO. --- SAMPLE DEPTH 28 cm
SAMPLE NO. ---
SPECIFIC GRAVITY, G_s, ---

SOIL SAMPLE WEIGHT

CONTAINER NO. ---
WT. CONTAINER + DRY SOIL IN g 847.0
WT. CONTAINER IN g 47.0
WT. DRY SOIL, W_s, IN g 800.0

TEST NO. 2
DATE May 20, 1975
TESTED BY J. Salituri

SIEVE NO.	SIEVE OPENING IN mm	WT. SIEVE IN g	WT. SIEVE + SOIL IN g	WT. SOIL RETAINED IN g	PERCENT RETAINED	ACCUMULATIVE PERCENT RETAINED	PERCENT FINER
20	.850	415.5	440.0	24.5	3.06	3.06	96.94
40	.425	377.0	412.0	35.0	4.38	7.44	92.56
60	.250	356.0	444.0	88.0	11.00	18.44	81.56
80	.180	358.0	505.5	147.5	18.44	36.88	63.12
100	.150	353.0	523.0	170.0	21.25	53.13	41.87
200	.075	332.0	662.0	330.0	41.25	99.37	.63
PAN	---	480.0	485.0	5.0	.63	100.00	--
				800.00			

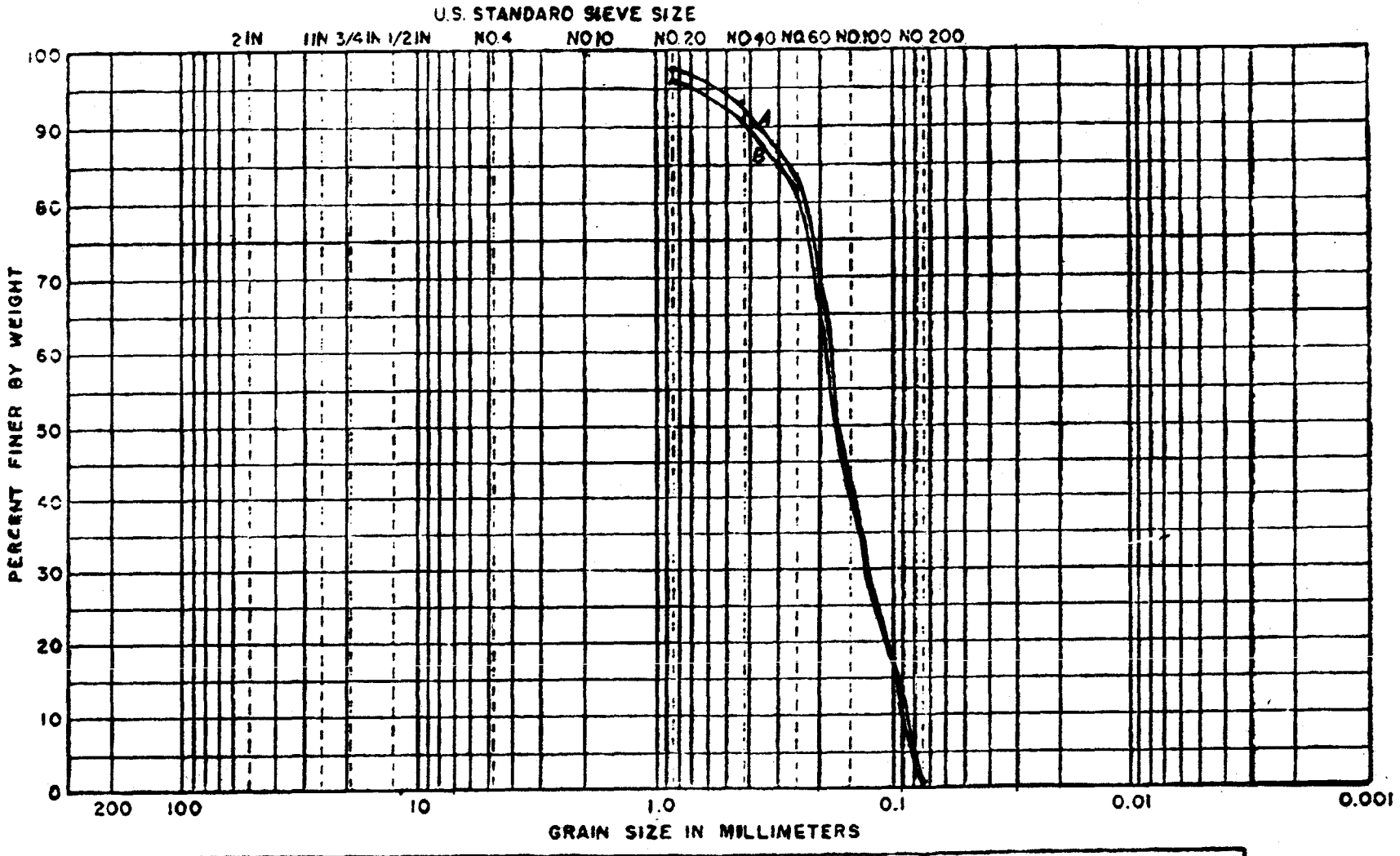
REMARKS

Table 11. Control Site

diameters were also extracted from this graph (table 12). The difference in the uniformity coefficient between the soil at the jetty site and the control site is 0.256. This difference is quite insignificant, as can be seen from the graph in figure 12. The difference in the mean diameters is 0.0075 millimeters. The difference in the median diameters is 0.005 millimeters and the effective diameters 0.009 millimeters. Looking at the curves, A and B, in figure 12, the extreme similarity between the soils of the two sample sites can be readily seen.

H. Statistical Analysis

A statistical analysis was applied to the chemical and physical parameters measured at all of the sample sites. For this analysis, the t-test was used to determine whether the differences between the average values of the parameters measured at the jetty site and the average values of the parameters measured at the control site were significant. A minimum level of significance of five per cent was established to be appropriate with four degrees of freedom. The corresponding value of t_{α} for this level of significance and degree of freedom is 2.776 (Mendenhall, 1971). A value of t was calculated using the data collected for all the parameters measured and the average values at the jetty site were compared to those at the control site (table 13). It is the hypothesis that if the value of the calculated t is



COBBLES	GRAVEL		SAND			SILT OR CLAY
	COARSE	FINE	COARSE	MEDIUM	FINE	

UNIFIED SOIL CLASSIFICATION SYSTEM

TEST NO	SYM.	MATERIAL SOURCE	REMARKS
			A - Control Site
			B - Jetty Site

Figure 12. Sieve Analysis For Jetty and Control Site Soil

	Jetty Site	Control Site
Uniformity Coefficient	2.353	2.097
Mean diameter	0.1975 mm	0.205 mm
Median diameter D_{50}	0.18 mm	0.175 mm
Effective diameter D_{10}	0.085 mm	0.094 mm

Table 12. Sieve Analysis - Jetty Site
- Control Site

greater than -2.776 and less than +2.776, then the value of the parameter at the jetty site does not deviate significantly from the value of the parameter at the control site. It can be concluded from the data shown in table 13, that all of the parameters measured are well within the limits of tolerance and can be assumed to be equal at the control site and the jetty site. We can, therefore, say that the parameters measured did not cause a difference between the growth of the manatee grass at the jetty site and the control site.

Parameter (Average Value)	Jetty $\bar{y}$	Control μ_o	s	Calculated t value
Turbidity	25.52	24	5.453	0.0623
Nitrate Nitrogen	0.0456	0.048	0.0430	0.125
Phosphate	0.0992	0.105	0.0244	0.532
Dissolved Oxygen	6.76	7.44	2.2345	0.681
pH	8.516	8.52	0.9117	0.01
Depth	27.5	28	0	
Salinity	23.55	24	1.002	1.004

$$S = \left[\frac{\sum_{i=1}^{n} y_i^2 - \left[\left(\sum_{i=1}^{n} y_i \right)^2 / n \right]}{n-1} \right]^{1/2} \quad , \text{(Mendenhall, 1971)}$$

$$t = (\bar{y} - \mu_o) \Big/ (s/(n)^{1/2}) \quad , \text{(Mendenhall, 1971)}$$

where:

s=standard deviation between sampling dates

n=number of sampling dates (5)

$\bar{y}$=average value at jetty sites

μ_o=average value at control sites

with:

level of significance=5 per cent

degree of freedom=n-1=4

Table 13. Statistical Analysis of the parameters at jetty site versus the parameters at control site, using the t-test

V. DISCUSSION

Cymodocea manatorum is widely dispersed throughout the tropics of the Caribbean Sea and thus has been considered a tropical species. It has also been shown not to be a stenothermic tropical species (Phillips, 1960). Winter water temperature observations from several stations in Florida, studied by Ronald C. Phillips, correlated with the period of leaf kill, indicate that Cymodocea leaves begin dying back when water temperature falls to approximately 20.0°C. No information has been found concerning the thermal effects on growth of manatee grass to date.

In a study done on the thermal effects on the Connecticut River, it was found that the result of exposure of the flora in the area to elevated temperatures appeared as (a) growth stimulation (increased standing crop), (b) development of synchrony in reproduction, and (c) community composition shifts (Foerster, et al., 1974).

Photosynthesis is an important factor in the growth rate of a sea grass. If the photosynthetic process is hindered, grass production will suffer. Photosynthesis is affected by gas exchange, temperature, turbidity and water depth.

Gas exchange may play an important role in control of photosynthesis in the marine system. CO_2 is much more soluble in sea water than is O_2. The solubility of O_2

decreases with increased water temperature (Slack and Clarke, 1965), as seen in tables 2 and 4. The low O_2 content would be favorable because all known types of photosynthesis function better under low O_2 concentration.

Photosynthesis increases with temperature in subtidal forms up to 30° C. At higher temperatures, photosynthesis declines sharply. Respiration increases with temperature and salinity (Biebl and Mc Roy, 1971).

During this investigation, turbidity did not have a hindering effect because of the relative clarity of the water. The water was very shallow, about 28 centimeters, so light penetration was very high.

The high concentrations of dissolved oxygen recorded were probably the result of the O_2 produced by the lagoonal benthic plants through photosynthesis, and the result of the shallow water, which favors atmospheric reaeration.

It was found by Phillips (1960) that Cymodocea manatorum requires a salinity of 20.0 to 25 parts per thousand and over. The salinity measured throughout this investigation was within this range.

The low concentrations of nutrients measured were typical for this area under these conditions (Lasater; Carey; 1974a, 1974b). It is possible and probable that the nitrogen is in organic form (Nevin and Lasater, 1972).

The technique used for the harvesting of the sea grass during this investigation was simple and proved to be

quite commendable. It could be made certain that all of the grass, both leaves and sub-substrate were harvested. Because the soil was also dug up along with the grass, the grass stayed intact until put into the plastic bags. There was, therefore, no loss of plants during the harvesting procedure. Siltation and retarded leaf production were not factors as in the blade cutting harvest procedure. This harvesting technique is recommended by the author when grass samples are needed for measurement of growth, and inspection of the plant in its entirety is required. Shallow water is a requirement for use of this technique.

Currents were not a factor in this investigation. There are no measurable currents in either the jetty site or the control site as indicated by dye testing. The waters in these areas are basically wind-driven and would be under equal conditions in both areas.

In the scope of this investigation, the algal growth, seemingly due to the rise in temperature, affected and hindered the growth of the manatee grass.

There has been evidence of thermal destruction to sea grasses in some areas as well. Biebl and Mc Roy (1971), in their study of Zostera marina, found that prolonged or frequent temperatures above 30°C could result in the destruction of the sea grass. A measurable reduction of the standing stock of eelgrass in Izembek Lagoon during the summer of 1964, was attributed to the effects of high temperatures (Mc Roy, 1966).

Each measurement was averaged, on each sample date, from five different sites at the jetty and three different sites at the control. This was done to minimize inaccuracies and to allow for more representative data.

Predation by animals, especially the manatee, was not noticed as a factor during this investigation.

VI. CONCLUSIONS

The growth rate of Cymodocea manatorum in brackish water of low turbidity is directly related to the temperature of the water. It can be seen, in figure 5, that where the temperature shows an average decrease between the second and third sampling date at the control site, growth of the grass is seen to drop off. When the temperature increase is greatest, especially when approaching the optimum temperature, the growth is greatest. It is also shown in figure 5 that the grass continued to increase in growth up to a temperature of 29°C. It was at this temperature where an algae bloom occurred. The algae which occurred at this location was identified as Hypnea cervicornis, a reddish-brown member of the family Hypneaceae. The alga covered much of the grass, acting as a light barrier, decreasing the sunlight supply and lowering the dissolved oxygen content. It is possible that the alga also acted as a barrier to an efficient gas exchange process. This reduction in the photosynthetic process resulted in a decrease in grass growth. It must also be stated that the blades of the grass that did remain, probably due to the natural selection process, were not only larger but continued to grow with the temperature in excess of 34°C. This grass was limited as shown in the drastic decrease in overall growth shown in figure 5. It is concluded, therefore that the destruction of the grass was not due directly to the

temperature level over 29°C, but due to the hindering effects of the alga which seems to undergo a bloom at this temperature in conjunction with the conditions present in the lagoon during this time.

The parameters measured, dissolved oxygen, pH, orthophosphates and nitrate nitrogen, turbidity and salinity, although showing some change at times, did not vary significantly between the jetty site and the control site. Temperature did vary significantly between these sites, which allows a relationship between temperature and grass growth to be defined.

Temperatures will increase in future months in both locations due to solar radiation. Due to the heat added by the power plant, the water temperatures at the jetty site will always be higher than those at the control site. As these temperatures increase over 30°C, photosynthesis will decrease. This will cause a reduction in the grass' productivity. With increasing temperatures, the metabolisms of the animals in the area will increase. This increase results in a higher food requirement for these animals which graze on the sea grass, resulting in a net reduction in the grass' biomass. During the late autumn months, when the temperatures begin to decrease in this area, the growth of the sea grass will increase. Due to the decreasing water temperatures, Manatees will be attracted to the warmer waters along the jetty where they graze, quite efficiently,

on the Cymodocea grass beds. Again the result will be a reduction in the grass' biomass.

Figure 5 shows that the net productivity of the grass at the jetty site, where the temperatures are higher than those at the control site, is less than the net productivity of the grass at the control site during the time of the investigation.

It can therefore be concluded that, on an annual basis, the net effect of the increasing temperatures in the area of the jetty reduces the net productivity of the sea grass, Cymodocea manatorum.

By running a sieve analysis on the soil from both the jetty site and the control site, it was concluded that the types of soil at each site were not factors affecting growth between the two sites.

The method of harvest can be considered an effective one when total and complete plant samples are required without damage to the plants and minimum upset to the rest of the grass bed. This method is recommended only in shallow water with low turbidity.

APPENDIX

Project: Thermal Effects on Growth of Manatee Grass Date of Sampling: Feb. 8, 1975

Location: Titusville, Florida Specific Area: Orlando Utilities Comm. Jetty

Site	Depth cm.	Sal. ‰	D.O. ppm	pH	Nitrate Nit. ppm	Phos-phate ppm	Turb. Jackson Units	Net Wet Wt. gms/ 572 cm^2	Net Dry Wt.gms/ 572 cm^2	Net Dry Weight gms/m^2			
1	27.5	22	8.0	8.0	0	.10	44	31.5	5.0	87.4			
2	27.5	22	8.0	8.0	0	.12	32	64.0	8.6	150.3			
3	27.5	22	7.5	8.1	0	.10	32	19.7	3.0	52.4			
4	27.5	22	7.5	8.0	0	.12	36	35.2	6.0	104.9			
5	27.5	22	9.5	8.3	0	.10	26	39.5	5.1	89.6			
CONTROL	SITES												
1	28	22	8.5	8.0	0	.12	30	9.4	3.5	61.4			
2	28	22	8.5	8.0	0	.13	28	11.0	3.1	54.2			
3	28	22	8.5	8.0	0	.11	32	14.9	3.9	68.2			

Appendix 1

Project: Thermal Effects on Growth of Manatee Grass Date of Sampling: March 8, 1975

Location: Titusville, Florida Specific Area: Orlando Utilities Comm. Jetty

Site	Depth cm.	Sal. ‰	D.O. ppm	pH	Nitrate Nit. ppm	Phos-phate ppm	Turb. Jackson Units	Net Wet Wt. gms/572 cm^2	Net Dry Wt. gms/572 cm^2	Net Dry Weight gms/m^2
1	27.5	24	7.5	9.6	0	.14	20	56.1	6.1	106.6
2	27.5	23	8.0	9.6	0	.13	20	127.4	12.6	220.3
3	27.5	24	8.5	9.6	0	.16	20	42.0	5.1	89.2
4	27.5	23	8.0	9.6	0	.12	22	64.0	9.0	157.3
5	27.5	23	8.5	9.6	0	.08	22	32.9	5.5	96.2
CONTROL		SITES								
1	28	25	8.0	9.6	0	.13	20	47.7	9.0	157.3
2	28	25	8.2	9.5	0	.12	20	66.0	9.2	160.8
3	28	25	7.8	9.5	0	.11	20	59.9	8.8	153.8

Appendix 2

Florida Institute of Technology — Oceanographic Data Sheet

Project: Thermal Effects on Growth of Manatee Grass — Date of Sampling: April 5, 1975

Location: Titusville, Florida — Specific Area: Orlando Utilities Comm. Jetty

Site	Depth cm.	Sal. ‰	D.O. ppm	pH	Nitrate Nit. ppm	Phos-phate ppm	Turb. Jackson Units	Net Wet Wt. gms/572 cm^2	Net Dry Wt.gms/572 cm^2	Net Dry Weight gms/m^2
1	27.5	24	9.6	8.8	.06	.06	22	91.9	20.7	361.9
2	27.5	25	8.6	8.8	.09	.08	22	99.7	18.2	318.2
3	27.5	25	8.0	8.8	.08	.07	20	60.1	12.7	222.0
4	27.5	25	9.3	8.8	.08	.06	20	63.4	12.2	213.3
5	27.5	24	9.1	8.8	.08	.04	20	49.4	7.5	131.1
CONTROL	SITES									
1	28	25	9.1	8.8	.10	.05	18	61.5	10.8	188.8
2	28	25	9.2	8.8	.10	.06	16	56.0	10.5	183.6
3	28	25	9.3	8.8	.10	.07	14	64.9	11.1	194.1

Appendix 3

Project: Thermal Effects on Growth of Manatee Grass Date of Sampling: May 3, 1975

Location: Titusville, Florida Specific Area: Orlando Utilities Comm. Jetty

* algal growth ** no samples taken because of stingrays at site

Site	Depth cm.	Sal. ‰	D.O. ppm	pH	Nitrate Nit. ppm	Phos-phate ppm	Turb. Jackson Units	Net Wet Wt. gms/ 572 cm	Net Dry Wt.gms/ 572 cm^2	Net Dry Weight gms/m^2
*1	27.5	25	4.0	8.9	.06	.06	32	38.9	6.3	110.1
2	27.5	24	4.2	8.9	.06	.10	20	105.0	20.8	363.6
*3	27.5	24	4.5	8.9	.06	.10	26	67.1	11.3	197.5
*4	27.5	24	4.8	8.9	.06	.10	22	53.3	10.8	188.9
**5										
CONTROL SITES										
1	28	24	5.9	9.1	.04	.10	26	127.3	21.8	381.1
2	28	24	6.1	9.1	.04	.10	28	116.0	20.2	353.1
3	28	24	5.7	9.1	.04	.10	24	119.9	23.4	409.1

Florida Institute of Technology — Oceanographic Data Sheet.

Project: Thermal Effects on Growth of Manatee Grass — Date of Sampling: May 31, 1975

Location: Titusville, Florida — Specific Area: Orlando Utilities Comm. Jetty

* algal growth ** no samples taken because of stingrays at site

Site	Depth cm.	Sal. ‰	D.O. ppm	pH	Nitrate Nit. ppm	Phos-phate ppm	Turb. Jackson Units	Net Wet Wt. gms/ 572 cm^2	Net Dry Wt.gms/ 572 cm^2	Net Dry Weight gms/m^2
*1	27.5	24	4.1	7.2	.09	.20	30	53.8	9.0	157.3
*2	27.5	24	4.4	7.2	.09	.08	26	76.7	12.3	215.0
*3	27.5	22	4.2	7.2	.09	.08	26	44.6	4.2	73.4
**4										
*5	27.5	24	4.5	7.2	.09	.06	26	84.5	14.8	258.7
CONTROL		SITES								
*1	28	24	5.6	7.2	.10	.10	28	87.6	21.0	367.1
*2	28	24	5.7	7.2	.10	.14	28	76.0	20.0	349.6
*3	28	24	5.5	7.2	.10	.12	28	84.9	22.0	384.6

Appendix 5

Date	Discharge Temp.(°F) Max.	Min.	Daily Average	(2/9-3/7) Period Average °F	°C	Average Flow gal./min.x10^5
				79.7	26.5	5.21
Feb. 9	83	73	78			
10	83	75	79			
11	79	75	77			
12	82	74	78			
13	81	75	78			
14	78	73	75.5			
15	80	73	76.5			
16	83	76	79.5			
17	84	76	80			
18	84	78	81			
19	89	78	83.5			
20	83	79	81			
21	86	78	82			
22	89	78	83.5			
23	86	82	84			
24	90	80	85			
25	86	77	81.5			
26	83	75	79			
27	82	75	78.5			
28	80	75	77.5			
Mar. 1	78	74	76			
2	80	73	76.5			
3	*	*	*			
4	*	*	*			
5	*	*	*			
6	*	*	*			
7	*	*	*			

* Recorder Failure

Appendix 6. Orlando Utilities Commission Cooling Discharge Water Daily Temperature Data - 1975

Date	Discharge Temp.(°F) Max.	Min.	Daily Average
Mar. 8	*	*	*
9	*	*	*
10	*	*	*
11	*	*	*
12	*	*	*
13	89	78	83.5
14	86	79	82.5
15	84	78	81
16	86	77	82.5
17	90	79	84.5
18	89	78	83.5
19	89	80	84.5
20	81	76	78.5
21	85	76	80.5
22	86	77	81.5
23	82	78	80
24	89	80	84.5
25	88	80	84
26	85	78	81.5
27	84	75	79.5
28	87	79	83
29	85	79	82
30	84	78	81
31	87	79	83
April 1	88	79	83.5
2	97	81	89
3	97	88	92.5
4	90	79	84.5

(3/8-4/4) Period Average: 83.1 °F, 28.4 °C

Average Flow, gal./min.x10^5: 5.21

* Recorder Failure

Appendix 7. Orlando Utilities Commission Cooling Discharge Water Daily Temperature Data - 1975

Date	Discharge Temp.(°F) Max.	Min.	Daily Average	(4/5-5/2) Period Average °F	°C	Average Flow gal./min.x10^5
				86.5	30.3	5.21
April 5	84	76	80			
6	83	75	79			
7	88	76	82			
8	94	78	86			
9	94	81	87.5			
10	94	83	88.5			
11	91	85	88			
12	89	84	86.5			
13	86	80	83			
14	95	82	88.5			
15	94	85	89.5			
16	89	82	85.5			
17	89	81	85			
18	94	83	88.5			
19	95	82	88.5			
20	96	83	89.5			
21	92	83	87.5			
22	92	83	87.5			
23	85	80	82.5			
24	86	79	82.5			
25	87	79	83			
26	88	80	84			
27	91	82	86.5			
28	92	86	89			
29	94	86	90			
30	95	82	88.5			
May 1	99	86	92.5			
2	101	86	93.5			

Appendix 8. Orlando Utilities Commission Cooling Discharge Water Daily Temperature Data - 1975

Date	Discharge Temp.(°F) Max.	Min.	Daily Average	(5/3-5/31) Period Average °F	°C	Average Flow gal./min.x10^5
				93.4	34.1	5.21
May 3	99	89	94			
4	97	88	92.5			
5	98	87	92.5			
6	98	86	92			
7	97	88	92.5			
8	98	88	93			
9	100	88	94			
10	97	89	93			
11	95	86	90.5			
12	98	86	92			
13	98	89	93.5			
14	99	86	92.5			
15	94	89	91.5			
16	92	87	89.5			
17	94	86	90			
18	96	87	91.5			
19	98	89	93.5			
20	98	89	93.5			
21	99	90	94.5			
22	100	89	94.5			
23	103	90	96.5			
24	101	90	95.5			
25	100	91	95.5			
26	102	91	96.5			
27	100	92	96			
28	101	92	96.5			
29	97	90	93.5			
30	98	88	93			
31	99	89	94			

Appendix 9. Orlando Utilities Commission Cooling Discharge Water Daily Temperature Data - 1975

1. Uniformity coefficient = $\frac{D_{60}}{D_{10}}$

Jetty site: $\frac{D_{60}}{D_{10}} = \frac{0.2}{.085} = 2.353$

Control site: $\frac{D_{60}}{D_{10}} = \frac{0.195}{0.093} = 2.097$

2. Mean diameter = $\frac{1}{2}(D_{16} + D_{85})$

Jetty site: $\frac{1}{2}(D_{16} + D_{85}) = \frac{1}{2}(0.095 + 0.300) = 0.1975$ mm

Control site: $\frac{1}{2}(D_{16} + D_{85}) = \frac{1}{2}(0.11 + 0.300) = 0.205$ mm

3. Per cent Retained = $\frac{\text{weight of Soil Retained}}{\text{total soil weight}}$ x 100%

D_{60} = Diameter in mm of the particles where the per cent finer is 60%.

Appendix 10. Calculations for Soil Analysis

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Section 1, Article 3

Benthic Species Diversity and Environmental Stability in the Northern Indian River, Florida

John R. Thomas

1974

BENTHIC SPECIES DIVERSITY AND ENVIRONMENTAL STABILITY IN THE NORTHERN INDIAN RIVER, FLORIDA

by

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B.Sc. in Biology, Dickinson College, 1966

Submitted to the Graduate Faculty

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Master of Science

in

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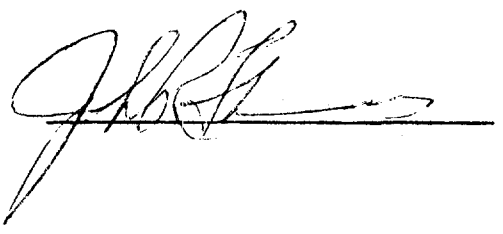

John R. Thomas
Oceanography

BENTHIC SPECIES DIVERSITY AND ENVIRONMENTAL STABILITY IN THE NORTHERN INDIAN RIVER, FLORIDA

Major Advisor: K.B. Clark

Species diversity in the benthic community of an evaporite estuary on the Florida east coast is examined for the summer of 1973. Samples were taken along a transect using a .05m^2 Ponar grab. Variations in species richness and evenness components of diversity were determined using several indices. Analysis of variance was used to determine variations in environmental parameters including temperature, dissolved oxygen, salinity, pH, and redox potential. Species richness and evenness were found to vary inversely when both were compared to water depth and species richness was found to correlate strongly with the redox potential of the sediments. Depth served to buffer the community from variations in temperature and dissolved oxygen but the availability of oxygen as interpreted from the redox

potential appears to play a greater role in determining species diversity than does the environmental stability.

Where oxygen was abundant, species were found to be closely coupled to their total environment as seen in trophic interactions and resource utilization by deposit feeders.

A biological indicator is proposed to aid in determination of sediment instability with respect to dredging activities. This indicator is used to demonstrate the apparent long term effects of the dredging of a navigational channel in this estuary.

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I. INTRODUCTION

A. Background

The research described in this paper was conducted as part of an ecological baseline study on the waters in and around the Kennedy Space Center, Merritt Island, Florida. The combined efforts of the Departments of Oceanography and Biological Sciences were focused on the assessment of biological, chemical, and physical water quality in terms of those parameters that are likely to be affected by man's activities.

Water quality is reflected in the species composition and diversity, population density, and physiological condition of indigenous communities of aquatic organisms (Standard Methods for the Examination of Water and Wastewater, 1971). Perhaps the most important reason for including the sampling of acquatic organisms in a water quality study is that they act as natural monitors. Aquatic organisms respond to their total environment. When that environment is stressed, organisms that cannot tolerate the stress are destroyed and the composition of the aquatic community changes. In general the use of biological indicators may reveal more about water quality than chemical analysis alone. Even the most specific chemical analysis can only indicate instantaneous conditions, whereas organisms used as indicators can represent

conditions extant over a period of months (Stein and Denison, 1967). It is important to recognize that biological assessment does not replace physical and chemical investigations. They all provide converging lines of information that supplement each other.

Qualitative and quantitative methods may be used to evaluate conditions in an aquatic community. The first consists of little more than a biological inventory or a listing of the species found in a community accompanied by notes on where they were found. Such an approach is particularly useful in studies where rare or commercially important species are of major interest.

In the field of pollution research attempts have been made to "quantify" the qualitative approach to the study of aquatic communities. This quantification is based on a precise taxonomic grouping of organisms according to their relative tolerance to the same stress. Beck (1954) developed a biotic index as a method of evaluating the effects of pollutants on benthic fauna. His index is simply the sum of the number of intolerant organisms, with the number of facultative organisms giving added weight to the former.

The evaluation of an aquatic community utilizing a saprobic system as proposed by Beck is weakly founded and less than universal in applicability. Knowledge of the tolerance levels of many organisms to various stresses is still severely limited. Tolerances for the same organisms may vary under different conditions, making categorization

somewhat subjective. This all-or-none concept of tolerance to stress neglects the principle of a continuum of tolerance (K. B. Clark, personal communication). Many of the so-called pollution tolerant species are also found in clean waters (Hynes, 1970). Therefore, the use of the mere presence or absence of a particular species as an indicator of water quality is ill-advised and no longer commonly accepted (Stein and Denison, 1967).

The quantitative approach in the use of aquatic biota to assess water quality is based on community structure as an indicator. Hairston (1959) defined community structure in terms of species frequency, species per unit area, spatial distribution of individuals, and numerical abundance of species. All of these parameters have been incorporated, either singly or in combinations, into the evaluation of a community in terms of species diversity.

Species diversity is most commonly equated with species abundance, or richness, relative to some base unit such as area or total population. The more species present in a community, the greater the diversity. Sanders (1968) and Whittaker (1965) describe such measures of diversity as "species diversity." Odum (1971), however, states that diversity can be defined mathematically by any function that has a maximum value when each individual belongs to a different species and a minimum value when all individuals belong to the same species. Such a mathematical definition appears to suggest a different view of

diversity which is independent of the number of species present. This measure of diversity is also widely used but the name given to the measure varies from author to author. Lloyd and Ghelardi (1964) provide the term "equitability" and Pielou (1966) uses the label "evenness." Sanders (1968) calls such a measure "dominance diversity" after the simpler and more common label of "dominance" used by Whittaker (1965). While all these adopted terms apply to the same concept of diversity, the positions given to the maximum values of the terms may be reversed. Maximum dominance or dominance diversity is equated to minimum evenness or equitability. The question arises then of which concept of diversity should be used as its measure. Hurlbert (1971) suggests that species diversity is, in fact, a function of both the species richness and the "evenness" components. In addition, Pielou (1966) suggests that depending upon the function used to mathematically define diversity, a third component may be introduced - population density, or more specifically, sample size.

A universally applicable mathematical definition of diversity would seem to yield a valuable statistic for the evaluation of the structure of a biotic community. But for the purpose of inter-community comparison, this statistic or diversity index must necessarily be independent of the population densities of the communities. Most of the formulae proposed as indices of diversity have been subsequently shown to be density dependent. Discussions concerning the history and fate

of these indices can be found in numerous publications including Whittaker (1965), Hairston (1959), and McNaughton and Wolf (1970) and will not be dealt with at length here. However, many of these indices are still used with due consideration given to their weaknesses. The formulae which are perhaps the most widely used by terrestrial and aquatic ecologists are those based on the concept of information content in communication theory. Originally proposed by Margalef (1957) as a measure of species diversity, the density independence of this series of equations remains argumentative. The proponent of this index argues that the results obtained are valid when the community under examination is reasonably homogeneous. This argument becomes somewhat circular when the index itself is the only measure of that homogeneity. Nonetheless, the generally widespread usage of the information theory indices of diversity demonstrates that they deserve a more detailed discussion at this point.

The underlying concept of the use of information theory as a measure of diversity lies in the assumption that individuals in a natural population are analogous to the letters of the alphabet contained in the words of some message. If all the letters in the message are scrambled and placed in a hat, they can be randomly selected one at a time. As each letter is drawn, it provides "bits" of information that will eventually lead to the meaning of the message. If there are a great number of the same letter, then theoretically more draws must be made to decipher the message. Each letter then provides only a few "bits"

of information about the message. Conversely, if the letters of the message cover a wider range of the alphabet with little duplication, less draws may be made to reveal the message content. Thus each letter drawn provides more "bits" of information. The parallel between repeated or different letters and dominant or diverse species is easily seen even though the similarity in the distribution of alphabetic letters in a message and the distribution of species in nature appears unlikely.

The use of information theory in ecological studies has led to various formulae. Beginning with the information function of Brillouin (1962):

$$H = {}^{1}/_{N} \log_2 N! - \sum_{i=1}^{s} \log_2 n_i !$$

where H is the index of diversity expressed as bits per individual, N is the total number of individuals in the sample, n_i is the number of individuals in the ith species and s is the number of species, Shannon and Weaver (1963) developed a special case formula

$$H' = - \sum_{i=1}^{s} p_i \log_2 p_i$$

where H' is the index of diversity and p_i is the fraction $n_i/_N$. As both Pielou (1966) and O'Connor (1972) point out, this second equation is applicable to cases where each n_i is relatively large so that Stirling's approximation to the logarithm of a factorial, in the form

$$\log N! \sim N (\log N - 1)$$

may be used with the result that H' is an approximation to H. Such a situation where all n_i are large is not often found in nature (Odum,

1971). Both of these equations dealt with the species richness aspect of diversity as well as the evenness of the distribution of organisms within those species. If one wished to consider only the evenness aspect, the ratio (J) of the observed diversity (H) to maximum possible diversity (H_{max}) at a given value of N and i may be used. Pielou (1966) discussed the use of this ratio and defined the maximum diversity by the equation

$$H_{max} = \frac{1}{N} \log_2 \frac{N!}{(m'!)^{s-r} \left[(m'+1)!\right]^{r}}$$

where N is as above, s is the number of species and $sm' + r = N$ (with m' and r as whole numbers and $r < s$) when s - r of the species are represented by m' individuals each and the remaining r species by m' + 1 individuals each.

A more recent approach to providing a density independent index of diversity has been advanced by Sanders (1968), which involves interpolation of the number of species found in various sample sizes by retaining a constant percentage of species composition. A detailed discussion of the method is undertaken at a later point in this paper. Still more recent approaches to a measurement of species diversity have been proposed by Simberloff (1972) and Fager (1972) using computer techniques to simulate the random sampling of a population one individual at a time. The use of these techniques enables one to determine the number of species present at any preselected sample size. While the simulation technique appears superficially to be Sanders'

method worked in reverse, it has led to the criticism that the latter method tends to exaggerate the species abundance estimates. This, in itself, does not disallow the use of Sanders' method as an index of diversity (Simberloff, 1972).

The concept of species diversity was accepted early in this century as an indicator of conditions in a biological community and has been used extensively ever since (Copeland, 1967). If diversity is a characteristic of a community, then it follows that that diversity is affected by either the community itself or by factors outside of and independent of the community. Application of the concept of diversity is often on a localized scale, that is in one localized community, but the generalized theories so far proposed to explain differences in diversity have been advanced on a global scale. These theories are reviewed by Pianka (1966) as theories to explain latitudinal gradients in diversity. There are six such theories summarized as follows:

The Time Theory - Diversity is low in a new or recently disturbed community. If allowed to develop undisturbed, the diversity of the community will increase with time.

The Theory of Spatial Heterogeneity - The more heterogeneous and complex the physical environment becomes, the more complex and diverse are the plants and animals supported by that environment.

The Theory of Climatic Stability - Regions with stable climates allow the evolution of finer specializations and adaptations than

do areas with more erratic climatic regimes, because of the relative constancy of resources.

The Competition Hypothesis - In temperate regions natural selection is controlled mainly by the physical environment whereas biological competition becomes a more important component of evolution in the tropics. Competition for resources is keener and niches are "smaller" in more diverse communities.

The Predation Hypothesis - There are more predators in diverse communities. These are able to hold down individual prey populations enough to lower the level of competition between and among prey species. This lowered level of competition then allows the addition of new prey types which in turn support new predators.

The Productivity Hypothesis - Greater production results in greater diversity, everything else being equal.

All of these concepts are difficult to test directly and thus all remain unproven exclusive of each other. There are however many objections to some of these concepts which tend to lessen their importance as determinants of diversity.

While the Time Theory is easily understood, it is largely unsupported as a major factor in community diversity. Geological catastrophies such as glaciation have, it is felt, allowed temperate regions less time for speciation and diversification than tropical regions which

were less affected. Evidence suggests, however, that temperate species were merely displaced further south during glacial periods rather than destroyed (Morris, personal communication). Thus, time would only be reflected in rates of colonization rather than rates of diversification. The paleoecological work of Simpson (1969) would seem to indicate the possibility of error in considering all past geological periods as being markedly less diverse than the present.

As shown by Stauffer (1937) spatial heterogeneity is an important aspect of diversity but it is insufficient explanation for latitudinal gradients within habitats (Pianka, 1966). It has been shown that environmental complexity in the form of foliage height is a good predictor of bird species diversity (MacArthur, 1964), but no explanation is provided for the vegetation diversity. It would appear that the effects of spatial heterogeneity may be habitat specific.

The hypotheses of predation and competition are by definition mutually exclusive (Pianka, 1966). Predation results in reduced competition in diverse communities while the competition hypothesis equates high diversity with high competition. Paine (1966) provides good evidence for the predation hypothesis in development of his "keystone species" concept. The intense competition and its resultant food web complexity provide little buffer against the damaging effects of the removal of a top carnivore from a highly diverse coral reef tract.

It is conceivable that hight competition would have its greatest effects when productivity is low. Where productivity is high, competition would be decreased at a given population density. Qualitative investigations of enriched, or "polluted," environments have indicated that exploitation and low diversity are more often associated with high productivity. It has been suggested that stability of production, rather than the rate, is a more realistic determinant of diversity (Valentine, 1971, Levinton, 1972).

The theory of climatic stability has found rather general acceptance as a determinant of diversity. But only once has a relatively successful attempt been made to correlate diversity with climate (Sanders, 1968). Perhaps the most important aspect of this theory is that of stability. The inclusion of this term in the productivity hypothesis has already been mentioned as a more viable alternative. Slobodkin and Sanders (1969) use the term predictability to include stability as a more general concept. Thus, the predictability of all the factors which may affect an organism or a community will ultimately affect the diversity. Unpredictable catastrophic effects such as glaciation or the wholesale removal of a key predator would have a deleterious effect on the diversity of a community. Predictability may be the general concept which unifies the six theories summarized above, all of which have been shown to play some role in the determination of diversity in a particular situation.

It may be interpreted that Sanders (1968) actually meant predictability in suggesting the time-stability hypothesis as a determinant of diversity:

> "Where physiological stresses have been historically low, biologically accommodated communities have evolved. As the gradient of physiological stress increases, resulting from increasing physical fluctuations or by increasing unfavorable physical conditions regardless of fluctuations, the nature of the community gradually changes to a predominantly physically controlled. Finally, when the stress conditions become greater than the adaptive abilities of the organisms, an abiotic condition is reached. The number of species present diminishes continuously along the stress gradient."

Sanders drew no conclusions as to the effect of fluctuations of constant magnitude and periodicity on diversity. But if his use of the term "stability" is interchanged with "predictability" the implication becomes obvious.

Demonstration by Sanders of the time-stability hypothesis as it affects the diversity of marine benthic communities revealed high diversity in tropical shallow water (10-40 meters) and deep sea continental slope samples. These locations are characterized by constant temperatures, salinities, and concentrations of dissolved oxygen. Significantly lower diversity values were seen for estuaries, boreal shallow waters, and disturbed tropical shallow waters. Nichols (1970) found lower diversity among marine polychaete assemblages at the mouth of an estuary than at deeper stations in Puget Sound, Washington. He concluded that this was the result of a shifting substrate and fluctuating salinities at the estuary mouth. In addition, the work of Rhoades and

Young (1970) and Levinton (1972) suggests that the high diversity of deposit feeders as opposed to the low diversity of suspension feeders in benthic communities is a function of the predictability or constancy of food supply. Deposit feeders rely on a detritus sink in which nutrients may be rapidly recycled and which acts as a buffer against any fluctuations in the "rain" of detritus from above. Suspension feeders, on the other hand, are subjected to changes in food availability by currents and seasonal plankton population changes.

If environmental stress and fluctuations are minimized or are predictable within the organisms' adaptive capabilities, biological accommodations will develop resulting in, or coinciding with, an increased diversity. Adaptive strategies can focus on the environment as a whole rather than on the parameter producing the stress. Member species of the community can become adapted to local conditions and to each other (Wilson, 1969). In a stressed or physically controlled community, adaptations of organisms are toward a broad spectrum of physical conditions and there can be no close coupling of a species to its environment (Sanders, 1968).

Low latitude environments are generally characterized by complex biological interaction and high diversity. But estuaries, even in the tropics, are subjected to severe environmental stresses such as low levels of dissolved oxygen (Odum, 1970), salinity fluctuations as a result of evaporation and fresh water input, and wide range daily temperature variations (Wood, 1965). Consequently many estuarine

organisms are living near the limits of their tolerance range (Odum, 1970) and even slight further alterations could result in considerable variation in local diversity within the estuary.

Sanders (1958) and Nichols (1970) found the sediment, particularly the percentage of clay, to be the most significant correlate of faunal distributions in the benthos. Sanders (1958) and Bloom, et al. (1972) related an optimum particle size to the distribution of suspension feeders. Nichols (1970) suggested the importance of the sorting of particle sizes to the diversity of polychaete assemblages. Sediment particle size and sorting coefficient are also probably related to the stability of the substrate and hence may be indicative of disturbances to that substrate although such use as indicators is of doubtful validity (Kalajian, personal communication). McNulty, et al. (1962) suggest that sediments may play a less important role in shallow waters of Florida. That conclusion is supported in part by Bloom, et al. (1972) in Tampa Bay, Florida.

Previous studies by Sanders (1958 and 1968), Lie (1974), and O'Connor (1972) were on a relatively large scale involving distances between stations in terms of miles. Such large scale studies may include unaccounted for differences in zoogeographical distributions and drastic changes in substrates. The work of Bloom, et al. (1972) was on a small spatial scale but diversity per se was not investigated due to limitations of sampling methodology.

The purpose of this study is to investigate species diversity in the benthic community of an evaporite estuary on a small scale with respect to parameters which may place physical stress on the community. In shallow water temperature, salinity, dissolved oxygen, and the nature of the substrate should represent the most significant environmental parameters whose fluctuations, either temporally or spatially, or relative presence would affect the distribution of the benthic fauna. The buffering of the community from these stresses, by increasing the water depth or the distance from shore, should result in increased biological interaction and higher diversity. Increases in biological interaction may be seen in the increase of significance of correlations between organisms and their environment.

B. Description of Study Area

The Indian River is part of the Intracoastal Waterway which extends along the east coast of Florida. The "river" is actually a lagoon separated from the ocean by a barrier island formed by wind and wave deposition of sand during recent geologic time (Brown, 1962). Little ecological research has been done in the waters of the Indian River although it has been an integral part of the recreational and commercial fishing industries of east coastal Florida.

The Indian River is bounded on the west by the Florida mainland and on the east by various barrier islands, the northernmost of which

is Merritt Island. On the north there is a connection with Mosquito Lagoon, another similarly formed lagoon. The Indian River extends from latitude 28° 48' about ten miles north of Titusville, Florida, southwards to latitude 27° 7' near Port Salerno, Florida, representing a total distance of approximately 123 miles.

Since a physical description of the entire Indian River is beyond the scope of this text, only some of the major features will be discussed here. Direct exchange of water between the Indian River and the Atlantic Ocean is accomplished through one man-made and two natural inlets, Sebastian Inlet, Fort Pierce Inlet and St. Lucie Inlet, respectively. North of Sebastian Inlet, the only contact with the ocean is indirect. Near Melbourne and Cocoa, Florida, the River connects with the Banana River, which, in turn, contacts the ocean through canal locks at Port Canaveral. North of Titusville, Haulover Canal links the Indian River with Mosquito Lagoon, which opens to the ocean at New Smyrna Beach.

Freshwater input in the form of rivers and streams is likewise limited. Of probable importance are: Turnbull Creek, at the extreme north end; the Eau Gallie River, Crane Creek, and Turkey Creek, in the vicinity of Melbourne; and the Sebastian and St. Lucie Rivers further south. Other significant freshwater inputs exist in the form of direct precipitation and run-off from adjacent land masses.

Two other man-made features are of probable significance. A total of seventeen causeways cross the River at various points along

its length. These causeways, the majority of which are the result of massive "fills," probably serve to divide the river into relatively discrete sections by impeding water circulation. Secondly, as previously mentioned, the Indian River provides a course for the Intracoastal Waterway practically throughout the total length of the lagoon. In addition to the relatively deep twelve-foot planned depth, the initial and maintenance dredging of this 100-foot wide channel has provided numerous small spoil islands paralleling its course. Lasater (1971) provides a comprehensive physical and hydrographical description of the Indian River and adjacent lagoons including further discussion of the points mentioned.

The portion of the Indian River directly encompassed by this study is the northernmost section as shown in Figures 1 and 2. This area was chosen for study for two reasons. First, as a result of the probable physical processes which formed the barrier islands this area should represent the geologically oldest part of the "river." Secondly, the shoreline, with some exception, is relatively free of human disturbance. As such, it was felt that this section may represent natural background conditions.

Man's influence is seen, however, in the railroad causeway which provides the northern boundary of the study area. The Intracoastal Waterway and its attendant spoil islands cut a diagonal course across the section from the railroad causeway in the south to Haulover Canal on the eastern shore. That portion of the shoreline from the causeway

FIGURE 1

Map of the

Indian River Lagoon

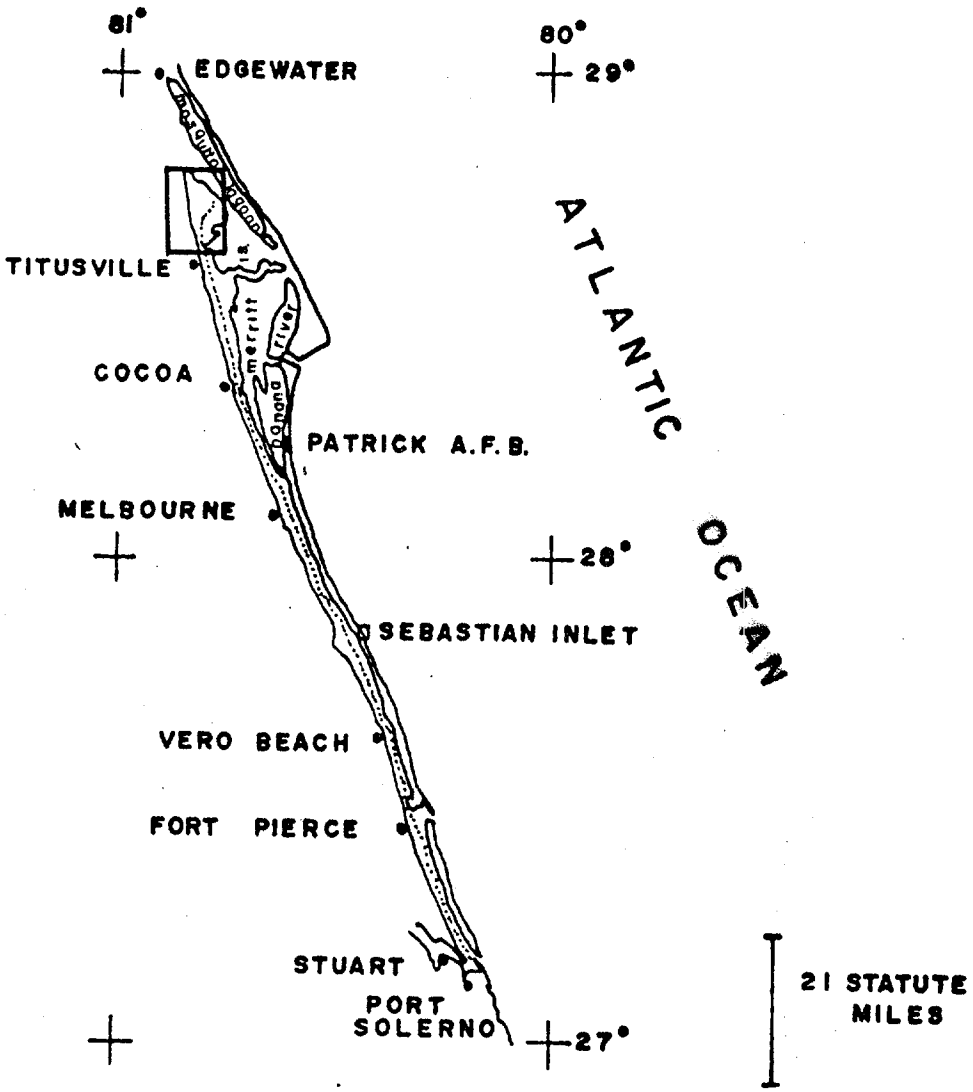
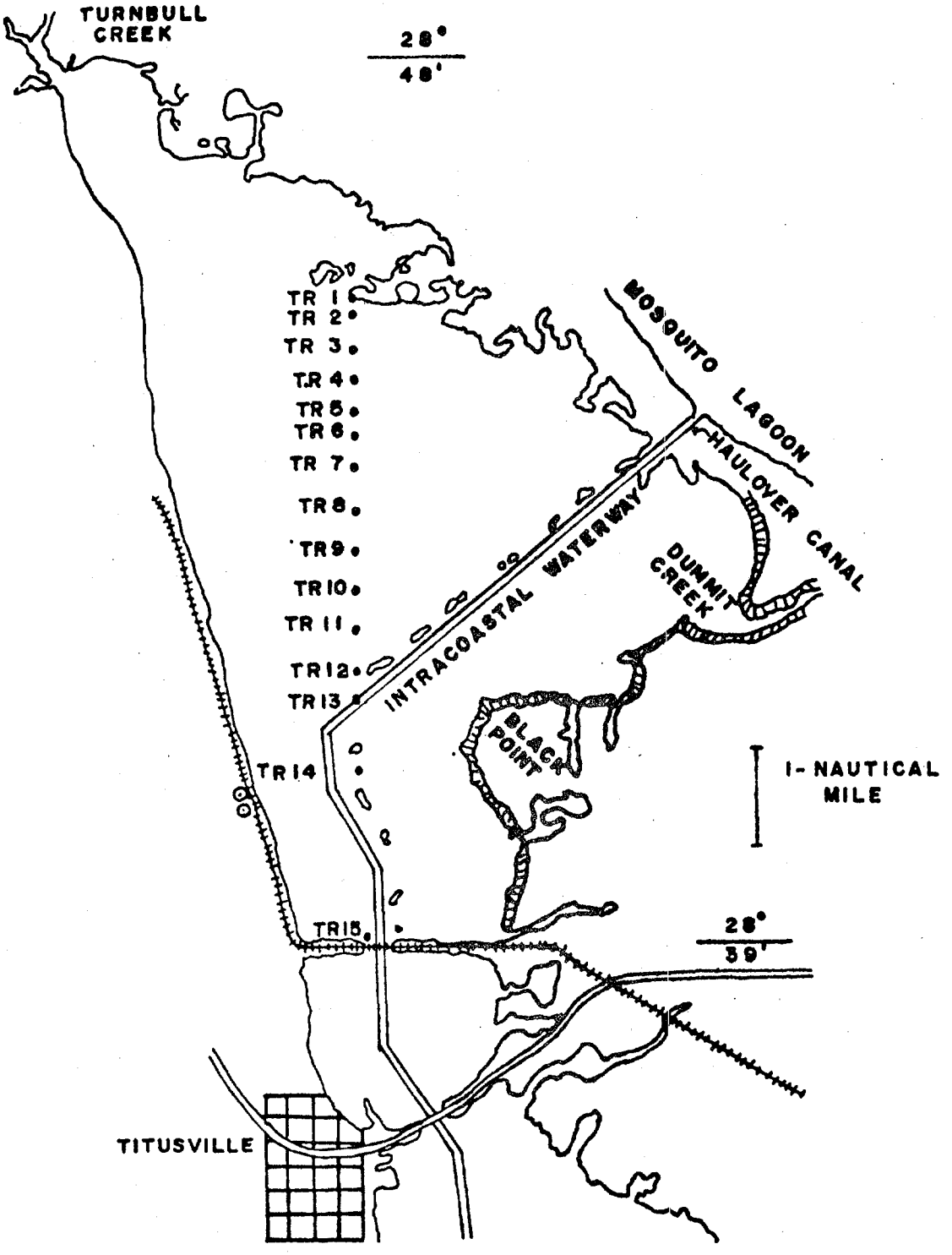

81°
80°
29°
28°
27°
EDGEWATER
TITUSVILLE
COCOA
PATRICK A.F.B.
MELBOURNE
SEBASTIAN INLET
VERO BEACH
FORT PIERCE
STUART
PORT SOLERNO
ATLANTIC OCEAN
Indian River
21 STATUTE MILES

FIGURE 2

Map of the Study Area in the north Indian River showing location of sample transect and stations.


TURNBULL CREEK
28° 48'
TR 1
TR 2
TR 3
TR 4
TR 5
TR 6
TR 7
TR 8
TR 9
TR 10
TR 11
TR 12
TR 13
TR 14
TR 15
MOSQUITO LAGOON
HAULOVER CANAL
INTRACOASTAL WATERWAY
DUMMIT CREEK
BLACK POINT
1- NAUTICAL MILE
28° 39'
TITUSVILLE

to Haulover Canal consits of stands of mangroves and Spartina marshes, both in discontinuous contact with the lagoon as a result of the construction of mosquito control impoundment dikes. The remaining shoreline, excluding the impoundment dikes, is similar and relatively undisturbed. An industrial facility is located on the west shore and a railroad bed runs along that shore from the causeway for approximately half the distance to Turnbull Creek.

Within the water body, the shallow waters fringing the shoreline are characterized by the presence of rather extensive seagrass beds. The shoals are dominated by Diplanthera (shoalgrass) which is displaced as the dominant at depths greater than 0.5 meters by manatee grass, Syringodium (= Cymodocea). Patches of Halophila, another seagrass, have been observed among the Syringodium beds. Also associated with the Syringodium beds are numerous algal species both free living, such as Gracilaria compressa, Acanthophora musciodes and Lyngbya sp., and epiphytic, such as Polysiphonia macrocarpa, Lyngbya sp., and Ceramium sp. (Hartman, written communication). Attached seagrasses were not observed at water depths greater than 1.5 meters. At such depths, the macro-producers appear to be predominantly macroalgal forms such as Gracilaria and Eucheuma.

Hydrographic data for this portion of the river was collected quarterly by Lasater and Nevin (unpublished) during the period from June, 1972, through December, 1973. Little variation of salinity was

observed, either temporally or spatially. At sample stations of greater than 1.2 meters depth bottom water salinity values ranged from 28-31 parts per thousand with a mean of 29. At shallower stations, the bottom salinity ranged from 30-33 parts per thousand with an average of 32. Bottom water temperature variation was somewhat greater, however, with ranges of 13-30.8° C. and 12-30.2° C. for depths greater than and less than 1.2 meters respectively. The average bottom water temperature for both deep and shallow stations was 24.9° C. over the entire period.

Since current patterns are determined by wind direction and velocity (Dill, 1974) in this portion of the Indian River, it is relevant to point out some general aspects of these driving forces. Lasater (1971) found that the strongest winds (average ten knots) occur during the fall and winter from September to March and are generally from the north. During the spring and summer prevailing winds are easterly and of lesser velocity (average seven knots). The mean annual wind direction and velocity are easterly at eight knots.

From this same data temperature and rainfall summaries have been obtained. The highest monthly mean temperatures occur during the months of July and August and the lowest during December, January and February. The maximum annual air temperature variation is about 41° C. from a low of -4° C. to a high of 37° C. Maximum rainfall occurs from June to October with an annual mean rainfall of about 48

inches. Brown (1962) classifies this area of Brevard County, Florida, as humid subtropical with normal monthly temperatures of about 17° C. for January and 28° C. for August. He records an annual monthly temperature of 22.5° C. and an average annual rainfall of about 50 inches accumulating mostly during the period from May through October.

These data suggest that the summer months may represent the maximum in climatological severity in relation to the marine life of the Indian River. Reduced circulation and mixing of the water column as a result of decreased wind velocities and higher temperatures may result in oxygen depletion in summer (Odum, 1970, and O'Connor, 1972). Higher temperatures accelerating evaporation in the shallow water and greater rainfall during this period may contribute to wider fluctuations of salinity.

II. METHODS AND MATERIALS

Bottom samples were taken during June and July, 1973, with a Ponar grab. This small sampler provides grabs of approximately $0.05 m^2$ surface area and depths of 2-8 cm depending upon the character of the bottom. The use of this grab as an all-sediment sampler is discussed and recommended by Flannagan (1970). Further analysis of this grab and its effectiveness in Indian River samples is discussed by Zarkanellas (1973). In terms of safety and technical simplicity, the Ponar grab was found to be more desirable than grabs of spring-loaded jaw design and other more mechanically sophisticated designs while working from a small open boat.

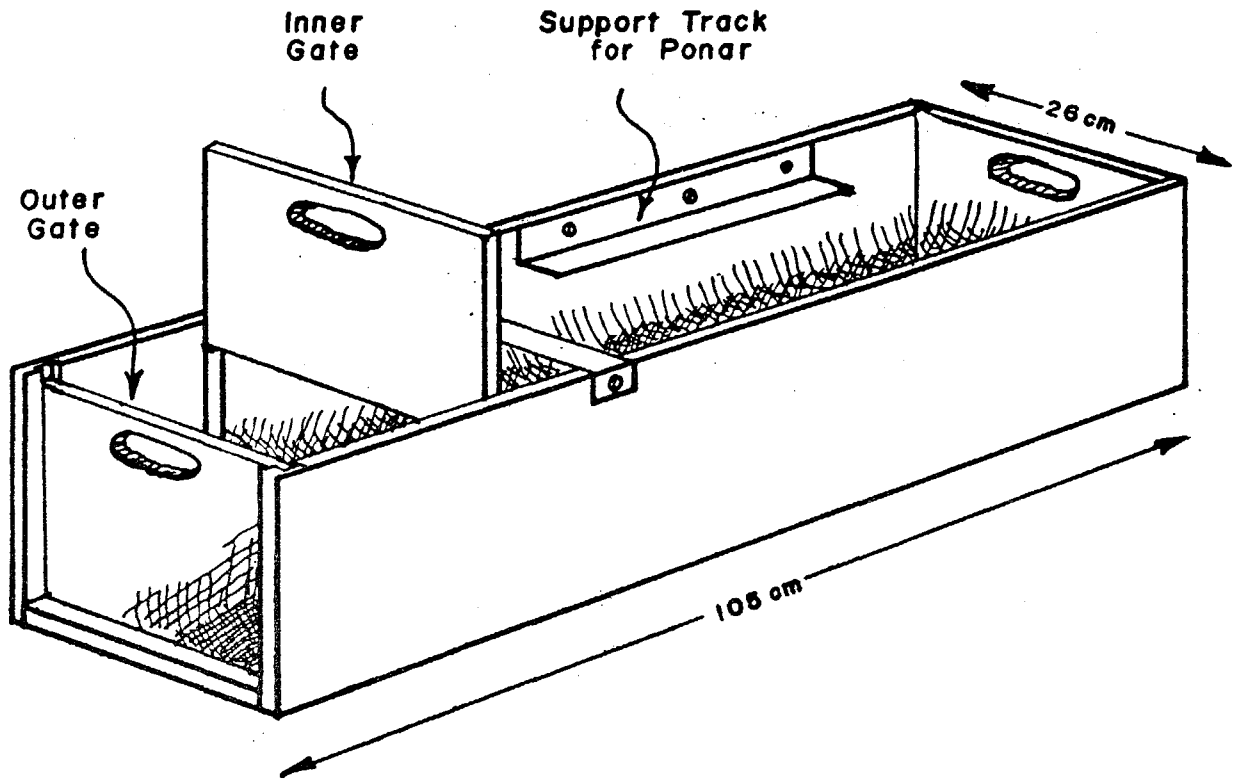
Sampling locations were selected along a north-south transect of approximately 6.4 nautical miles in length. The transect sampling scheme was selected in preference to a grid or random site sampling to ensure a gradient in depth and distance from shore. Locations of the fifteen sample sites along this transect are shown in Figure 2.

It is generally accepted that aggregated populations commonly occur in nature. Small samples taken from areas exhibiting such distributions would either exaggerate or neglect species importance depending upon where in the distribution pattern the sample was taken. Increasing the sample size or number of samples taken at each site

tends to recruit additional species according to a curve, exponential in form (Longhurst, 1959). In an effort to decrease the probability that additional species could be recruited, five grabs were taken at each site. These replicate grabs were then pooled in a "sluice-box" and mixed by hand to provide an homogeneous and, theoretically, a random distribution throughout the pooled sample. The sluice box shown in Figure 3 was designed to take an aliquot equal to $^1/_5$ x total area sampled by closing the inner gate subsequent to mixing. Such an aliquot reduces sorting effort while the theoretically random distribution of the organisms in the sample allows the use of the aliquot as an estimate of the total sample. By removing the outer gate the aliquot was washed into a fiberglass tub modified from a method used by Sanders, et al. (1965). Organisms floated out of the tub were captured on a stack of screens; the smallest mesh size was 0.42 mm. Organisms were fixed in 10 per cent buffered formalin after relaxation for 10-20 minutes in six per cent $MgCl_2$. The formalin was replaced after a minimum of twenty-four hours by 70 per cent ethyl alcohol for preservation. The samples were then carefully sorted in the laboratory, identified to species when possible, and counted. Only non-colonial species were counted. The convention used for counting provided that organisms or fragments of organisms that included the "head" should be counted. If no fragments of a species were found with a "head" that species was quantified as a single occurrence. A few hours prior to sorting, Rose Bengal stain was added to the samples. This protein

FIGURE 3

Sketch of "Sluice Box" showing inner gate in open position for mixing of pooled samples.


Inner
Gate
Support Track
for Ponar
26 cm
Outer
Gate
105 cm

stain allowed easy detection of small invertebrates among the shell debris in the sample resulting in an estimated recovery of almost all of the organisms present.

Taxonomic nomenclature used in this study follows Abbott (1954), Andrews (1971) and Warmke and Abbott (1962) for Mollusca, Hedgepeth (1948) for pycnogonids, Renaud (1956) for some polychaetous annelids and Smith (1964), Miner (1950), and Gosner (1971) for other polychaetes and all other taxa. Individual exceptions are noted in parentheses following the binomial.

At each station, bottom water and sediment temperatures were measured in situ with a thermister probe. Water samples were taken using a modified VanDorn bottle (Wildco). Dissolved oxygen concentration was determined by Winkler titration (Standard Methods for the Examination of Water and Wastewater, 1971). Salinity was measured by means of a handheld optical refractometer. Beckman Model G pH meters were used for measurement of pH and redox potential, using platinum and calomel electrodes for the latter. Sediment samples were taken from the unused portion of the pooled grab samples for analysis of particle size distribution and organic carbon content. These sediment analyses follow methods described by Holme and McIntyre (1971).

Statistical analyses were performed on a Monroe programmable calculator. Statistical program packages included one-way analysis of variance (4021 J), two-way analysis of variance (4500 J) and linear regression (4505 J) provided by the Monroe Calculator Company.

Diversity curves were calculated using the rarefaction method described by Sanders (1968). The species in a sample are ranked by abundance, and the percentage composition of each species and the cumulative percentage are plotted. Using the data collected in this study from sample Station TR 14 as an example (Table 1), there are 100 individuals and 12 species. To determine the number of species at the 50-individual level, the percentage composition remains the same as in the original sample, but the number of individuals is reduced to 50. Since 50 specimens in this reduced sample represent 100 per cent of the individuals present, then each individual specimen forms two per cent of the sample. In the original sample, seven species each comprise two per cent or more, and in total they compose 95 per cent of the sample by number. Therefore, each of these seven species will be present in the reduced sample. This leaves a residue of five per cent of the original sample comprising the remaining five species. Because none of these species forms more than two per cent of the original sample, those species of this group that will appear in the reduced sample cannot be represented by more than one individual. Since one speciment comprises two per cent of the reduced sample, therefore 5%/2% = 2.5 species; 7 + 2.5 = 9.5 species (which may be rounded off to 10 species) present per 50 individuals.

The determination of species per 25 individuals is as follows:

(1) since each individual represents four per cent of the sample, then

TABLE I

Sample from station TR 14 with
100 individuals and 12 species.

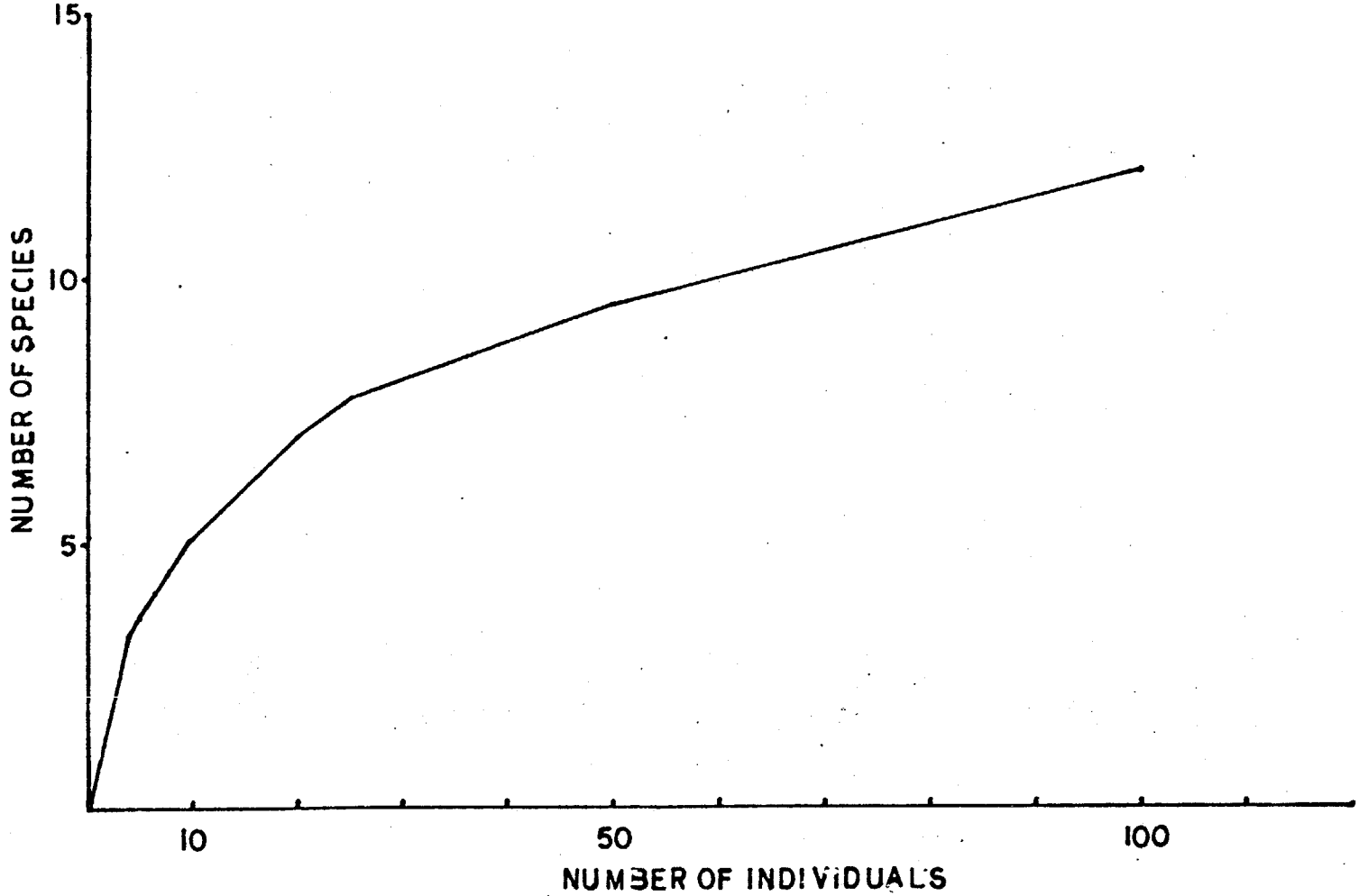
Rank of Species by Abundance	Number of Individuals	% of Sample	Cumulative of Sample %
1.....	43	43	43
2.....	26	26	69
3.....	8	8	77
4.....	8	8	85
5.....	4	4	89
6.....	3	3	92
7.....	3	3	95
8.....	1	1	96
9.....	1	1	97
10.....	1	1	98
11.....	1	1	99
12.....	1	1	100
Total Number	100		

(2) five species in Table 1 each comprise $\leq$ 4% of the fauna and cumulatively = 89% of the sample; (3) the residue = 11% of the sample; 11%/4% = 2.75 species; and (4) 5 + 2.75 = 7.75 species per 25 individuals.

Using this technique, arithmetic plots of the number of species at different population levels up to the total number of individuals are made. The plot for Station TR 14 is shown in Figure 4. The curvilinear nature of the line is due to the fact that individuals are being added at a constant rate but progressively rarer species are added at a continuously decreasing rate. The curve itself gives the interpolated number of species at the different population levels. Each environment seems to have its own characteristic rate of species increment (Sanders, 1968).

FIGURE 4

Arithmetic plot of the number of species at different population levels using the rarefaction methodology for the sample from station TR 14.


15
10
5
NUMBER OF SPECIES
10
50
100
NUMBER OF INDIVIDUALS

III. RESULTS

Since the sampling program in this study was carried out on a relatively small scale, it was important to determine if any significant changes are detectable both in the biological parameters and the physical and chemical parameters. To accomplish this throug. statistical analyses it was necessary to divide the data into two or more groups. Rather than choosing a random grouping sequence, it was decided that more relevant grouping might be accomplished if ordered according to any faunal associations that may be present.

The method most frequently used to demonstrate the grouping of individual samples into discrete aggregates is through the use of a trellis diagram formed by comparisons of the values of some index of similarity between samples taken two at a time for all possible combinations of samples. Several different measures of association have been discussed by Nichols (1970) with the conclusion that the value of a particular index depends on the use to which it is put. For the purpose of this study, only the existence of associations in terms of the species shared among the various samples was sought. To this end, the index of similarity proposed by Bray and Curtis (1957) was chosen without their subsequent modifications to reflect the relative success of shared species between stations. This index of similarity (S) is similar to that

of Sorenson (1948) and is represented by the formula

$$S = 100 (2w / a + b)$$

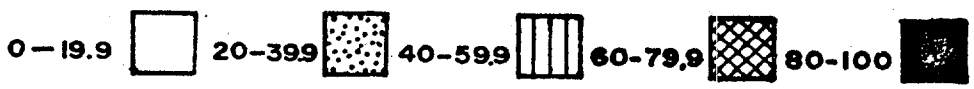
where a and b are the numbers of species at two stations and w is the number of species common to the two stations. The score thus determined actually represents the percentage of species shared by the two stations compared. The major disadvantage of this index as used in this study is that it generates no statistic that can be utilized to determine the significance of the differences or similarities (Nichols, 1970), but, as will be shown later, statistical significance of differences between the assemblages can be shown using other faunal indices.

The trellis diagram shown in Figure 5 was generated from the species distribution list in Appendix A using the Bray and Curtis index of similarity as discussed previously. The diagram shows at least two relatively distinct communities based on species similarities alone. The first assemblage, A_{1-4}, consists of Stations TR 1 through TR 4. A second assemblage encompasses Stations TR 5 through TR 12. Within this second assemblage a further, less distinct, separation occurs in the vicinity of Stations TR 8, TR 9, and TR 10. To facilitate statistical comparisons, this assemblage has been separated into two sub-assemblages, A_{5-8} and A_{9-12}. The relatively weak similarities shown in Stations TR 13, TR 14 and TR 15 either among themselves or when compared to all other stations indicate either that they represent samples from another distinct community or that they are portions of

FIGURE 5

Trellis diagram generated by index of similarities between sample stations along the transect.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1		77.1	83.3	72.9	55.1	52.8	52.3	45.4	48.4	47.5	37.7	41.4	0.2	31.4	37.1
2			72.2	68.5	59.6	53.3	56.6	44.4	56.0	51.1	43.9	47.8	0.3	30.8	58.6
3				80.5	59.2	54.0	53.7	50.0	53.1	52.5	40.0	43.3	0.3	34.0	58.3
4					58.3	53.3	47.1	46.4	52.3	48.4	35.7	45.9	0.3	22.2	54.8
5						74.6	69.2	67.9	53.1	60.9	45.0	48.9	0.5	31.6	56.1
6							65.5	64.3	57.7	57.1	51.2	54.2	0.6	34.2	56.7
7								69.4	62.2	57.1	50.0	58.5	0.7	35.3	56.6
8									65.2	55.8	59.5	52.4	1.1	34.3	59.3
9										71.8	60.8	52.6	0.6	38.7	64.0
10											60.0	62.9	0.8	35.7	59.6
11												62.1	2.2	54.5	43.9
12													2.2	37.0	47.8
13														3.8	2.6
14															41.0
15															



the same community subjected to a different set of environmental conditions. These stations are, therefore, treated separately from the first twelve stations.

On the basis of recognition of at least two distinctly separate assemblages the transect can be divided, arbitrarily, into two biotopes. Assemblage A_{1-4} represents the fauna of the first biotope, characterized by dense vegetation. The assemblages A_{5-8} and A_{9-12} represent the fauna of the biotope having sparse or no vegetation. Using these divisions, with the assumption that their differences are significant, analyses such as analysis of variance can be used to examine the various environmental parameters which may be associated with the differences between these assemblages.

A. Depth

This segment of the Indian River is relatively shallow with a naturally-occurring maximum depth of about 2.25 meters. A maximum dredged depth of 3.25 meters along the transect was obtained at Station TR 13 in the channel. Since stations along the transect were selected with respect to depth, no statistical treatment of this parameter would be valid. On the basis of the assemblage groupings it would appear that convenient divisions of the transect at one meter depth intervals are acceptable. Assemblage A_{1-4} is represented by stations in less than one meter of water. Assemblage A_{5-8} is made up of stations at

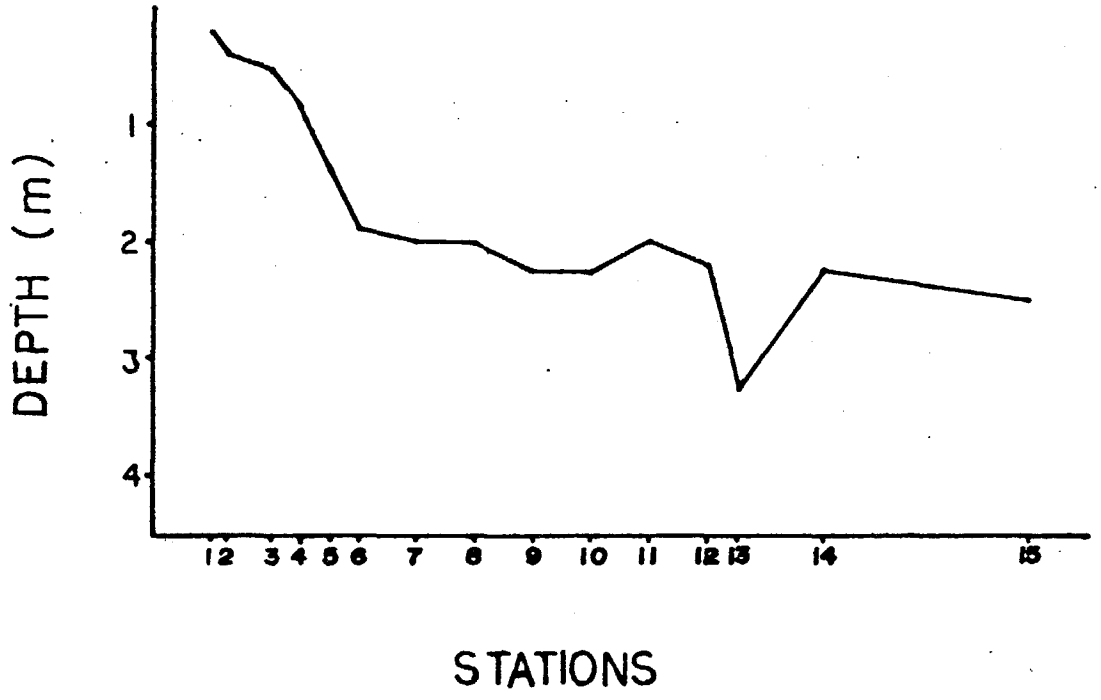
depths in the range of 1-2 meters. The remaining stations are located at depths of two meters or more. Station TR 13 again was the only station in more than three meters of water (Figure 6).

B. Sediments

Several authors, as mentioned previously, have found that the nature of the substrate is the most significant physical parameter affecting the distribution of benthic fauna. Conversely, McNulty (1962) and Bloom, et al. (1972) concluded that the sediment character appears to play a less important role in determining faunal distributions in two Florida bays. The difference appears to lie in the sampling scale. Sanders (1958) and Lie (1974) sampled very large areas encompassing a wide variety of sediment types. The studies of McNulty and Bloom covered somewhat smaller areas where sediment characteristics were not so variable. The results of the sediment analysis of this study reveal an average median grain size for all stations along the transect of slightly less than .125 mm (3.07 Φ) indicating the predominance of a very fine grained sand. This value changed little when only the first twelve stations were considered (3.06 Φ). Without exception, the only particles exhibiting a grain size of greater than 0.25 mm in diameter were shell debris and aggregates of polychaete worm tubes. When two-way analysis of variance was used to compare the sediment parameters of median grain size, sorting coefficient, and per cent of silt and clay

FIGURE 6

Depth contour along transect. Vertical distortion is approximately 2000:1. Sample stations are placed at approximate distances along the transect.


DEPTH (m)
1
2
3
4
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
STATIONS

among the three assemblages, no significant differences between the variances were revealed ($\alpha = 0.05$). The variations between stations within the assemblages were greater than the variations between assemblages. While the greater variations between stations were not significant either ($\alpha = 0.05$) these variations would seem to indicate that sediment characteristics over a relatively small spatial scale are the resultant of very localized effects. It is probable that the redistribution of the sediments is greatly dependent upon the shallow water currents which are primarily wind driven (Dill, 1974). With this resultant uniformity in sediment characteristics, no strong variations in faunal indices would appear attributable to the physical nature of the sediment in terms of particle sizes.

C. Salinity

In general, the transect sampling demonstrated a salinity gradient from north to south as shown in Figure 7. Except where otherwise stated, all the water parameters are those measurements taken at the bottom of the water column within 20 centimeters of the water-sediment interface. The salinity variations appeared to be only weakly significant ($\alpha = 0.05$) spatially along the transect but more so than salinity variations with respect to time (Table 2). Two stations (TR 3 and TR 7) along the transect were arbitrarily selected for investigation of seasonal as well as diurnal fluctuations in water parameters. Diurnal

FIGURE 7

Salinity values measured along the transect. Stations are shown at approximate distances relative to one another.

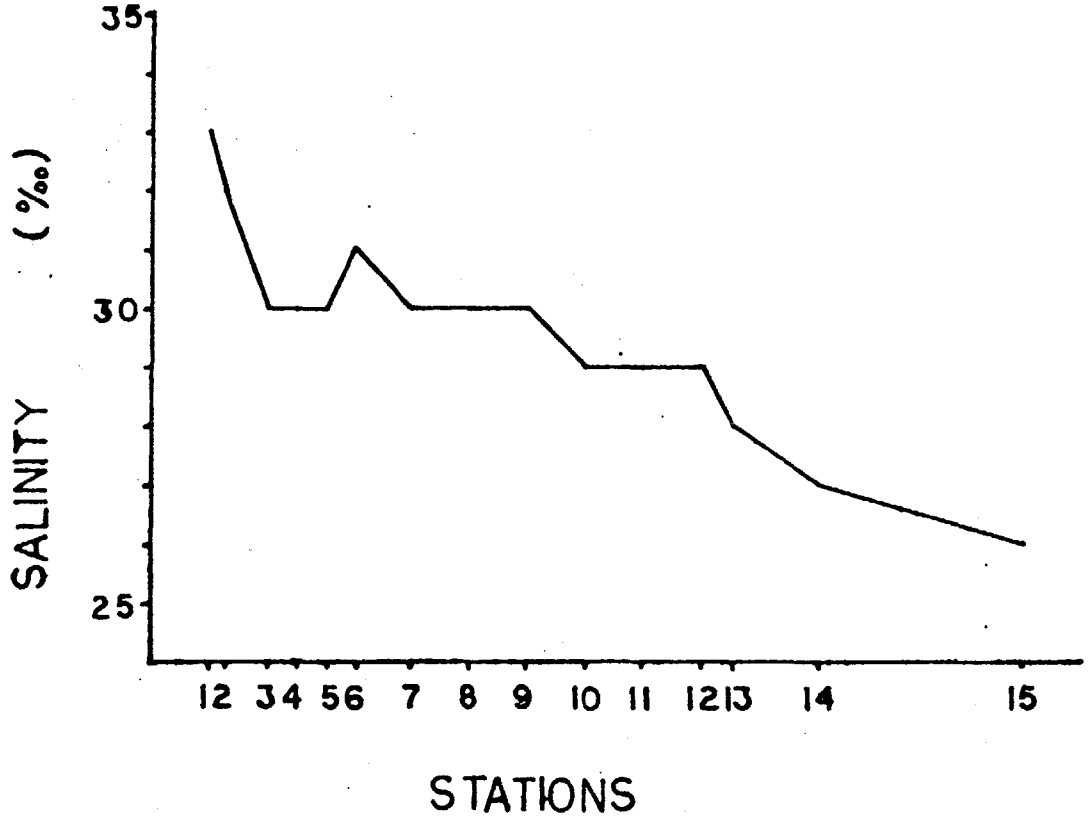

35
30
25
SALINITY (‰)
12 34 56 7 8 9 10 11 1213 14 15
STATIONS

TABLE 2

Spatial differences in the variances of salinity. Stations grouped according to faunal similarities using the F test.

Assemblages Compared	Calculated F	Tabulated F at $\alpha = 0.05$
$A_{1-4} : A_{5-8} : A_{9-12}$	4.36	4.26
$A_{1-4} : [A_{5-8} + A_{9-12}]$	5.85	4.96
$A_{5-8} : A_{9-12}$	8.00	5.99

variation in salinity was 0.1 per cent for both summer (2.8-2.9 per cent) and winter (3.0-3.1 per cent) and the maximum seasonal variation for the two reference stations was 0.3 per cent. Hutchinson (1973) calculated the instrumental error of the refractometer used in these studies as $\pm$ 0.12 per cent. Thus it seems the observed temporal variations may be more of a result of experimental error rather than real variations.

The data of Lasater and Nevin (unpublished) agree in part with these observations, in that their stations north of the Intracoastal Waterway showed bottom salinity fluctuations over the period 1972-1973 of only 0.1 per cent, again within the range of experimental error. But in the vicinity of the railroad causeway, temporal fluctuations of 0.75 per cent salinity were observed. This would seem to indicate that the effects of precipitation and rate of evaporation in the shallow northern area are in temporal equilibrium while the water in the vicinity of the causeway is subjected to dilution as a result of fresh water run-off from the causeway. If Turnbull Creek indeed represents a major freshwater input to the Indian River in this sector, then it's influence appears to be localized near its mouth with the shallow waters beyond its mouth rapidly dampening its impact.

D. Temperature and Dissolved Oxygen

The third important environmental factor which affects benthic faunal distributions is temperature. In the estuarine environment, temperature appears to affect an organism's ability to withstand reduced salinities (Hedgpeth, 1957). Temperature directly affects marine organisms in such areas as metabolic rates and enzyme activity, and indirectly, temperature affects organisms through its effect on the solubility of oxygen in water. As a result of this last effect, these two parameters will be discussed together.

When the values of dissolved oxygen and temperature obtained during the transect sampling (Figure 8) were subjected to analysis of variance, the only significant difference ($\alpha = 0.05$) between areas represented by faunal assemblages occurred between the vegetated (A_{1-4}) and sparsely vegetated ($A_{5-8} + A_{9-12}$) areas (Table 3). This difference was sufficiently weak so that the null hypothesis (i.e., no difference) would be accepted at $\alpha = 0.01$.

Since these samples were taken on different days and at different times of the day, it appeared possible that the observed difference might be the result of temporal rather than spatial variations. To test this possibility, two reference stations were selected for diel and seasonal sampling. Station TR 3 was selected to represent the vegetated area and TR 7 was selected to represent the area with no rooted vegetation. Station TR 3 showed a weakly significant seasonal variation in

FIGURE 8

Temperature and dissolved oxygen values measured at stations along the transect.

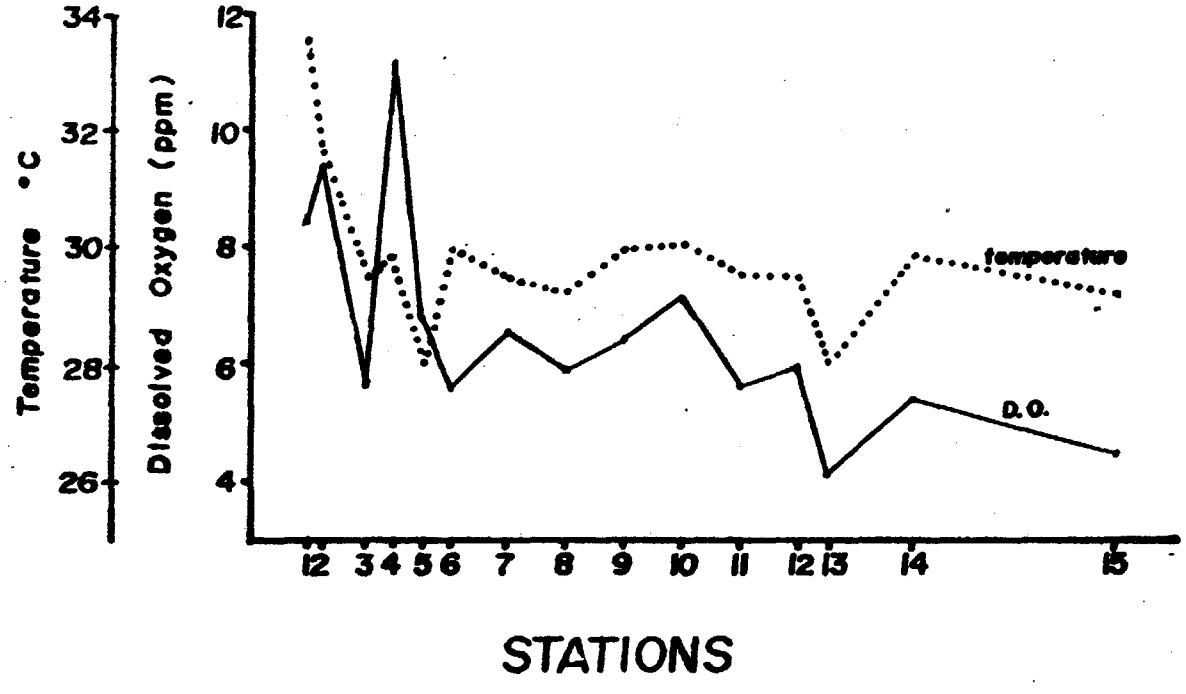

Temperature °C
Dissolved Oxygen (ppm)
34
32
30
28
26
12
10
8
6
4
temperature
D.O.
12 3 4 5 6 7 8 9 10 11 12 13 14 15
STATIONS

TABLE 3

Analysis of the variances of bottom water temperature and dissolved oxygen between station assemblages characterized by attached vegetation on those with little or no vegetation in the summer using the F test.

	Calculated F	Tabulated F α=0.05	α=0.01
Dissolved Oxygen	8.41	4.96	10.04
Temperature	6.03	4.96	10.04

temperature while Station TR 7 did not (Table 4). Diel temperature variation was not significant at either station. Dissolved oxygen values showed strongly significant differences ($\alpha = 0.01$) seasonally at both stations and weakly significant ($\alpha = 0.05$) differences over a 24-hour period at Station TR 3 only (Table 5). Per cent oxygen saturation values calculated from the same data revealed that the daily range at the shallow station was from 26 to 74 per cent during the summer and 65 to 113 per cent in winter. During the summer, the oxygen saturation at the deep station ranged from 32 to 45 per cent and during the winter from 100 to 116 per cent.

A comparison between Stations TR 3 and TR 7 for each season revealed no significant differences in the variances of temperature or dissolved oxygen. However, a comparison of the mean values of these parameters, using Student's t test, gave different results. The mean diel temperature and dissolved oxygen concentration was significantly higher at Station TR 3 in the summer sampling (Table 6). Among the winter samples there was no significant difference between the stations in terms of mean diel temperature but,in terms of dissolved oxygen, Station TR 7 now displayed a significantly higher mean diel value. The winter and summer temperature and dissolved oxygen profiles over the 24-hour periods are shown in Figures 9 and 10 respectively.

In summary then, daily temperature variations were not significant at either station and only the shallow station revealed a significant

TABLE 4

Two-way analysis of variance of diel and seasonal variations in temperature at shallow (TR 3) and deep (TR 7) stations using the F test.

Station	Type of Variation	Variance	Calculated F	Tabulated F	Level of Significance (α)
TR 3	Seasonal	51.98	19.6	7.71	0.05
	Diel	2.92	1.1		
TR 7	Seasonal	0.96	52.45	224.58	0.05
	Diel	3.83	209.82		

TABLE 5

Two-way analysis of variance of diel and seasonal variations in dissolved oxygen at shallow (TR 3) and deep (TR 7) stations using the F test.

Station	Type of Variation	Variance	Calculated F	Tabulated F	Level of Significance (α)
TR 3	Seasonal	27.19	82.64	21.2	0.01
	Diel	3.98	12.1	7.71	0.05
TR 7	Seasonal	72.36	734.63	21.2	0.01
	Diel	0.25	2.57	7.71	0.05

TABLE 6

Comparison of mean daily water temperature and dissolved oxygen concentration between deep and shallow stations by season using Student's *t* test.

Parameter	Season	Calculated t	Tabulated t	Level of Significance (α)
Dissolved Oxygen	Summer	16	3.355	0.01
	Winter	272	3.355	0.01
Temperature	Summer	25.3	3.355	0.01
	Winter	1.9	2.306	0.05

FIGURE 9

Temperature profiles at shallow and deep stations over a 24-hour period in summer and winter.

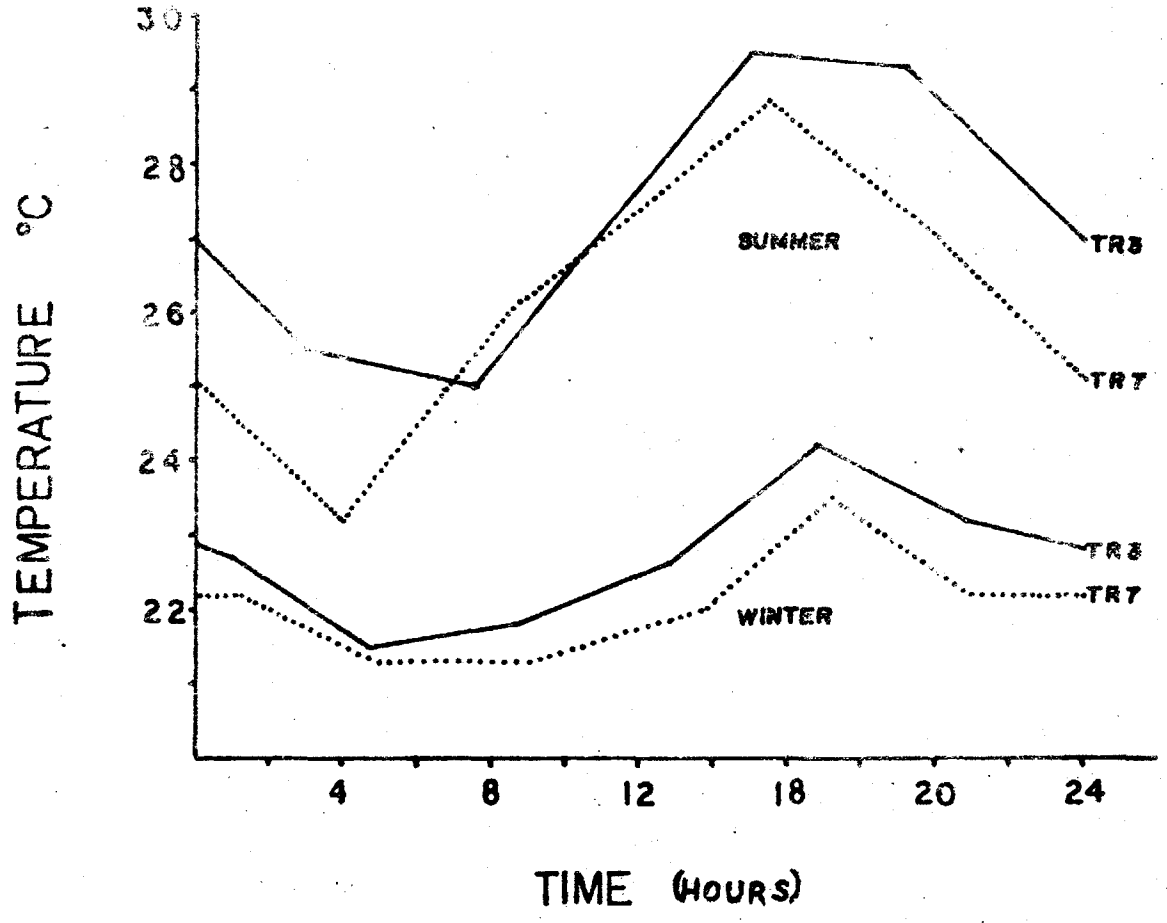
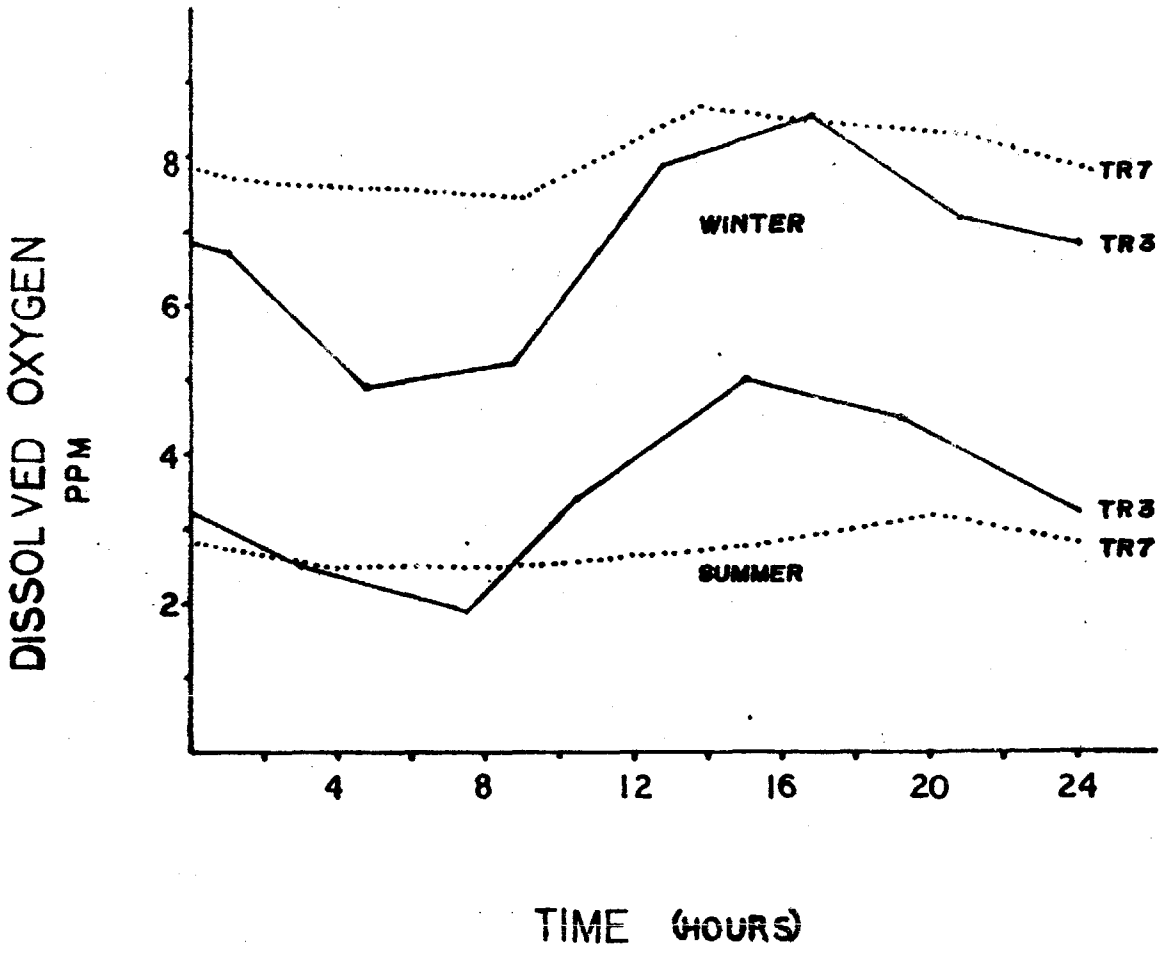

TEMPERATURE °C
30
28
26
24
22
SUMMER
TRS
TRT
WINTER
TRS
TRT
4
8
12
18
20
24
TIME (HOURS)

FIGURE 10

Dissolved oxygen concentration profiles at shallow and deep stations over a 24-hour period in summer and winter.


DISSOLVED OXYGEN
PPM
8
6
4
2
WINTER
TR7
TR3
TR3
TR7
SUMMER
4
8
12
16
20
24
TIME (HOURS)

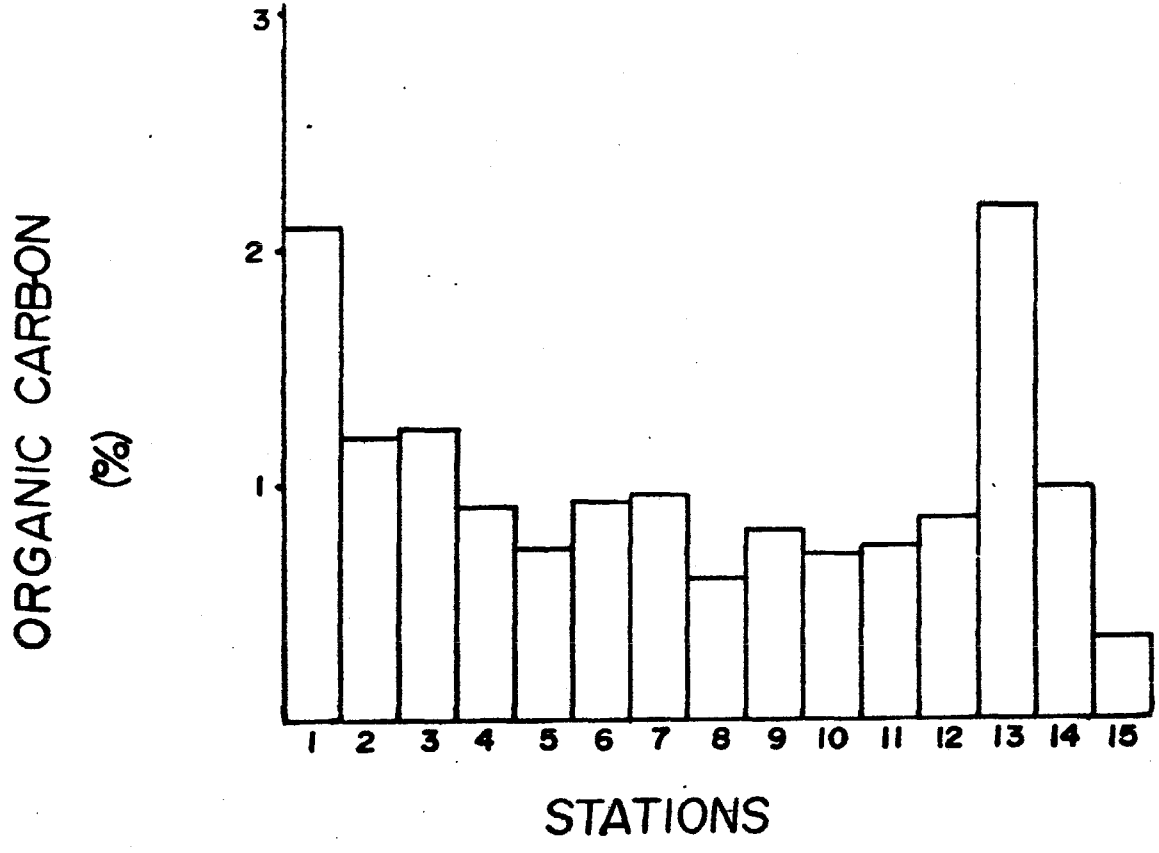
seasonal variation. Mean diel temperature was significantly higher in the shallow station than in the deep station during the summer while no difference was observed between the shallow and deep stations in winter. Dissolved oxygen concentration and oxygen saturation values varied significantly both seasonally and dielly in the shallow vegetated station, whereas only seasonal variation was seen in the deep station. The average dissolved oxygen concentration and saturation over a 24-hour period at the shallow station was the higher value during the summer and the lower value during the winter. Relatively stable conditions with respect to oxygen and temperature appear to occur in the deeper water compared to the widely fluctuating conditions of the shallower waters.

E. Organic Carbon

Using the values obtained for the organic carbon content of the sediments (Figure 11), three areas of difference are distinguishable. The first of these is the sandy bottom devoid of rooted vegetation. The percentage of organic carbon in these sandy sediments was uniformly less than one per cent, and no significant variation in organic carbon content was distinguishable between groups of stations representing assemblages A_{5-8} and A_{9-12}. The mean value for these samples was 0.8 per cent. A significant difference ($\alpha = 0.05$) was evident between these samples and the ones taken from the grass flats. The stations represented in assemblage, A_{1-4} revealed a mean value of

FIGURE 11

Organic carbon content of sediment
at stations along the transect.


ORGANIC CARBON
(%)
3
2
1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
STATIONS

1.36 per cent organic carbon in the sediments. The values for samples from vegetated areas were, with one exception, greater than one per cent.

The third area of difference in organic carbon content of the sediments is represented by only one sample. Station TR 13, located directly in the channel exhibited the highest organic content of all stations, with a value of 2.18 per cent. Higher values of organic carbon content were obtained in samples taken from dredged borrow pits in the nearby Banana River (4.0 and 8.9 per cent) indicating that these dredged "holes" become sedimentary traps. The lower values obtained from the navigational channel at Station TR 13 is probably the result of the periodic maintenance dredging which removes the trapped sediments to spoil areas outside the channel.

However, located close to the channel in the gap of the railroad causeway, Station TR 15 provided the sample with the lowest organic carbon content (0.34 per cent).

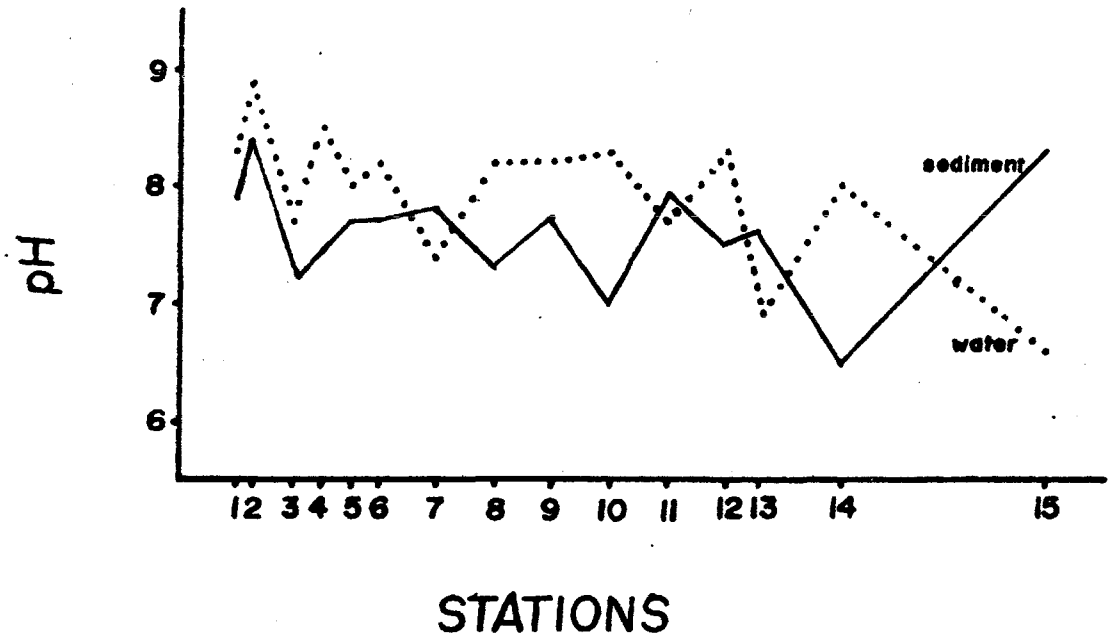
F. pH

Measurements of pH were taken at each station and at the reference Stations TR 3 and TR 4 during the 24-hour study periods to determine possible changing conditions within the carbon cycle. As the carbon cycle equilibrium is disturbed, a change in pH may reflect the direction and possibly the magnitude of such a change. For instance,

in a closed system or one with minimum circulation, the removal of CO_2 from the water by photosynthetic activity would result in a rise in pH. In tidal pools dominated by green algae during periods of high photosynthetic activity, values of pH = 10 may be experienced (Zottoli, 1973). In this study, pH values for bottom waters ranged from 6.62 to 8.75 with a mean value of pH = 7.94 (Figure 12). The highest value (pH = 8.75) occurred at Station TR 2 which was shallow (41 cm) and had the highest density of attached seagrass (358 dry wt/m^2). Since removal of CO_2 results in a rise in pH, the addition of CO_2 under the same conditions by high community respiration would be expected to produce a lowering of the pH. Thus it is not surprising that the lowest values for the pH of bottom water were found at the two deepest stations. However, neither temporal nor spatial variations in pH values were found to be significant ($\alpha = 0.05$). Apparent pH of the sediments was measured along the transect and were found to be generally slightly lower than the pH of the bottom water with a mean pH of 7.59. This is probably the result of the respirational activity of microorganisms involved in the breakdown of the organic detritus in the sediment. The highest pH value for the sediments (pH = 8.35) was found at Station TR 2. Station TR 15 which had the lowest pH value for the bottom water had a very high sediment pH value (8.30). While this represents an apparent anomaly, it may be explained by the low percentage of organic carbon (0.34 per cent) resulting in lower community respiration and perhaps,

FIGURE 12

pH of bottom water and subjacent sediments along the transect.


pH
9
8
7
6
sediment
water
12 3 4 5 6 7 8 9 10 11 12 13 14 15
STATIONS

in part, by the observed evidence of a considerable amount of shell fragments in the sediment. The latter is evidence of long-term high pH conditions (K. B. Clark, personal communication).

Since a primary value of pH measurements in aquatic systems is as an indicator of photosynthetic activity versus community metabolism (Zottoli, 1973), it was somewhat disappointing to find no diel fluctuations in pH during the 24-hour studies conducted in January, 1974. During this study, equipment malfunctions forced the selection of a pH color comparator to be used in the measurements. A range of pH values from 8.4 - 8.6 over the entire 24-hour sampling period at both stations appears to allow only two hypotheses: (1) the low sensitivity of the test precluded the observation of expected changes, or (2) the possibility of increased circulation in the winter provided an uniformity of mixing thus preventing localized "buildup" and reduction in either time or space. The temperature and dissolved oxygen fluctuations, or lack of them, observed during this period provide considerable support for drawing the latter hypothesis to a conclusion.

It should be mentioned here that the sampling schedule prevented the addition of pH measurements to the 24-hour sampling period during the summer of 1973. The few samples taken at that time did not differ appreciably from those values obtained during the original transect sampling.

G. Redox Potential

For the twelve stations north of the dredged channel, no significant spatial variation in the redox potential of the bottom waters was found ($\alpha = 0.05$). All values were greater than zero (i. e., positive) with a mean value of Eh = $\pm$ 172 mv (Figure 13). Only the three stations in proximity to the channel (TR 13, TR 14, and TR 15) exhibited values less than zero with a mean Eh of −533 mv. Conversely, with only one exception, all the sediment values were less than zero (i. e., negative) with a mean Eh of −442 mv. The exception, Station TR 2, having a sediment with an Eh of + 192 mv is probably explainable in terms of the high apparent photosynthetic activity as evidenced by the high plant biomass, the high pH discussed previously and the highest dissolved oxygen concentration (9. 4 ppm) measured along the transect. While no significant difference in sediment redox potential was demonstrated between vegetated and non-vegetated areas, this was the only significantly different environmental parameter other than salinity between the two non-vegetated areas represented by assemblages A_{5-8} and A_{9-12}. The calculated F value for analysis of variance of 34. 14 was greater than the tabulated value of F = 13. 74 at the one per cent level of significance. The agreement between a grouping of the stations according to the sediment Eh values and the divisions of faunal assemblages can readily be seen by comparing the bar graph in Figure 14 with the assemblage groupings in Figure 5. The lack of any apparent agreement

FIGURE 13

Redox potential of bottom waters along the transect.

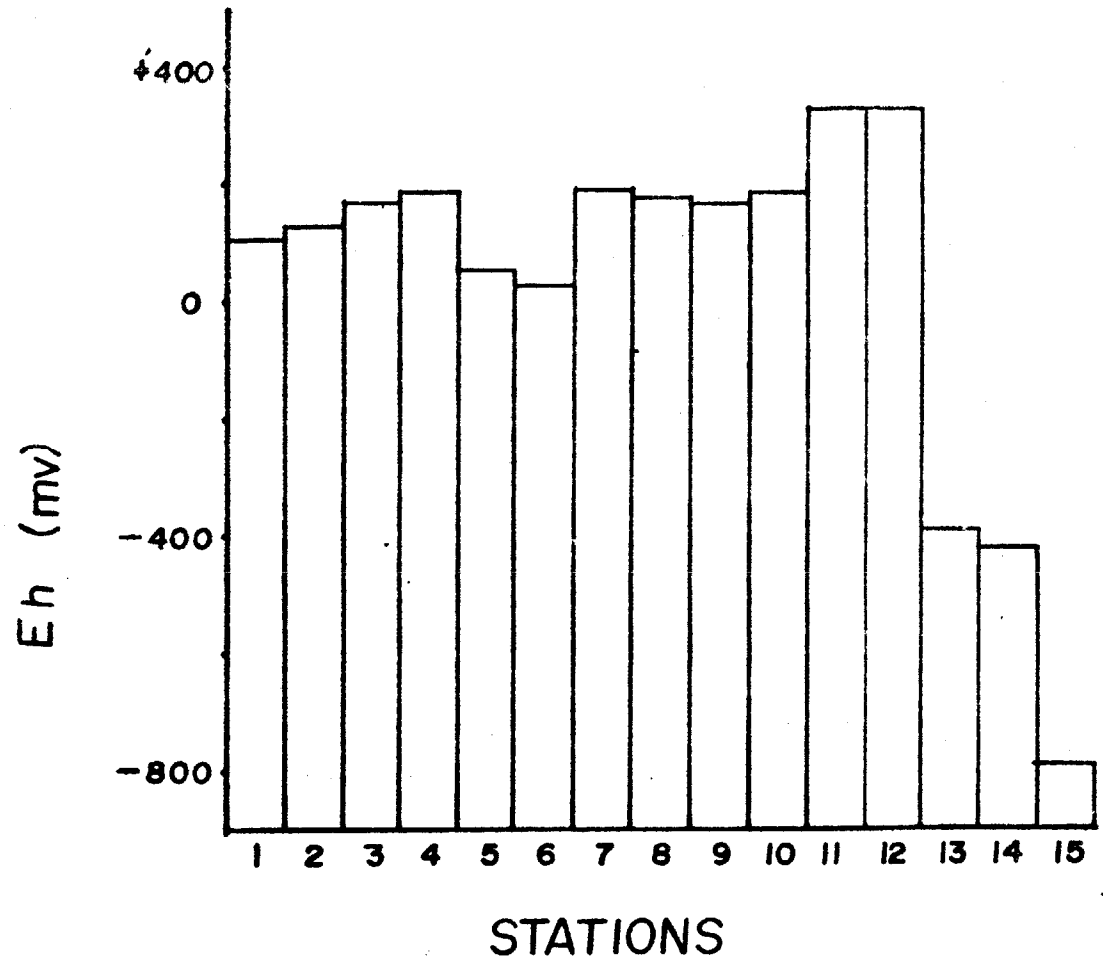
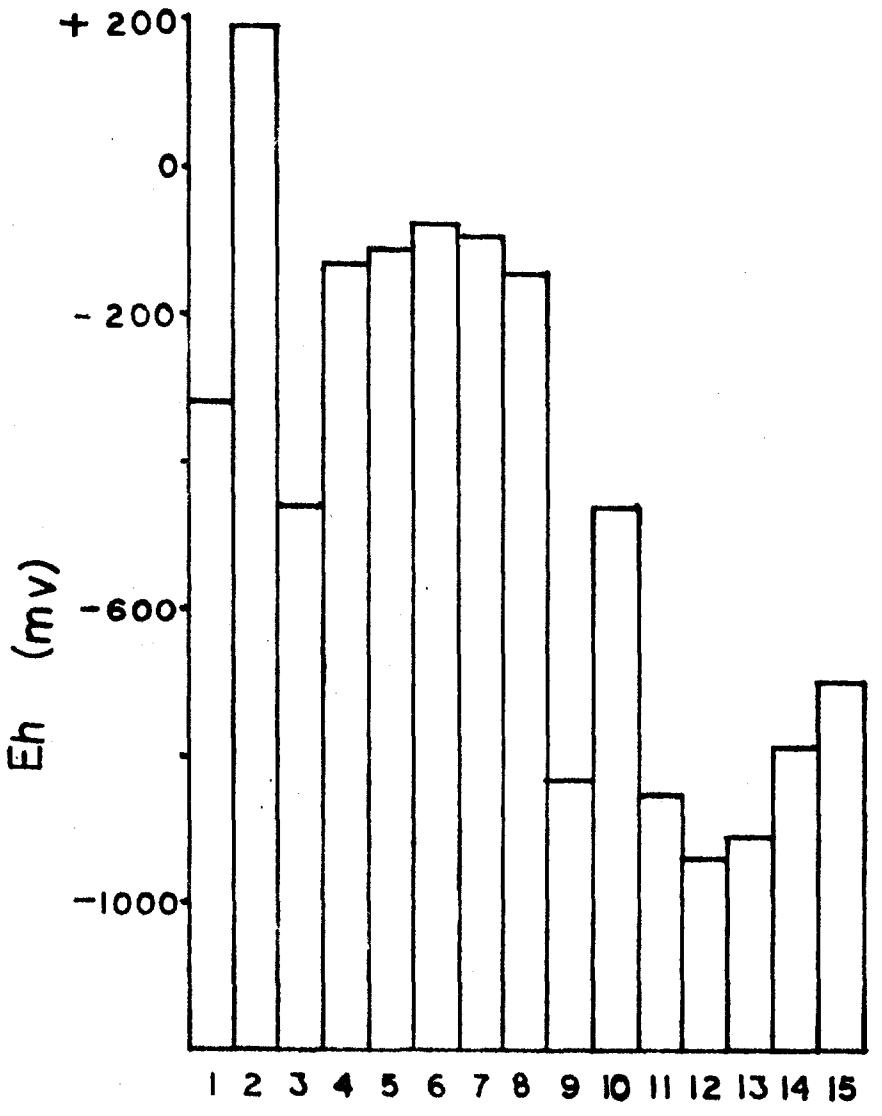

+400
0
-400
-800
Eh (mv)
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
STATIONS

FIGURE 14

Redox potential (Eh) of sediments at stations along the transect.


+ 200
0
- 200
-600
-1000
Eh (mv)
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
STATIONS

between the faunal assemblages and the sediment redox potential in the high vegetation areas is perhaps explainable by the presence of the rooted vegetation itself. In a detritus based food chain energy availability for detritus feeders is low in newly deposited plant detritus although organic carbon is high. (Odum and de la Cruz, 1967). This is apparently due to the not easily assimilable lignin and cellulose of the plant cells. Time and the activity of plant scavengers such as isopods are probably required to breakdown the plant detritus into forms or particle sizes more easily attacked by microbes. Thus a lack of a correlation between total organic carbon and sediment Eh may be anticipated in such areas. Considering the above arguments, it is suggested that the organic carbon content in these areas may be more closely related to the diversity and density of the organisms involved in reworking the plant detritus.

Dissolved oxygen concentration per se of the water column above the sediments would not necessarily be correlated with either the total organic content or the redox-potential of the sediment. This would be especially true in the grassy areas. It should be apparent, however, at this point that some relationship does exist. Both Eh and organic carbon are commonly used as indicators of oxygen availability or stress (Odum, 1971, and O'Connor, 1972). It is proposed that the Eh may be used as an indicator of the resultant effects of the availability of both oxygen and assimilable food to the community, since the redox potential

is affected by both inputs of oxygen (e. g., as a result of photosynthesis) and community metabolic activity (e. g., the reduction of organic materials to easily oxidizable forms) (Odum, 1971, and Zottoli, 1973).

If oxygen is less available at depth either as a result of reduced photosynthetic input or reduced circulation from the surface waters, and if organic detritus is transported to deeper waters and becomes more "trapped" at depth a relationship may be seen between the sediment Eh and depth. Figure 15 shows that as the depth of stations along the transect increases, the redox potential of the sediment decreases. This correlation is significant at $\alpha = 0.05$.

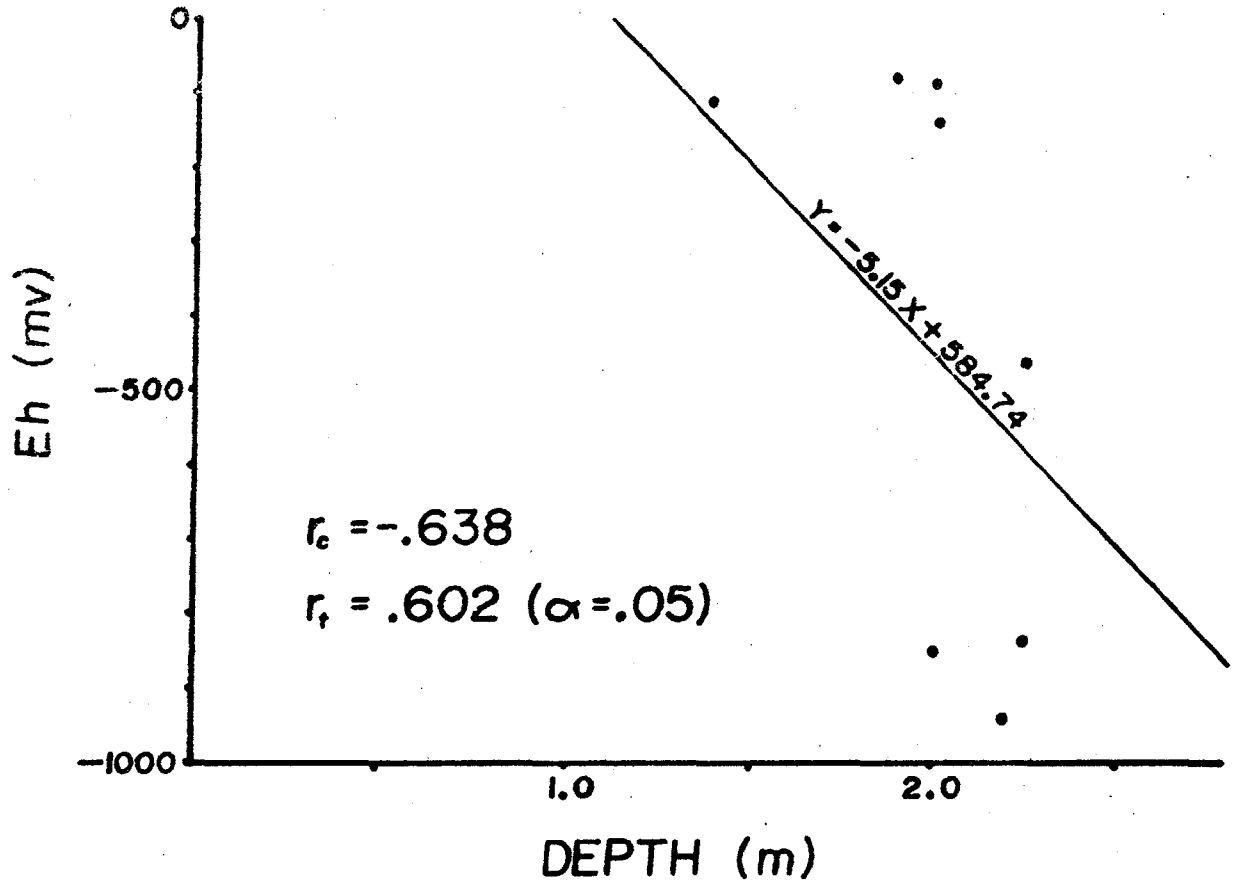
H. Diversity Indices

Some of the problems inherent in the selection of a suitable index of diversity have been discussed previously. In addition to those problems, it has been suggested that, as a result of definitional differences there is no reason to suspect that any two indices of diversity will correlate with one another (DeBenedictis, 1973). In view of this, a variety of diversity indices have been used in this study, each one being suited to a particular task.

The mathematically simplest and most direct index of diversity used is the number of species per station. Since all samples were taken by means of a grab which sampled a uniform area of the river bottom in each case, the number of species at each station can be

FIGURE 15

Linear regression of sediment Eh on depth at stations with sparse to no vegetation.


0
-500
-1000
Eh (mv)
Y = -5.15X + 584.74
r_c = -.638
r_t = .602 (α = .05)
1.0
2.0
DEPTH (m)

related to a unit of area (0.05 m^2). The question of sample size independence is not directly encountered since the number of individuals is not part of the proportional fraction (species/area). This type of index of diversity has been used by Whittaker (1965) for terrestrial plant communities. The limited motility of benthic organisms relative to the motility of terrestrial and pelagic aquatic organisms allows the use of plant methods of quantification as long as the sampling area is sufficiently large to allow the inclusion of dominant and rarer species. Whittaker (1965) suggests that such a means of determining diversity is the most convenient way to compare diversities in different communities.

The component of diversity that is represented by the number of species per unit area is most properly called species richness. Table 10 shows the species richness value for all stations along the transect. The species richness for the stations included in the assemblages identified in the trellis diagram were compared by analysis of variance in three combinations. The results are shown in Table 7. The significance of the differences in the variances of the three assemblages in terms of species richness is sufficient to support the assumption of a significant difference among the assemblages.

Species richness varied significantly among all three assemblages considered separately as well as between the assemblages at stations characterized by rooted vegetation and sparse or no vegetation. Between the two assemblages found in the absence of vegetation, species

TABLE 7

Comparison of species richness values between faunal assemblages.

Faunal Assemblages Compared	Calculated F Value	F Value at $\alpha = 0.01$
$A_{1-4} : (A_{5-8} - A_{9-12})$	17.46	10.04
$A_{5-8} : A_{9-12}$	34.14	13.74
$A_{1-4} : A_{5-8} : A_{9-12}$	23.99	8.02

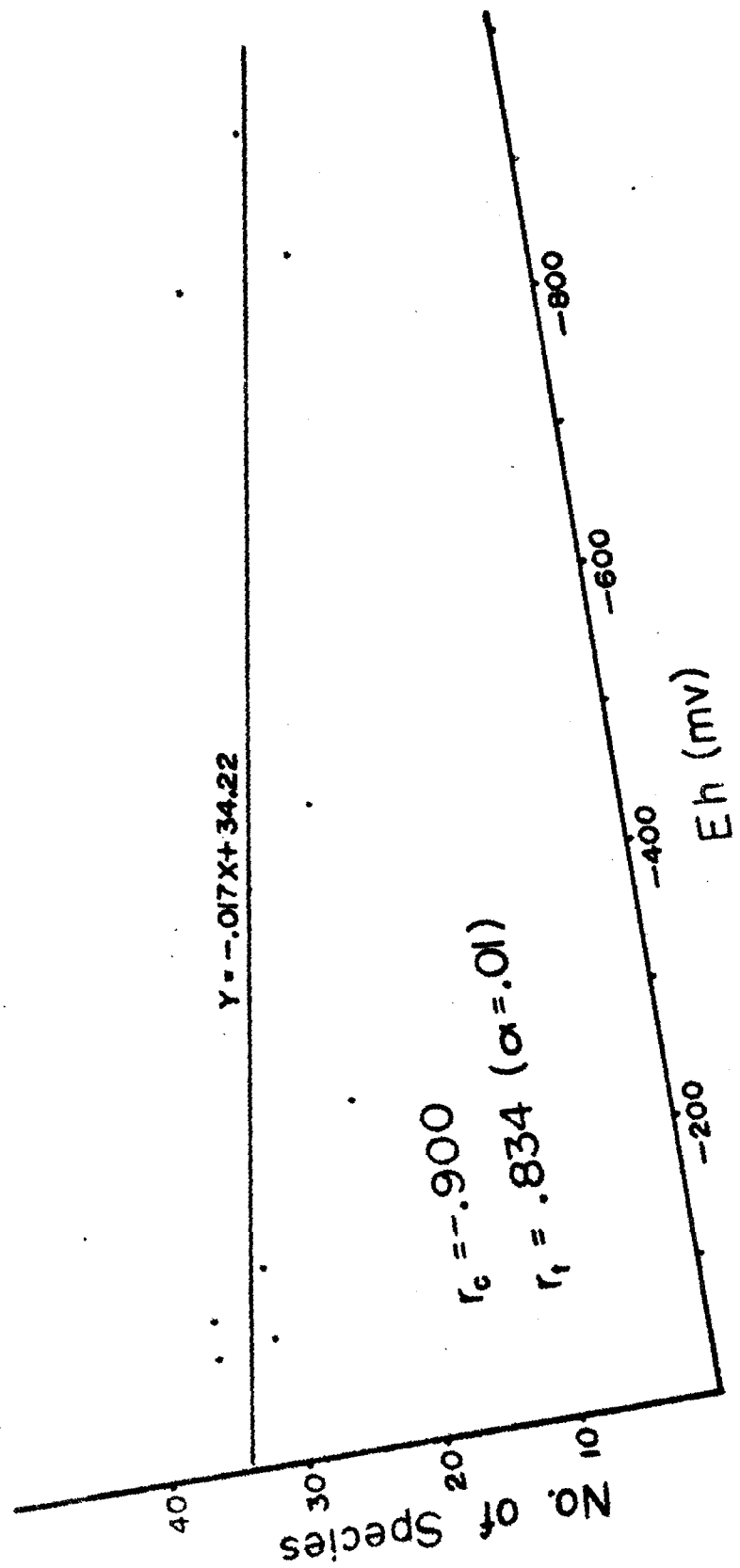
richness was the only faunal diversity index that differed significantly. It was shown previously that the only physical parameters that had significantly different variances between assemblages A_{5-7} and A_{9-12} were salinity ($\alpha = 0.05$) and sediment Eh ($\alpha = 0.01$). Linear regression analysis was performed to determine any correlation between species richness and these two physical parameters. No significant correlation ($\alpha = 0.05$) was observed in the regression of species richness on salinity but species richness was significantly correlated with sediment Eh (Figure 16). As the reducing environment of the sediment increased there is a resultant decrease in the number of species present. It appears, then, that the absence of the rooted vegetation to directly supply higher concentrations of dissolved oxygen in the face of high metabolic activity in the sediments limits the number of member species that can exist.

The second index of diversity used is one based on information theory to determine the evenness component of diversity. As a measure of evenness of finite collections, the ratio H/H_{max} is preferable (Pielou, 1966). In such a ratio, the value of $\underline{N}$ (sample size) becomes irrelevant since for large $\underline{N}$, $H_{max} \sim \log s$. Values for H, the observed species diversity, were calculated using the formula of Brillouin (1962). Logarithms of factorials were taken from published tables (Rohlf and Sokal, 1969) for values up to 500. Stirling's approximation to the logarithm of a factorial in the form

$$\log N ! \sim N (\log N - 1)$$

FIGURE 16

Linear regression of species richness on sediment Eh for stations with sparse or no rooted vegetation.


No. of Species
40
30
20
10
Eh (mv)
-400
-200
-600
-800
Y = -.017X + 34.22
r_c = -.900
r_t = .834 (α = .01)

was used for any $N \geq 500$. Values for H_{max} were also calculated directly for all $N < 500$. The approximation to maximum possible diversity of a population of a given $\underline{N}$ and $\underline{s}$ (the number of species) in the form

$$H_{max} \sim \log s$$

was used where $N \geq 500$. The possible range for the evenness ratio extends from zero to one. The higher the value, or as the value approaches unity, the greater the evenness of distribution among the species. Values for the species evenness at all stations along the transect are shown in Table 8. In general, as with species richness, species evenness was greater in the seagrass flats than in sandy bottom stations without rooted vegetation.

As can be seen in Table 8, the highest evenness value as well as the lowest species richness value was obtained at Station TR 13, the deepest station along the transect. Although depth variations were not significant among the sparsely vegetated Stations TR 5 through TR 12, the effects of depth as a buffer against climatological fluctuation is a major component of this thesis. Therefore, the occurrence of distinctly opposing values of the two components of diversity led to the comparison of both species richness and evenness with depth using those stations with little or no vegetation.

Water depth appears to be strongly correlated with species richness and evenness but in opposite directions. In the absence of vegeta-

TABLE 8

Information diversity values for stations along the transect.

STATION	Diversity (H)*	Evenness (J)**
TR 1	4.53	.81
TR 2	4.99	.98
TR 3	5.44	.98
TR 4	4.24	.75
TR 5	1.66	.32
TR 6	3.50	.68
TR 7	3.45	.70
TR 8	2.93	.62
TR 9	3.73	.80
TR 10	3.95	.88
TR 11	2.14	.56
TR 12	2.35	.59
TR 13	0.90	1.00
TR 14	2.28	.70
TR 15	3.70	.81

*Brillouin index, see text

**Pielou's evenness index, see text

tion the number of species decreases with increasing depth (Figure 17) and the evenness increases (Figure 18).

While it is difficult at this point to determine whether these opposite relationships between species richness and evenness with depth are real or artifactual, the possibility of such an occurrence is stated by Hurlbert (1971). If these two components of diversity increase in opposite directions with respect to the same parameter, the net effect on diversity appears to be determined by sample size. From the formula for H_{max} in the form

$$H_{max} = \frac{1}{N} \log_2 \frac{N!}{(m'!)^{s-r}\left[(m'+1)!\right]^{r}}$$

the distribution of m' individuals among $\underline{s}$ species is weighed. This corresponds to the evenness component of diversity. However, for large $\underline{N}$ the maximum possible diversity is approximated as a function of the species richness only. Thus it is implied that the evenness with which individuals are divided among the species decreases in importance as sample size increases. This trend will be seen again in the rarefaction curves used as indices of diversity. As a result, with diverging values for species richness and species evenness, the former will have the greater influence on diversity in large samples and the latter will be more important in small samples.

The rarefaction method of determining species diversity (Sanders, 1968) was employed in this study for two purposes. First, the method provides graphical representation of species diversity independent of

FIGURE 17

Linear regression of species richness on depth.

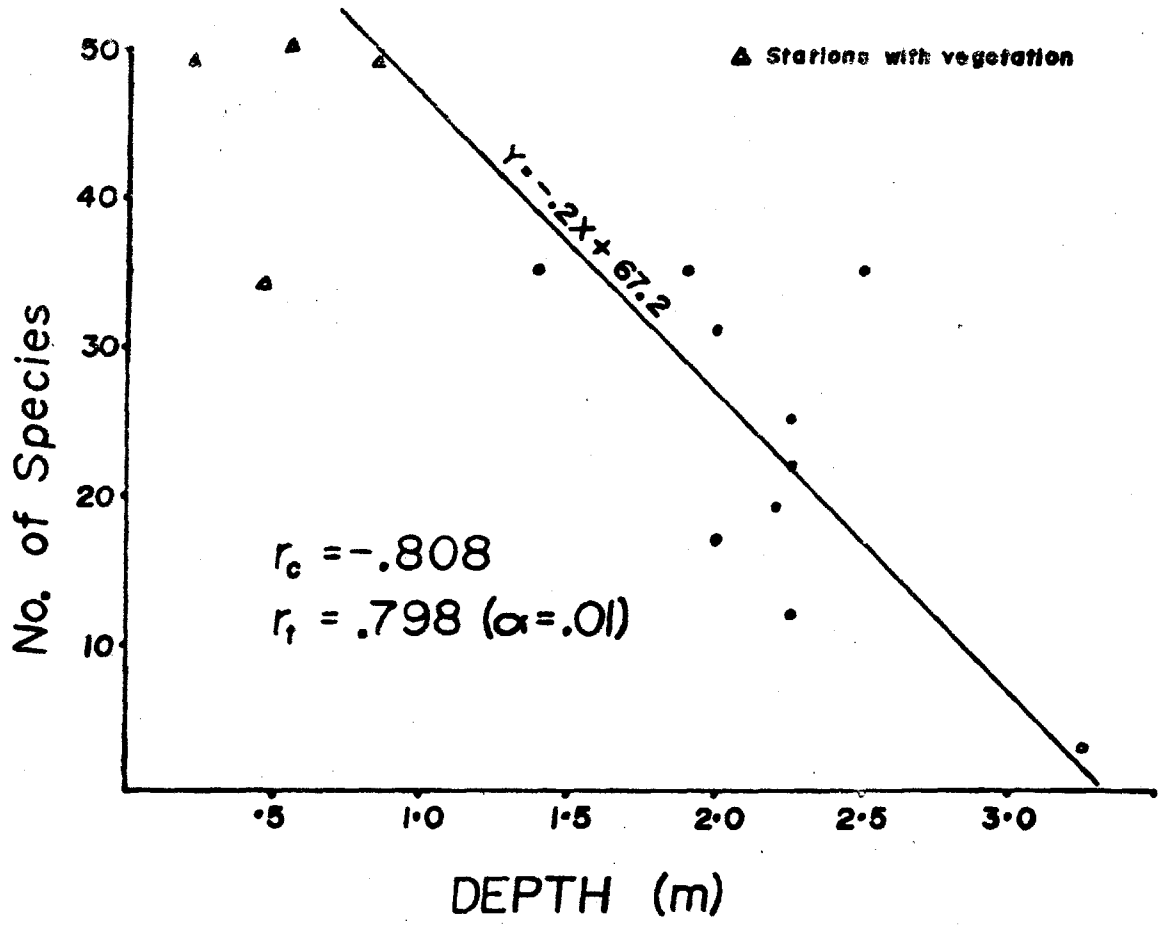
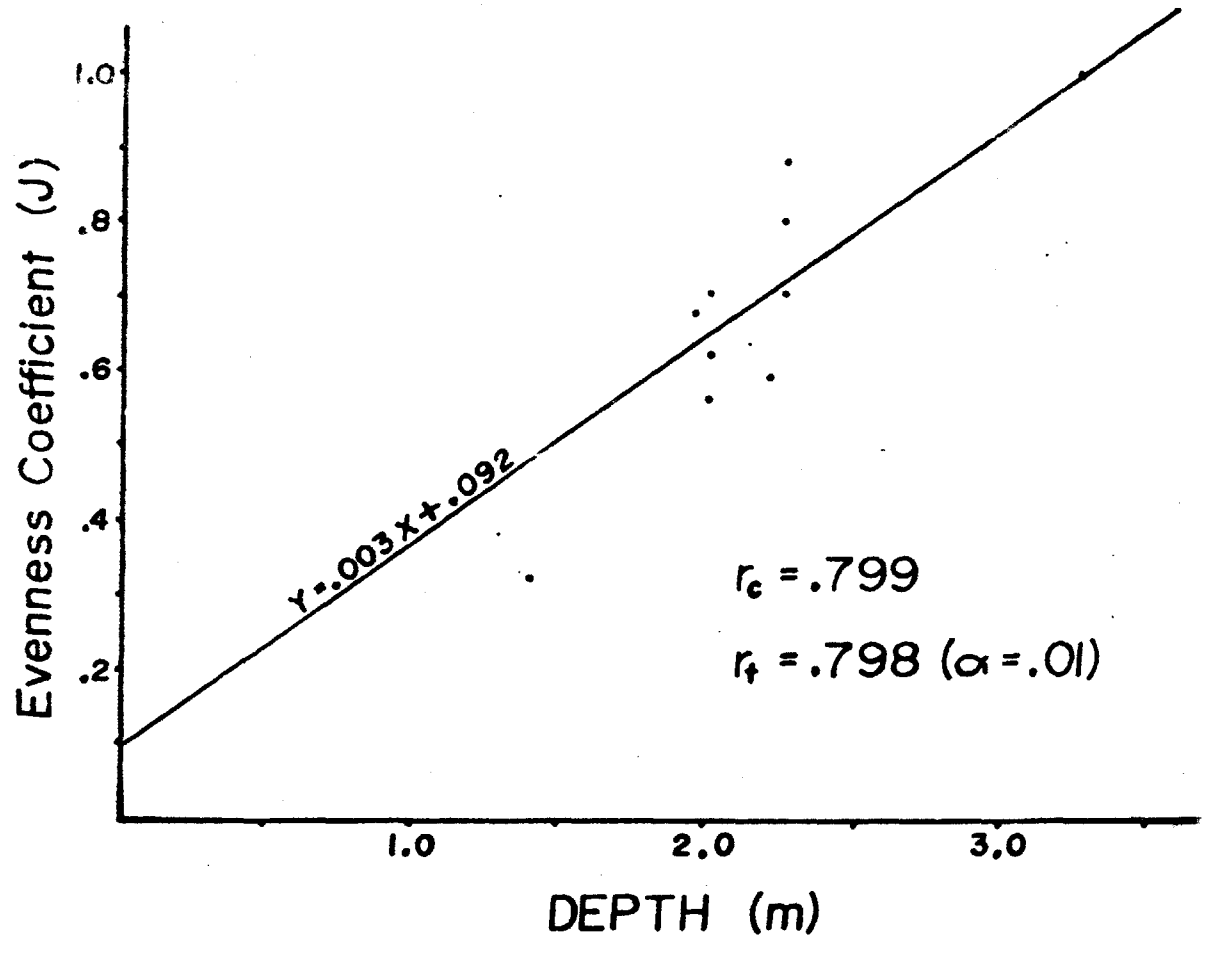

▲ Stations with vegetation
Y = -.2X + 67.2
r_c = -.808
r_t = .798 (α = .01)
No. of Species
50
40
30
20
10
·5
1·0
1·5
2·0
2·5
3·0
DEPTH (m)

FIGURE 18

Linear regression of species evenness on depth.


Evenness Coefficient (J)
1.0
.8
.6
.4
.2
Y=.003X+.092
r_c = .799
r_t = .798 (α = .01)
1.0
2.0
3.0
DEPTH (m)

density or sample size. This facilitates comparison of data from studies in other geographical locations. Second, the curves obtained provide a relative measure of bilogically accommodated versus physically controlled portions of the total community. According to Sanders, the closer a curve approaches the abcissca, the more biologically accommodated is the community. Conversely, the closer the curve approximates the ordinate, the greater the role that physical factors may be expected to play in species distribution. The shape of the curve is determined by the evenness component and the final value by the species richness. Thus at small sample sizes the evenness component is of considerable importance in determining diversity. As sample size increases, the species richness component becomes increasingly more important.

The curves generated by the data from each of the fifteen stations along the transect are shown in Figure 19 and the corresponding data tabulated in Table 9. The curves provide the same general indications as did the previous diversity indices. High diversity is found at those stations characterized by dense rooted vegetation, that is Stations TR 1 through TR 4. The end point of the curves represents the actual number of species and individuals sampled at each station.

Four of the stations exhibited distinctly higher curves, and by Sanders' definition are subject to a greater degree of biological accommodation than the other stations. This means that one might expect a

FIGURE 19

Rarefaction curves for all stations on the transect.

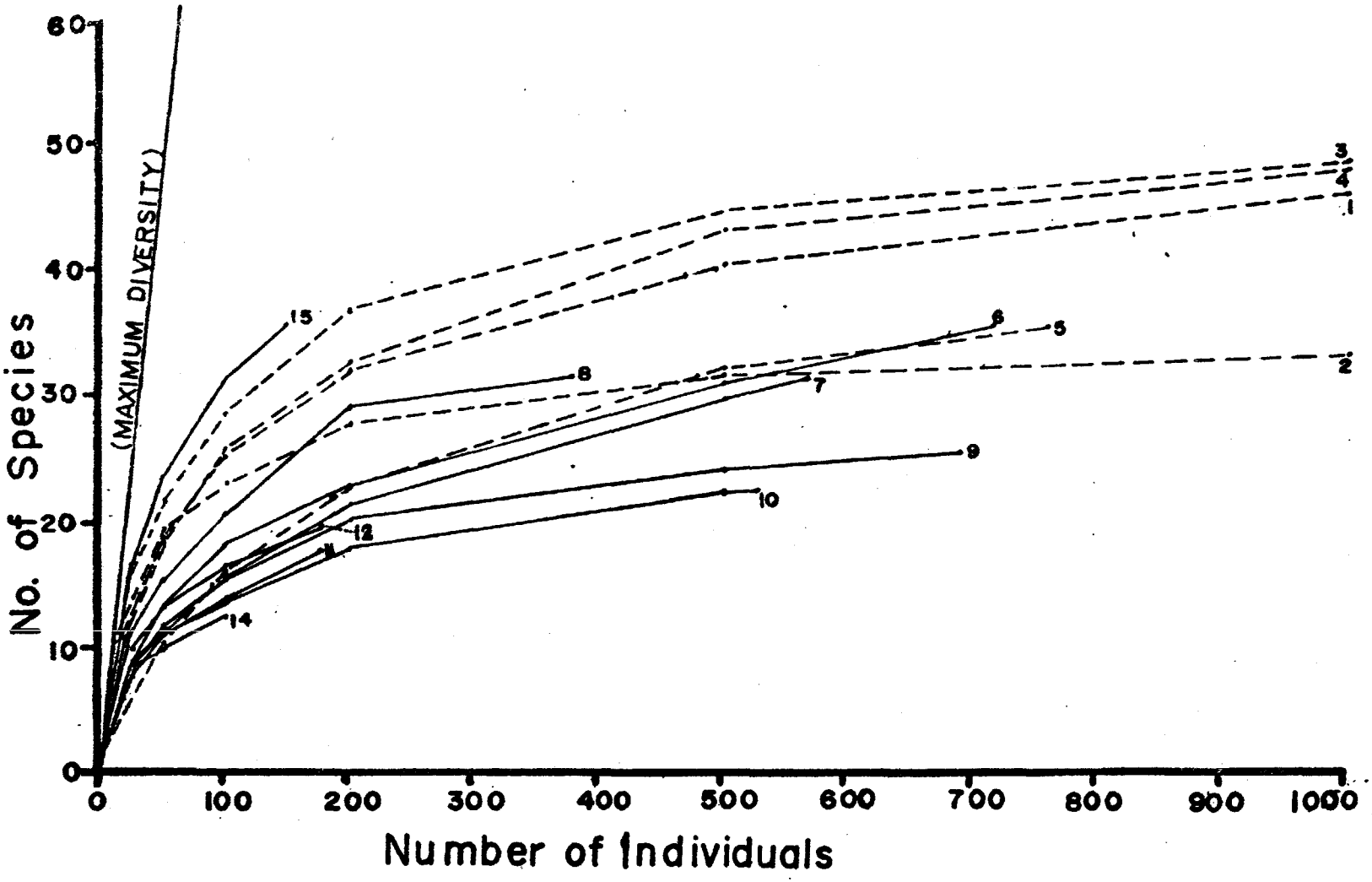

No. of Species
Number of Individuals
(MAXIMUM DIVERSITY)
0
10
20
30
40
50
60
0
100
200
300
400
500
600
700
800
900
1000
1
2
3
4
5
6
7
8
9
10
11
12
14
15

TABLE 9

Rarefaction data for all stations on the transect.

Station	Actual # Indiv/Spec.	2000	1000	500	200	100	50	25	20	10	5	4
TR 1	2008/49		45.5	40	31.5	24.7	18.2	11.8	10.3	6.8	4.4	3.8
TR 2	1463/34		32.7	31	23.7	22.4	18.1	13.2	11.6	7.4	4.4	3.7
TR 3	1361/50		48.1	44.2	36.3	28.0	21.1	15.5	13.6	8.7	4.0	3.2
TR 4	1314/49		47.6	42.6	32.1	25.1	17.8	12.0	10.6	6.6	4.0	2.4
TR 5	759/35			31.6	22.3	15.5	9.8	5.5	4.6	2.8	1.9	1.7
TR 6	716/35			30.4	22.4	17.7	12.8	8.4	7.2	4.1	2.6	2.2
TR 7	568/31			29.3	20.7	15.0	11.2	7.9	6.9	4.3	2.6	2.3
TR 8	376/31				25.9	20.1	15.0	10.8	9.6	6.4	3.8	3.2
TR 9	689/25			23.6	19.8	15.1	10.7	8.2	7.1	4.6	3.3	2.8
TR 10	527/22			21.8	17.5	13.1	10.5	7.3	6.4	4.2	3.1	2.8
TR 11	175/17					13.1	10.4	8.1	7.2	4.6	3.3	2.8
TR 12	177/19					16.0	12.8	9.4	8.4	5.5	3.2	2.8
TR 13	4/3											3
TR 14	100/12					12	9.5	7.8	7	5.1	3.6	3.2
TR 15	148/35					30.8	23.2	15.8	13.5	8.0	4.8	3.0

closer coupling between species and their total environment. Such coupling might be detected in the significance of correlations between organisms and some parameter that may influence their distribution.

In order to test the above hypothesis, some general assumptions must be made. While remaining cognizant of the fact that morphological features do not provide unquestionable proof of an organism's position in a food chain, it is possible to divide organisms into basic trophic feeding types such as deposit feeders, suspension feeders, carnivores and scavengers (Bloom, et al., 1972, Sanders, 1958, Rhoades and Young, 1970). Such a breakdown was accomplished for each station sampled. (Table 10). Information on feeding habits of the various species was obtained from the various taxonomic references as well as Bloom, et al. (1972), Barnes (1963) and Zottoli (1973). In addition to assuming that organisms may be so distinctly divided according to feeding type, it must also be assumed that at a given level of environmental stability, the number of organisms that may be supported in a community is dependent upon the amount of energy available as food. If the organic carbon content of the sediment may be used as a measure of the amount of food available to deposit feeders, it follows, then, that as stress on a community is reduced the number of deposit feeders will be correlated with the amount of organic carbon in the sediment.

As seen in Figure 19, Stations TR 15, TR 3, TR 4 and TR 1 are the most biologically accommodated or, in other words, the least

TABLE 10

Summary of abundance of trophic feeding types at each station (DF = deposit feeders, SF = suspension feeders, C/S = carnivores/scavengers, H/S = herbivores/scavengers, EP = ectoparasitic, C = carnivores).

TROPHIC FEEDING TYPES DISTRIBUTION

Sta. #	DF	SF	C/S	H/S	EP	C	TOTAL	% SF	% DF
1	1700	79	171	25	25	8	2008	3.94	84.7
2	756	488	126	90	3	0	1463	33.36	51.7
3	970	128	219	29	3	12	1361	9.4	71.3
4	865	279	102	60	4	11	1310	21.30	66.0
5	716	17	20	3	3	1	758	2.2	94.4
6	642	56	15	1	2	0	716	7.8	89.7
7	514	39	13	2	0	0	568	6.9	90.5
8	291	56	27	0	2	0	376	14.9	77.4
9	632	36	21	0	0	0	689	5.2	91.7
10	482	28	17	0	0	1	527	5.3	91.5
11	160	7	8	0	0	0	175	4.0	91.4
12	152	1	24	0	0	0	177	.6	85.9
13	4	0	0	0	0	0	4	0	100.0
14	68	2	30	0	0	0	100	2.0	68.0
15	104	34	9	1	0	0	148	22.97	70.3

stressed stations. Using linear regression, a significantly ($\alpha = 0.05$) positive correlation was found between the number of deposit feeders and the organic carbon content of the sediments for these stations (Figure 20). A similar regression was performed between the number of deposit feeders and the organic carbon content of the sediments for Stations TR 9, TR 10, TR 11, TR 12, and TR 14 which were selected to represent more physically controlled or stressed stations. This correlation was negative but not significant (Figure 21). Acceptance of the null hypothesis often only implies that there were not enough data to permit rejection. However, since more data points were used in the latter test, acceptance of the null hypothesis, with the conclusion that no correlation in fact exists, is probably valid.

I. Comparisons with Other Studies

While uniformity of methodology remains something to be hoped for in studies of the marine benthos, the methods used herein provide the capability of limited comparison with at least two previous studies.

Using the rarefaction techniques, some comparison is possible with the work of Sanders (1968). In sampling a wide variety of communities, Sanders established ranges of rarefaction curves for both boreal and tropical estuaries. Since Sanders used only polychaete and bivalve species in his calculations, similar curves were calculated from the Indian River data (Figure 22). The curves for Sanders'

FIGURE 20

Linear regression of the number of deposit feeders at biologically accommodated stations on the organic carbon content of the sediments.

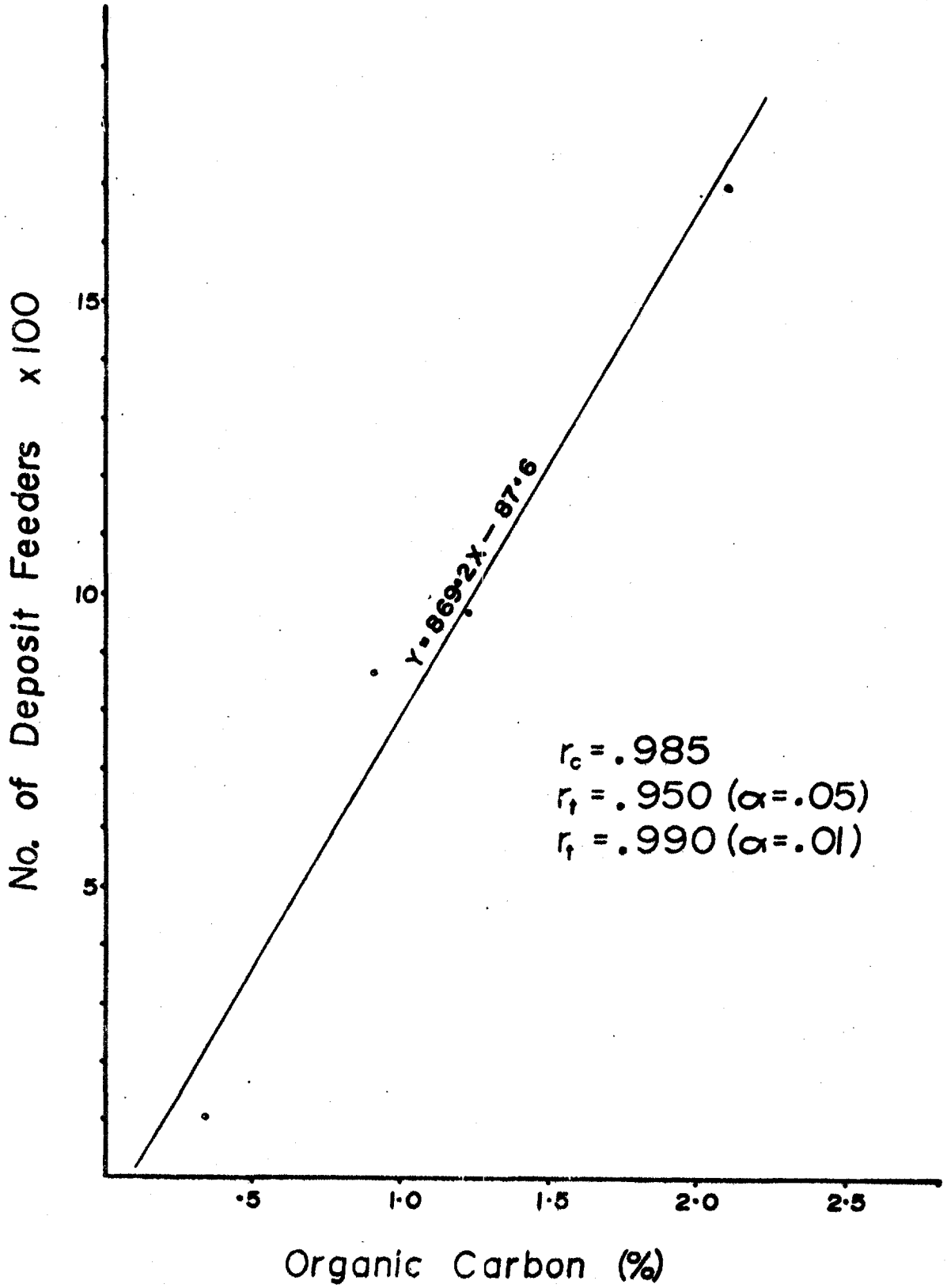

No. of Deposit Feeders x 100
15
10
5
Y = 869·2X − 87·6
r_c = .985
r_t = .950 (α = .05)
r_t = .990 (α = .01)
·5
1·0
1·5
2·0
2·5
Organic Carbon (%)

FIGURE 21

Linear regression of the number of deposit feeders at physically controlled stations on the organic carbon content of the sediments.

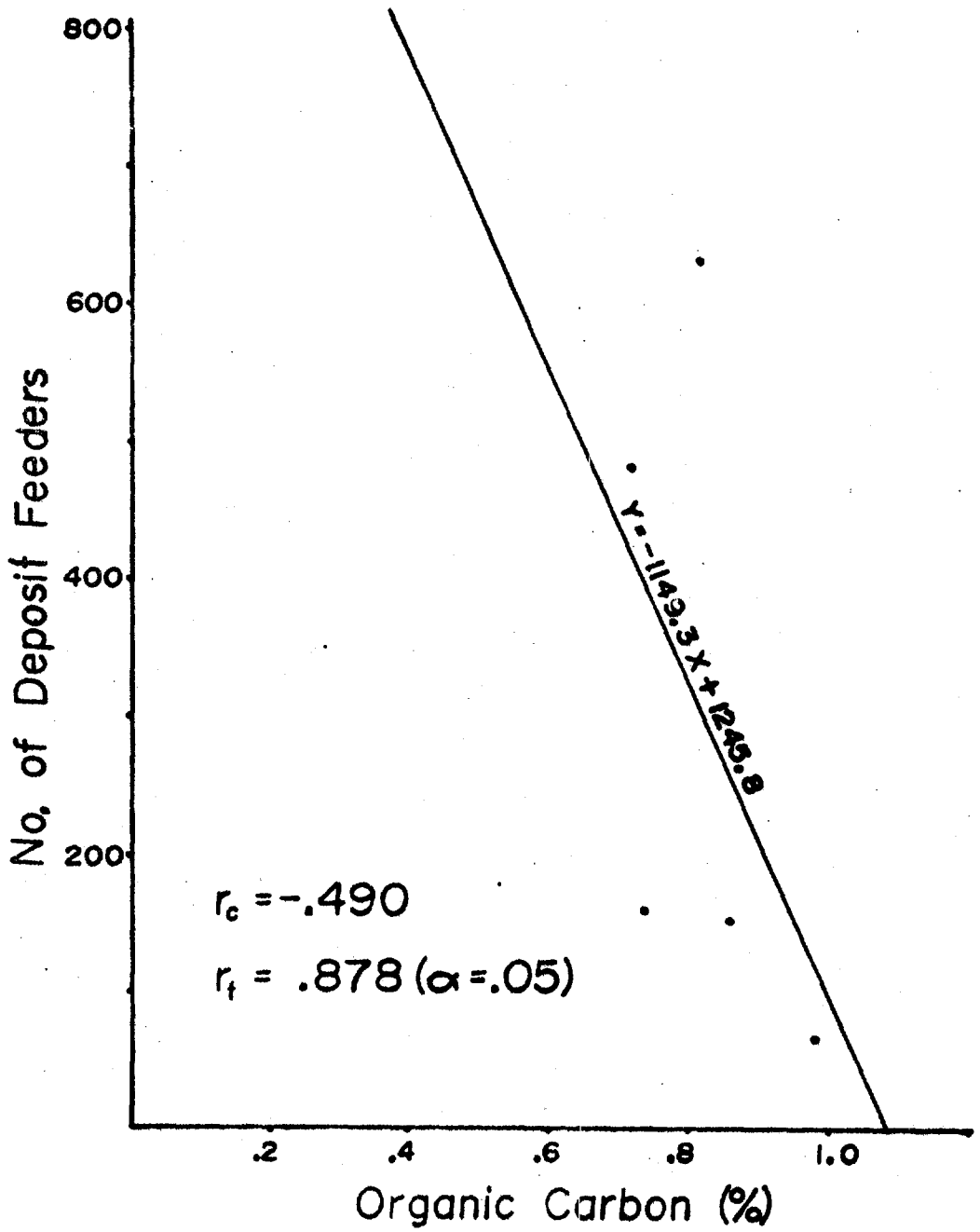
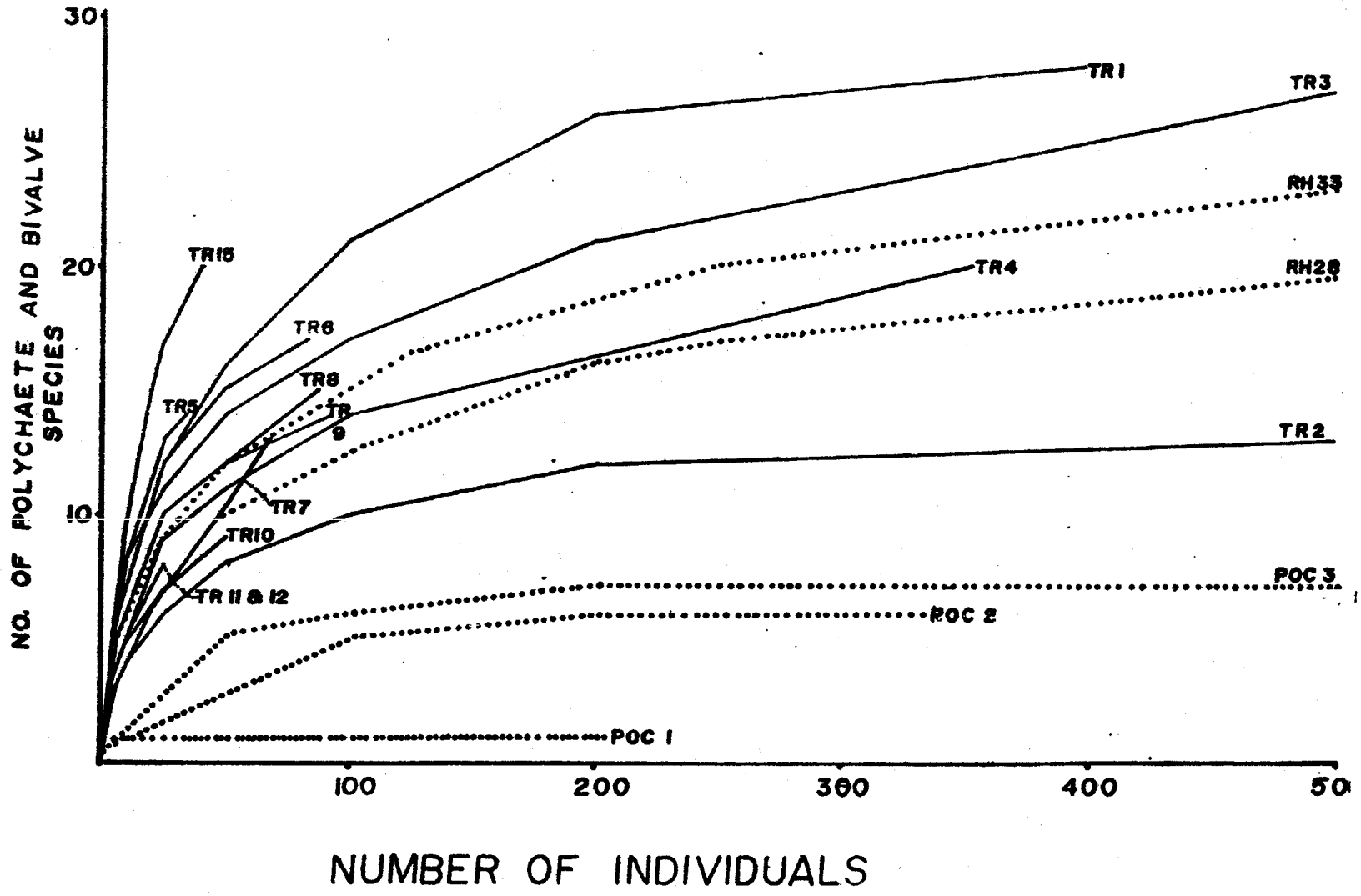

800
600
400
200
No. of Deposit Feeders
Y = -1149.3X + 1245.8
r_c = -.490
r_t = .878 (α = .05)
.2
.4
.6
.8
1.0
Organic Carbon (%)

FIGURE 22

Rarefaction curves for Indian River samples and boreal and tropical estuaries from Sanders (1968). Only polychaete and bivalve species are used.

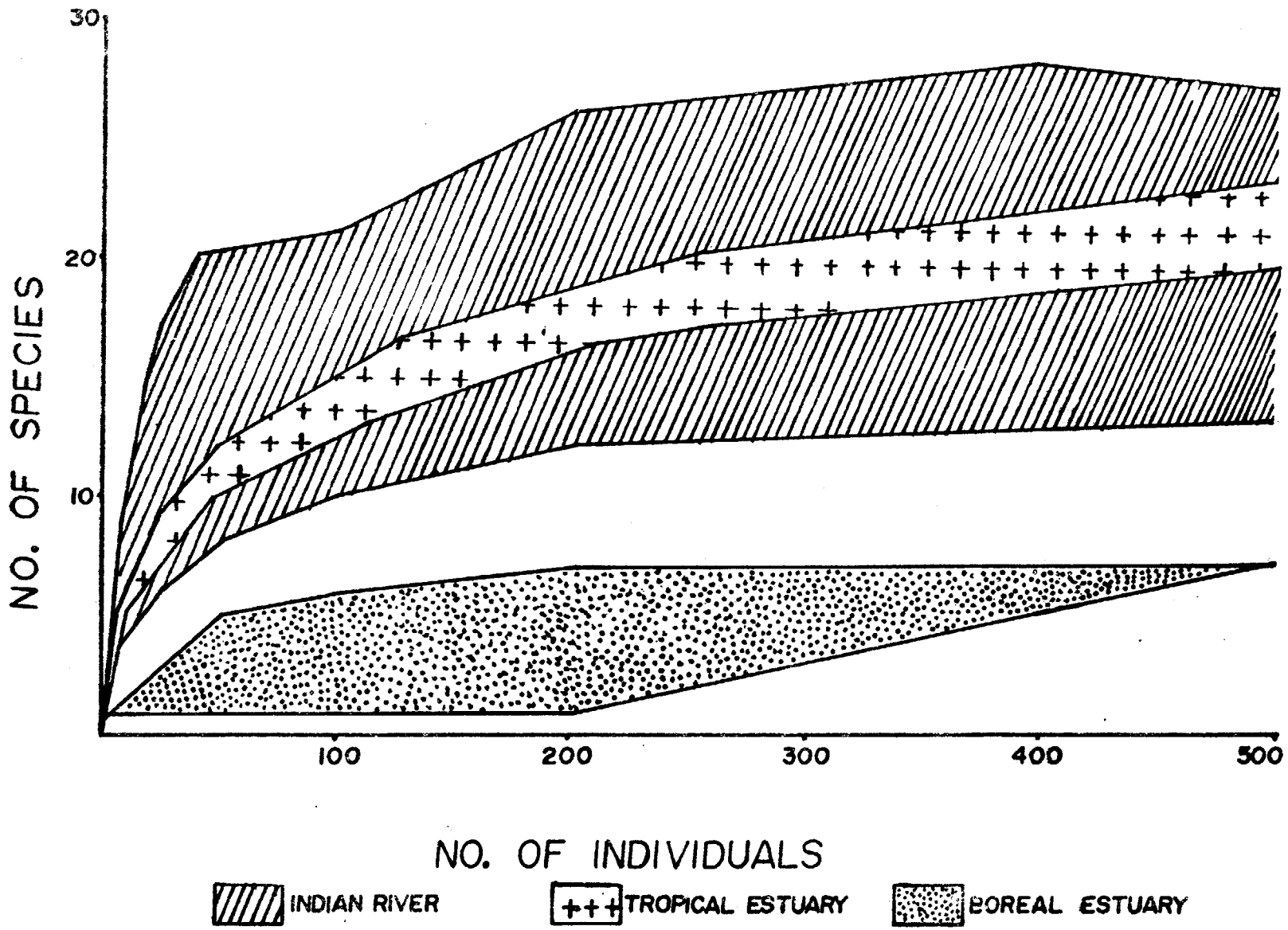

30
20
10
NO. OF POLYCHAETE AND BIVALVE SPECIES
TR1
TR3
RH35
RH28
TR4
TR2
TR16
TR6
TR8
TR5
TR9
TR7
TR10
TR 11 & 12
POC 3
POC 2
POC 1
100
200
300
400
50
NUMBER OF INDIVIDUALS

tropical estuaries (RH28 and RH 33) fall well within the range of the curves for the Indian River. The boreal estuary curves (POC 1, 2, and 3) fall distinctly below those of the tropical estuaries. Sanders denies the usefullness of attempting to ascribe confidence limits to the curves as a measure of statistical validity but instead uses a graphical demonstration of the distinct separation between the different communities. A similar method of comparison is shown in Figure 23. While the similarity is immediately apparent, the range of curves for the tropical estuaries sampled by Sanders is considerably narrower than that of the Indian River. Such a variation is probably attributable to the relative sample sizes. Therein lies the only difference in methodology. A Ponar grab was used in this study while Sanders used a modified anchor dredge which provided much larger samples and thus less variation in data.

Another study which used a Ponar grab was performed by O'Connor (1972). In that study, duplicate grabs and a one mm screen were used making it less comparable to the Indian River work. Brillouin's information measure was used to calculate diversity in that study in Moriches Bay, New York. The use of the larger sieve, as well as the more severe temperature climate should have provided a lower diversity than the present study, but such was not the case. The average diversity for Moriches Bay, excluding the dredged channels was 4.6 as compared to 3.3 for the Indian River samples. The dredged channels

FIGURE 23

Comparison of ranges of rarefaction curves from Indian River samples with those of boreal and tropical estuaries studied by Sanders (1968).


30
20
10
NO. OF SPECIES
100
200
300
400
500
NO. OF INDIVIDUALS
INDIAN RIVER
TROPICAL ESTUARY
BOREAL ESTUARY

yielded diversity values of 1.3 and 0.9 for Moriches Bay and the Indian River respectively. In the light of present theory, such discrepancies are not reconcilable.

IV. DISCUSSION

The major areas of emphasis in this study are faunal diversity and the coupling of organisms to their environment. Before further discussing these areas, certain limitations characterizing the methods used should be clarified. The mesh size (0.42 mm) of the sieves used, while smaller than that commonly used for benthic studies (1 mm) is still too coarse to adequately determine the total faunal diversity. Interpolating from the data of Reish (1959) one might expect to retrieve 100 per cent of the Nemerteans and Mollusks, 95.5 per cent of the Polychaetes and only 65.2 per cent and 3.75 per cent of the Crustacea and Nematodes respectively. Although only about 70 per cent of the fauna can be expected to be retained on the 0.42 mm screen, this is an increase of 47 per cent over the retention on the one mm (1 mm) screen used by O'Connor (1972), Bloom, et al. (1972), and others.

The statistical validity of the aliquot has not yet been tested as an estimate of the total population. Some bias may be expected in a comparison between samples with dense rooted vegetation and sparsely vegetated sandy samples. However, subsequent work with this method has shown repeatedly similar samples with respect to faunal diversity values over relatively long periods of time (Thomas, unpublished data). Combining this with the similarities between stations in this study supports the proposition that the method is acceptable in the face of the

overwhelming task of individually sorting the 75 grabs that were taken along the transect.

Seasonal changes in diversity were not addressed in this study although such an investigation is presently underway. It is recognized that this study may not represent optimum conditions in the Indian River, since Odum (1970) and O'Connor (1972) have discussed the effects of the summer season on various estuarine ecosystems in terms of the relative stress that that season places on the benthos. The faunal diversity values described herein, then, may well represent minimum values.

The statistical tests employed in this study are generally well accepted. Significance was, by convention, acknowledged at the five per cent level. That is, that there is only a five per cent chance that one is in error in rejecting the null hypothesis. Significance has been often qualified in the discussions as being "strong" or "weak." These are purely subjective terms implying only that either the one per cent or the five per cent levels of significance, respectively, were used to determine the significance. Acceptance of the null hypothesis, of course, can never be conclusive since more data may be all that is required to reject it (Neville and Kennedy, 1964). On the other hand, rejection of the null hypothesis is only slightly more conclusive since additional data may only strengthen the probability of rejection. Thus weakly significant ($\alpha = 0.05$) relationships may become strongly significant ($\alpha = 0.01$) with additional data.

Mention should also be made at this point concerning the sorting efficiency of the samples. The addition of the Rose Bengal stain to the preserved samples provided an excellent contrast between the organisms and the shell debris in the sample. This allowed even untrained technicians to remove and save only the "pink things." Two samples were chosen arbitrarily to examine the sorting efficiency. All shell debris following the initial sorting of these samples was retained and re-sorted. In one of these samples from Station TR 6, three ostracods, one bivalve, and three nematodes were missed in the initial sorting. Since nematodes were not quantified in this study, the remaining organisms constituted less than one per cent of the total sample. In the other sample from Station TR 12, one ostracod, one polychaete and four nematodes were found by re-sorting. The ostracod and polychaete represented approximately one per cent of the total sample. These percentages of error would tempt one to estimate the sorting process to be about 99 per cent efficient. Neither of these samples, however, were taken from grass beds where more error may be introduced since the grasses also tend to incorporate the stain. It is suggested that, when all samples are considered, sorting efficiency approaches the range of 85 to 90 per cent. This is considerably higher than the 75 per cent efficiency considered to be desirable for such studies (holme and McIntyre, 1971).

The final note limitations in methodology is directed toward the use of the rarefaction method of determining species diversity.

According to Sanders (1968) the method was developed for comparisons of within habitat diversity rather than the diversity between habitats. This implies that the diversities of soft bottom benthic invertebrates may be compared on a global scale while the diversities of the benthos and the plankters within the same body of water cannot be compared. A second limitation is the effect imposed by aggregation of species. The occurrence of clumped population may distort the diversity curve. Thus a large aggregation of the diminutive polychaete Fabricia sabella which comprised about 32 per cent of the sample at Station TR 2 was probably responsible for the aberrent positioning of the curve for that station. A similar situation is cited by Sanders (1968).

The initial effort in this study was directed toward investigating species diversity with respect to those parameters which may place a physical stress on the benthic community. The most significant are generally considered to be salinity, temperature and the nature of the substrate (Nichols, 1970). In turn, the depth of the water may significantly affect the effects of these parameters on the benthos by acting as a buffer against rapid or extreme fluctuations in the environment.

In this segment of the Indian River, the physical character of the sediment was shown to be sufficiently homogeneous so as to have little effect on the diversity and faunal distribution of the benthos. The physical or "abiotic" parameters of the sediment have been shown in other studies to be a significant determinant of the benthic community but these parameters (median grain size, sorting coefficient, and

per cent of silt and clay) do not vary significantly over the length of the transect from Stations TR 1 through TR 12.

Salinity, while it obviously plays a role in determining which species may inhabit the estuary as a whole, was so homogeneous temporally and spatially as to account for no demonstrable effect on the benthic fauna. Nichols (1970) found that salinity variations between 2.53 and 3.05 per cent were not able to account for the distribution of polychaetes except at one station in the mouth of a fresh water-influenced bay. At this station, daily salinity fluctuations as well as sediment transport due to tidal action were quite severe. That the polychaete assemblages throughout his study seemed dependent upon the physical nature of the substrate probably places most of the responsibility for stress with the constantly shifting substrate at that station. Since estuarine species are commonly euryhaline in comparison to their oceanic relatives, it would seem unlikely that small salinity fluctuations of 0.5 per cent would have an effect on the localized distributions of the residents. Further support of this conclusion is provided by the fact that higher temperatures facilitate acclimation to lesser salinities (Hedgepeth, 1957). Thus the higher temperature range of the water in this portion of the Indian River (12-30.2° C.) as compared to that of the York River (0.6 - 29.4° C.) which has a similar benthic faunal composition (Warinner and Brehmer, 1966) implies that salinity minimums would have less effect in the Indian River.

While the physical nature of the substrate was not significant as a determinant of diversity in the benthos, the same cannot be said for the biotic characteristics of the substrate. Significant differences could be seen in the components of faunal diversity dependent upon the presence of rooted vegetation. Higher values of both components of diversity, species richness and evenness, were found in areas so vegetated. According to Odum (1970) the primary advantage of these seagrasses to the benthos is in the provision of more stable sediments by action of the roots. Seagrasses also provide additional niches to be filled in terms of attachment sites and food types (Gosner, 1971), thus allowing a higher diversity. As documented by Stauffer (1937), the removal of rooted macrophytes resulted in a drastic decrease in diversity and complexity of the community.

Although the presence of these plants benefits community diversity, they complicate further the separation of the effects of the physical parameters of the environments. The distribution of these plants appears to be limited by water depth since no rooted macrophytes were found in samples from depths greater than 1.5 meters. A discussion concerning the cause and effect relationships between the occurrence of rooted vegetation, depth, and the quantity of suspended material in the water limiting light penetration tend to become too circular to include within the scope of this study.

The occurrence of rooted seagrasses and small variations in depth have widely divergent effects on the diversity. As stated previously, higher diversity occurs in the shallow grass flats where the water depth is less effective as a buffer against climatic variations such as temperature. The more constant temperatures obtained at a depth of two meters as compared to the daily and seasonal temperature variations in the shallower grassy station would appear to indicate that some other parameter is more worthy of consideration. It may be argued, however, that these temperature variations are predictable and as such do not qualify as an environmental stress. This argument does not deny the possibility that such variation, even though predictable, should place a greater requirement on organisms for a flexible adaptive strategy than constant conditions.

Two of the parameters measured appear to coordinate the effects of the seagrasses, temperature, and depth. These parameters are dissolved oxygen concentration and sediment redox potential (Eh). Dissolved oxygen stress is common to estuaries, especially during summer (Odum, 1970). The sources of dissolved oxygen to aquatic organisms are primarily through photosynthetic activity and diffusion across the air-water interface (Sverdrup, et al., 1942). During the summer, the reduced solubility of oxygen due to higher water temperatures and the reduced wind velocities of that season (Lasater, 1971) would tend to reduce both interfacial exchange and vertical mixing. To

aquatic organisms, dissolved oxygen is a major limiting factor (Odum, 1971) and the presence of the rooted seagrasses in the shallow water relieves this stress. In the deeper water where grasses are absent and temperature and dissolved oxygen concentration are both lower and more constant, the amount of dissolved oxygen available for respiration serves to limit the number of member species.

In a detritus-based food chain, rooted submerged or emergent plants generally serve as autotrophs in the benthic community. Direct herbivory among the invertebrate members of the benthic community is often absent in this case. Instead, grasses are broken off by wave action, grazing by larger herbivores such as manetees, or by feeding activities of water foul, etc. These grass fragments are deposited on the bottom where aerobic microbial activity may break them down to a form assimilable by detritus feeders. Whether detritus feeders utilize the oxidizable carbon directly or act as non-selective predators on the bacteria is unimportant to this discussion. In either case, the amount of oxidizable organic carbon represents the quantity of available energy produced by the autotrophs. In the grass beds this quantity of available food is understandably greater than in the deeper sandy areas where it must be transported by water currents. The amount of oxidizable organic carbon may be measured directly or it appears to be preferable at this point to determine a resultant of the combined effects of the amount of oxidizable organic carbon and the availability of dissolved oxygen. While microbial metabolism is probably highest in the grass

flats, especially in the warmer summer temperatures, the photosynthetic activity provides sufficient oxygen so that no appreciable difference can be seen, in terms of the resultant redox potential, between the grass flats and the sandy, sparsely vegetated areas. In the absence of the rooted seagrasses, the species richness is seen to decrease linearly with the redox potential. An increase in oxidizable carbon in the presence of limited oxygen over relatively long periods of time results in a decrease in the number of species able to exist in the environment. The possibility of resuspension of deposits by wave or current action decreases with depth and hence deeper bottoms may tend to become sinks or traps for large quantities of oxidizable organic carbon. If dissolved oxygen is not readily available to these deeper areas, then the oxidation of this material by microbial metabolism places an oxygen stress on the macrofauna. Such an oxygen stress has been postulated by O'Connor (1972) to result in a decrease in microfaunal biomass. Faunal biomass was not directly measured in this study but size comparisons gave indications that macrofaunal biomass would be less than anticipated given the numerical abundances of species. As an example, polychaetes, although many species have distinct respiratory structures, often use their entire body surface for gaseous exchange (Barnes, 1963). Many of the polychaete species found in this study were considerably smaller in size than described in the taxonomic references. As shown in Table 11, the smaller size of the three species used as examples provides an approximate increase

TABLE 11

Comparison of sizes of some polychaete species with expected sizes from taxonomic descriptions.

Species	Described Size* in mm. (Length x Width)	Ratio (S. A. / Vol)	Mean Size from Samples in mm. (Length x Width)	Ratio (S. A. / Vol)	Approximate Ratio Increase
Glycera americana	370 x 13	0.15	68 x 3	0.67	4 X
Podarke obscura	40 x 3	0.67	5 x 1	2.0	3 X
Platynereis dumerili	75 x 6	0.67	6 x 1	2.0	3 X

* From Gosner, 1971

in body surface area to volume ratio of three to four times. This is a significant adaptation to periods of oxygen depletion and as such would lead to the lower faunal biomass values postulated by O'Connor. Sanders (1968) attributes a decrease in species richness to a similar oxygen stress. Thus it appears that the redox potential of the sediment may serve as an indicator of conditions in the benthic invertebrate community of the Indian River. Caution is advised, however, in attempting to compare sparsely or non-vegetated areas with shallow water grass flats.

Species diversity is a function not only of the number of species present but also of the distribution of the number of organisms among those species. Under most conditions, these two components are assumed to vary directly. In the sandy, sparsely vegetated samples, however, the species richness decreases with increasing depth and decreasing Eh while under the same conditions the evenness component is seen to increase. The possibility of such an occurrence is proposed by Hurlbert (1971). With sufficient oxygen available, such as in the grass flats, species evenness as well as species richness is high. As oxygen becomes less available and both the number of individuals and the number of species decrease; the evenness of distribution among the species present increases. High evenness values are suggested to be the result of isolation or territoriality (Odum, 1971). Isolation or territoriality, defined by Odum (1971) as any active mechanism that spaces individuals or groups apart from one another, is usually the result of

(1) interindividual competition for resources in short supply, or (2) direct antagonism. This sort of isolation tends to reduce competition, since competition is most likely between proximal individuals (McNaughton and Wolf, 1970), and thus conserves energy during critical periods and prevents overcrowding and exhaustion of resources. Trammer (1969) suggests that communities from rigorous or physically controlled environments will vary in diversity according to their evenness components while diversity in biologically accommodated environments will be a function of the number of species. The data from the Indian River supports this suggestion provided that the major factor providing the degree of physical control is the availability of dissolved oxygen. This factor appears to predominate over the degree of environmental stability provided by the constancy of temperature, salinity, and dissolved oxygen concentration in the deeper water.

The possibility of this relationship between the effects of species richness and species evenness on diversity being an artifact of methodology has already been implied. That species evenness is of greater importance in smaller samples and is thus merely a function of sample size rather than a result of a biological acclimation to the rigors of the environment implies a negative correlation between the two. Such an implication is not supported by the data from this study in that the correlation, although negative was not found to be significant ($\alpha = 0.05$).

The second major emphasis in this study is the close coupling of species to their environment in biologically accommodated communities.

It should be understood that no community can be expected to be entirely either biologically accommodated or physically controlled. Each community represents a point along the time-stability gradient exhibiting the resultant effects of both biological accommodations and physical control. One of these factors may be more prominent than the other and thus serve as a basis for comparison.

With the amelioration of stresses, such as oxygen availability, organisms are able to develop their adaptive strategies toward their total environment. One aspect of this has already been examined: that of the relationship between the number of deposit feeders and the amount of food contained in the sediments as oxidizable organic carbon. With the reduction of oxygen stress the number of deposit feeders, representing the numerical counterpart of biomass, was seen to increase with the amount of available food. In the physically-controlled stations, where low dissolved oxygen availability produced a stress, the number of deposit feeders were not so closely coupled to the food supply. Sanders (1958) found a weak correlation between deposit feeders and sediment organic carbon. He contributed the weakness to the fact that the presently available methodology does not distinguish assimilable forms of oxidizable carbon from non-assimilable forms such as coal. While this problem is presently being pursued, the data herein indicates that such a weakness in correlation may be due to environmental stress.

It was postulated by Sanders (1958) that deposit feeders may correlate with food availability while suspension feeders may be dependent upon either grain size or the patterns of water currents. Rhoades and Young (1970), however, suggest a closer relationship between deposit feeders and suspension feeders. The reworking of sediments by the burrowing activities of deposit feeders results in an unstable sediment surface layer that is easily resuspended by weak wave and current action. This unstable sediment layer may preclude the presence of large numbers of suspension feeders through the reduction of stable attachment sites, clogging of gills or other respiratory structures, and burying of newly settled larvae. This hypothesis of trophic exclusion would probably be more effective in muddy sediments and probably less so in coarse sands, shell debris or in sediments stabilized by rooted grasses. In less favorable sites, smaller numbers of suspension feeders should be evident in the absence of other environmental stresses. Such evidences of trophic exclusion may be considered to be an indication of the effects of biological interaction.

The samples representing the more biologically accommodated stations can be compared to those of the more physically controlled stations in terms of trophic exclusion by again borrowing the techniques of the terrestrial plant ecologists. Using a simple ordination technique the samples from both physically controlled and biologically accommodated stations are ranked according to decreasing percentage composition of deposit feeders and increasing percentage composition of

suspension feeders. At the biologically accommodated stations, good agreement is seen between increasing percentage of suspension feeders and a decreasing percentage of deposit feeders (Table 12). The ranking of Stations TR 4 and TR 15 resulted in a reverse order since a high number of suspension feeders occurred concomittantly with a high number of deposit feeders at Station 15. This is probably due to the geographic position of that station. The sediment at Station TR 15 was a hard packed sand with a considerable amount of surface shell debris. This station had the lowest sediment values for both organic carbon and silt and clay content. These factors combined with the location of the station at the narrow navigational gap in the railroad causeway illustrate the probability that current velocities at this station may be greater than at other stations. Increased current velocities would facilitate suspension feeding as well as scour the sediment surface, rapidly removing the unstable sedimentary particles as they are reworked by the deposit feeders.

Among the samples representing physically controlled stations, no such easily explained agreement is seen (Table 13). No evidence of trophic exclusion of suspension feeders by deposit feeders occurred in sediments where the member species are limited in their distribution by other physical, density independent, controlling factors.

Stations TR 13, TR 14, and TR 15 are all located in proximity to the Intracoastal Waterway and probably represent the effects on the benthos by man's most significant influence in this segment of the

TABLE 12

Ranking of biologically accommodated stations according to the percentage composition of deposit feeders and suspension feeders

Decreasing Deposit Feeders (%)	Increasing Suspension Feeders (%)
TR 1	TR 1
TR 3	TR 3
TR 15	TR 4
TR 4	TR 15

TABLE 13

Ranking of physically controlled stations according to the percentage composition of deposit and suspension feeders.

Decreasing Deposit Feeders %	Increasing Suspension Feeders %
TR 9	TR 12
TR 10	TR 14
TR 11	TR 11
TR 12	TR 9
TR 14	TR 10

Indian River. All three stations are in water depths greater than two meters and contain the only station along the transect where dissolved oxygen concentration was initially found to be less than five parts per million in the bottom water.

It is reasonable to assume that the factors which contribute to the success of suspension feeders at Station TR 15 may also contribute to its high diversity. The possibility of increased circulation as a result of the through-causeway currents would be expected to prevent the accumulation of oxidizable detritus and hence preclude the possibility of dissolved oxygen stress. The low dissolved oxygen concentration (4.5 ppm), however, does not support this possibility. The lack of accumulated detritus may contribute to diversity in another way. Benthic organisms in a detritus based system are provided with a stable, non-fluctuating food supply (Rhoades and Young, 1970). The removal of detritus by current scouring would provide an improverished environment in terms of available food, and Station TR 15 yielded the smallest value for sediment organic carbon composition (0.34%) along the transect. In relating species diversity to resource supply, Valentine (1971) suggests that the highest diversity would be found in an environment where resources are found in low but stable quantities. The species harbored would be those selected for competitive ability and interactions with other species (k-selection). The data for Station TR 15, especially as shown in the rarefaction curves, demonstrates such a situation.

While the sediment at Station TR 15 is stable and supports a high diversity, the opposite may be said of Station TR 13 located in the Intracoastal Waterway. Samples taken from Station TR 13 yielded high amounts of silt and clay and organic carbon. Dissolved oxygen concentration in the bottom water at this station was the lowest of any of the transect stations sampled. The low sediment Eh suggests the probability of oxygen stress. All the faunal indices, except evenness, exhibited their lowest values at this station. The presence of only four organisms, all of which were relatively motile crustaceans, also indicates stressed conditions.

Dredged navigational channels such as the Intracoastal Waterway must be periodically re-dredged as a result of redeposition and entrapment of sediments in the channel. Spoils removed during this maintenance dredging are commonly deposited parallel to and proximal to the channel forming the spoil islands shown in Figure 2 and characterized by Station TR 14, samples from which contained two per cent suspension feeders only. While much of these spoils are probably stabilized in time, they are probably the major contributors to redeposition in the channel (Odum, 1970). As a result of this unstable condition of the substrate, many organisms, especially sus ension feeders or any other attached forms, may be excluded from these areas. The sample from Station TR 13 contained no sessile or suspension feeding forms.

The effects of sediment instability may not be limited to the immediate vicinity of the channel. Wind driven currents may widely

distribute these spoil derived materials affecting a larger area of the river within a zone of sediment redeposition. Current methodology for sediment analysis does not provide a suitable measure for determination of such sediment instability or its effects within the possible zone of redeposition (Dr. E. Kalajian, personal communication). A biological index is then proposed as a measure of sediment instability and redeposition by extending the trophic exclusion hypothesis of Rhoades and Young (1970). Since suspension feeders may be excluded or at least reduced in numbers as a result of sediment instability, they must be used as an index of that instability. The lack of suspension feeders in the samples from Stations TR 13 and TR 14 supports the proposal. Further support is found in the contrasting high incidence of suspension feeders at Station TR 15 and at the more biologically accommodated stations at the northern end of the transect. The distribution of suspension feeders does not appear to be the direct result of the activities of deposit feeders at those stations which are more physically controlled. Using the ordination technique, the stations ranked according to their relative distances from the channel may be compared to the same stations ranked in order of the increasing occurrence of suspension feeders as seen in Table 14. Good agreement with the proposed index is found as far north along the transect as Station TR 8. Redeposition of the sediments eroded from the higher contours of the spoil areas may also serve to limit the success of suspension feeders over both a large area

TABLE 14

Comparison of stations ranked according to increasing distance from the Intracoastal Waterway to stations ranked in order of increasing abundance and percentage composition of suspension feeders.

Distance from Channel	Suspension Feeders	
	Number	Percent
TR 13	TR 13	TR 13
TR 12	TR 12	TR 12
TR 11	TR 11	TR 11
TR 10	TR 10	TR 9
TR 9	TR 9	TR 10
TR 8	TR 8	TR 8

and time span. Through the combined effects of this stress and the possible inducement of oxygen stress by resuspension of the sediments (Odum, 1970) and the reduction of oxygen availability in the deeply dredged areas, channelization may constitute one of man's most insidious contributions to the benthic ecology of the Indian River.

V. SUMMARY

During the summer months, the northern portion of the Indian River supports a benthic community with a diversity approximating that of a tropical estuary. Species diversity is variable along depth gradients where the availability of dissolved oxygen to the macroinvertebrates is the primary limiting factor. Long term oxygen availability measured in terms of the redox potential of the sediment appears to mask any effects produced by environmental variability or conversely environmental stability in terms of temperature, salinity or physical nature of the substrate.

In more biologically accommodated portions of the benthic community, the stress of oxygen availability is ameliorated. There organisms appear to be more closely coupled to their environment as measured in terms of abundance of deposit feeders relative to their food supply and in terms of exclusion interactions between deposit and suspension feeding forms.

Man's intrusion into this portion of the Indian River has been, as is most often the case, detrimental to the benthic community through the construction of the Intracoastal Waterway.

APPENDIX A

Species List and Distribution

SPECIES	Feeding Type	STATIONS 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Molluska																
Gemma sp.	SF	4														
Tagelus divisus	SF						1									1
Lynosia hyalina	SF	26		1												
Chione cancellata	SF				4								1			1
Brachidontes exustus	SF	18	5	8	174	2	9		9	6	2	5				3
Amygdalum papyria	SF	1	1		1											
Nucula proxima	DF										1		1			1
Mulina lateralis	SF	5	4	4	6	6	31	37	43	25	12					1
Tellina sp.	SF		1	2				1	1	2		1			1	1
Laevicardium sp.	SF			1	2	3	1									
Anomalocaadia cuneimeris	SF	3														
Turbonilla interrupta	Parasitic (?)	20		1												
Crepidula convexa	SF	13		12	2											
Mitrella lunata	S	1		2											1	
Retusa canaliculata	DF	37	35	8	11	9	7	8	3	9	2	3	5			1
Haminoeia sp.	C			3	3											
Cerithiopsis emersonii	C				3											
Caecum pulchellum	DF	2	30	42	64	14	35	38	37	134	121	34	16		4	9
Nassarius vibex	NSDF				3		1									
Prunum apicinum	C/S	35	12	13	27	8	1		3	7	10	1	14		3	1
Cerithium muscarum	DF	1	10	2	1											

SPECIES	Feeding Type	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Molluska (continued)																
Odostomia 1	Parasitic(?				3	3	2		2							
Odostomia 2	Parasitic(?	5	3	2	1											
Polychaeta																
Sphaerodorids	DF	63		40											1	
Exogone hebes	C/S	63	56	123	17					3						1
Podarke obscura	C/S	2	1	3	2	2		1	1							1
Platynereis dumerili	C/S	2	3	16	11	1	2	1					1			
Eteone heteropoda	NSDF	3		9				1	1							2
Scolecolepsis sp.	C/S		7	10	6	1	1	2	3	7	4	6	5			
Prionospio sp.	C/S	9	28	25	10	4	3	1			1		3		26	2
Polydora ligni	C/S	1	19	4	2											1
Fabricia sabella	SF	2	476	61	67											2
Marphysa sanguinea	C/S	33		5	1											
Tharyx sp.	DF	1					7	18	3	4						
Aricidea jeffreysi	DF	20	42	95	1					4			4			
Pista palmata	DF	6	9	9	2											2
Glycera americana	NSDF	2		2	4	1	1	2	1			1	2			
Glycinde solitaria	NSDF					1	1		1						1	2
Leiochone dispar	DF	51	108	58	17	1	2	1		36	18					5
Diopatra cuprea	C/S	1		3	2		3		2	1	1	1	1			2
Sabella microphthalma	SF	3		33	14		12	1		1	11	1			1	2

SPECIES	Feeding Type	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Polychaeta (continued)																
Potamilla sp.	SF						1		3							
Maldone sarsi	SDF	10	2													
Hypaniola grayi	DF	43	8	17			1									
Stauronereis rudolphi	DF			1												
Scoloplos sp.	NSDF			1		2	1	1	1	1	1					2
Odontosyllis fulgurans	C/S	23		8	3	1			1							
Pectinaria gouldii	SDF				1			1	1	4	2		10			5
Syllis gracilis	C/S			7	7				1							
Armandia agilis	DF					3	3									5
Sabella crassicornis	SF					3	1									
Lepidonotus sp.	C/S					1		4	9							
Scoloplos rubra	NSDF						12	2					1			
Aglaophamus verrilli	C/S					1	4	4	7	3						1
Arthropoda																
Erichsoniella attenuata	H/S	11	41	4	20	1		1								1
Sphaeroma quadridentatum	SDF	7	7	6	20	4	1	1	2	2		1	2	2	3	5
Cyathura sp.	H/S	14	49	25	40	2	1	1								
Oxyurostilis smithi	SF	4	1	6	6	3				1	3					
Tanais sp.	DF	5	8			14	14	12	18		2	1	1			
Panopeus herbstii	C/S	1														
Callepallene brevirostrum	C	8		8	2	1					1					
Mysidacea	NSDF													1		

SPECIES	Feeding Type	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Arthropoda (continued)																
Cylindroleberis mariae	NSDF	589	107	181	530	621	493	382	168	377	291	95	98		43	36
Sarseiella americana	NSDF	456	195	271	112	2	9	4	3	3		1				5
Cythereis sp. (?)	NSDF	3	11	9	11	9		2				1				2
Cystisomid	DF			1		2		3	1							
Corophiid	DF	146														
Ampeliscid	DF	13	4	5		2		3	3	4	2	8	3			2
Melita fresnelii (Johnson and Snook, 1955)	DF	41	95	58	18	19	15	1	23	27	13	9		1	8	10
Lysianopsis alba	DF				19	2	1	1	1		3					1
Caprella equilibra	C			1	3											
Echinodermata																
Leptosynapta inhaerens	NSDF	10	12	3	2		1									
Ophiophragmus filograneus	NSDF	3	22	45	10	8	8	14	11	2	2		1			4
Sipuncula																
Phascolion strombi	DF	188	51	107	42	2	30	19	13	25	24	6	8		8	5
Cnidaria																
Actinothoe gracillima	SF				5					1						23

APPENDIX B

Plant Biomass
(gram dry wt/m^2)

Sta. No.	g/m^2
TR 1	77
TR 2	358
TR 3	279
TR 4	270
TR 5	2

APPENDIX C

Sediment Analyses Data

STATION #	Median Grain Size (Md O)	Sorting (Qd O)	% Silt-Clay
TR 1	3.70	.66	39.08
TR 2	2.74	.52	9.88
TR 3	2.70	.45	7.20
TR 4	2.64	.36	6.72
TR 5	2.57	.36	5.92
TR 6	2.89	.64	9.52
TR 7	3.19	.60	11.24
TR 8	3.07	.64	8.36
TR 9	3.19	.55	9.36
TR 10	3.23	.52	5.72
TR 11	3.67	.40	27.60
TR 12	3.13	.57	8.00
TR 13	3.49	1.09	36.20
TR 14	2.85	.62	16.44
TR 15	3.06	.89	3.80
Mean	3.07		13.67

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Section 1, Article 4

The Sediments of the Indian River and the Impounded Waters near Kennedy Space Center

Joyce M. Daggett

1973

The Sediments of the Indian River and the Impounded Waters near Kennedy Space Center

By

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ABSTRACT

Several relationships between the chemical and physical properties of marine and fresh water sediments reported in the literature were observed for the sediments of the Indian River and impounded waters near Kennedy Space Center, Merritt Island, Florida. The results indicated that the distribution of organic carbon in the sediments is controlled by the mean grain size, the sedimentation rate of the area, the decomposition rate of the organic matter, and its availability. The ratio of organic carbon to hydrogen was obtained for the samples and used to indicate the degree of oxidation of the organic matter in the sediments, while the color, odor, and banding of the cores suggested that the first few centimeters of water above the sediment is probably deficient in dissolved oxygen. Changes in the environmental conditions over the past years are indicated by the irregular depth profiles of the cores.

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I. INTRODUCTION

Marine sediments consist of a complex mixture of inorganic and organic compounds which may be present in a variety of different forms. The majority of the organic matter in the sediments is adsorbed onto the surface of mineral particles, while the remaining portion of organic matter is present in the interstices between the mineral grains or is connected with the bottom-dwelling animals and bacteria (Bordovskiy, 1965). Studies on the marine sediments of the Bering Sea have indicated that the type of organic matter and its distribution in the sediments were most intimately connected with the biological activity and the morphological characteristics of the area, especially in coastal and restricted waters (Bordovskiy, 1965).

The organic content of marine sediments has been studied in detail for only a few isolated cases. Results of these studies indicated that the organic carbon content of marine sediments was inversely related to the grain size for clays and silts (Bordovskiy, 1965), and directly related to the water content (Kogler, 1967).

The purpose of this study was to investigate the distribution of carbon in the sediments of fourteen cores taken from the Indian River and impounded waters near the Kennedy Space Center (KSC), Florida, and to determine if any correlations exist between the organic and carbonate carbon of the sediments, the mean grain size and the water content of the samples. Relationships between carbon content, depth into core and location of cores were also investigated.

II. BACKGROUND

A. Chemical and Physical Relationships of the Sediments

One of the most common correlations between chemical and physical properties of marine sediments reported in the literature is that between the distribution or organic carbon and the mean grain size of the sediment. In general, the organic carbon content of the sediments increased as the mean grain size decreased (Bordovskiy, 1965). As a result, the organic content of silts and clays was considerably higher than that of sands. It was estimated that silts contain twice the organic content, and clays four times that of sands (Bordovskiy, 1965). Gross (1967) reported that the sands of the Northeast Pacific contained less than 1% organic carbon, while the clays contained 2 to 3%, and suggested that the grain size of the sediment could limit the maximum amount of organic carbon present. Similar values were reported by Biggs (1967) for the sediments of the Chesapeake Bay, with 0.95% for the shallow silty-sands, and 3.4% for the silty clays. These results indicated that the relationship between grain size and organic carbon exists for shallow estuarine sediments as well as deep sea sediments.

If most of the organic matter in sediments is adsorbed on the surface of the mineral particles, as suggested by Bordovskiy (1965), then the relationship between organic carbon content and mean grain size of the sediment should exist for any type of sediment, marine and fresh water, since the smaller particles have greater surface area, and therefore, a higher capacity for adsorption, regardless of the type or depth of the water. Bordovskiy (1965) also found that factors such as morphology of the area and sedimentation rates could modify this relationship between carbon content and grain size to a slight extent.

The possibility of water depth controlling, to a small degree, the grain

size of the sediments was observed when Bordovskiy (1965) found that the coarsest materials of the Bering Sea were located in the cores collected from shallow waters, while the cores from the deep waters consisted mainly of silt-clay oozes. Biggs (1967) noted a similar trend in the sediments of the Chesapeake Bay, and proposed that the greater values of organic carbon in the deep waters of the Chesapeake Bay may be attributed to four factors: (1) the dilution of the organic matter in the shallow waters as a result of higher sedimentation rates; (2) higher oxygen content of the overlying waters, and larger sediment grain size resulting in a higher rate of inorganic oxidation of organic matter, and a greater circulation of water through the sediments of shallow water; (3) the greater scavenging activity of organisms in shallow waters; and (4) the resuspension of fine organic matter in shallow waters due to the greater physical energy of the area.

Both, the sediments of the Bering Sea and those of the Chesapeake Bay, exhibited a general decrease of organic content with increased depth into the core (Bordovskiy, 1965; Biggs, 1967). This trend suggested that the clay and silt-sized particles of the sediments were located toward the top of the core near the sediment water interface, and the sand-sized particles toward the bottom. No data on grain size distribution with depth into the core were cited.

Another correlation reported in the literature was that of an increase in organic carbon content with increasing water content of the sediments (Kogler, 1967). Kogler (1967) reported a maximum water content of 293% of dry sediment weight for the sediments of the Arabian and Baltic Seas which corresponded to the maximum organic carbon value of 6.5%. The lowest water content value of 25% was found for a core which had organic carbon values less than 2%. In general, the water contents of these cores decreased with depth into the core.

The studies of the sediments of the Northeast Pacific (Gross, 1967) and

the Arabian and Baltic Seas (Kogler, 1967) suggested still another relationship for organic carbon content. Data from these studies indicated that the highest values of organic carbon were found in the samples which contained the lowest carbonate values, and vice versa. Gross (1967) found the highest organic carbon value of 3% to correspond to carbonate values of less than 2%, while organic carbon values of less than 1% were found in sediment with carbonate values between 5 and 10%. Similar values were reported by Kogler (1967) with a maximum organic carbon value of 6.5% found for a carbonate content less than 2%, and values of less than 2% organic carbon corresponding to carbonate values between 3 - 6%. The majority of the carbonate values for both studies were below 5%, and most of the organic carbon values were below 2%.

A very interesting color relationship was reported by Biggs (1967) in his study of the sediments of the Chesapeake Bay. The color of the sediment and the structure of the core were related to the oxygen content of the overlying water. In general, black, grey-green, banded cores corresponded to a low oxygen content in the water column, while light brown, homogeneous cores were indicative of a well aerated situation. A strong hydrogen sulfide odor was usually associated with the black, grey-green sediments, which contained a higher organic content and a higher water content than the grey sediments when both were located at the sediment water interface.

A considerable portion of the organic matter of marine sediments is composed of humic acids and "residual" organic matter (Bordovskiy, 1965). Very little work has been done to determine the chemical structure of the "residual" organic matter which is mainly bonded with the mineral skeleton of the sediment. Detailed studies, however, have been done on the humic acids of marine sediments, and the results indicated that they are condensed aromatic systems incorporating carbon,

hydrogen, oxygen, and sulfur (Bordovskiy, 1965). Humic acids occur widely in natural accumulations of organic matter such as peats, and several subaqual deposits. According to Bordovskiy (1965), the humic acids result from the condensation of carbohydrates and proteins, and are relatively resistant to biochemical oxidation in semi-aerobic conditions. In well aerated soils the hydrogen content of the acids is lower than in less aerated sediments such as that of marine basins (Bordovskiy, 1965). The ratio of organic carbon to hydrogen, C/H, can be used to indicate the degree of condensation of the acid. For the bottom sediments of the Bering Sea, Bordovskiy (1965) reported a C/H range of 6.8 to 8.8. The typical range for soils is 12-21.4. The lower C/H range for the bottom sediments indicates a lower degree of condensation which is probably the result of a more anaerobic condition. Generally, the C/H is higher in deep water sediments than in shallow water deposits, which could be due to the fact that the deep water deposits are more mature and are in a more advanced state of transformation (Bordovskiy, 1965).

B. Analytical Techniques for Organic and Inorganic Carbon Determinations

The majority of the carbon present in sediments occurs as carbonates and a variety of organic compounds. The basic principle behind both carbonate and organic carbon determination is the measurement of carbon released as carbon dioxide, CO_2. There are several variations in both the methods of conversion of carbon to carbon dioxide, and the methods of measurement of the released CO_2. Volborth (1969) has stated that the most universal method for the determination of carbon is to release the carbon as carbon dioxide by acid attack for carbonates, and by combustion for organic and total carbon. The freed carbon dioxide can then be determined volumetrically, or by absorption on a suitable medium. The carbonate carbon in the sample can also be determined by the method of Shapiro and Brannock (Volborth, 1969) which is a variation of the classical acid attack method. A special gas collecting tube developed by Shapiro and Brannock is utilized in the method. Several other variations of the Volborth method are mentioned at the end of this section.

Volborth (1969) has suggested that a direct combustion in an oxygen atmosphere, followed by purification of the evolved gases and gravimetric determination of the carbon dioxide should be employed when the sample contains organic carbon. For best results when employing a combustion train, the following advice should be considered (Volborth, 1969). If carbonate carbon is present in the sample, the oven should be maintained at 900°C. The flow of oxygen should be regulated to 2-4 bubbles per second by means of a bubbler of concentrated sulfuric acid, which should be connected to the tube containing the carbon dioxide absorbent in order to protect the system from moisture. A tube of magnesium perchlorate or calcium chloride should be placed before the tube containing the carbon dioxide absorbent to trap any moisture which is produced during the combustion. A suitable absorbent for carbon dioxide

is sodium hydroxide (NaOH).

For best results, a porcelain, mullite, or platinum combustion tube should be used, and the sample placed in a porcelain, alundum, or zirconium oxide combustion boat. Platinum boats should not be employed if metals and sulfides are present, or if copper oxide is mixed with the sample. Manganese oxide should be loosely packed in the end of the tube down train from the sample in the cool part of the oven to remove any oxides of sulfur or nitrogen from the product gases. Copper oxide is generally mixed with the sample and placed in the hot part of the combustion tube to catalyze the oxidation of carbon monoxide to carbon dioxide.

The system should be flushed with oxygen for five minutes before the sample is introduced into the combustion tube. A combustion time of 10-15 minutes should be sufficient.

If just the organic carbon in the sample is desired, the carbonate carbon is first removed by an acid attack method and the sample is then dried and placed in the combustion train. The acid attack method consists of treating the dried sample with a suitable acid which will convert the carbonates in the sample to carbon dioxide which is then measured either volumetrically or gravimetrically.

Several variations of the dry combustion have been reported in the literature. Gross (1967) in his study of the marine sediments of the Northeast Pacific, determined the organic carbon of the sediments by subtracting the carbonate carbon from the total carbon. The carbonate carbon was determined by the absorption of the carbon dioxide released when the dried sample was treated with 10% phosphoric acid. The total carbon of the sediments was obtained by a dry combustion process in an oxygen atmosphere. An appropriate catalyst was reacted with the gases to convert the carbon monoxide to carbon dioxide, and manganese dioxide

was added to remove any oxides of sulfur and nitrogen from the gaseous products. A coefficient of variation of 10% of the amount of organic carbon, and a reproducibility of 2% for the carbonate method was reported.

In a recent study of the sediments of Lake Mendota, Bartleson (1972) determined the total carbon content by a dry combustion process, and measured the carbon dioxide released by the organic and carbonate compounds with a thermal conductivity cell. The calcium which was dissolved by $HF-HNO_3-HC1O_4$ acid was measured and converted to its carbon equivalent, which was then subtracted from the total carbon to yield the amount of organic carbon in the sample.

The organic content of the sediments of the Chesapeake Bay (Biggs, 1967) was obtained directly from a dry combustion of the sediments which had first been treated with hydrochloric acid to remove all the carbonate. Biggs (1967) reported recoveries of 99.9%, and a precision of $\pm$ 0.19 for this procedure.

Buchan (1967) determined the carbonate content of the North Atlantic sediments with a Collins Calcimeter. The process involved treatment of the dried, powered, sample with hydrochloric acid in a closed system, and volumetric measurement of the amount of carbon dioxide evolved.

A much more sophisticated method of determining the organic carbon in the sediments was reported by Hobson (1969), which consisted of treating a 2 gram sample of dry sediment with hot 0.3N trichloroacetic acid to remove the carbonates, and then determining the amount of organic carbon with an elemental analyzer. By measuring the amount of carbon dioxide evolved from the acid treatment, the amount of carbonate carbon could also be obtained. The total carbon would simply be the sum of these two results.

III. CORING AREA

A. Description of Coring Area

The sediment samples analyzed in this study were taken from fourteen cores which were collected from portions of the Indian River and the impounded waters surrounding Kennedy Space Center, Merritt Island, Florida (Figures 1, 2, 3). The exact locations of the fourteen cores analyzed are indicated on Figures 4 and 5 by means of a number code. Area 1 was located in the Indian River between Titusville and the Orsino Causeway. The cores collected from this area were designated as 1- followed by a core number (Figure 4). The number of 100+ refer to the sites for the impounded waters in this area. Three of the cores used in this study were obtained from Area 1 near the mouth of Banana Creek, and six from the impounded waters in the same general area. Four cores analyzed were from Area 2, designated with 2- and located in the Indian River north of Titusville (Figure 5). Only one core, 3-12, from Area 3 near Haulover Canal in Mosquito Lagoon was studied (Figure 5).

The impounded waters on Merritt Island are the result of an effort to reduce the two species of salt water mosquito, Aedes sollicitans and Aedes taeniorhynchus. These mosquitos possess the unique trait of laying their eggs on dry land. The eggs hatch when the land becomes temporarily flooded, as in a tidal marsh. Until 1960, the shore lines of Merritt Island provided a tidal marsh area ideal for the breeding of these two species. In order to prevent the mosquitos from laying their eggs, dikes were constructed to permanently flood the area. This project was initiated by the Brevard County Mosquito Control Division, and completed with the assistance of NASA. These dikes have probably altered the characteristics of the impounded waters and the sediments of this area.

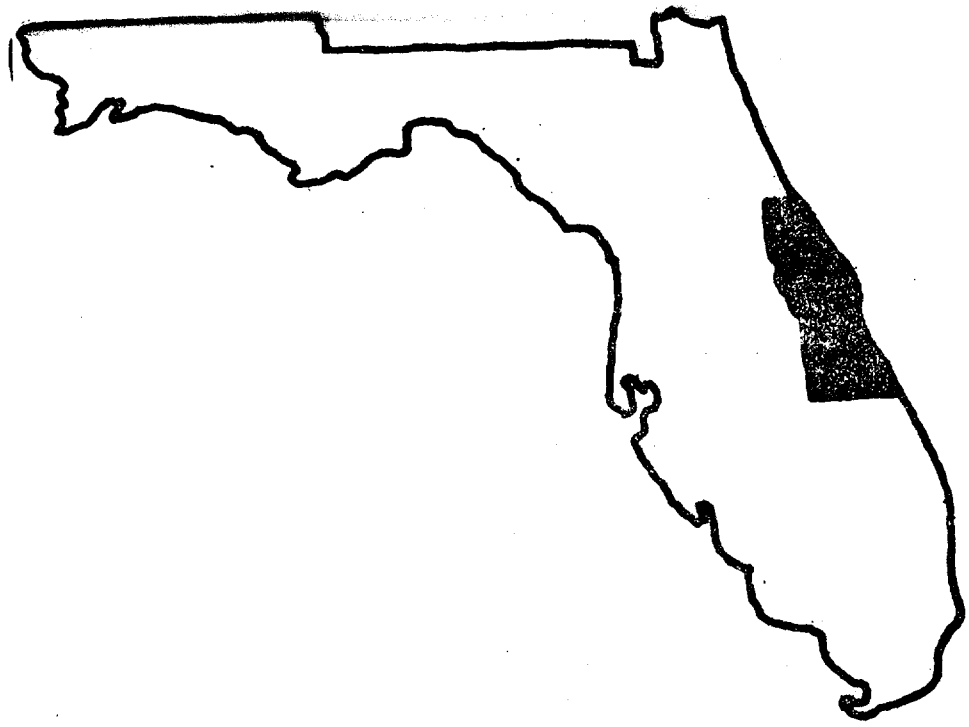


Figure 1. Florida State Map

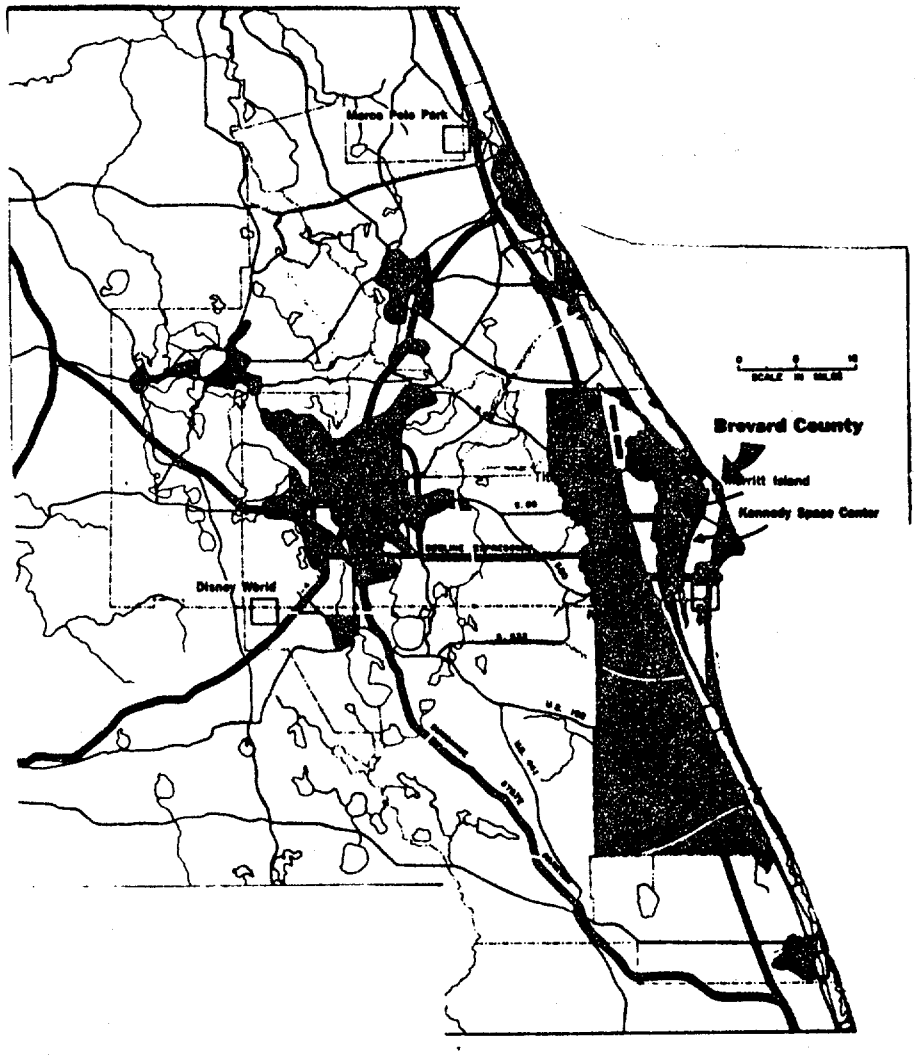


Figure 2. Brevard County

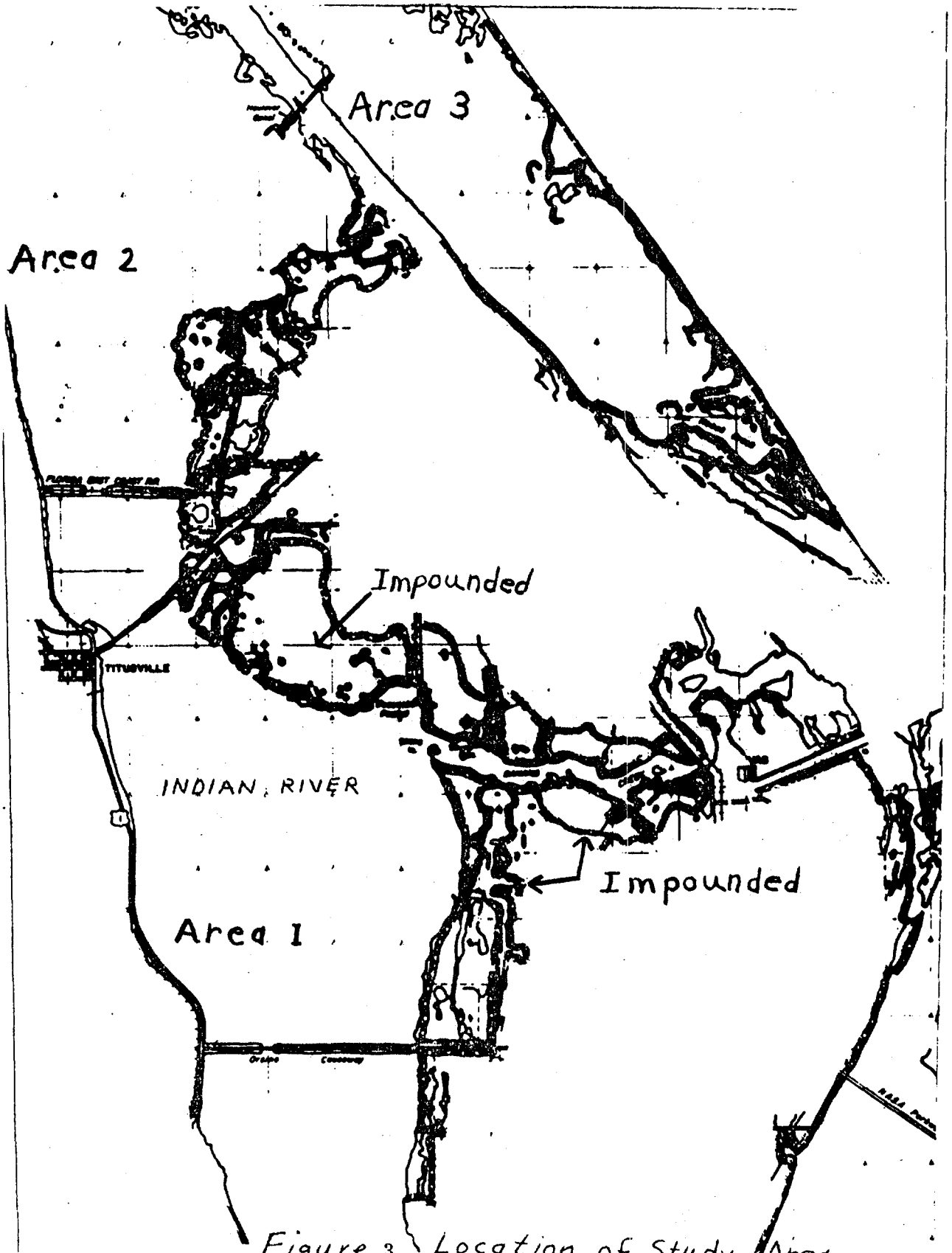


Figure 3. Location of Study Area

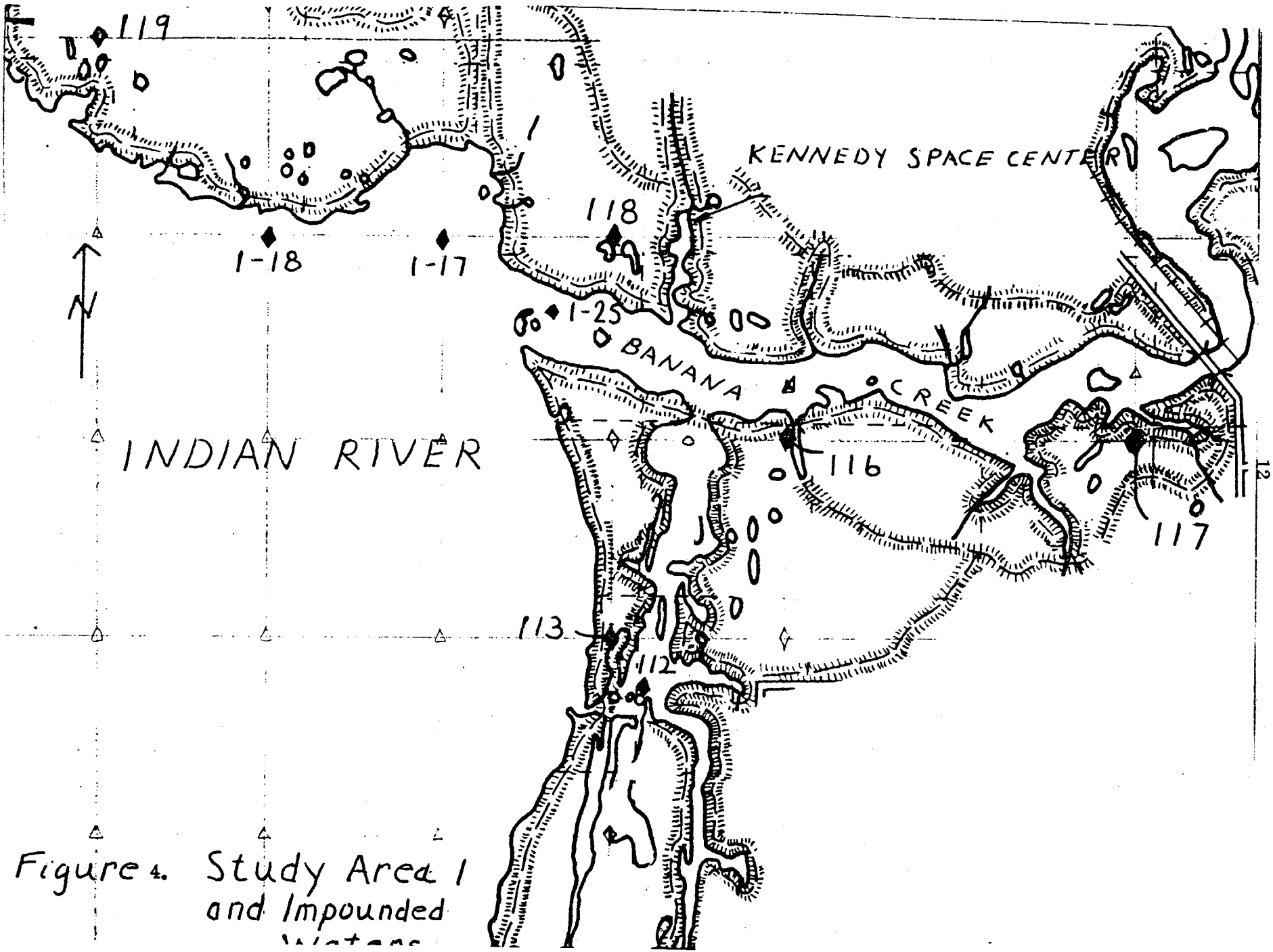


Figure 4. Study Area 1 and Impounded Waters

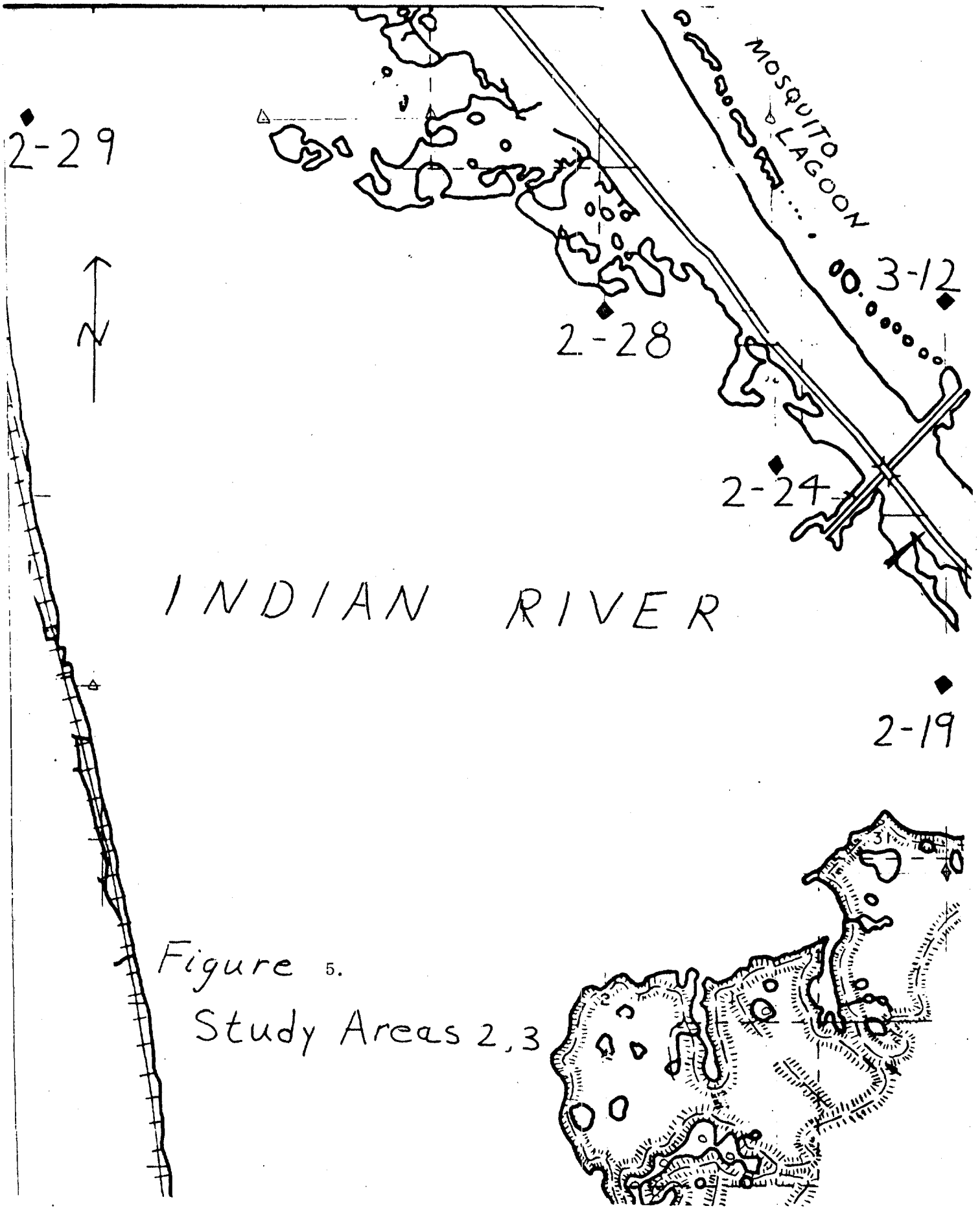


Figure 5.
Study Areas 2, 3

B. Collection of Cores

The cores used were collected between July and September of 1972 by the students and faculty of Florida Institute of Technology (FIT), Melbourne, Florida. The collection of these cores was undertaken as a portion of the previous mentioned NASA project (see Acknowledgment).

Samples were obtained using a coring device developed by two FIT students and consisting of a two inch polyvinylchloride pipe equipped with a ball check valve (Figure 6). The corer was manually driven into the sediment by means of a T-handle, and the collected samples were virtually undisturbed. A recovery of 87.7% calculated as length of core recovered/total penetration was obtained.

Immediately upon collection, the cores were capped and taped to prevent any loss of moisture, and sealed with wax as soon as they were brought to the lab. The cores were analyzed within a few days after collection.

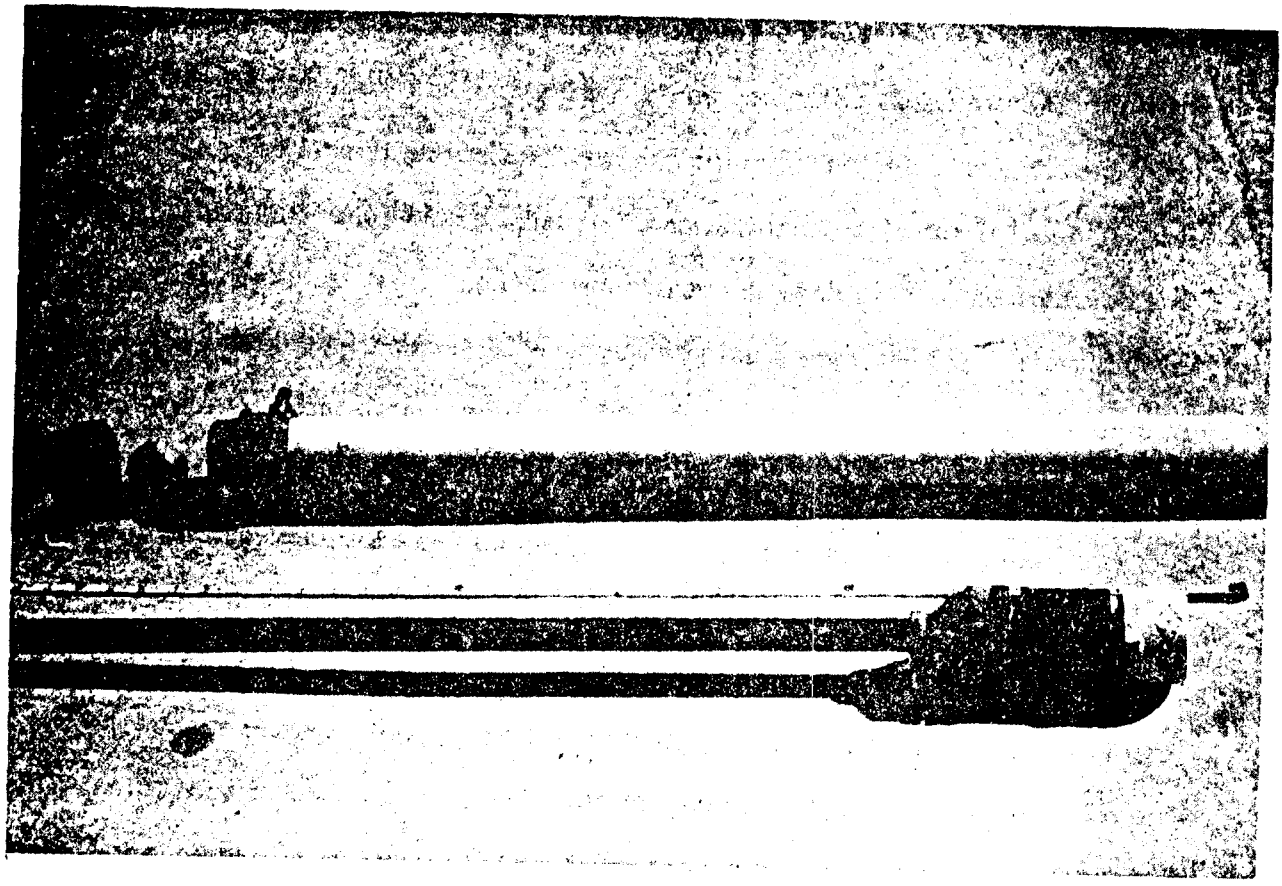


Figure 6. Coring Device

IV. LABORATORY ANALYSIS

A. Physical Characteristics of the Samples

The preliminary analysis of the cores consisted of longitudinal splitting, photographing, and examination for odor and color. The color was determined by means of a Munsell color chart. Figure 7 shows core 2-29 after it had been split for analysis. Samples from the different layers of each core were obtained and dried at 100° C. for 24 hours. The dried samples were used for grain size analysis and water content determinations. The mean grain size of the sediments was obtained by standard sieve analysis, and the water content was recorded in percent weight of water/weight of dry sample.

B. Chemical Composition of the Sediments

Chemical analysis to determine the amount of total carbon, organic carbon, carbonate carbon, and hydrogen were done on at least three samples from different layers in each core. These samples were obtained either from the sediment not passing the #40 or #60 sieve from the grain size analysis, or from the water content cans. The dried sediment was homogenized by grinding with mortar and pestle before analysis.

The total carbon of the sediment was determined by a dry combustion method as described by Volborth (1969). Figure 8 shows the combustion train employed for this analysis. A similar procedure was followed by Gross (1967) in his study of the surface sediments of the Northeast Pacific.

First the two drying tubes, one containing the magnesium perchlorate ($MgC10_4$), and the other the sodium hydroxide (NaOH), were weighed to the nearest milligram using semimicro analytic technique. Next the weighed tubes were connected to the combustion train, and the entire system flushed with oxygen for

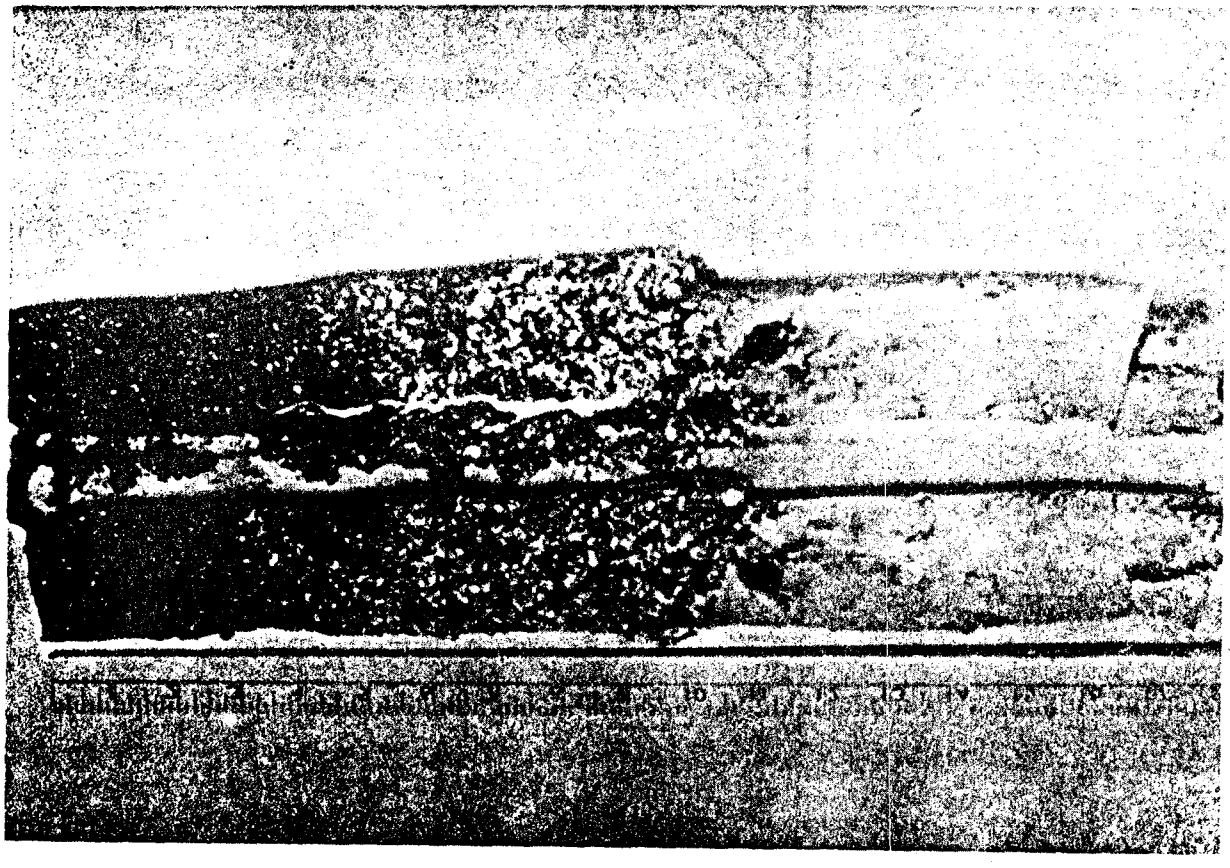


Figure 7. Core 2-29

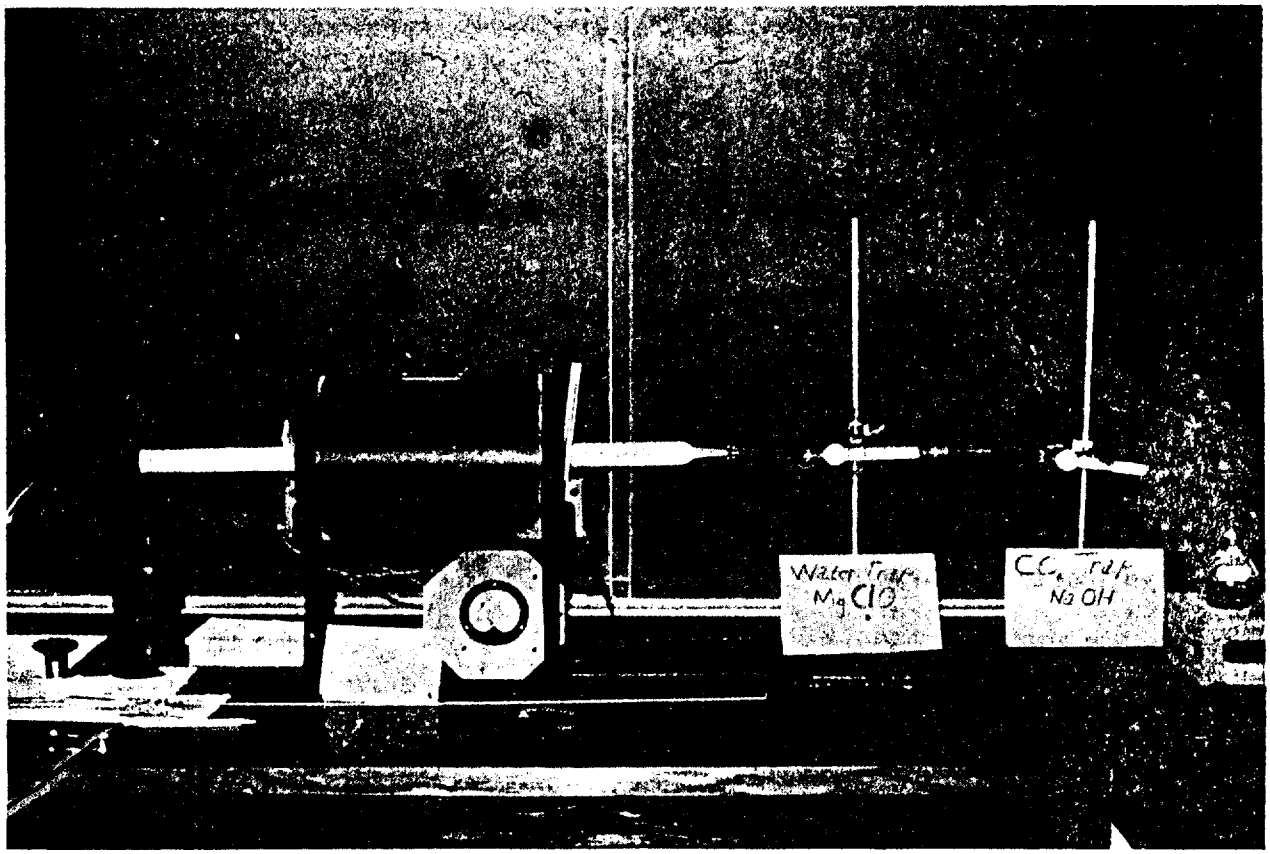


Figure 8. Combustion Train

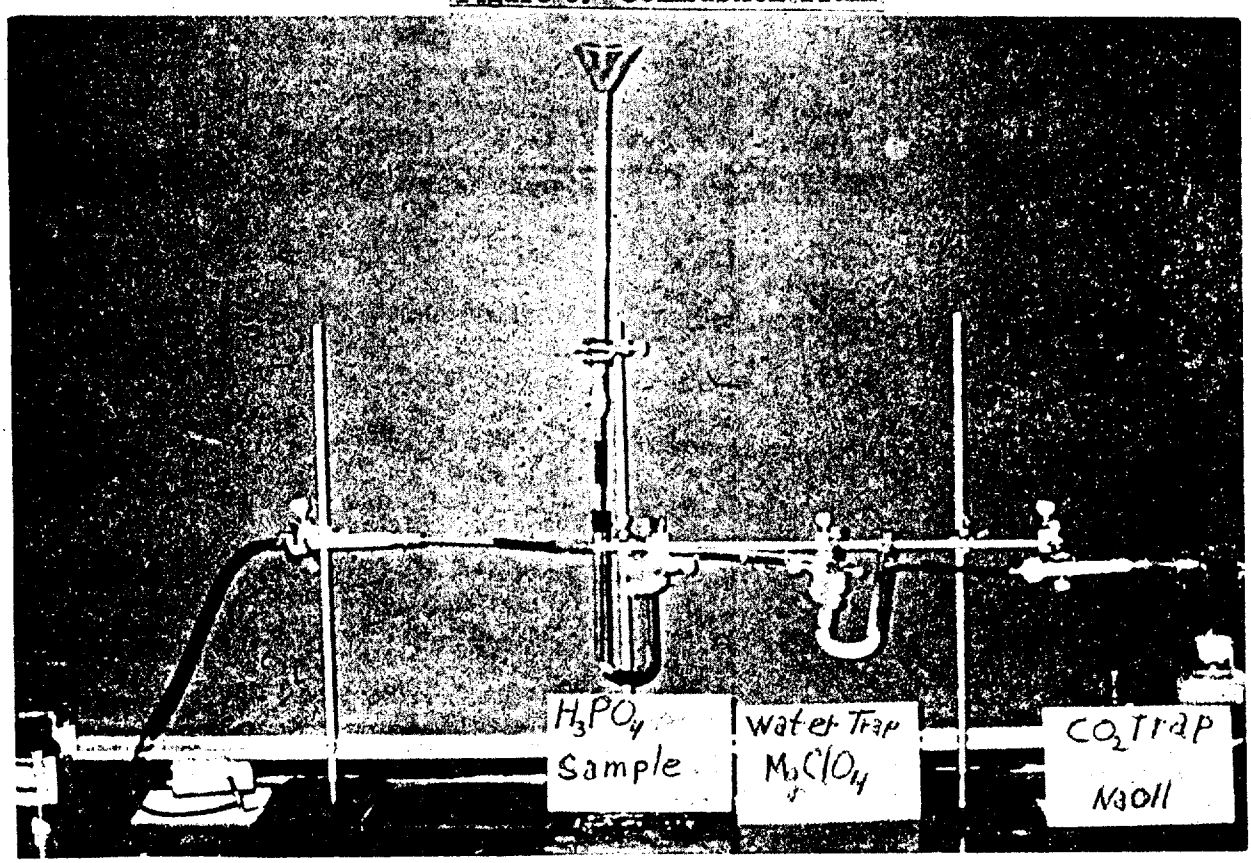


Figure 9. Carbonate Analysis

approximately five minutes. About one gram of dried sample was placed in a porcelain combustion boat and introduced into the oven, which was maintained at approximately 900° C. Hot copper oxide was used as a catalyst to insure complete oxidation of carbon monoxide to carbon dioxide. Manganese dioxide (MnO_2) was packed in the end of the combustion tube to remove any oxides of sulfur and nitrogen from the gaseous products. After a combustion time of a half hour, the two drying tubes were removed and reweighed. The water from the sediment was trapped by the magnesium perchlorate and used to determine the percentage of hydrogen in the sample. The carbon dioxide released from the organic compounds and carbonates was absorbed by the sodium hydroxide and used to obtain the total carbon. The following calculations were performed:

$$\%\text{Total Carbon} = \frac{\text{weight } CO_2 \text{ evolved}}{\text{weight original sample}} \times \frac{12 \text{ grams C}}{44 \text{ grams } CO_2} \times 100$$

$$\%\text{Hydrogen} = \frac{\text{weight } H_2O \text{ evolved}}{\text{weight sample}} \times \frac{2 \text{ grams H}}{18 \text{ grams } H_2O} \times 100$$

To check the reproducibility of the method, several samples were run in duplicate or triplicate. The values of total carbon for three runs of sample 1-25-7 were: 0.59%, 0.64%, 0.64%. For comparison purposes this same sample was given to KSC Micro Chemical Analyst Lab for total carbon determination using the Carbon-Hydrogen-Nitrogen Analyzer. The results indicated a total carbon of $0.68\% \pm 0.22$. Additional results from KSC are reported in the Results section of this presentation (page 38).

One major difficulty was encountered with the total carbon determination. Samples 1-1, 1-18, 1-25-7, 2-2-41, and 2-2-62 produced a yellow residue upon

combustion, which was picked up by the magnesium perchlorate. This yellow residue interfered with the normal combustion process causing the total carbon values to be less than the carbonate values. Thus it was impossible to obtain an organic carbon result for these samples. This caused considerable concern, and an effort was made to identify the yellow residue. A sample of the residue was taken to KSC and analyzed by X-Ray spectrometry and infrared absorption. The residue was not identified by either of these methods, but there was a sharp IR band at 8.9 microns which indicated a possible sulfur-oxygen and/or halogen bonding. The results from the X-Ray study indicated that there was a trace of titanium at the top of the drying tube, and a slight variation in the amount of chlorine from top to bottom of the drying tube.

After consideration of the available equipment, the experimental set-up in Figure 9 was used for the carbonate analysis. This method is a modified version of the acid attack used by Gross (1967). The tube containing sodium hydroxide located at the far right of the set-up was used to absorb the evolved carbon dioxide from the reaction. After the tube was carefully weighed, it was connected to the set-up. The system was then flushed with dry, carbon dioxide-free air for five minutes to remove any carbon dioxide or moisture that might be present. The dried sample was treated with 50% phosphoric acid, and a reaction time of a half hour was allowed. The dry, carbon dioxide-free air was used both as a carrier gas for the evolved carbon dioxide, and as a means of mixing the sample and acid. A tube of magnesium perchlorate was placed before the sodium hydroxide absorbent to pick up any moisture produced from the reaction. In order to trap any oxides of sulfur and nitrogen produced, a tube of manganese dioxide was placed between the sodium hydroxide and magnesium perchlorate tubes. The most appropriate sample size for this determination was between 0.8 and 1.0 gram.

The amount of carbonate and inorganic carbon was calculated as follows:

$$\%\text{Carbonate} = \frac{\text{Weight } CO_2}{\text{Weight sample}} \times \frac{60 \text{ grams } CO_3}{44 \text{ grams } CO_2} \times 100$$

$$\%\text{Inorganic C} = \frac{\text{Weight } CO_2}{\text{Weight sample}} \times \frac{12 \text{ grams C}}{44 \text{ grams } CO_2} \times 100$$

The method was standardized with a sample of calcium carbonate, and a recovery of 100% was obtained. The flow of the carrier gas had to be regulated for each determination to prevent any acid mixture from being pushed into the drying tubes. Several reactions were so vigorous that the air flow had to be completely stopped to prevent this overflow.

Originally the organic carbon was to have been determined by subjecting the residue from the acid attack procedure to the combustion-train process. In this way, the acid attack would yield carbonate and inorganic carbon, while the combustion would give the organic carbon directly.

Unfortunately, the residue from the carbonate analysis would not dry at 100° C., and it was felt that higher temperatures might have driven off some organic components. As a result, Gross's method (1967) of subtracting inorganic carbon from total carbon to obtain organic carbon was utilized.

V. RESULTS

A. Physical Properties

All the sediments studied were either grey or black in color with various green and brown hues. Most clays and sands were grey, while the peat and humus layers were black. There were however, some black sands found at the sediment water interface for the cores from area 2. Generally the cores from this area were darker at the top of the core than at the bottom. All of the cores studied exhibited color banding, and some of the cores from area 1 showed mottled areas of grey and black. The grain size of these mottled areas appeared uniform.

Layers ranging from 2 to 6 inches in thickness and composed entirely of shell occured at a depth of approximately 15 inches in the cores from area 2, and at depth of 6 to 14 inches inthe cores from area 1. Some of the cores contained two such layers, and no shells were found in the sediment immediately below the second layer.

The mean grain size of the sediments obtained from the 50% finer value on the sieve analysis curve ranged from 0.2 mm for the fine sands to 0.02 mm for the clays. The majority of the sediments from the study areas were classified as fine sands, with an occasional clay or silt layer in the cores from area 1 and the impounded waters.

Most of the cores studied exhibited a hydrogen sulfide odor, which was classified as mild, moderate, or strong. There were, however, some samples which had no noticeable odor at all. Core 1-25 had a definite sewage-like odor, while cores 1-17, 1-18, and 1-25 had a very strong hydrogen sulfide odor at the top. The hydrogen sulfide odor of the cores from area 2 were generally milder than that of the other study areas. A "humus" odor was noticed in several of the cores from

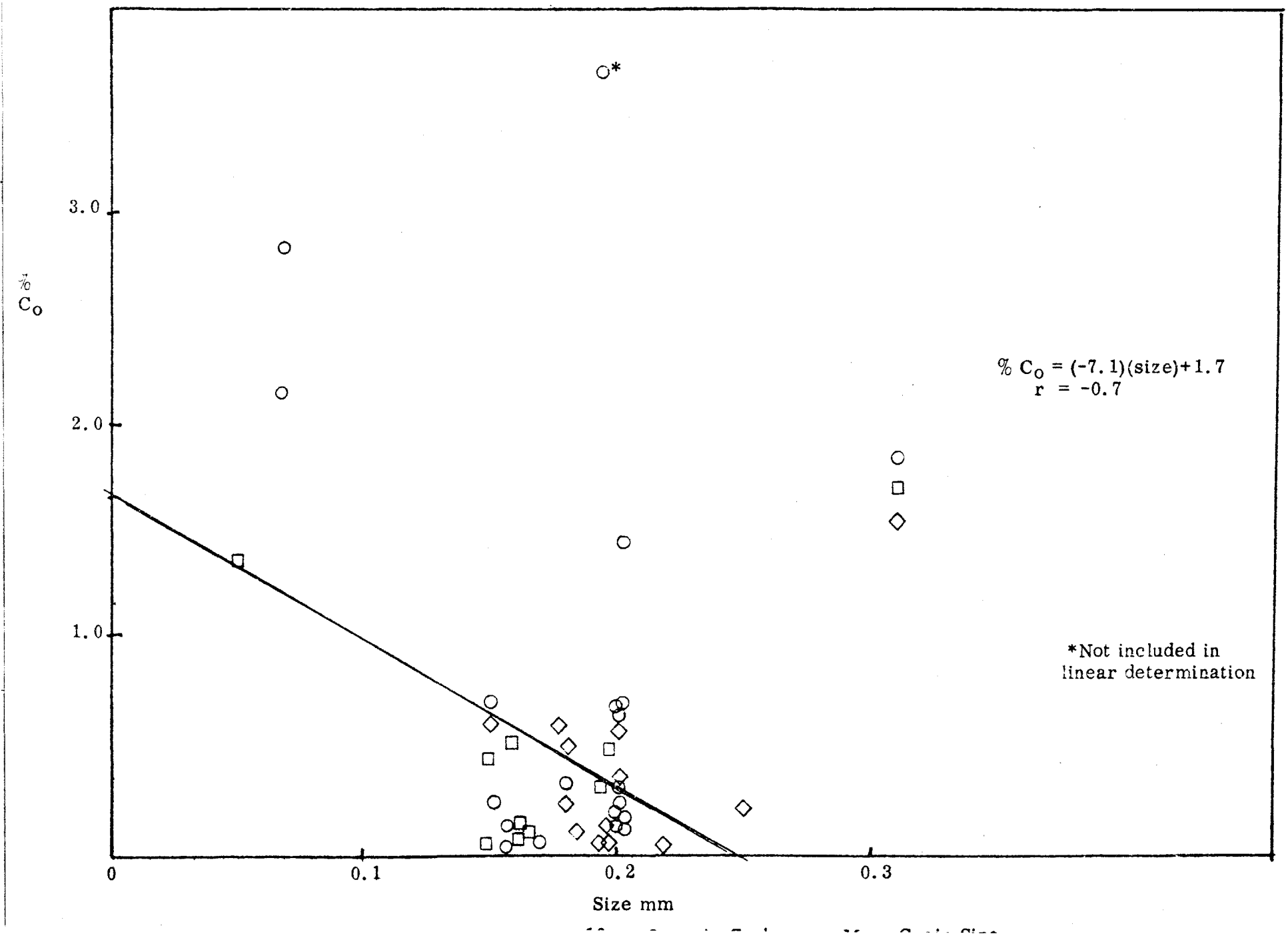
the impounded waters.

B. Chemical Results

The organic carbon values ranged from 0 to 3.56% with the majority of the values less than 0.5% (Appendix). Of the forty-three values obtained, thirty-two were less than 0.5%, five were between 0.5 and 1%, five between 1 and 3%, and only one value was greater than 3%. This maximum organic carbon value of 3.56% was found for a humus layer located at the top of core 118. Core 113 also contained a surface humus layer which gave a value of 1.86%, and core 119, a peat layer at a depth of twelve inches had a value of 2.07%. All other values of organic carbon larger than 1% were found for clays and silts. The highest values of organic carbon were obtained for the cores from the impounded waters, while Area 2 gave no value greater than 0.5%, and Area 1 had only one value greater than 1%. This value was found for a grey clay layer located at the bottom of core 1-25.

An inverse relation between organic carbon and grain size of the sediment was observed (Figure 10). The organic carbon values for clays and silts with mean grain size between 0.02 mm and 0.07 mm ranged from 1.39% for core 1-25 to 2.9% for core 117. For the sands with a mean grain size greater than 0.1 mm all the organic carbon values were less than 1%, and did not exhibit any particular relationship in this size range. The only exceptions to this trend were the two humus layers which had a grain size of 0.2 mm yet gave organic carbon values of 1.56% for core 113, and 3.56% for core 118 and the peat layer of core 119. This high organic carbon content for humus was expected, and does not invalidate the trend between mean grain size and organic carbon content for the clays and silts.

A negative correlation between organic carbon and depth into the core for the sediments from the impounded waters can be observed on figure 11. This general decrease of organic carbon with depth into the core is probably due to the fact that


3.0
2.0
1.0
% C_o
0
0.1
0.2
0.3
Size mm
% C_o = (-7.1)(size)+1.7
r = -0.7
*Not included in linear determination

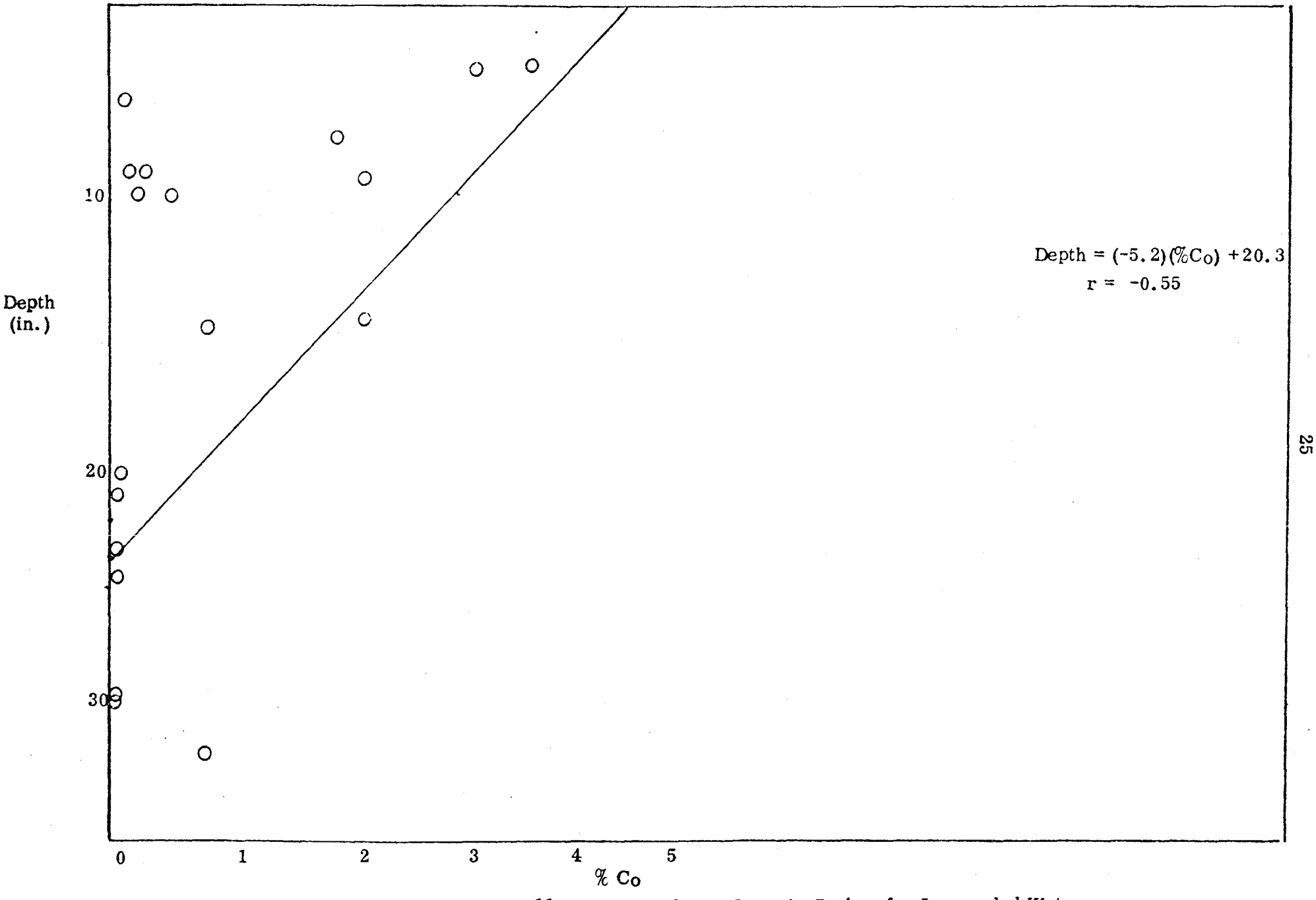


Figure 11. Depth vs. Organic Carbon for Impounded Waters

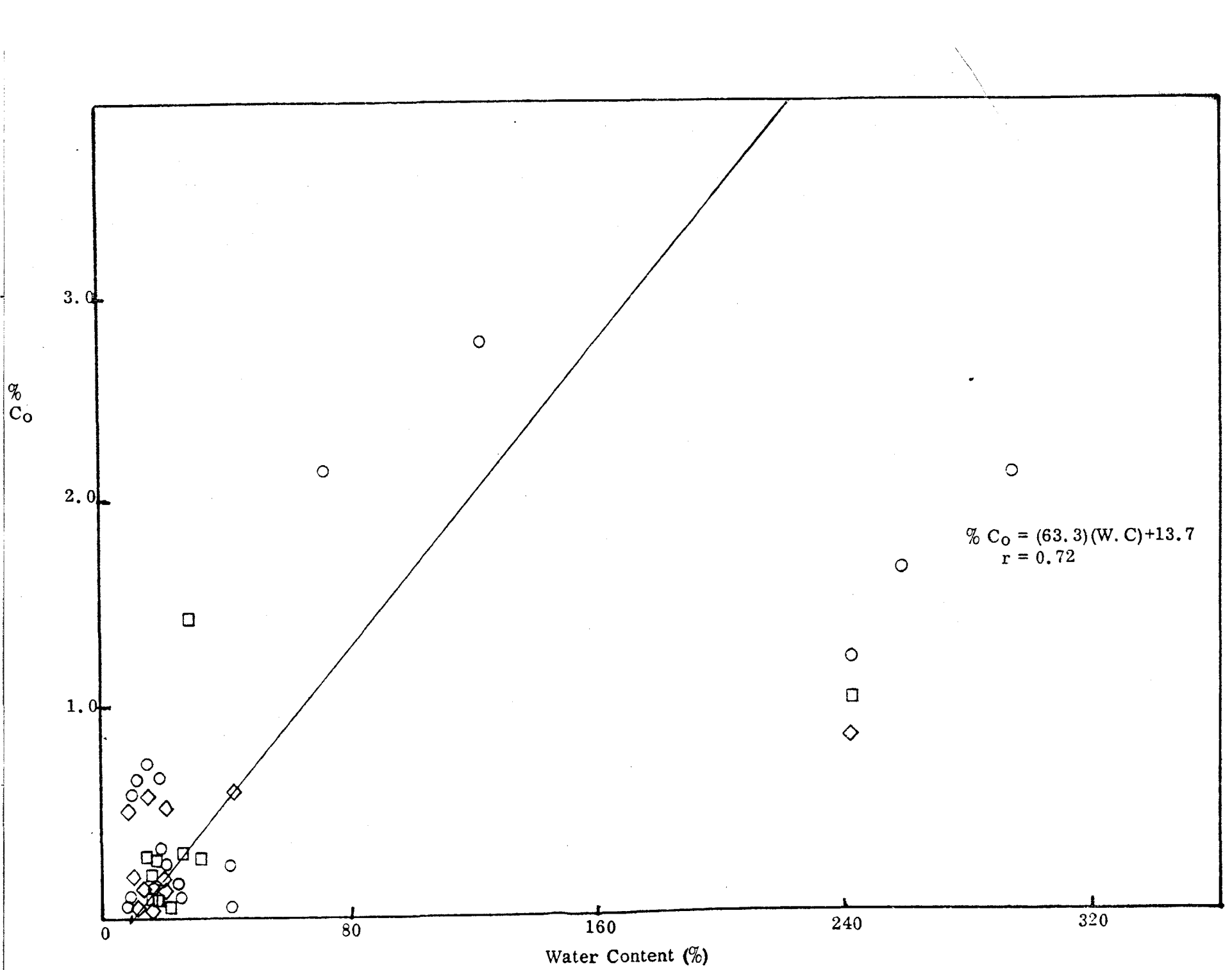


Figure 12. Organic Carbon vs. Water Content

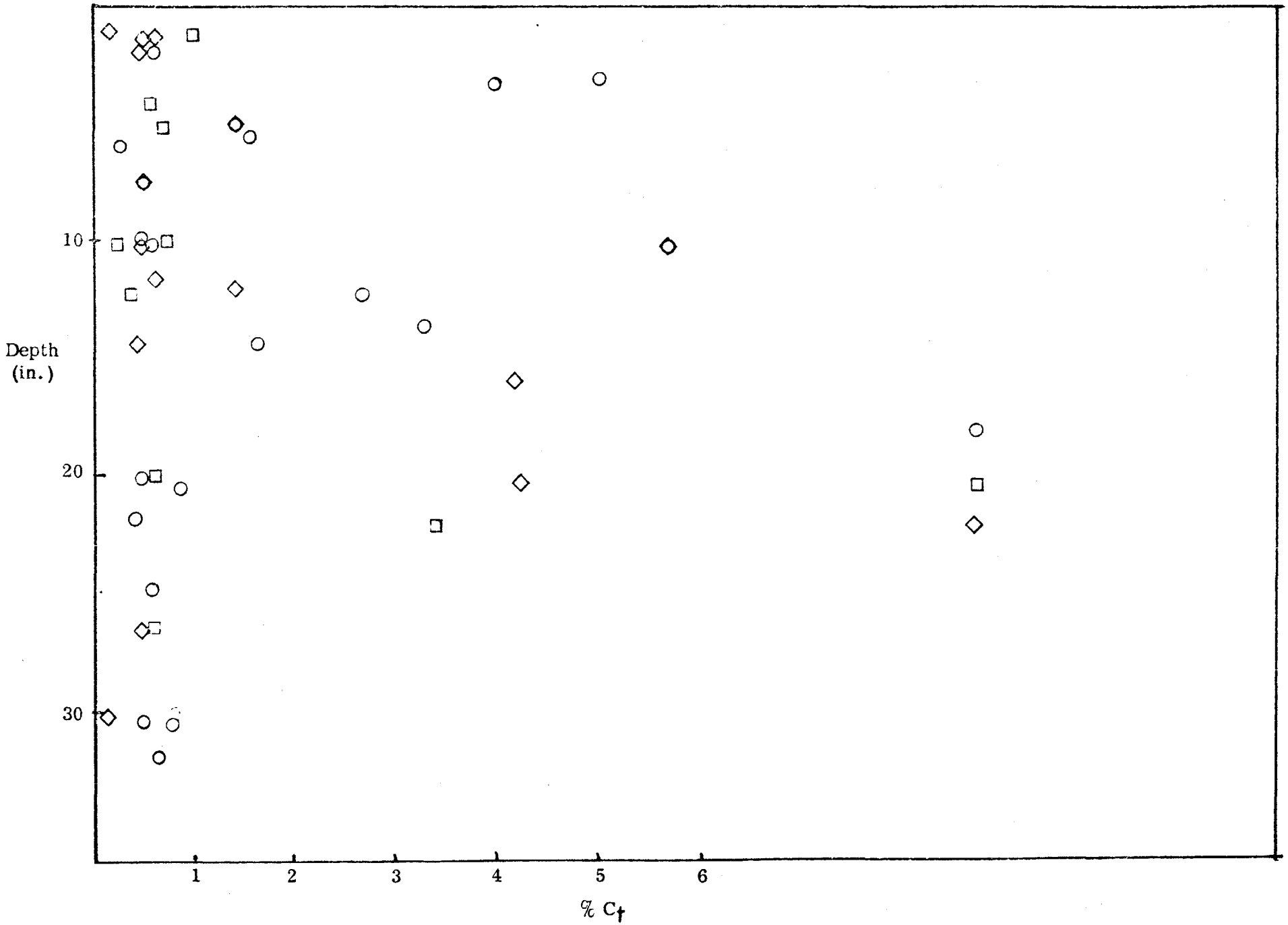


Figure 13. Depth vs. Total Carbon

the clay, humus, and peat layers were located at the top half of these cores, while the fine sands were located at the bottom of the cores. Above a depth of fifteen inches the organic carbon reached a maximum value of 3.5%, yet did not exceed 1% below this depth. No similar trend was observed for the cores from Areas 1 and 2.

A positive correlation was observed between the organic carbon content and the water content of the sediments (Figure 12). The maximum water content of 300% of dry sample weight was obtained from a humus layer located in core 113, and corresponded to an organic carbon value of 2.07%. Core 119 contained a peat layer which had a water content of 263% and an organic carbon content of 1.56%. The range of water content for the clays and silts was between 35% and 130%, which was lower than that of the peat and humus layers, but higher than that of the sands. The water content of a clay layer from core 117, for example, was determined to be 130%, and corresponded to an organic carbon value of 2.9%, while the water content of a clay from core 119 was 69% and the organic carbon was 2.19%. The range of water content for the sands was from 18% to 50%.

A slight variation of total carbon with depth into the core was observed. Figure 13 shows that the maximum value of 5.58% total carbon was located at a depth of ten inches in core 112. At depths above twenty inches the carbon values ranged from 0.2% to 5.7%, with fourteen values exceeding 1%. On the other hand, at depths greater than 20 inches all the values were 1% or less.

The carbonate carbon values ranged from 0.15% for core 116 to 25% for core 112. Although the maximum value was obtained for a sand located at a depth of ten inches in core 112, the carbonate values for clays and silts were generally higher than that of the sands and humus layers, and ranged from 5.05% to 20.8%. This is probably an indication that the clays are carbonaceous in this area. In general, the carbonate values for sands were less than 3%, as indicated on Figure 14.

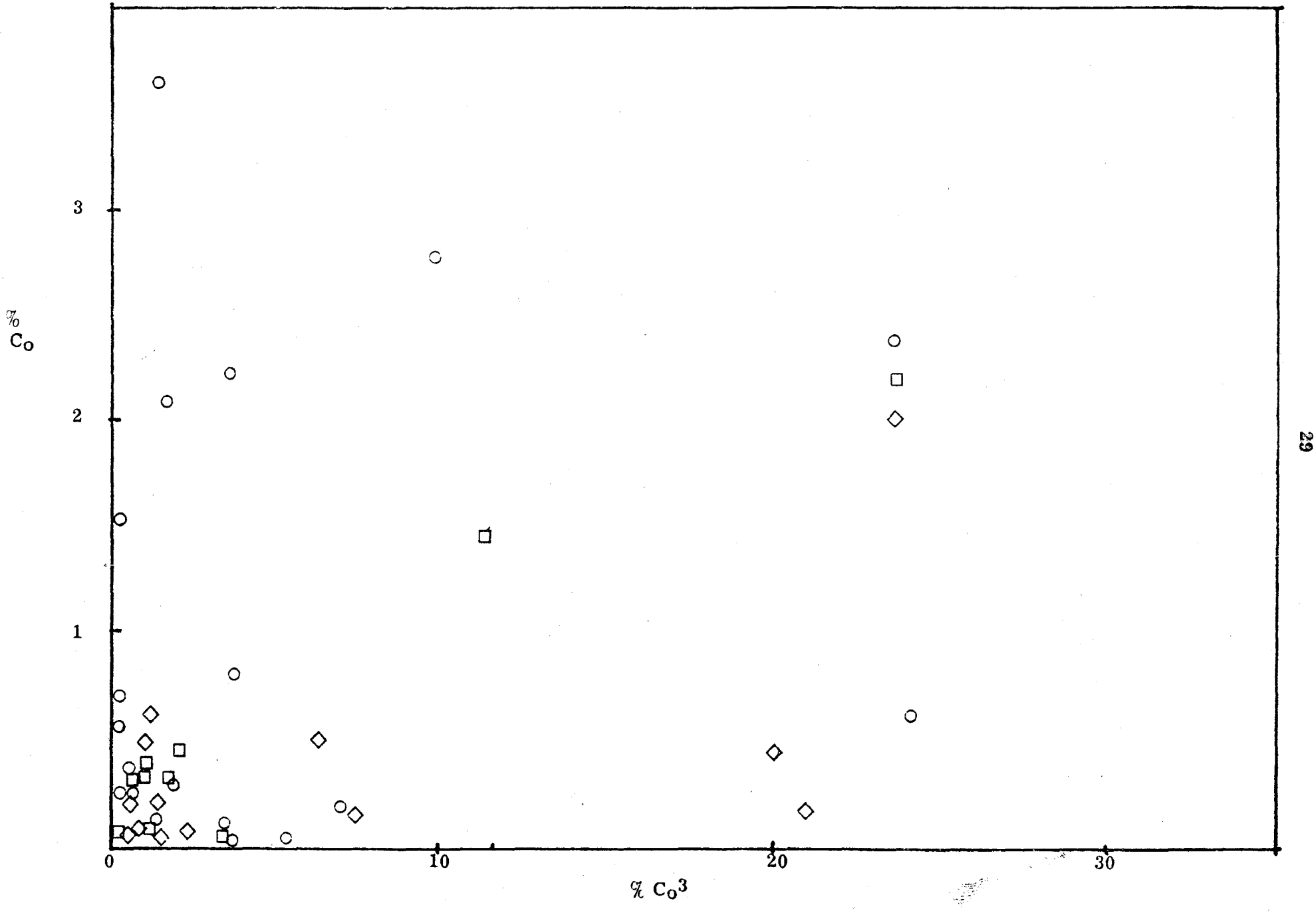


Figure 14. Organic Carbon vs. Carbonate Carbon

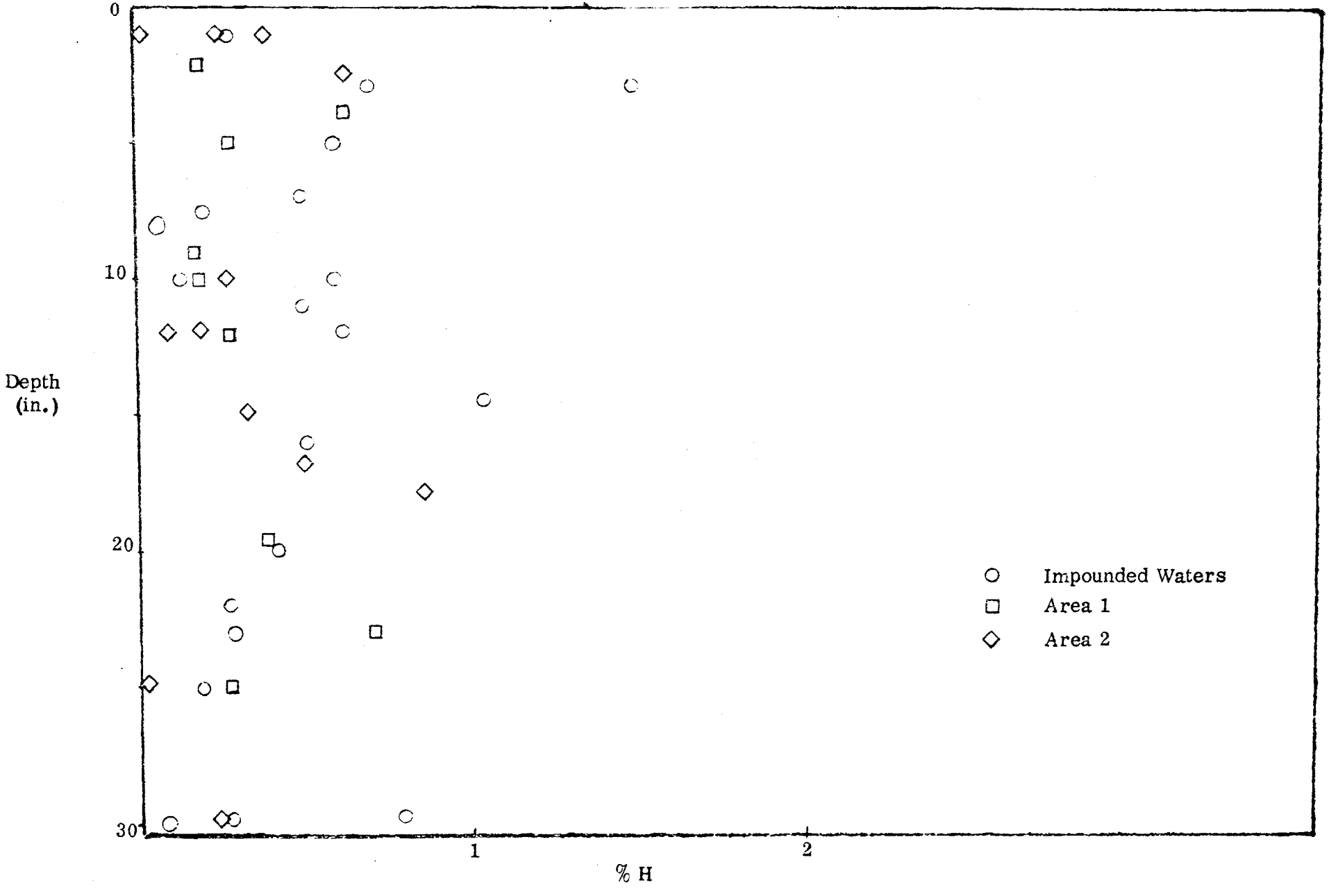


Figure 15. Depth vs. Hydrogen Content

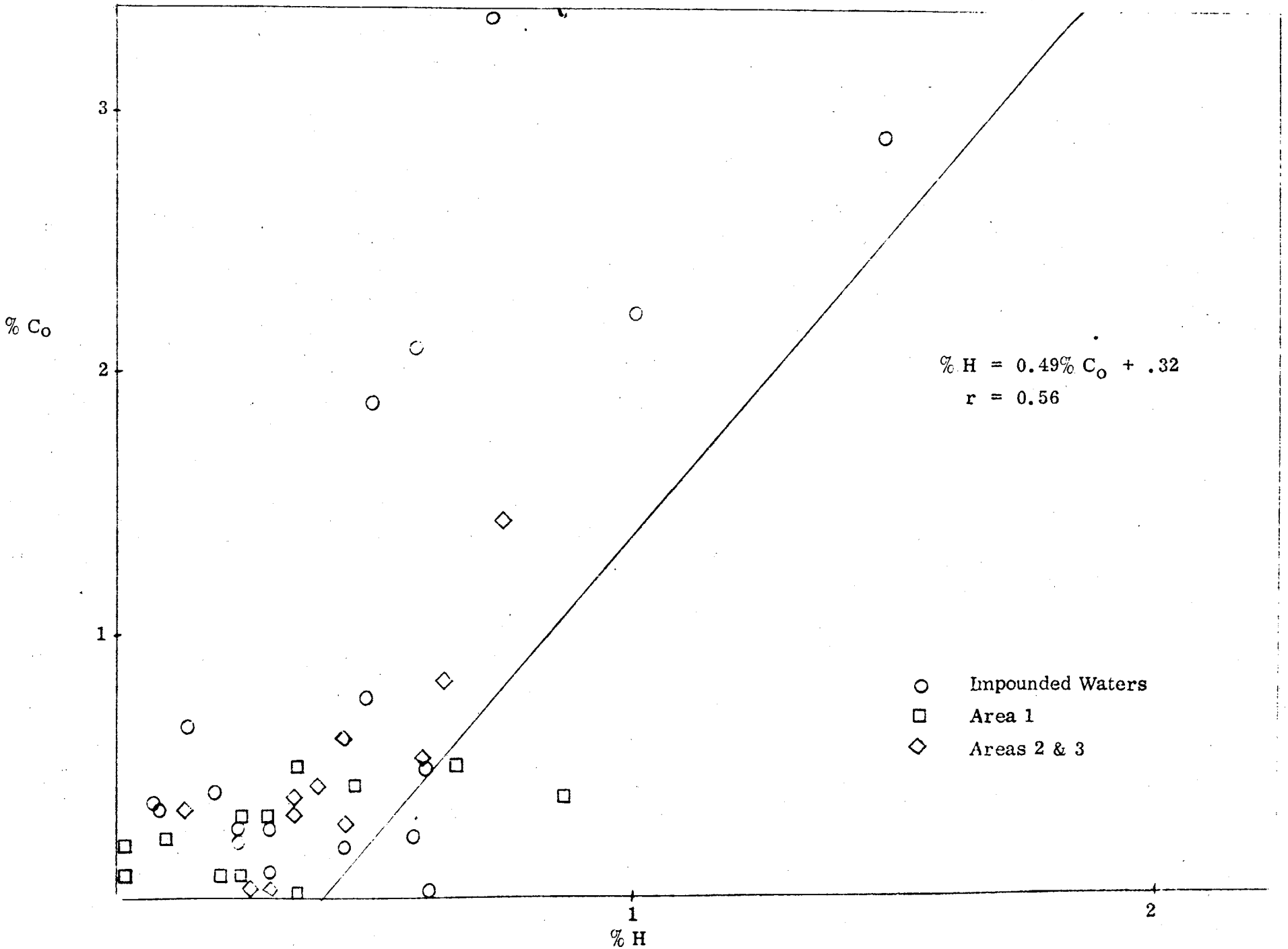


Figure 16. % H vs. % C_o

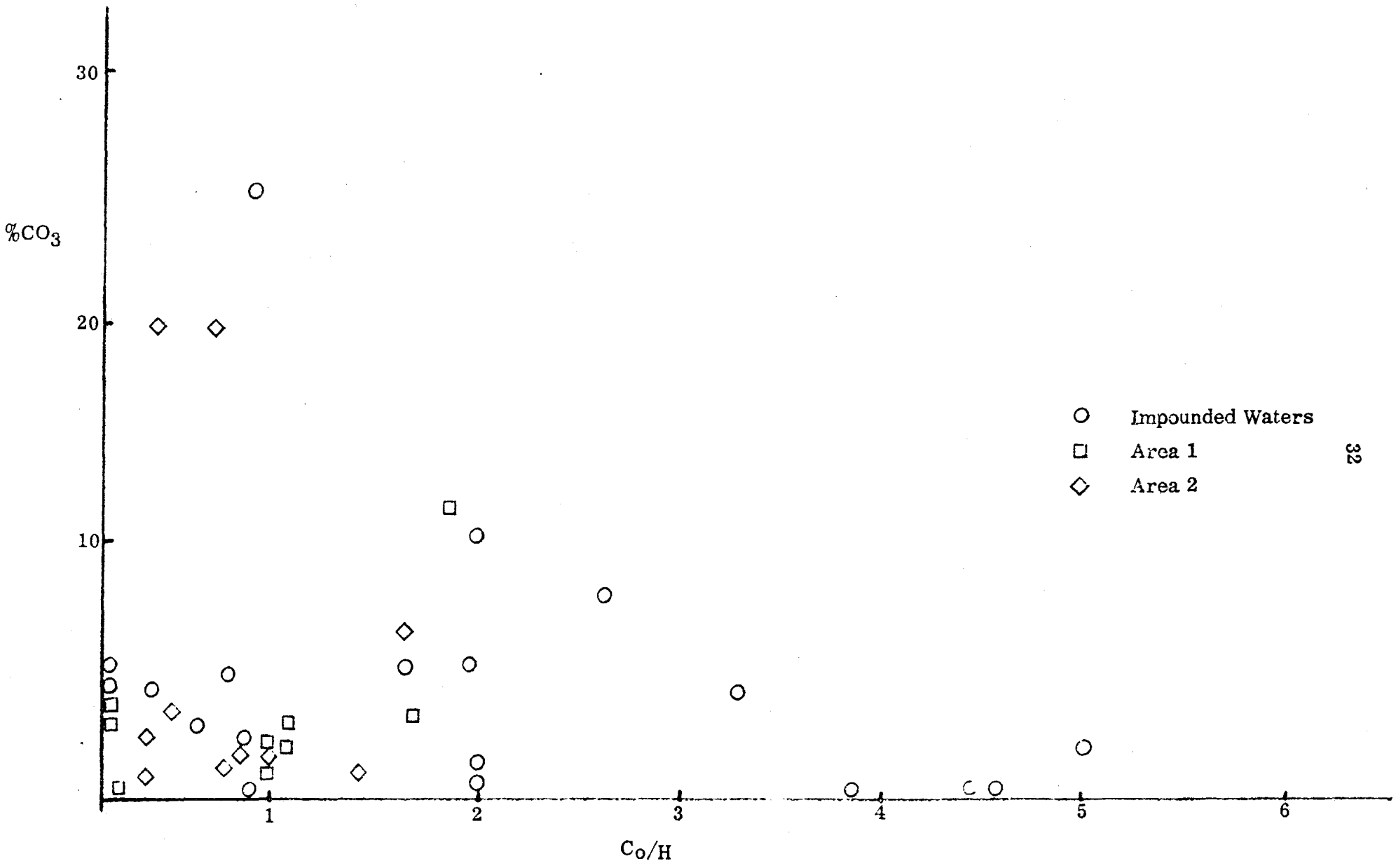


Figure 17. Carbonate vs. Co/H

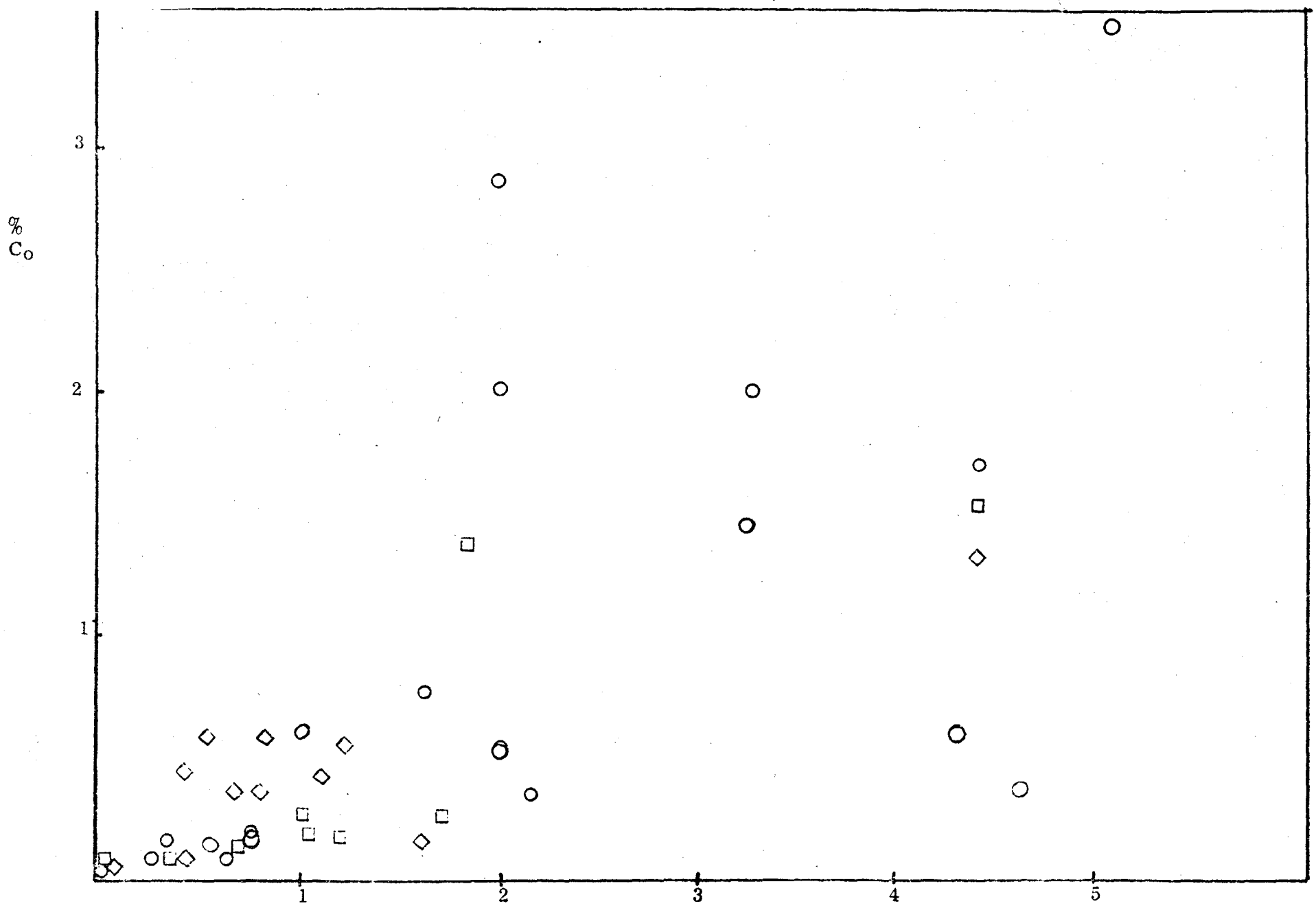


Figure 18. Organic Carbon vs. C_o/H

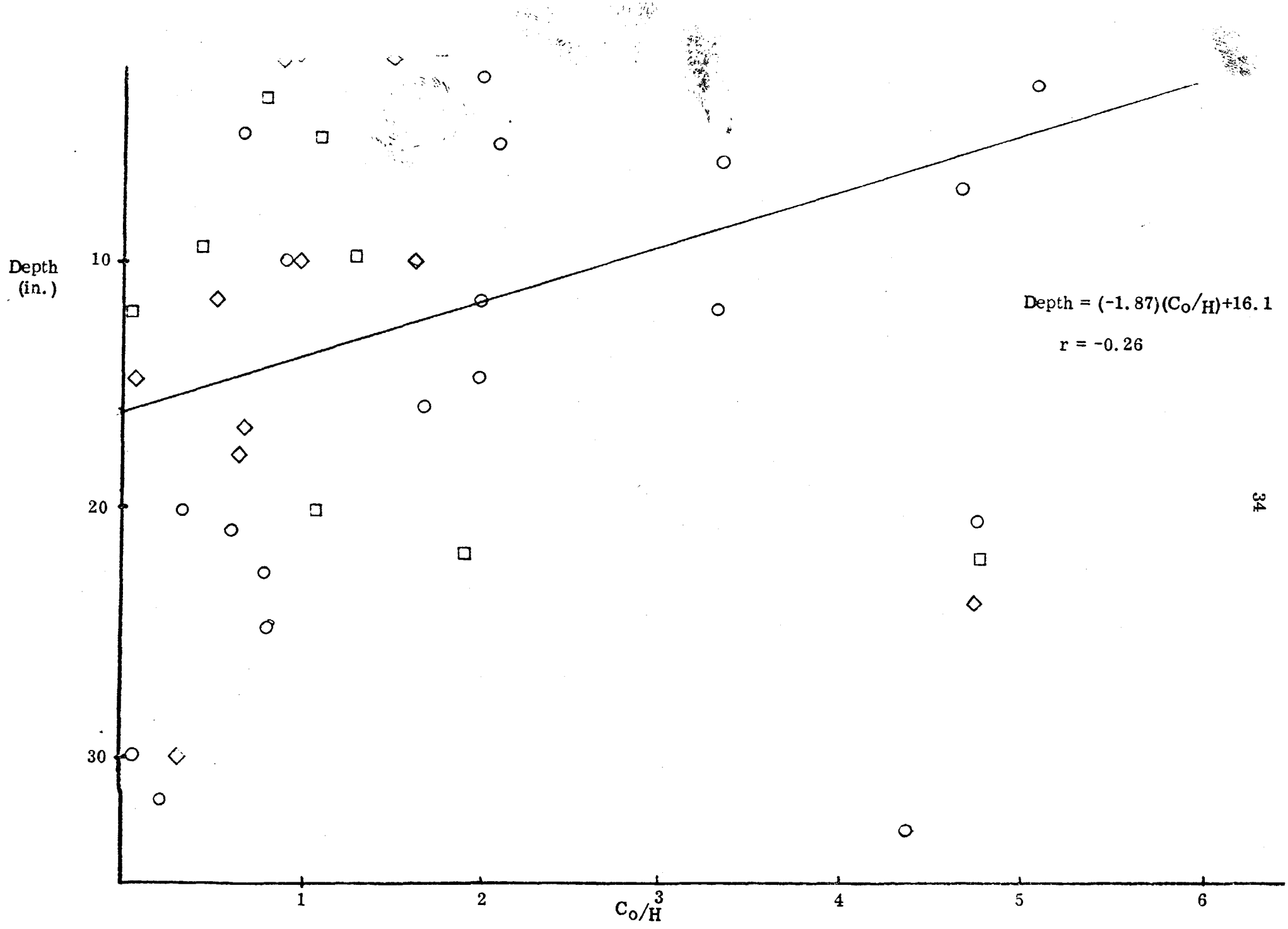


Figure 19. Depth vs. C_o/H

Of the five carbonate values between 10% and 20%, four were obtained for clay layers.

The percentage of hydrogen in the sediment showed a very slight decrease with depth into the core (Figure 15). Only two values exceeded 1%, one was found for a clay layer from core 119 and the other for a silt layer in core 117. The %H for clays, silts, and humus layers was slightly higher than that of the sands. A linear relationship exists between organic carbon and the amount of hydrogen in the samples (Figure 16). This trend was most pronounced for the cores from the impounded waters with the exception of a humus layer from core 118.

The ratio of organic carbon to hydrogen was calculated for all the samples. These ratios ranged from 0.05 to 19, with the majority of the values being between 1 and 3, and only one above a ratio of 5. Figure 17 shows a slight indirect variation of C_O/H with carbonate carbon values. For example, the three carbonate values greater than 20% correspond to a ratio less than 2, while all the ratios from 3 to 5 correspond to carbonate values below 5%. The relation between organic carbon and C_O/H can be seen on Figure 18. The C_O/H of 5.1 occured in a humus layer from core 118 which exhibited the maximum organic carbon value of 3.56%. The maximum C_O/H of 19 occured in an olive-grey sand at a depth of 26 inches into core 2-24 and corresponded to a % C_O of 0.2.

With the exception of two points, an indirect relation between the C_O/H and depth into the core can be observed from Figure 19. The majority of the ratio values greater than 2 were found for silts, clays, and humus layers at a depth of less than fifteen inches, while all of the C_O/H values except for two, for sediments below fifteen inches were less than 2. This relationship is even more regular for the impounded waters (Fig. 20). All the samples with water contents greater than 60% which were clays, silts, and humus layers, corresponded to a ratio greater than 2 with no exception (Figure 21).

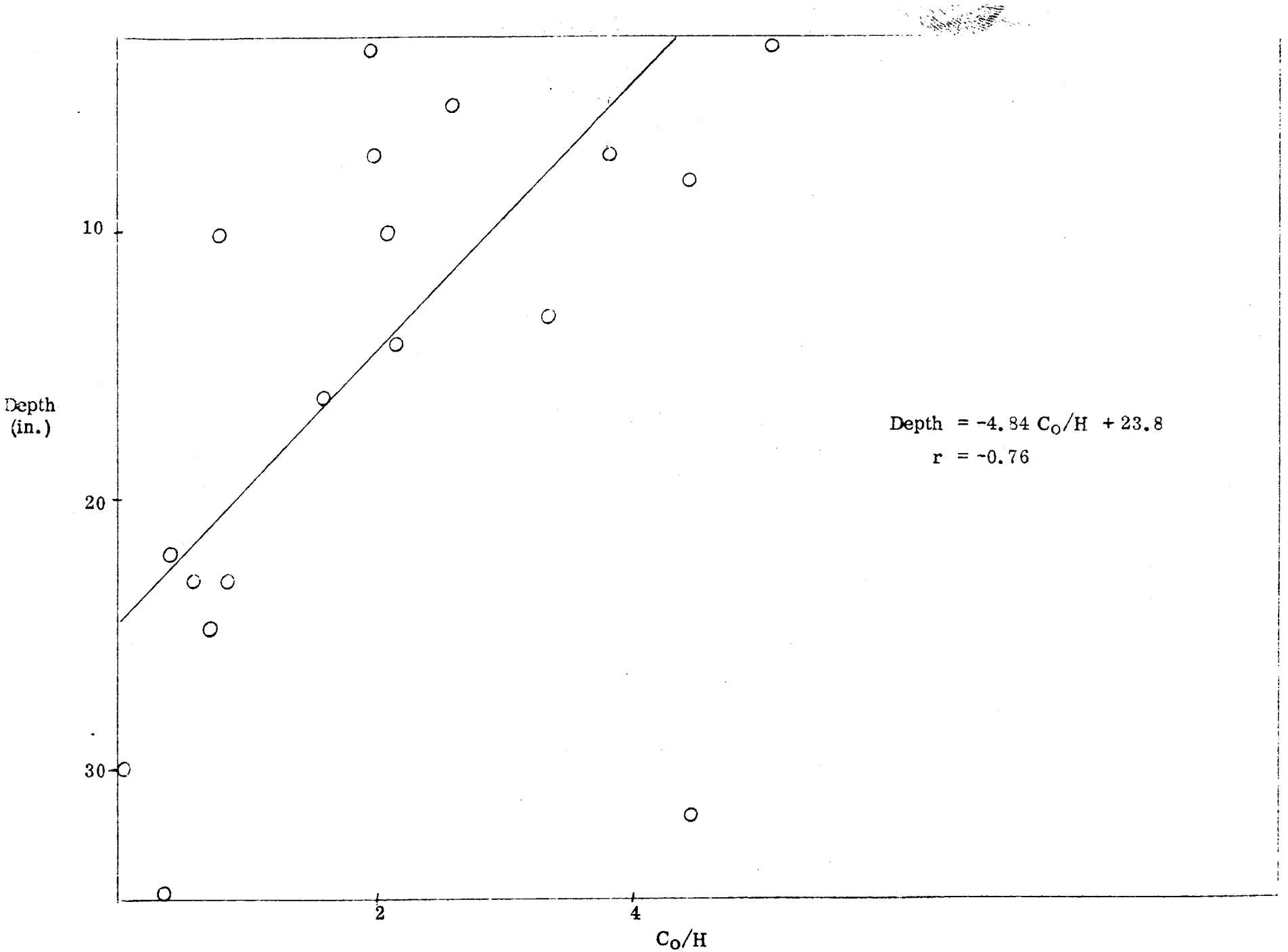


Figure 20. C_o/H vs. Depth for Impounded Waters

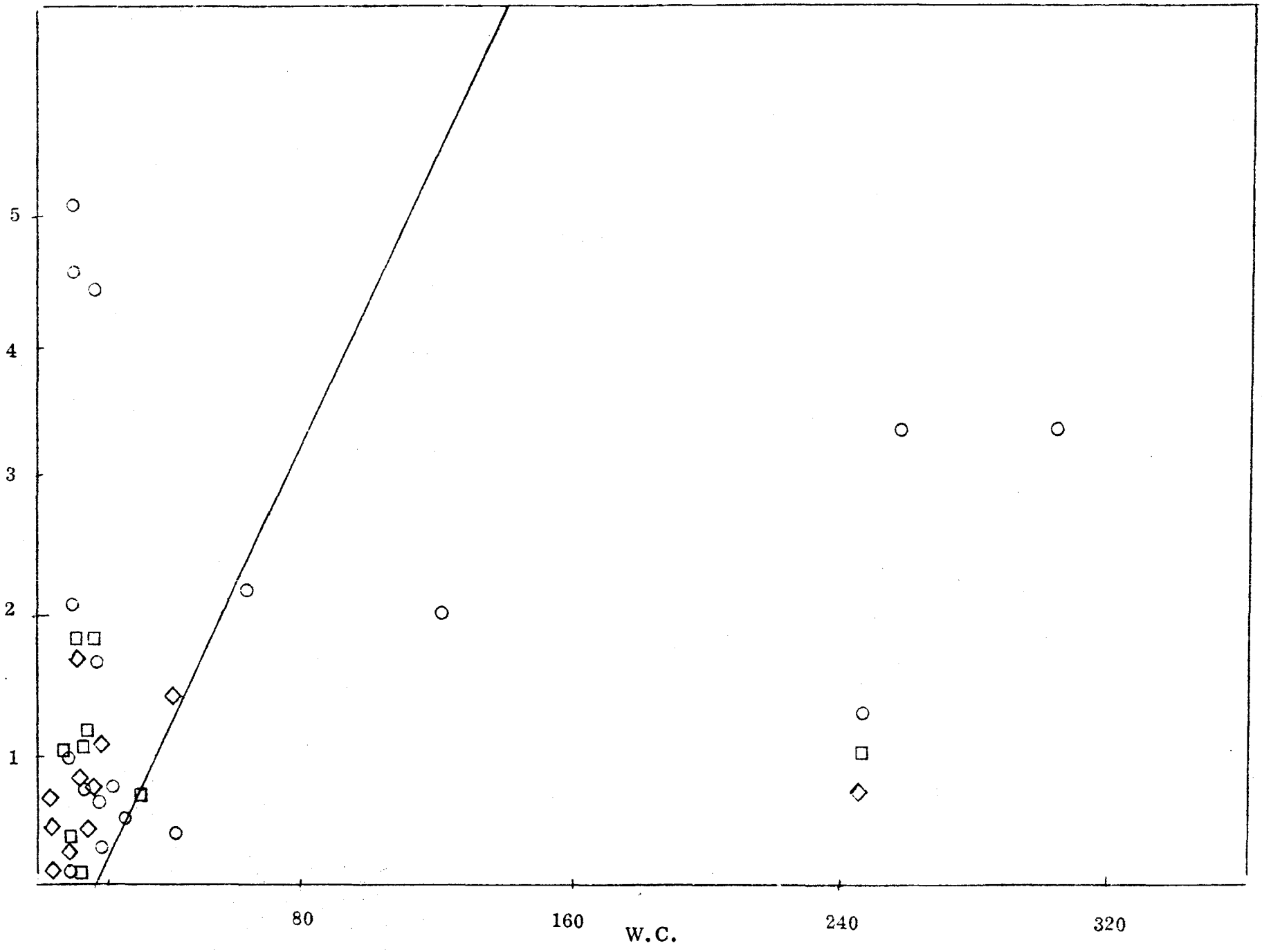


Figure 21. C_o/H vs. Water Content

C. Results from Kennedy Space Center

The results of the total carbon content of six selected samples by the Carbon-Hydrogen-Nitrogen Analyzer at KSC are presented in Table I. The lower limit of four of the six determinations agree closely with the values obtained from the combustion method employed in this study.

A few selected samples were analyzed at KSC for elements using semi-quantitative emission spectroscopy. The results are given in Table II. All the samples analyzed were fine sands. The source of each sample is indicated on Figures 22, 23. Although both 113D and 117C were obtained from the impounded waters near Banana Creek, it is obvious from the map of the area that they were taken from two very different locations, which is reflected in the different elemental content of these two samples. Sample 117C contained the highest value of aluminum, iron, and magnesium of all the samples analyzed. It is possible that the elemental composition is connected to the location of the sample site. There appears to be a progressive decrease in aluminum content from core 117 to 1-18 as indicated on Figure 22, and a simultaneous increase in calcium content. The similarity between the composition of samples 1-17 and 1-18 could be attributed to their similar location at the mouth of Banana Creek. Sample 2-2 (Figure 23) was obtained from a very different location and appears to be unique in its composition, especially in calcium content, which was the highest value obtained.

Table I. CHN Analysis of Selected Samples at KSC

Sample	Combustion %C	CHN %C	% Standard Deviation
1-25-1	3.63	4.08%	0.28
117-D	0.67	1.19	0.39
117-C	0.58	1.45	0.29
1-1-A	----	0.818	0.042
113-D	.71	1.19	0.31
1-25-7	.61	0.686	0.224

Table II. Elemental Analysis % $\pm$ 100% of value reported

Core No.	113-D	117-C	1-25-7	1-17	1-18	1-1	2-2
Element							
Al	0.1	1.25	0.5	0.25	0.25	0.1	0.75
B	0.001	0.005	0.01	0.005	0.001	0.01	---
Ca	0.1	0.5	0.5	1.0	1.0	0.2	5.0
Cu	0.001	0.001	---	0.005	0.005	0.001	0.005
Fe	0.1	0.75	0.1	0.1	0.1	0.25	0.1
Mg	0.01	0.1	0.05	0.005	0.01	0.001	0.001
Mn	0.01	0.005	0.005	0.005	0.01	----	0.001
Na	0.1	0.5	0.1	0.1	0.5	0.1	0.01
Zn	0.1	0.1	0.1	0.05	0.01	****	0.01
Ti	0.1	0.075	0.05	0.05	0.05	0.001	0.005
Zr	0.1	0.005	0.05	0.001	0.01	-----	----

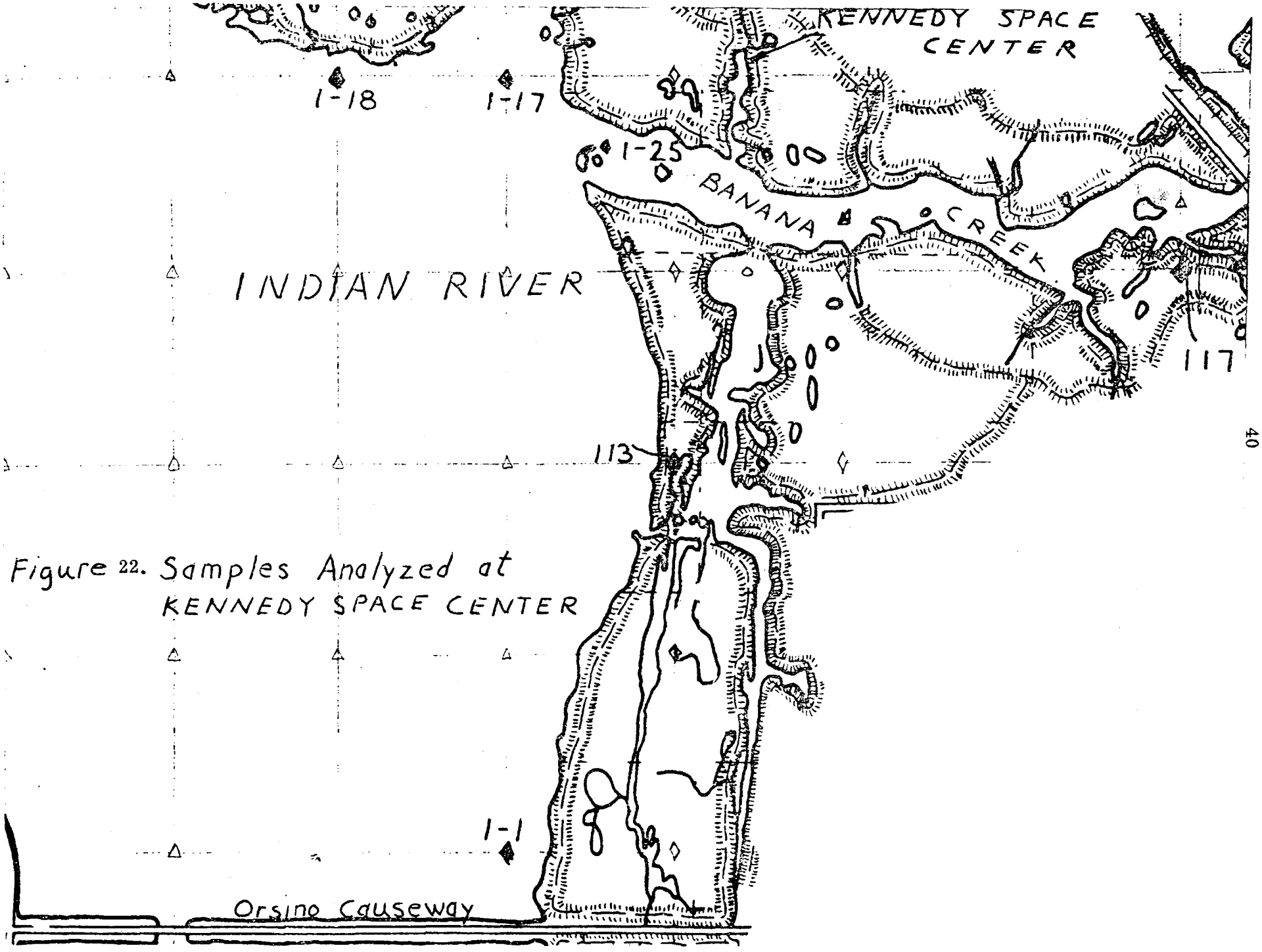


Figure 22. Samples Analyzed at KENNEDY SPACE CENTER

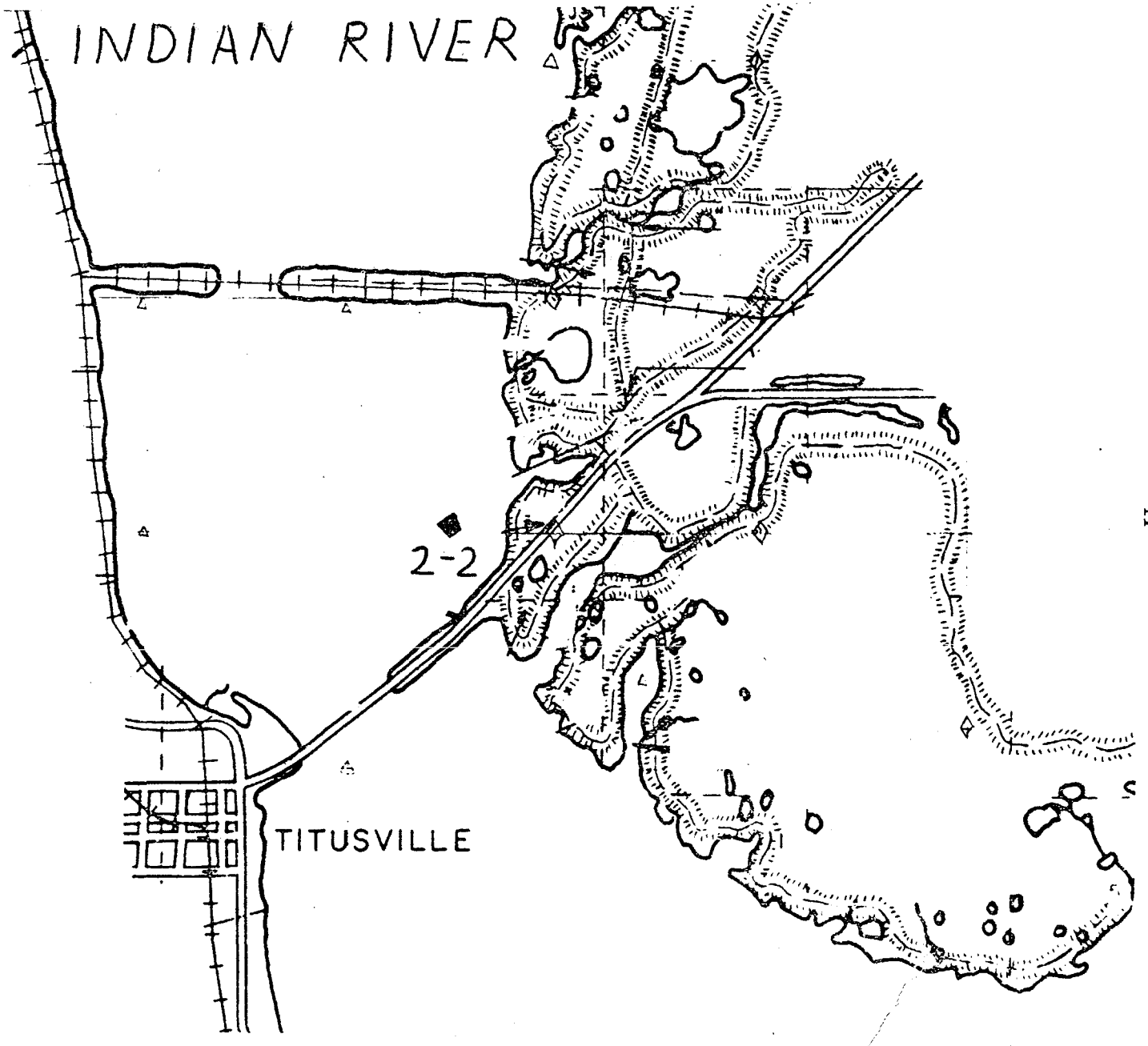


Figure 23. Samples Analyzed at KENNEDY SPACE CENTER

VI. DISCUSSION

Several results obtained in this study agree with those reported in the literature. For example, the organic content of the silts and clays was 3 to 4 times greater than that of the sands, which was less than 1% (Figure 10). This result agrees with the data presented by Biggs (1967), Bordovskiy (1965) and Gross (1967) and is probably due to the fact that organic matter is usually transported and deposited with fine grained material. According to Riley (1965), the higher organic content of clays and silts implies poor ventilation of the bottom water and a low rate of exchange with sediment. Consequently, a large part of the organic matter is not decomposed and is preserved and buried in the sediment. The preservation of organic carbon is also favored by anaerobic conditions. The sands are poor in organic matter because they generally accumulate in agitated, well-ventilated water, and do not get washed away like the lighter clay and silt particles.

Grain size of sediment is not the only factor controlling the amount of organic matter. The influence of sedimentation rate on the organic content of the sediments studied was evidenced by the fact that the samples with the highest organic carbon content contained the lowest carbonate carbon and vice versa (Figure 14). Gross (1965) found the same relationship for the sediments of the Northeast Pacific, and presented a curve very similar to Figure 14. In areas where sedimentation rates are low calcareous remains predominate due to the oxidation of organic matter. Where the rate of sedimentation is rapid, the organic carbon predominates because there is not much time for oxidation before the organic matter is buried in the sediment (Gross, 1965). The results of this study might indicate that the sedimentation rate in Area 2 is lower than that of the impounded waters since the highest carbonate values were found for cores 2-29 and 2-19, while the highest organic carbon values were found for cores

117, 118, 119, 113 (Figure 14). The high organic values for cores 113, 118, and 119 were located in humus and peat layers and could also be attributed to the greater terrigenous nature of this area, while the high value for core 117 was found for a silt layer and might be more dependent on sedimentation rates and ventilation of bottom water.

The organic content of the sediment could also be indicative of the rate of decomposition by bacteria. It has been found (Bordovskiy, 1965) that the granulometric composition of the sediment affects both the distribution and physiological activity of the bacteria in the sediment. Bordovskiy (1965) reported that 95% of the organic matter in sands is decomposed in 40 days from bacterial action, while only 75% of the organic matter in clays is decomposed in the same time. The difference in decomposition rates is due to the fact that the majority of bacteria in fine grained sediments are adsorbed on the mineral particles and their functions are restricted. In coarse sediment, the bacteria are located between the particles and are in a freer state (Bordovskiy, 1965). Of course the availability of the organic matter will also influence the decomposition rate.

The general decrease of organic carbon with depth into the core (Figure 11) was also reported by Biggs (1967), Bordovskiy (1965), and Bortleson (1972). This decrease in organic carbon is probably due to the decay of organic matter with time. In general, the decrease is irregular but most pronounced in the top ten inches of the core. According to Bordovskiy (1965) the process is slowed down below the first few inches due to a change in environmental conditions. In the upper layer of sediment the biological activity is the main decomposing agent. Lower down the core the bacteria are reduced mainly because the nutrient reserve is used up, and other factors predominate such an increasing toxicity of medium, and biochemical agents like enzymes. The decrease of organic carbon with depth into the core is most regular for

the cores from the impounded waters and Area 1. Probably the organic matter in these areas was more available for bacterial oxidation than that of Area 2 in the past years.

It is difficult to attribute the trend in organic carbon content to any one factor. It is the result of the combined effects of sedimentation of carbonate carbon, organic carbon, and inorganic compounds; the production of organic matter; and its introduction from external sources.

Several relationships between the C_o/H of the sediments and other parameters were presented in the Results section (page 35). The C/H for humic acids was discussed in detail by Bordovskiy (1965, see Background), but no mention was made in the literature of the C_o/H for all of the organic matter in the sediment. Possibly the C_o/H of the sediment could be used to indicate the degree of oxidation of the organic matter, with a high C_o/H indicating a more oxidized state of organic compounds and a small C_o/H indicating a more reduced state, or a considerable amount of hydrated compounds.

The C_o/H values for the impounded waters ranged from 0.3 to 5, with nine values between 2 and 5. In Area 1 the values ranged from 0.04 to 1.9, with only three less than 1, and in Area 2 from 0.05 to 19 with seven values below 1. These results might indicate that the organic matter in the impounded waters was more available for bacterial oxidation and is in a more oxidized state than that of Areas 1 and 2. A higher C_o/H might also be indicative of a more aerobic condition, since oxygen is needed for bacterial decomposition. The low C_o/H ratios might indicate that there are hydrated compounds in these sediments.

In general the C_o/H decreased with depth into the cores, indicating that the organic matter is being transformed with time to the precursors of crude oil. This transformation of organic matter to a more reduced state in the lower layers of

sediment is a natural phenomenon (Riley, 1965).

VII. CONCLUSION

A summary of the correlations obtained and their statistical significance is presented in Table III. A relationship is considered significant when the probability, P, is 0.05 or less that the value of the correlation coefficient, r, will occur by chance. The relationship between organic and carbonate carbon is not linear but in agreement with that reported by Gross (1967) and Kogler (1967). When the relationship agreed with the literature, the reference is given.

From the general appearance and odor of the split cores one would probably conclude that the first few centimeters of water directly above the surface sediments is deficient in oxygen. All the cores contained color banding ranging from light grey to dark grey and black, with green hues. According to Biggs (1967), this banding along with hydrogen sulfide odor are indicative of a lack of dissolved oxygen in the overlying water. Area 2 in particular contained cores which were extremely dark on the top at the sediment water interface, and lighter on the bottom. Dark followed by light banding indicates deposition during alternating anaerobic, and aerobic conditions.

The higher organic carbon and C_O/H values for the surface sediments of the impounded waters suggests a more rapid rate of sedimentation along with a more aerated condition than that of Areas 1 and 2. The more pronounced decrease of organic carbon with depth into the core for the impounded waters might indicate that the organic matter in this area was more available to bacterial oxidation.

The irregular profiles of the various parameters with depth into the core (Appendix), especially organic carbon, might be indicative of changes in sedimentation rates and productivity in the past, and could probably be used to trace the influence of cultural activities of man on the area.

TABLE III

Summary of Results

Parameters	m	b	r	P	Reference
C_o, Size	-7.13	1.73	-0.7	0.001	1, 2, 5
C_o, Depth	-5.22	20.3	-0.55	0.01	1, 2
Co, Water content	63.35	13.7	0.72	0.001	7
C_o, H	0.49	0.32	0.56	0.001	
C_o/H, Water content	18.59	20.1	0.41	0.01	
C_o/H, Depth, Imp.	-4.84	23.8	-0.76	0.001	
*C_o/H, Depth, All	-1.87	16.1	-0.26	0.1	
*C_o/H, CO_3	-0.5	4.54	-0.14		
*H, Depth	-4.4	14.88	-0.13		
*C_t, Depth	-0.63	13.61	-0.09		
C_o, CO_3	not linear				5, 7
Grey-black, banding, H_2S Odor					1

*not statistically significant

It is a general feature of clays, silts, humus, and peat to have considerably higher water contents than sands. The linear relationship between organic carbon and water content (Figure 12) was expected and a similar trend was reported by Kogler (1967).

Too few samples were analyzed for elemental composition to obtain any significant trends or agreement with the literature. According to Bortleson (1972), the amount of aluminum, potassium, magnesium, and calcium depend upon the rate of supply of particulate and dissolved mineral matter, the biological or chemical precipitation of carbonates, and variations in the accumulation of the sediment. In general, calcium is more easily leached from the soil than magnesium. The distribution of iron and manganese is strongly influenced by the redox conditions in addition to the supply of dissolved and particulate matter, and accumulation of sediment. Iron is usually associated with clay minerals and sulfides.

No correlation between iron content and clay content could be obtained since all the samples analyzed were fine sands. The higher values of aluminum, iron, and magnesium for core 117 might suggest higher rates of supply of dissolved and particulate matter to this area, but more data is needed to conclude this hypothesis. Cores 2-2, 1-17, 1-18 contained a higher shell content than the others analyzed and might explain the higher calcium values for these cores. The major trend observed for the elemental composition of the sediments was that a regular composition corresponded to a similar location (see Results).

VIII. RECOMMENDATIONS

According to Gross (1967), the dissolved oxygen in the bottom waters may control, to a large extent, the amount of organic carbon in the sediment. At certain depth intervals, the amount of organic carbon in the sediment is inversely related to the concentration of dissolved oxygen in the overlying water. In order to obtain a complete understanding of the sediments of the Indian River and the impounded waters, dissolved oxygen values should be determined for the water above the collected cores.

The redox state of the environment should also be determined when studying sediments. Biggs (1967) suggested that the sulfate to chlorinity weight ratios in the interstitial waters be determined. In reducing environments, the ratio is lower than 0.14 due to the breakdown of the sulfate molecule (Biggs, 1967).

Finally, in order to obtain a complete understanding of the environment, the pH and E^h should be obtained. These two parameters have been used by many authors to obtain information about compositional changes, chemical reactions, biological populations, diagenesis, and sediment color (Biggs, 1967; Bordovskiy, 1965).

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APPENDIX

Variation of Organic Carbon, Grain Size, Carbonate Carbon, Hydrogen, Water Content, Total Carbon, and C_O/H with Depth into Core.

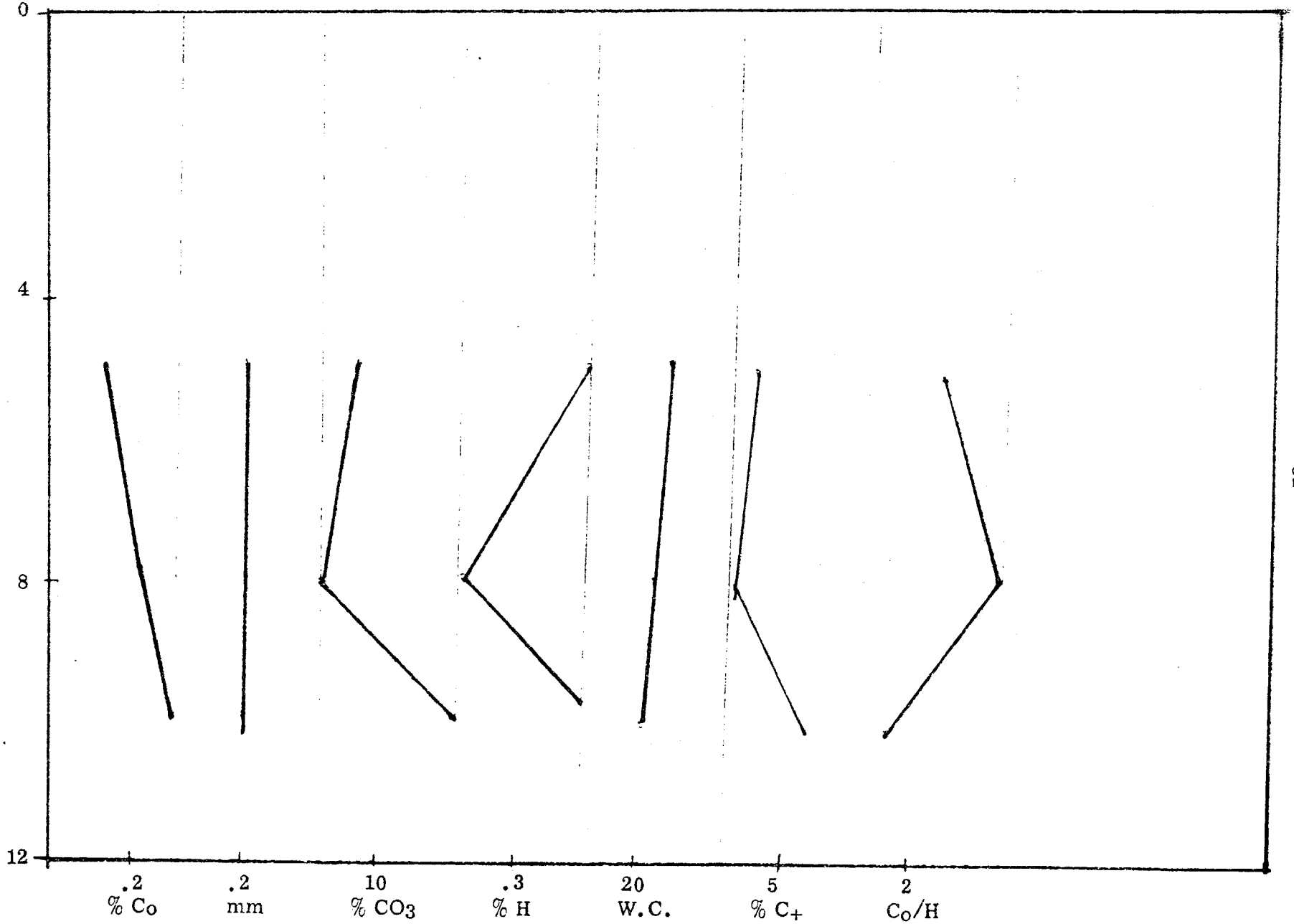


Figure A. Core 112

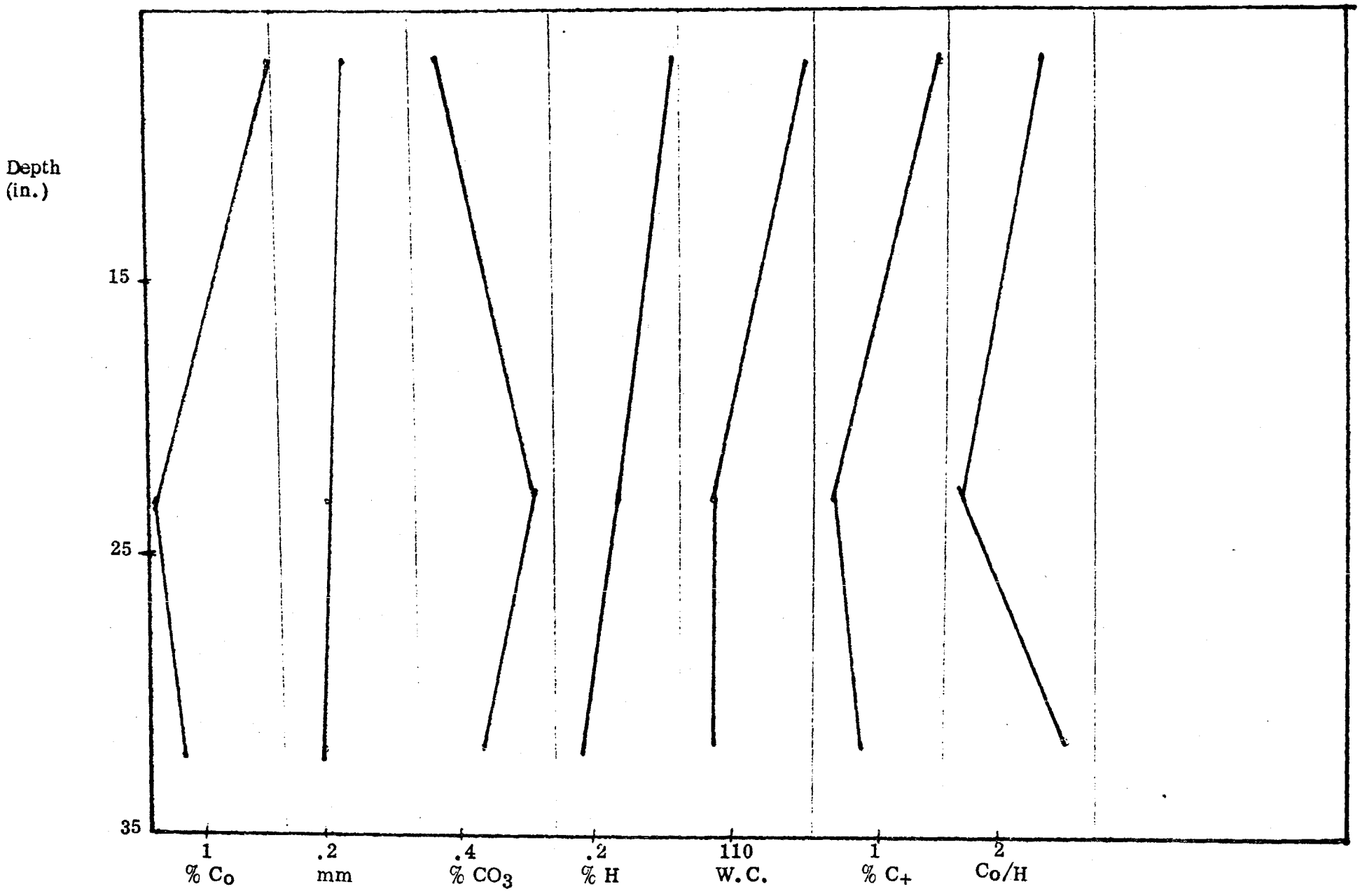
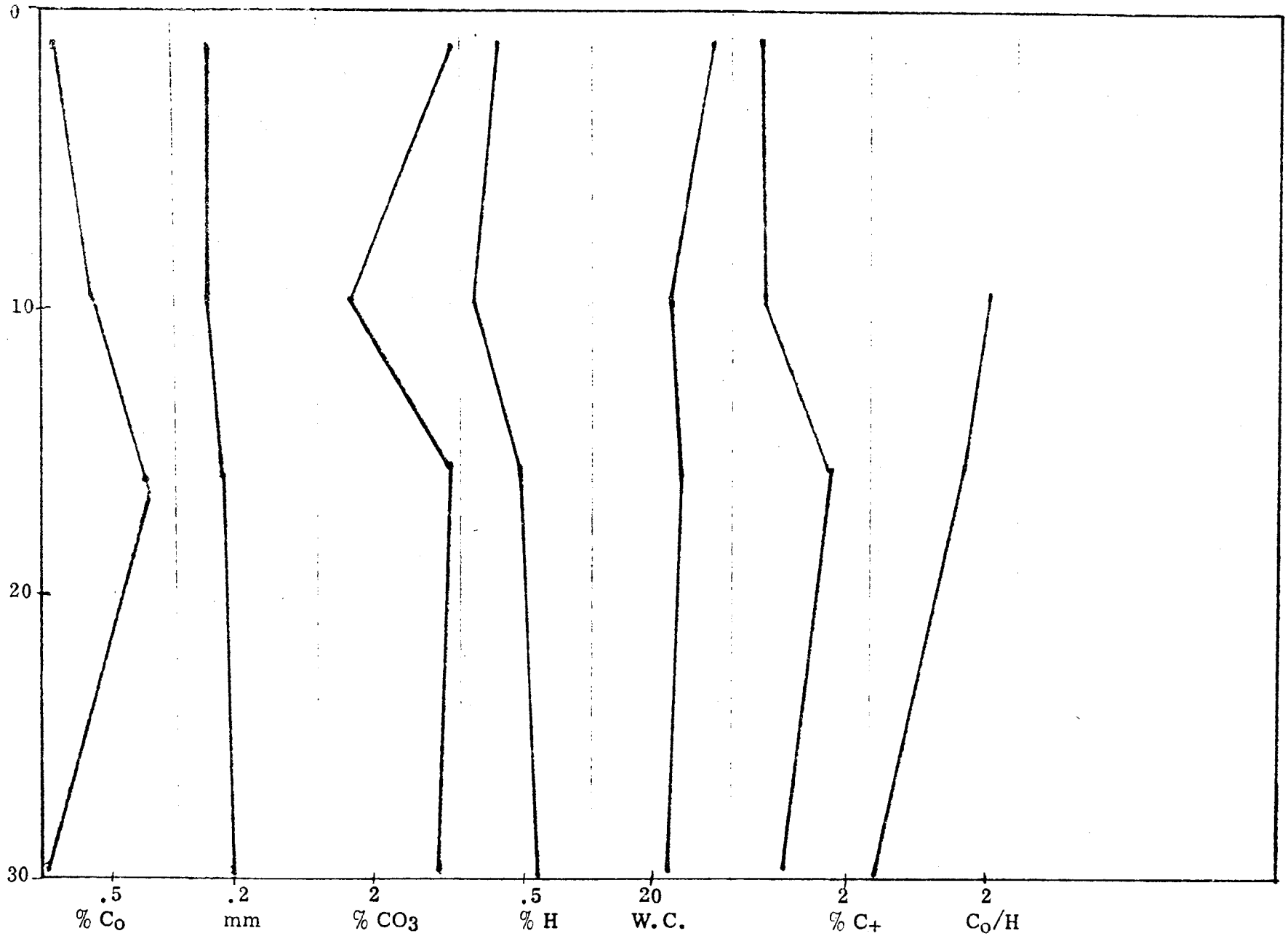


Figure B. Core 113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(in.)
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mm
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.5
% H
20
W. C.
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% C+
2
Co/H

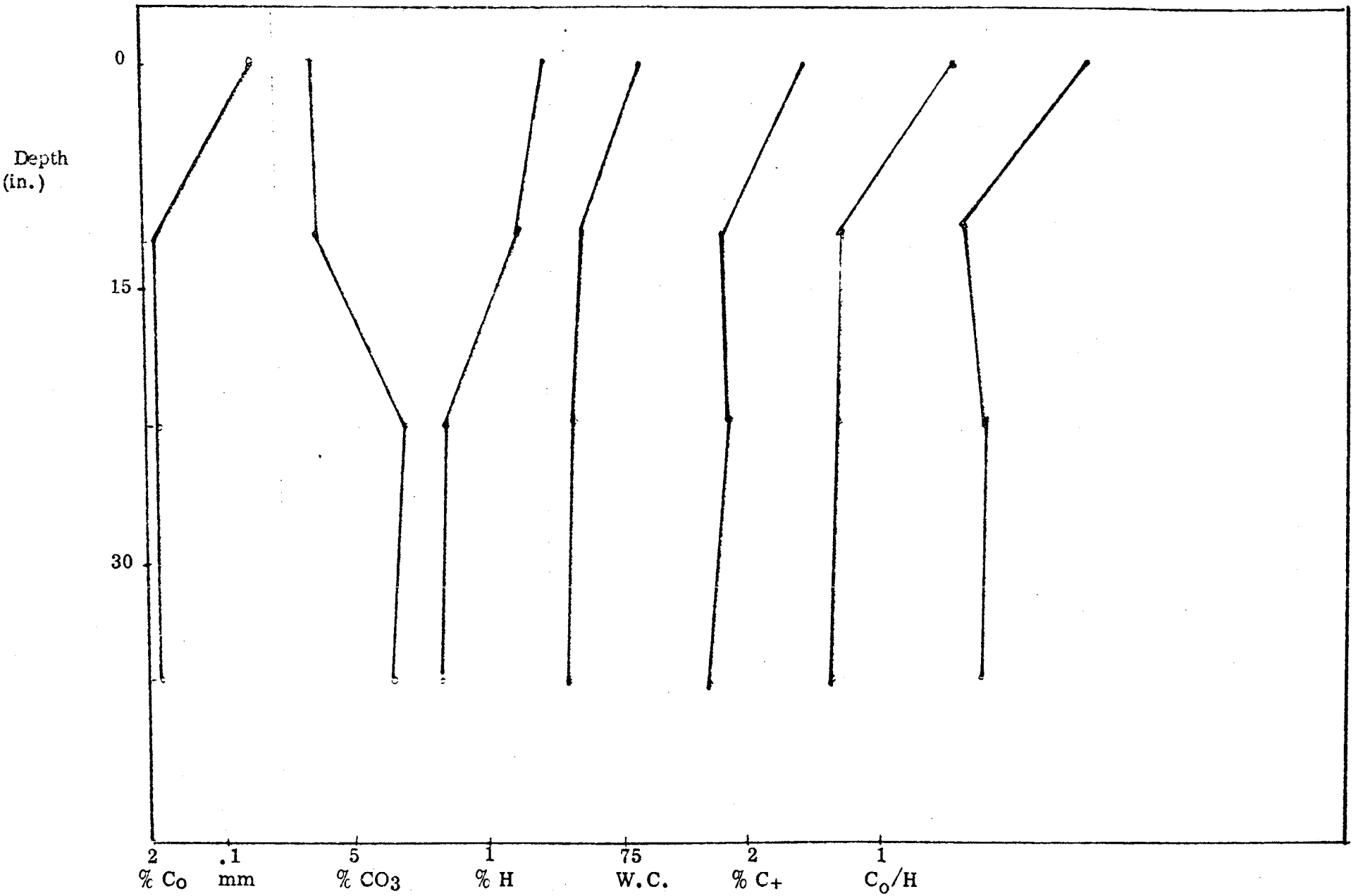
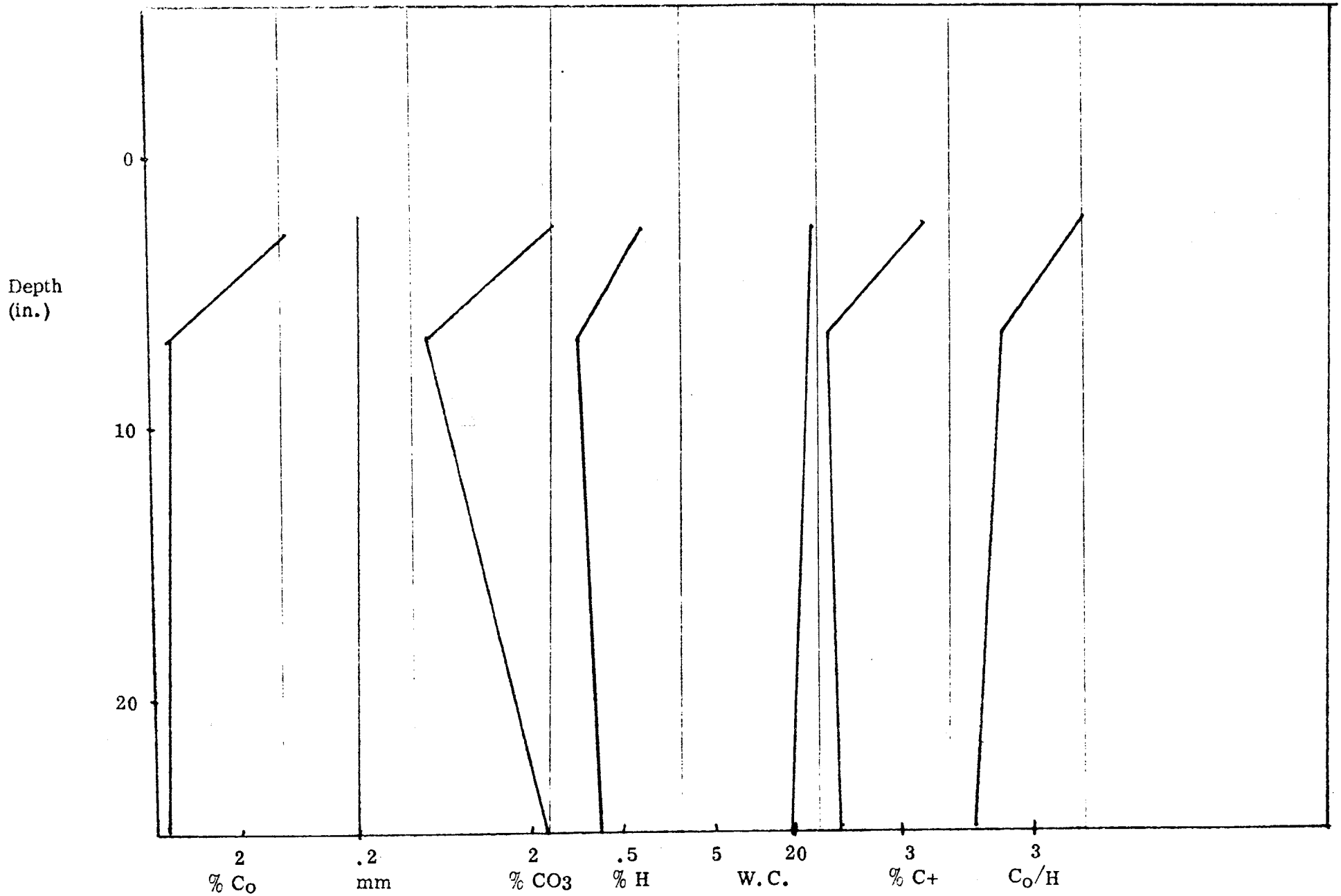


Figure D. Core 117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% C+
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Co/H

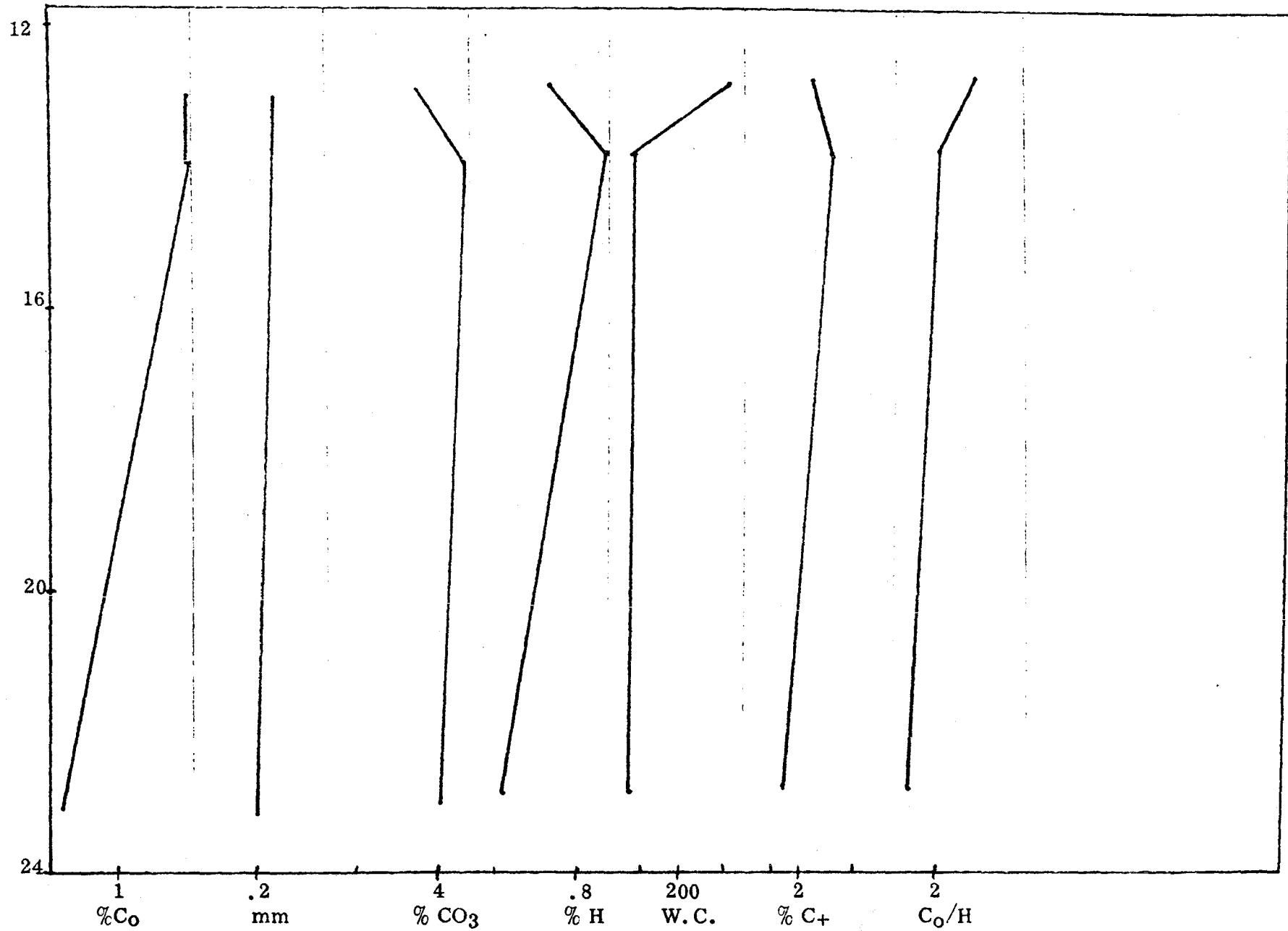
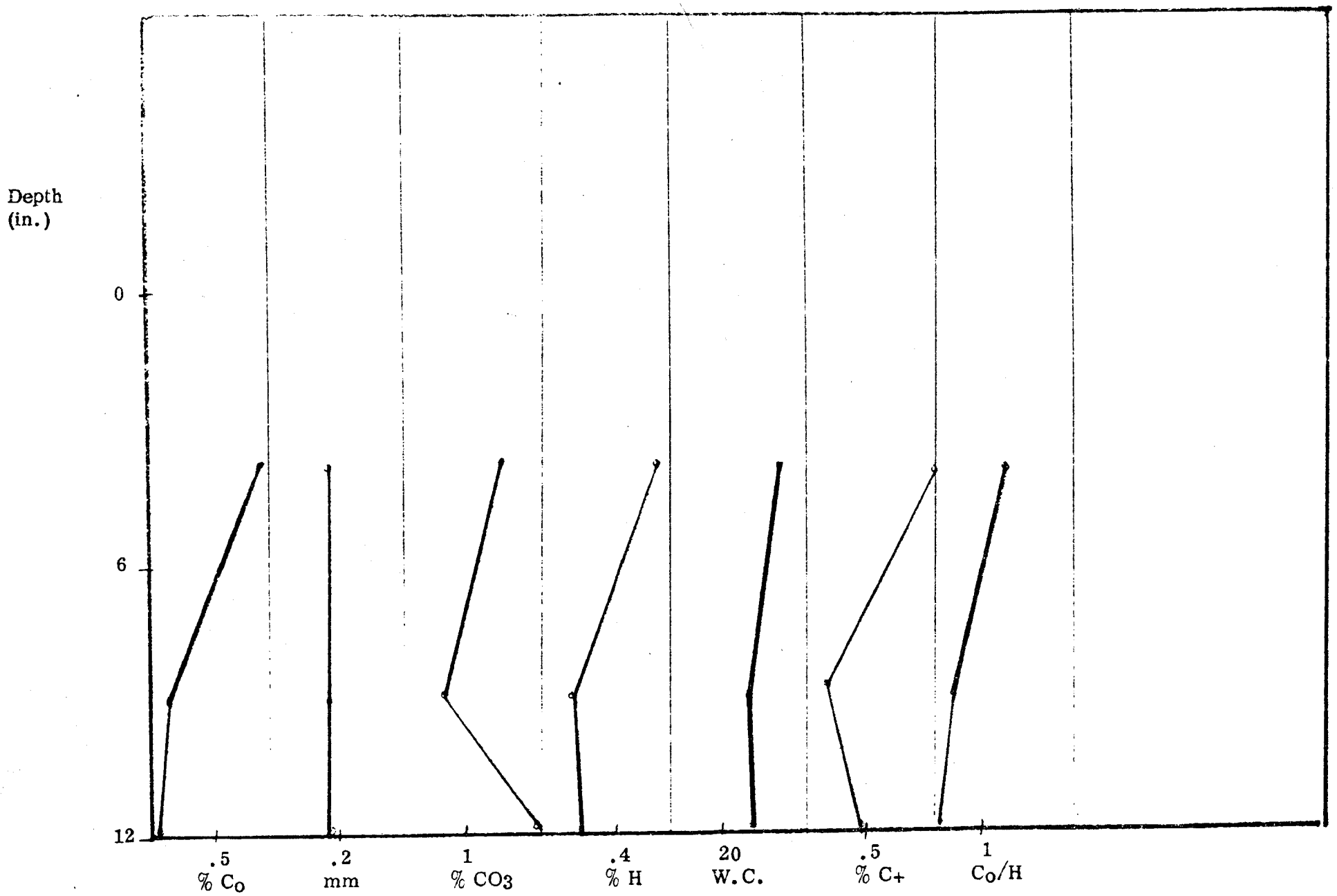


Figure F. Core 119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Co/H

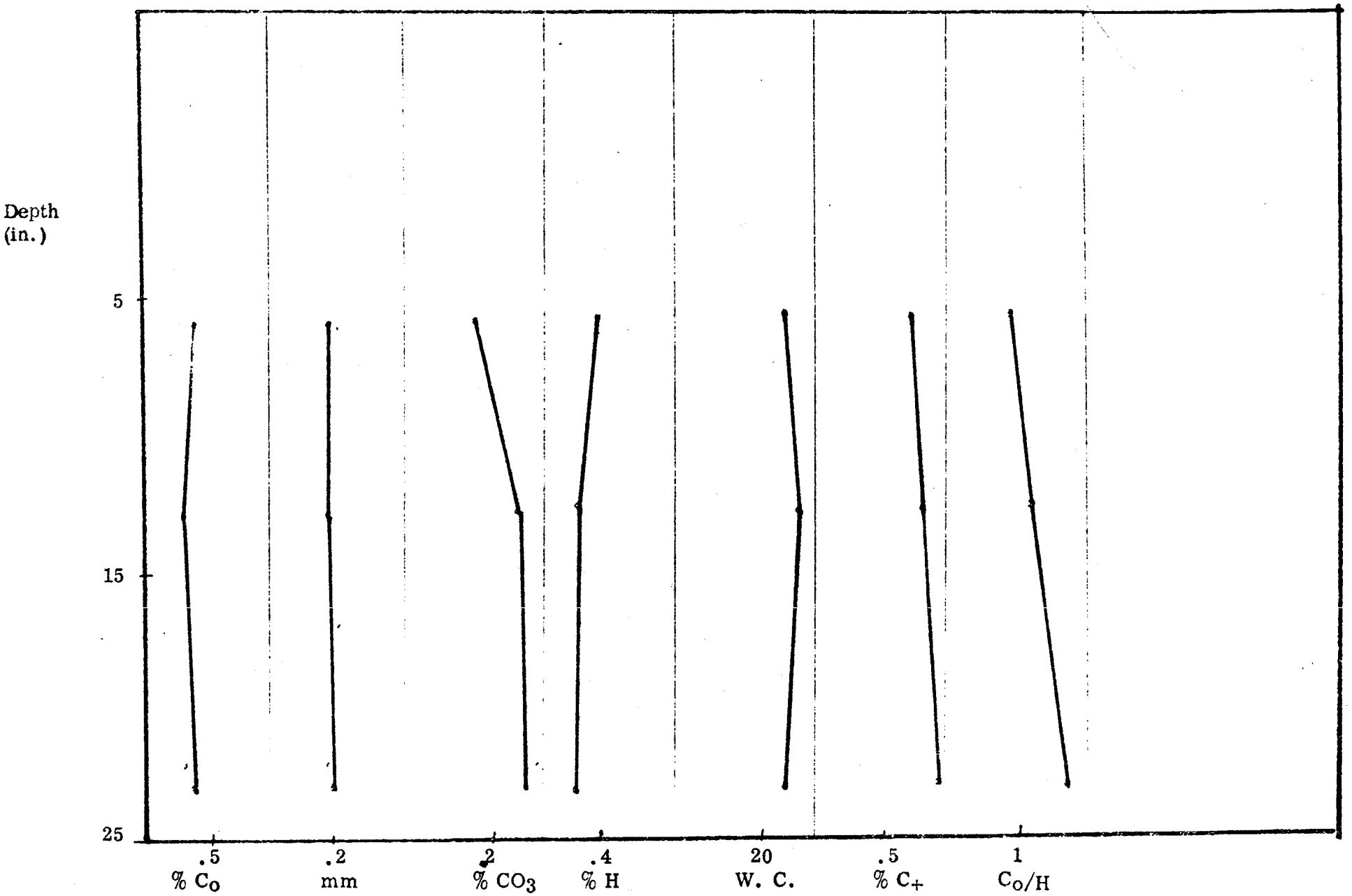

Figure H. Core 1-18

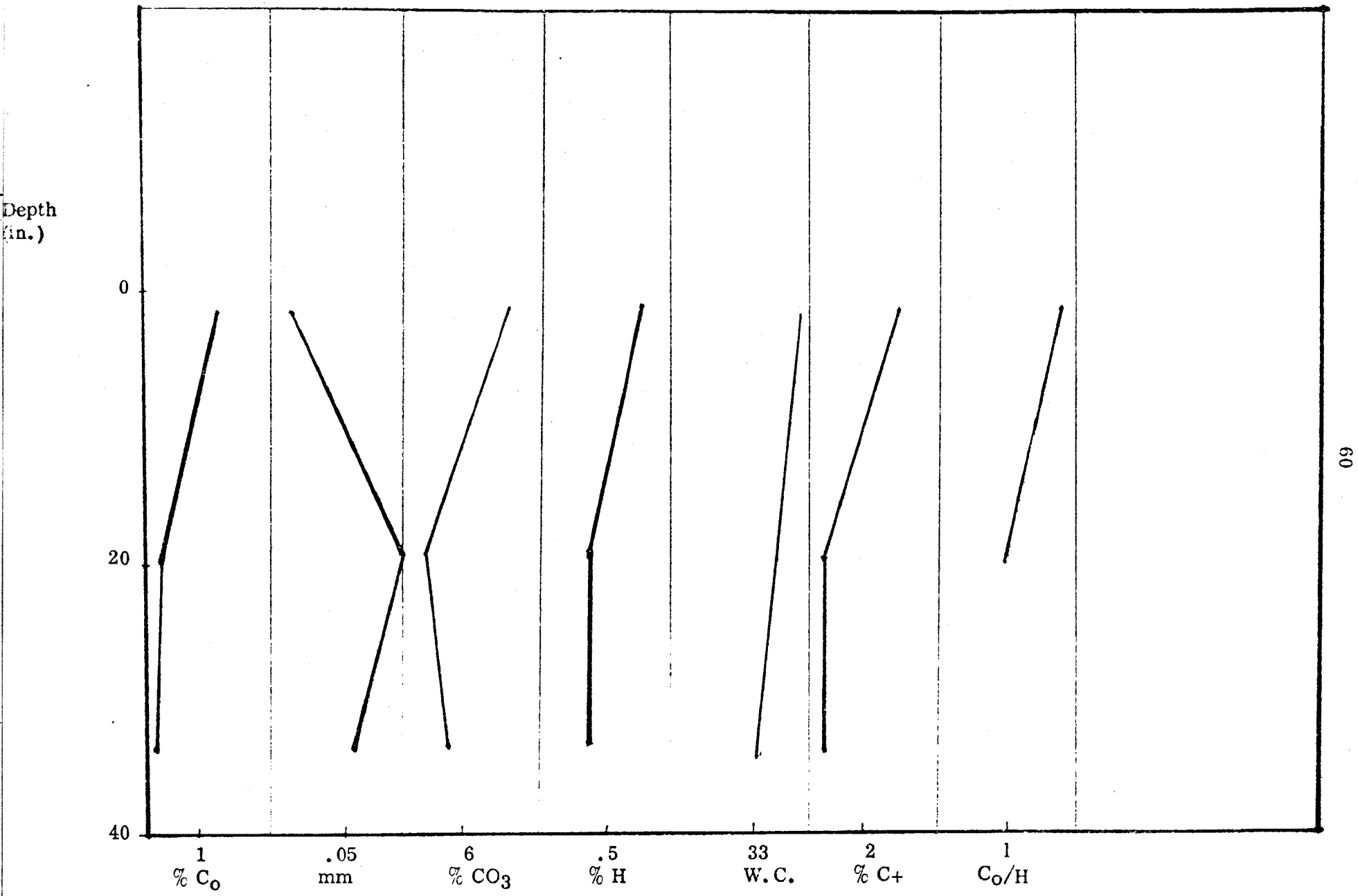

Figure I. Core 1-25

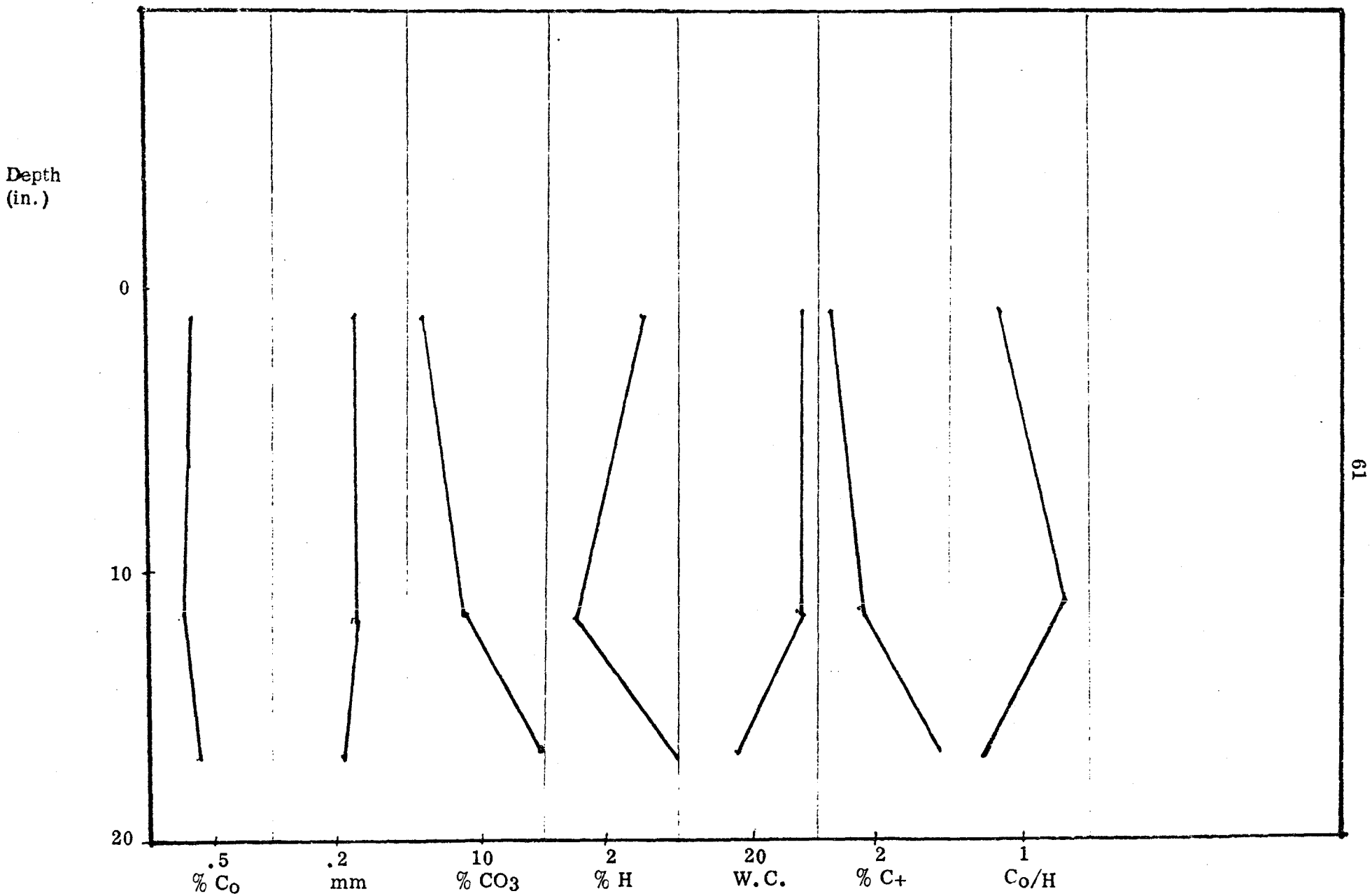

Figure J. Core 2-19

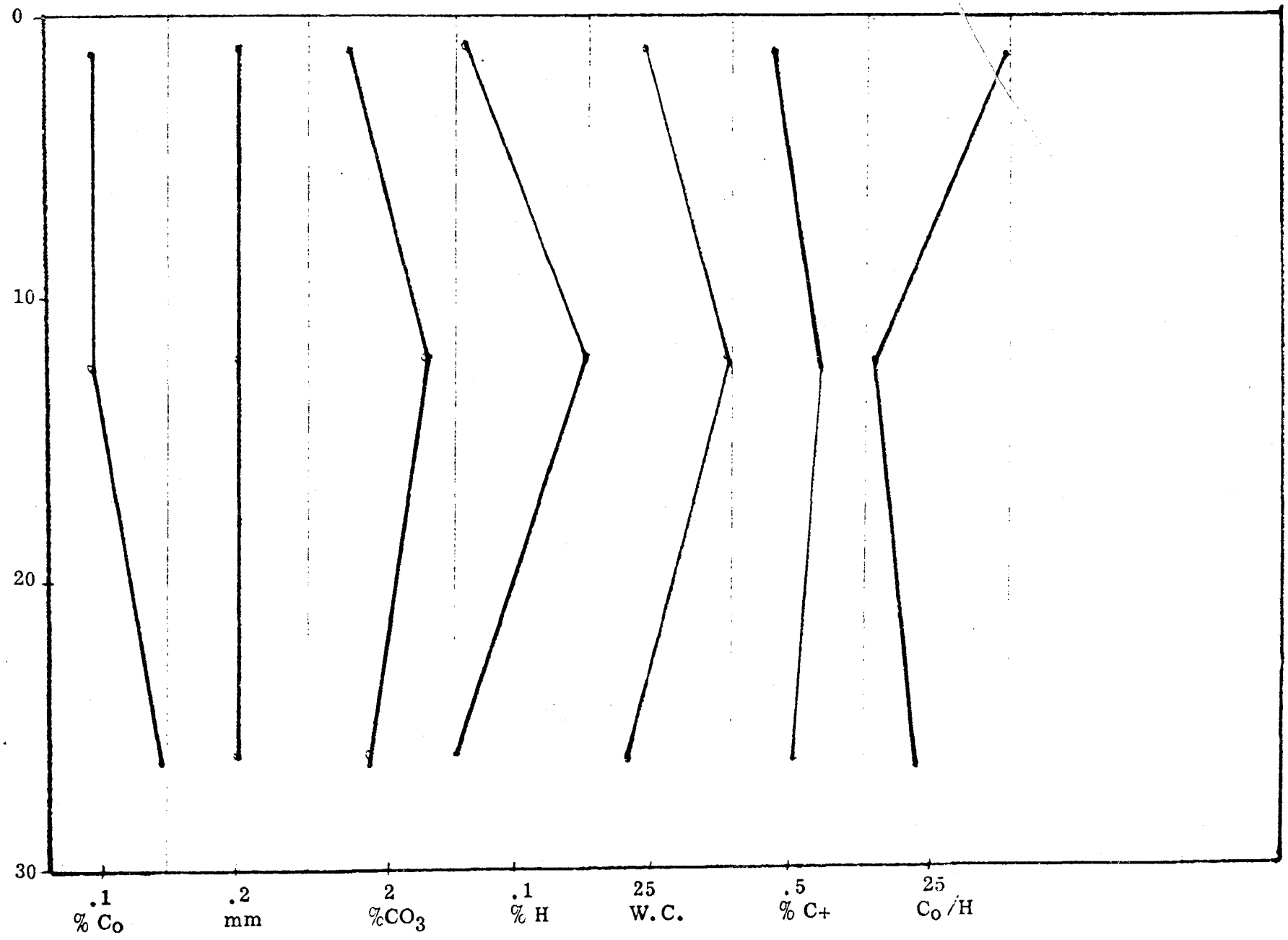

Figure K. Core 2-24

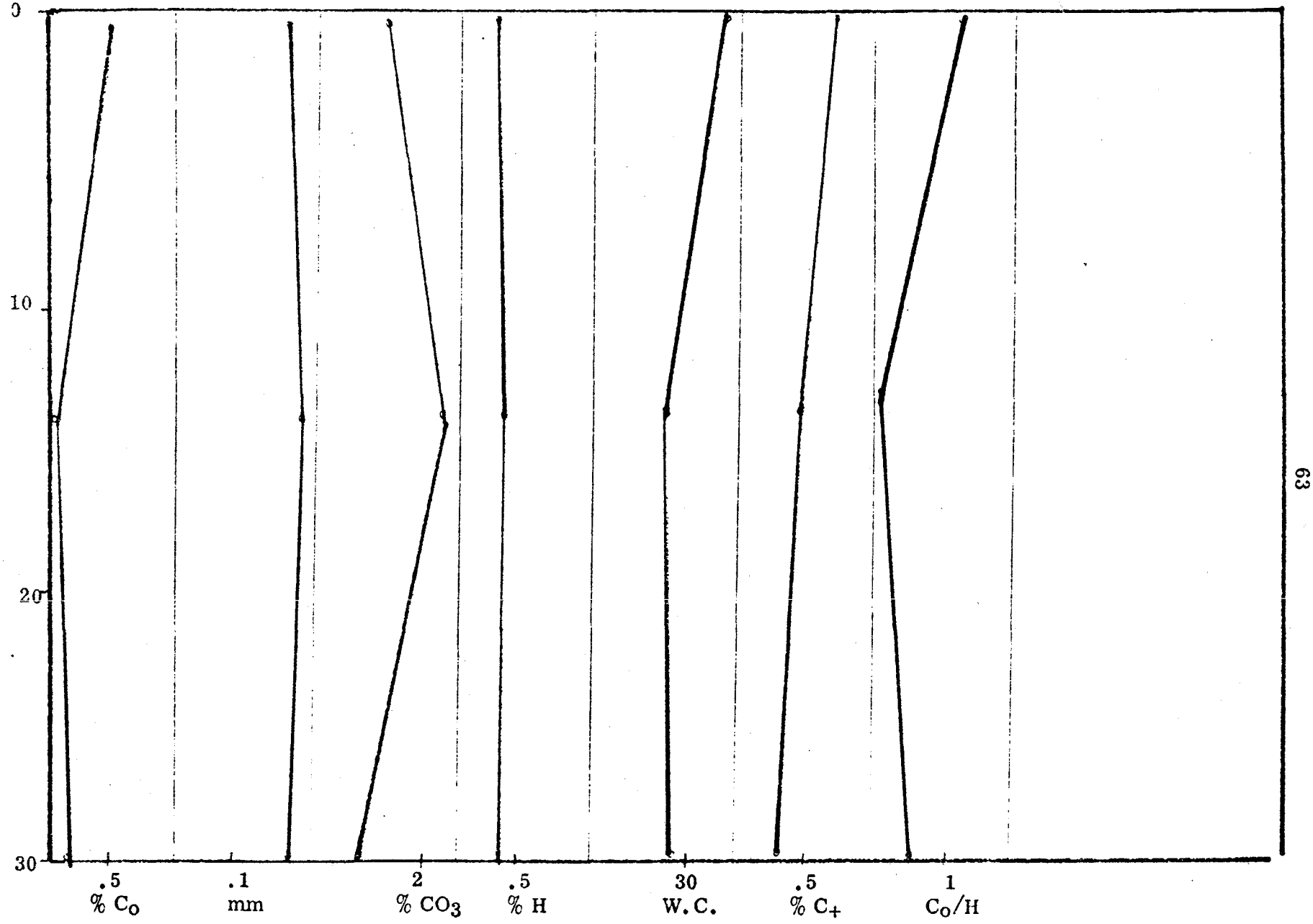

Figure L. Core 2-28

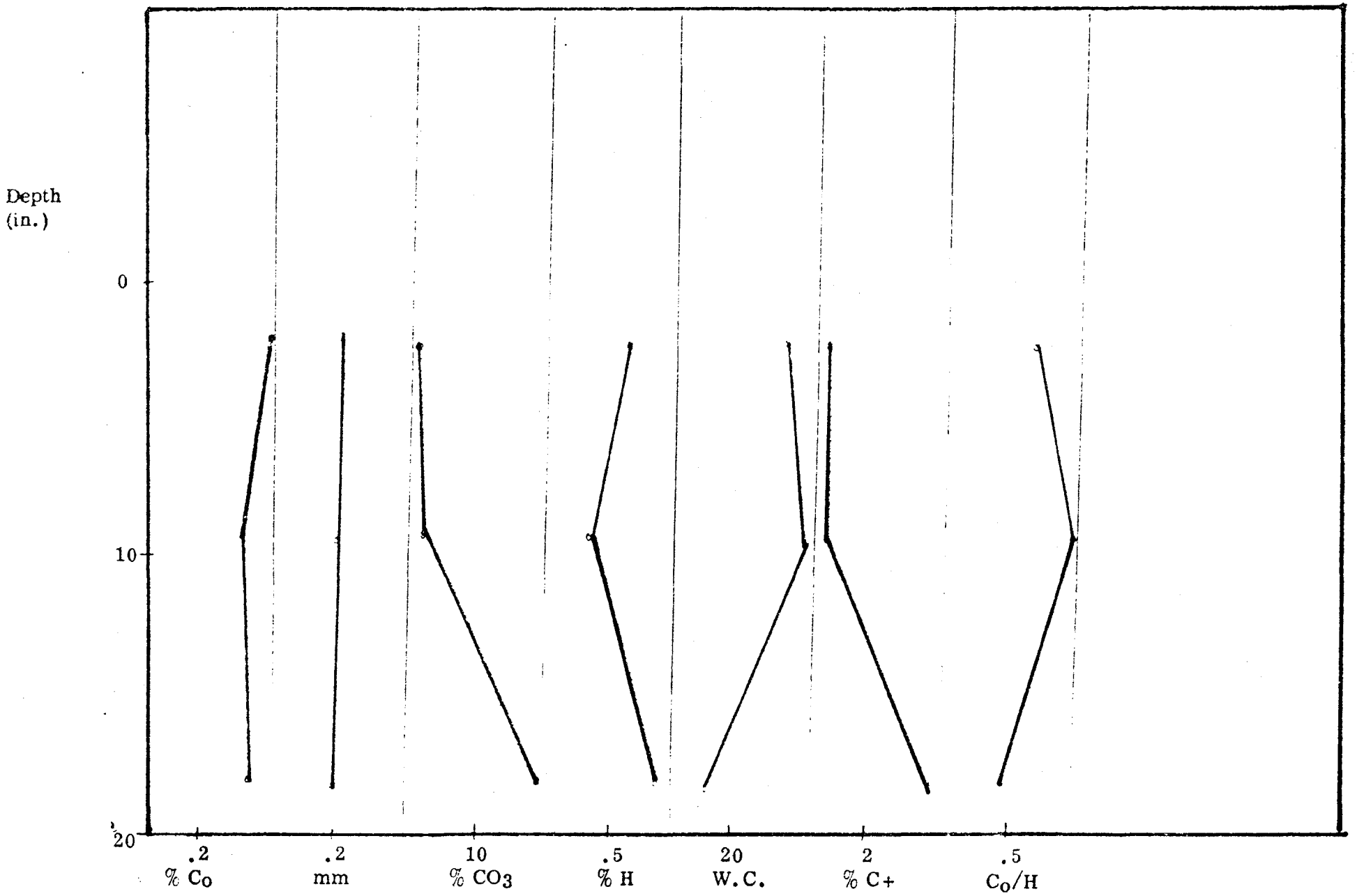

Figure M. Core 2-29

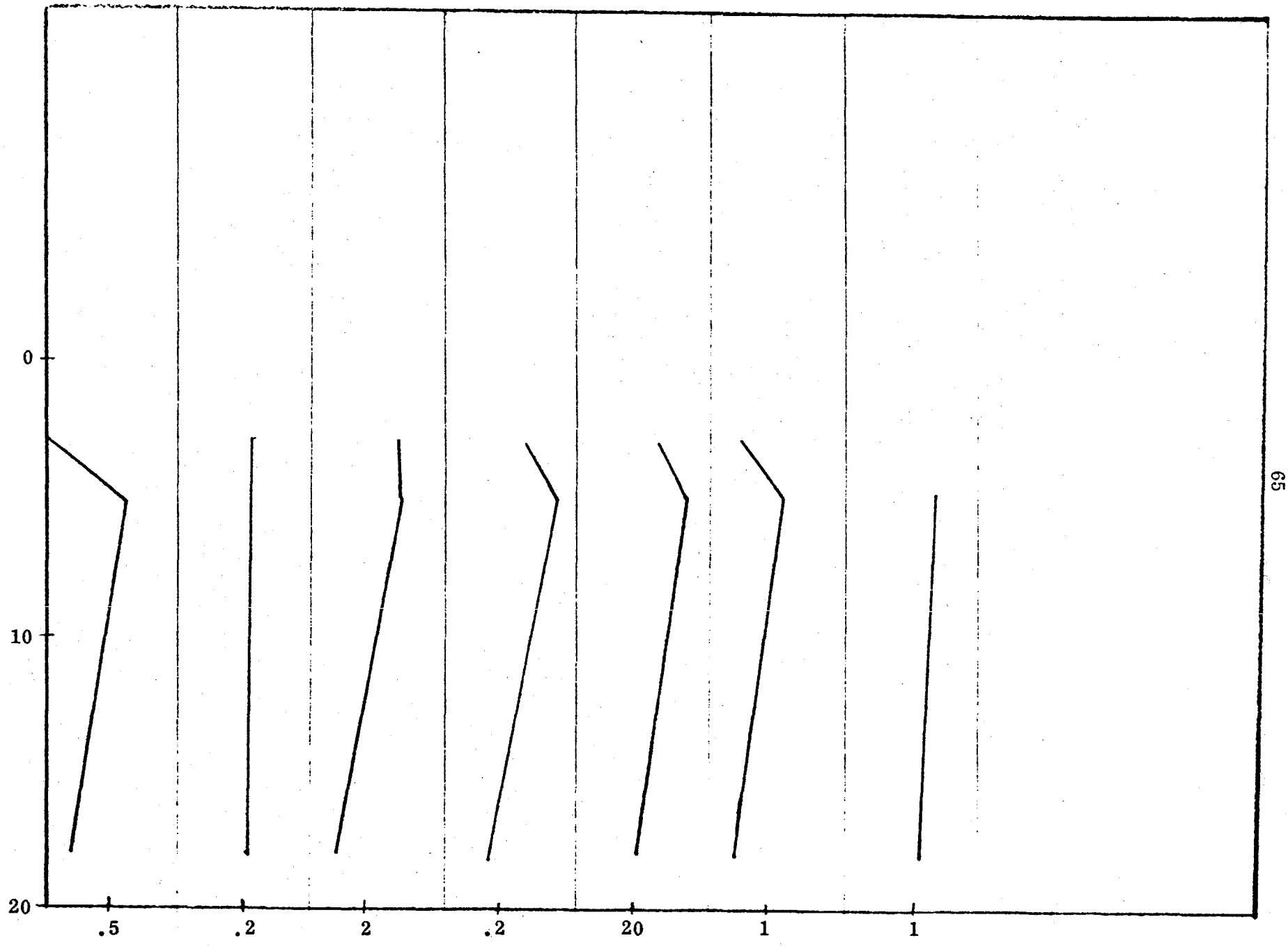

Figure N. Core 3-12

Section II, Article 5

A Study of the Distribution of the Cultivable Bacteria in Lagoonal Waters and Sediments

Robert W. Beazley

1973

A STUDY OF THE DISTRIBUTION OF CULTIVABLE BACTERIA IN LAGOONAL WATERS AND SEDIMENTS

by

Robert W. Beazley
B.S. in Biology, Siena College, 1969

Submitted to the Graduate Faculty
in partial fulfillment of
the requirements for the degree of

Master of Science
in
Oceanography

Florida Institute of Technology
1973

ABSTRACT

Relatively large bacterial populations were encountered in areas of restricted water movement in and around the Kennedy Space Center. The sediments within the areas of restricted water movement contained relatively high concentrations of hydrogen sulfide. Cultures made from these sediments yielded sulfide producing organisms that were gram-positive, spore-forming, rod shaped anaerobes.

In order to establish a relationship between bacterial numbers and hydrogen sulfide production, it was necessary to determine the best indicator applicable for estimating the numbers of sulfide producing bacteria in mixed cultures. In doing so, the distribution of sulfide producing bacteria in representative segments of the Indian River lagoonal system might be useful as an indicator of the transport of carbonaceous materials into the segment.

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FOREWORD

The program was supported in part by NASA Grant Number 10-015-008.

Special acknowledgement is due Mr. J. R. Puleo, Director of the Planetary Quarantine Laboratory, and his staff for their assistance in confirming the identity of certain organisms isolated during this study.

The author is especially indebted to Dr. Thomas A. Nevin, Research Professor of Microbiology. Without his forbearance and diligence, this study could not have been accomplished.

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I. INTRODUCTION

The lagoonal system on the East Coast of Central Florida, which encompasses the Kennedy Space Center, consists of the Indian River, the Indian River Lagoon, and the Banana River. The system extends from Ponce de Leon Inlet near New Smyrna Beach to the St. Lucie Inlet (Fig. 1). The representative water depth is approximately six feet except for the width of the Intracoastal Waterway. The water is lagoonal and estuarine. The salinity, depending on rainfall and fresh water runoff, ranges between 12 and 36 parts per thousand (7). Such water movement as occurs is generally wind driven.

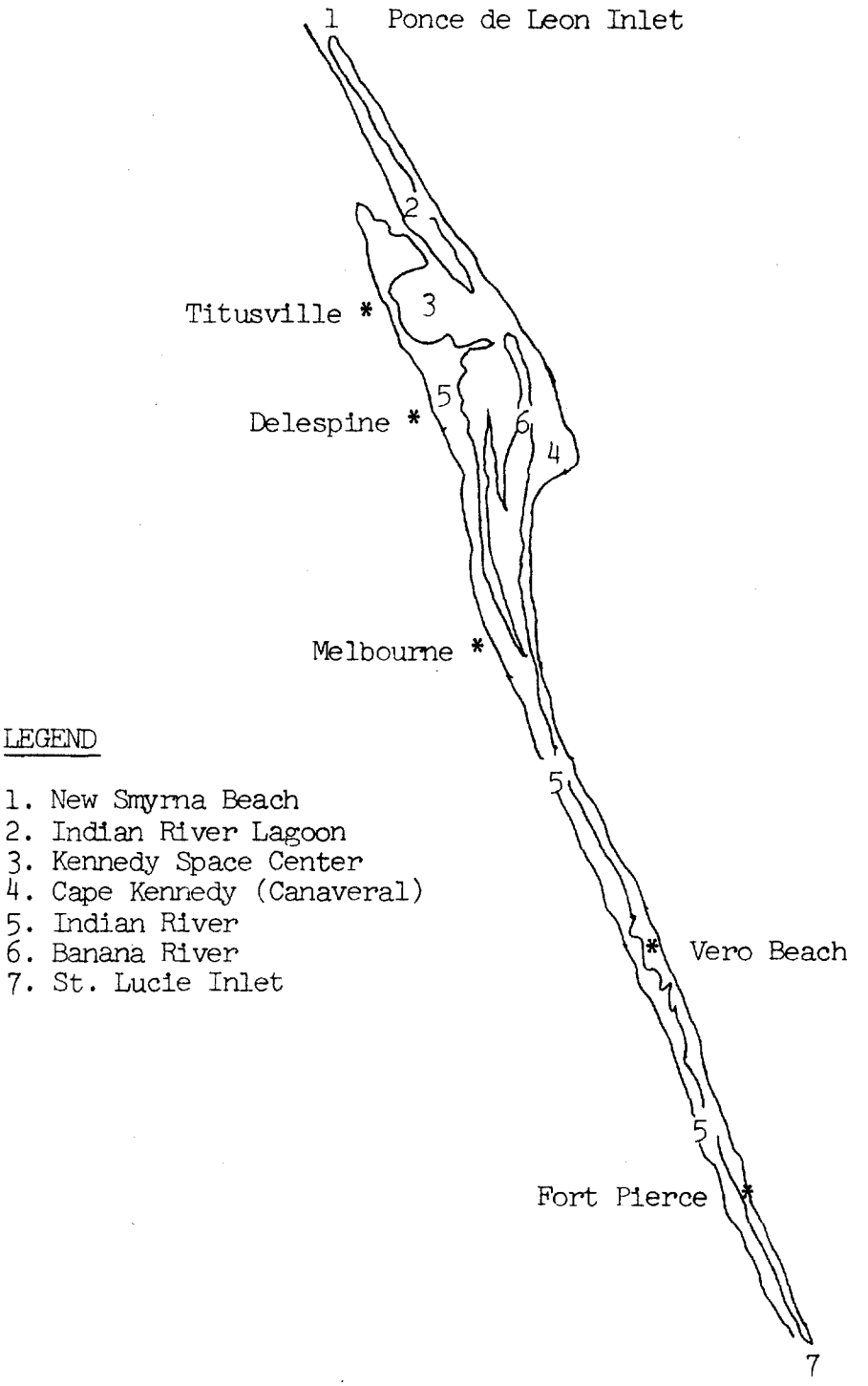
In a study of the channels and man-made canals of the west central coast of Florida, Betz (2) cultured the sediments for Clostridium perfringens using a selective medium developed by McClung (6) for the study of food contamination and reported:

> "We have detected C. perfringens specifically in the presence of many other potentially similar organisms and our statement of their concentrations is a significant though very conservative minimum, defensible against any reasonable doubt."

C. perfringens is a gram-positive, rod shaped, spore-forming, obligate anaerobe that produces hydrogen sulfide in suitable culture, and is known to cause gas gangrene in humans.

Sherman (12) also isolated gram-positive, spore-forming, rod shaped, anaerobic organisms from sulfide sediments collected on or near the Kennedy Space Center. These organisms, shown to be members of the genus Clostridium, produced hydrogen sulfide in culture, using ethion, a commercial pesticide,

FIGURE 1 INDIAN RIVER LAGOONAL SYSTEM



LEGEND

1. New Smyrna Beach
2. Indian River Lagoon
3. Kennedy Space Center
4. Cape Kennedy (Canaveral)
5. Indian River
6. Banana River
7. St. Lucie Inlet

as the only source of sulfur.

The prior investigation of sulfide ion concentrations in the sediments of the Indian River collected near Delespine and near Vero Beach by Akimoto (1), indicated that low levels, less than 4 mg. per cent, could be expected in most of the lagoonal sediments. Further, higher levels might be expected in samples which were collected from sites under six or more feet of water.

It seemed reasonable, therefore, to anticipate the isolation of Clostridium species, and to ascribe to them a role in the microbiology of the lagoons.

II. STATEMENT OF THE PROBLEM

Bacteriological surveys of the lagoonal waters in and around the Kennedy Space Center were conducted during 1972 to locate areas of relatively high bacterial populations. When such areas were encountered, a study of the water columns and the underlying sediments was conducted in order to determine the predominant types of bacteria and to gain some insight into their activities.

III. METHODS AND MATERIALS

A. Sample Sites

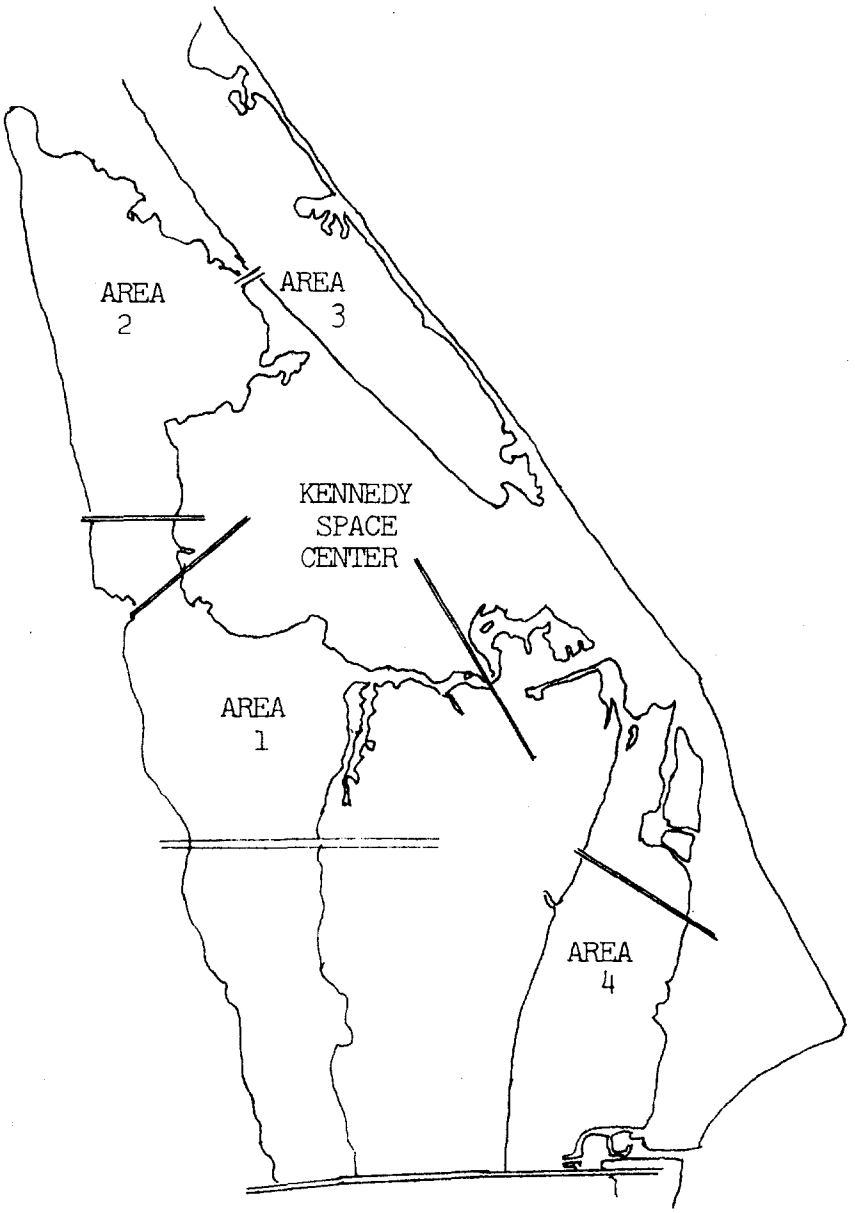
Predesignated sample sites were used for the bacteriological survey of the Kennedy Space Center. The intersections of longitudinal and latitudinal lines drawn at one minute intervals on the National Fish and Wildlife Service Chart Number 4R-FLA-632-406, "Merritt Island National Wildlife Refuge," served to locate them. Other sites which did not occur on the resulting grid were selected to satisfy specific interests.

As shown in Figure 2, the sites were labelled numerically and prefixed with the numbers 1 through 4 in accordance to the general sampling area, Area 1 included the waters of the Indian River north of the Orsino Causeway and south of the Titusville Causeway, as well as Banana Creek. Area 2 included the waters of the Indian River north of the Titusville Causeway. Area 3 consisted of the southern portion of the Indian River lagoon below the Haulover Canal. Area 4 included the waters of the Banana River north of the Bennett Causeway and the turning basins within Port Canaveral.

Sample sites for the studies at the Vero Beach Municipal Power Plant and the Orlando Utilities Commission Power Plant had been located and identified previously (9, 10) using the United States Department of Commerce Nautical Charts 843-SC, "Intracoastal Waterway, Tolomato River to Palm Shores, Florida," and 845-SC, "Intracoastal Waterway, Palm Shores to West Palm Beach, Florida."

Related studies on the west coast were conducted at Punta Gorda, Florida. Specific local maps were used in locating the actual sample sites

FIGURE 2 SAMPLE AREAS ADJACENT TO THE KENNEDY SPACE CENTER



employed by other investigators. The sampling area consisted of four groups of sites (8):

1. Four sites within the open waters of Charlotte Harbor
2. Six sites in a canal system having no access to open waters
3. Four sites within a canal system having access to the open waters of Charlotte Harbor and adjacent to the closed canal system
4. Four sites within an established (more than ten years old) canal system having access to Charlotte Harbor.

FIGURE 3 ORLANDO UTILITIES COMMISSION POWER PLANT SAMPLING AREA

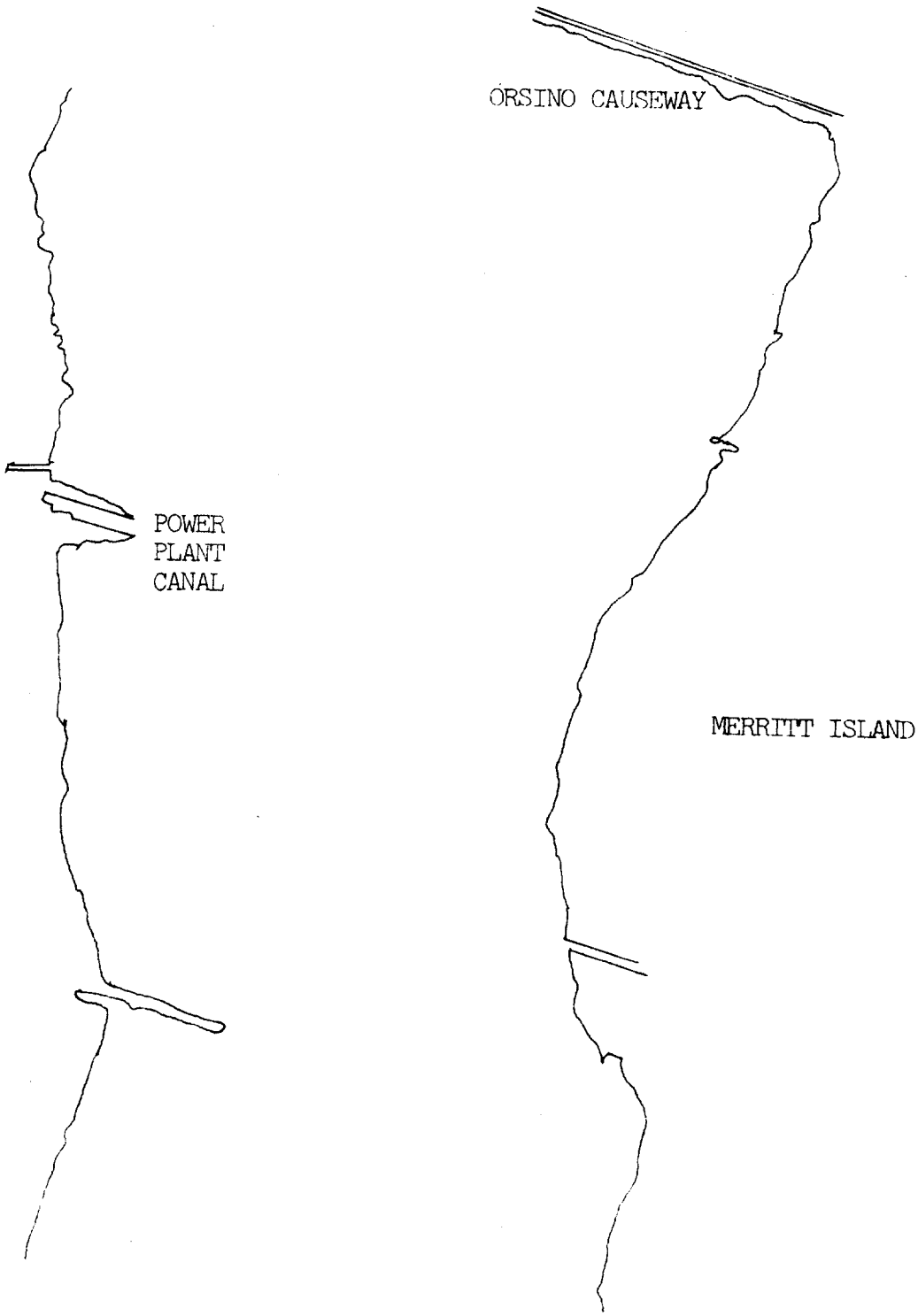
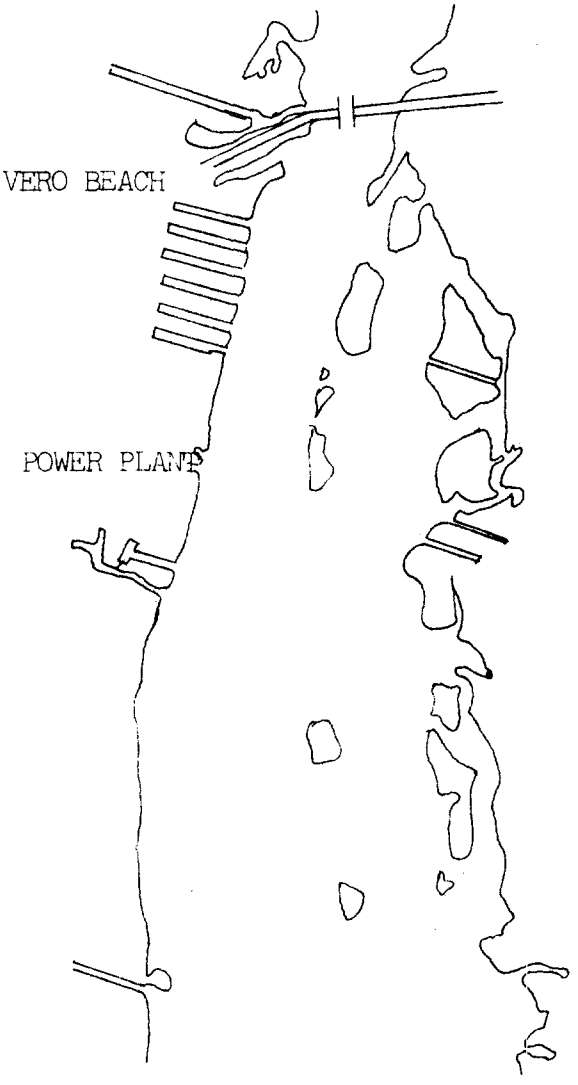


FIGURE 4 VERO BEACH MUNICIPAL POWER PLANT SAMPLING AREA



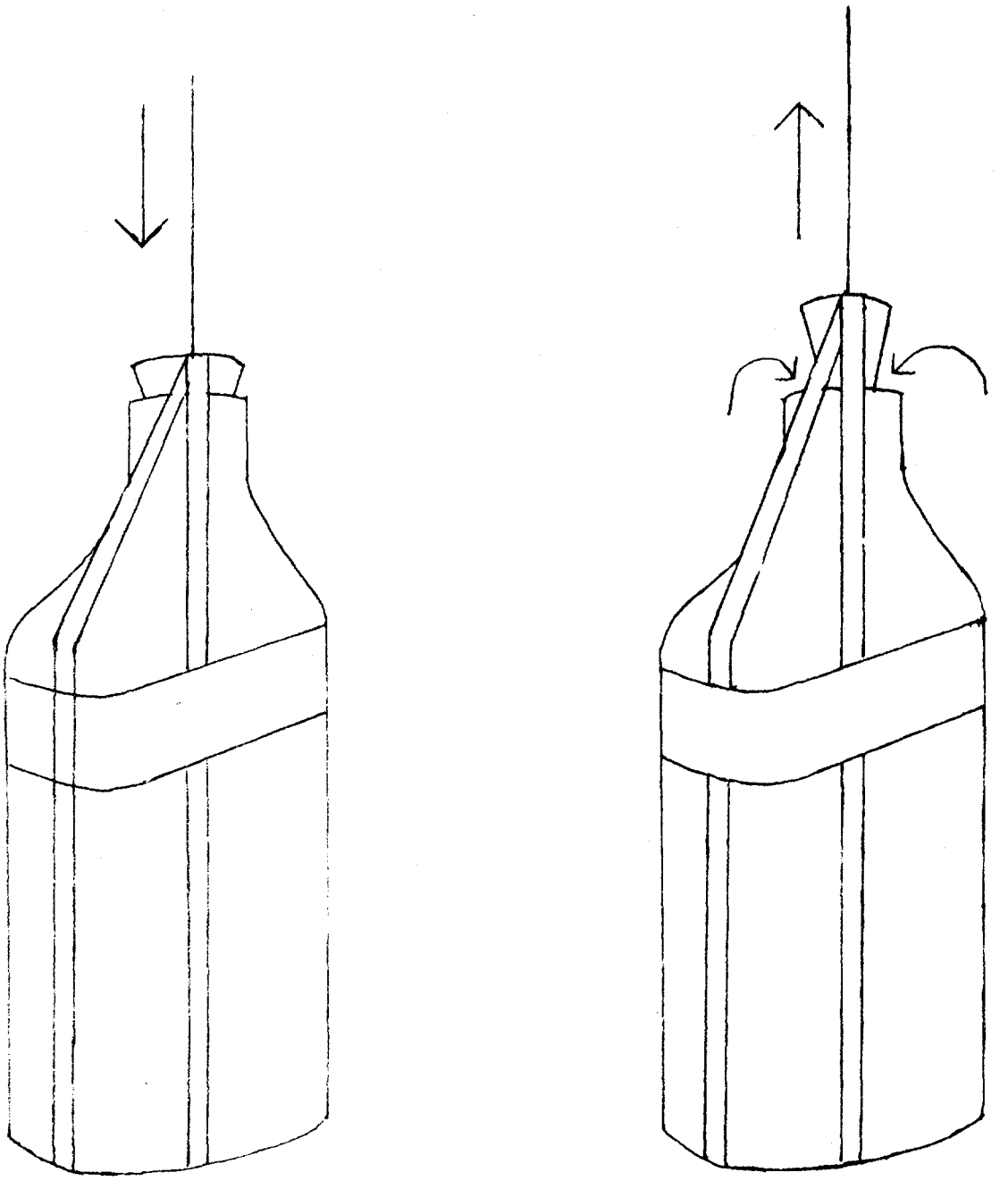
B. Sample Collection

Surface water samples were collected in sterile, plastic, 100 ml. bottles from a depth of six inches below the surface. The capped bottles were immersed, uncapped, filled and recapped underwater to avoid collecting airborne contaminants.

Water column studies conducted within Banana Creek required that samples be collected from the bottom sediments and from the water at two foot intervals between the bottom and surface. The water samples were collected from preselected depths by means of a self-sealing glass water bottle and holding device. A twenty foot length of monofilament fishing line (80 lb. test) was attached to a rubber stopper. The stopper was placed in the mouth of a three ounce glass medicine bottle and secured with two rubber bands as shown in Figure 5. The bottle was then placed in a paper bag, sealed, and sterilized in an autoclave for 20 minutes at 15 lbs. pressure (150^{o}C.).

The holding device was constructed of PVC plastic and fiberglass screening. A six inch length of four inch diameter PVC pipe was capped at one end. A hole, large enough to accomodate the bottle neck, was drilled through the cap. A one inch piece of four inch diameter PVC pipe was covered with fiberglass screening and attached to the bottom of the device by using additional fiberglass screening as a flexible hinge. The device was then attached to the end of a three foot length of three-quarter inch diameter PVC pipe. The opposite end of the pipe was outfitted with a screw-type connector as shown in Figure 6. Four additional three foot lengths of pipe were fitted with alternating male and female screw-type connectors and

FIGURE 5 DEEP WATER SAMPLE BOTTLE AND CLOSURE



marked at one foot intervals for collecting samples at depths greater than three feet.

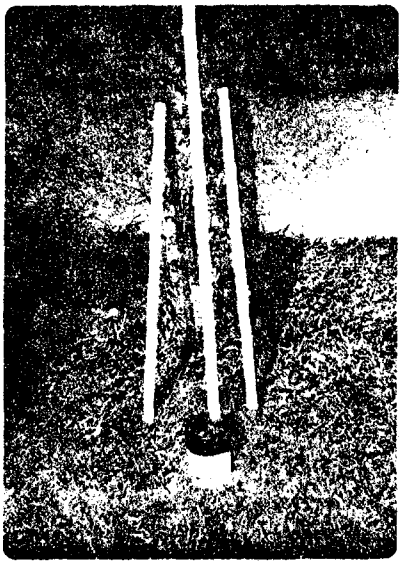
When ready for use, a sterile sample bottle was removed from the paper bag. The bottle was placed in the holding device with the rubber stopper and line protruding through the hole in the cap. The hinged bottom was then closed and fastened with a rubber band. The end of the line was held in hand and the device lowered to the desired depth. The line was pulled, dislodging the stopper and allowing the bottle to fill. When the line was released, the rubber bands forced the stopper back into the bottle mouth, sealing the bottle.

Sediment samples were obtained by one of two methods. The most convenient method was to drag a standard Danforth anchor and collect the sediment sample adhering to it after raising. At sites where the sediment samples could not be collected this way, a length of three-quarter inch diameter PVC pipe was used as a simple coring device. The sample was removed from the anchor or from the pipe, placed in a plastic bag, and sealed with a wire tie.

C. Sample Storage

All samples were processed in a mobile laboratory which was usually available in the sampling area. Inoculations were initiated within four hours of collection. When the mobile laboratory was not available, the samples were refrigerated in an ice chest and returned to the laboratory facilities at the Florida Institute of Technology for processing. The time elapsed between collection and processing rarely exceeded six hours.

FIGURE 6 HOLDING DEVICE FOR COLLECTING WATER SAMPLES AT DEPTHS



6a HOLDING DEVICE AND ADDITIONAL POLES

6b SAMPLE BOTTLE

6c SAMPLE BOTTLE BEING INSERTED INTO HOLDING DEVICE

Sediment samples collected simultaneously for sulfide ion analyses were alkalinized immediately with sodium hydroxide pellets in order to trap volatile hydrogen sulfide as non-volatile sodium sulfide, this preventing any loss of hydrogen sulfide during transport and preliminary treatment.

D. Sample Preparation

Using sterile techniques and standard procedures, 10 ml. of each water sample were diluted in ten-fold series from 10^{-2} through 10^{-6}, inclusively, in suitable sterile water blanks. When sediments were studied, one gram, wet weight, of each sample was suspended in 100 ml. of sterile distilled water blanks and diluted in ten-fold series from 10^{-3} through 10^{-7}, inclusively. One ml. aliquots of each dilution were then used to inoculate tubes of NIH Thioglycollate medium (Difco) and 10 ml. aliquots to inoculate Lactose Broth (Difco).

Alkalinized sediment samples for sulfide ion analyses were placed in suitable containers and dried in an oven at 100°C. for 48 hours. Twenty-five grams of sediment were weighed out and processed as described by Akimoto (1).

E. Analytical Methods

The initial survey and subsequent studies of the lagoonal waters and sediments near the Kennedy Space Center employed the following tests:

1. 25 Tube MPN (most probable number) of total bacteria (11)
2. Multiple (5) Tube Presumptive Coliform MPN
   a. EMB- E. coli, confirmation
   b. E.C. - E. coli, fecal types

3. Microscopic examination of Gram-stained smears made from MPN cultures

Details of these methods are presented in the Appendix.

In addition to the above, SS agar (Difco), Sabourad's agar (Difco), and Nutrient agar (Difco) were inoculated with one ml. aliquots of each diluted sample collected from the Banana Creek area during a water column study.

The sediments collected from the Banana Creek area were categorized as follows:

1. "Sulfide muds" - any sediment that offered olfactory evidence of hydrogen sulfide. Usually grey clays to brown and black silty sands.

2. "Fine sands" - usually fine uniform sands with little evidence of plant material, regardless of color.

3. "Sands" - usually fine to medium sands with some shell fragments; various colors.

The distribution of the sediment types in the Banana Creek area is demonstrated in Figure 7.

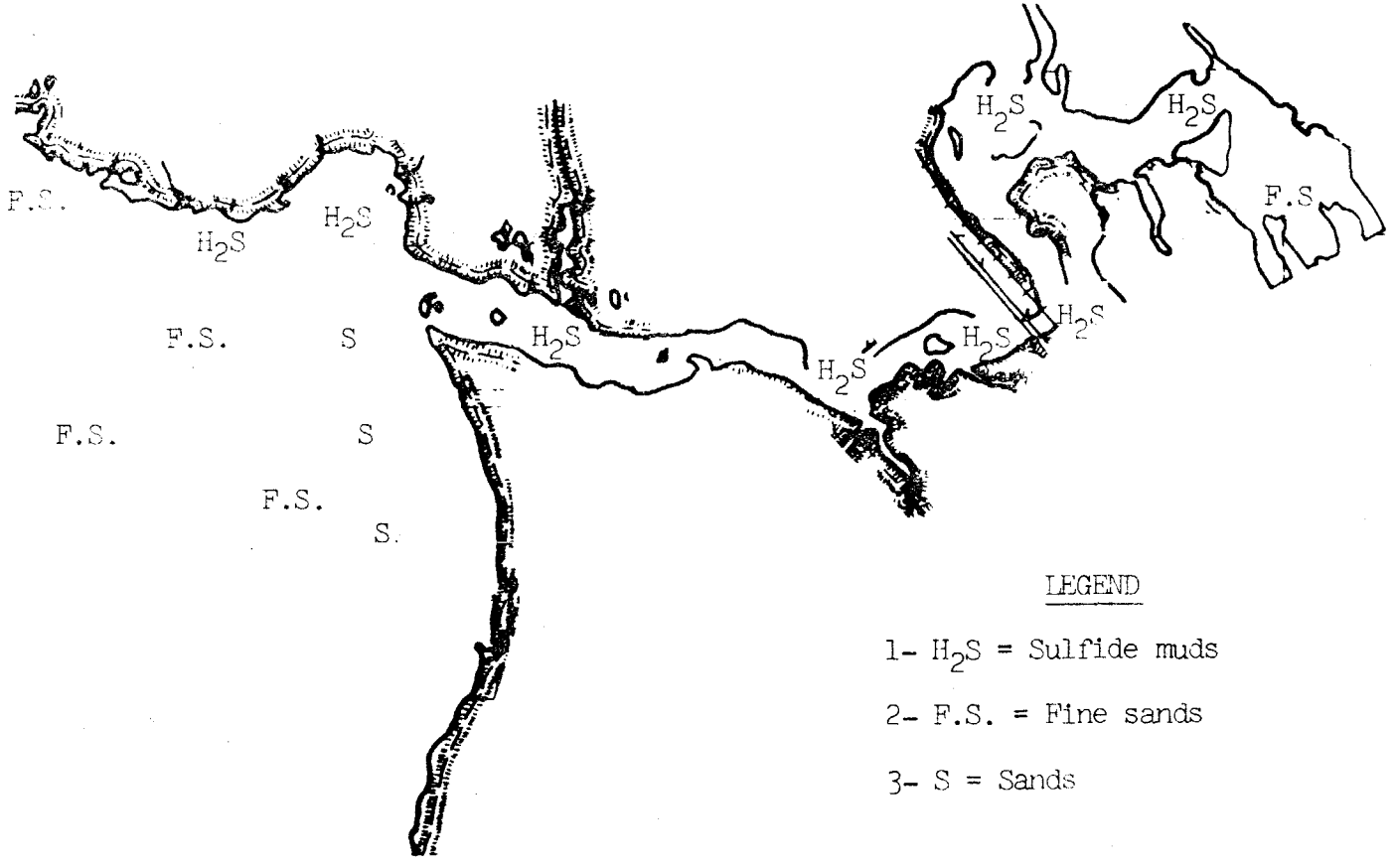
In determining the relative numbers of sulfide producing organisms, a procedure using iron wire was employed. The wire was cut into two inch lengths and cleaned in hydrochloric acid, rinsed several times with distilled water, and then sterilized in a flame. One strip was then placed in each inoculated tube which had been incubated and in which growth had occurred. The tubes were reincubated at room temperature for 24 hours. After this time, the appearance of black iron sulfide was considered indicative of sulfide production. The most probable number of sulfide producing bacteria was then estimated using Porter (11) as a guide.

A parallel test was conducted using lead acetate paper. Strips of lead acetate paper were placed in a paper bag, sealed in aluminum foil, and sterilized in an autoclave for 20 minutes at 15 lbs. pressure (150°C.). One strip of paper was then placed in the neck of each inoculated thioglycollate tube which had been incubated and in which growth had already occurred. The paper was held in place by the plastic cap. Again after reincubating at room temperature for 24 hours, the strips were inspected for the appearance of black lead sulfide.

Cultures growing in the tubes exhibiting evidence of sulfide production were streaked on petri plates containing 1.5% agar with NIH Formula Thioglycollate (Difco) medium as a nutrient source. The plates were then incubated anaerobically for 48 hours at 35°C. in a disposable system (GasPak-BBL). Fresh tubes of fluid thioglycollate medium were inoculated from isolated colonies that were checked for purity by microscopic examination of gram-stained preparations, and then forwarded to an independent laboratory for confirmation of generic identification.

The chemical procedures for sulfide ion analyses of the sediments were conducted according to Standard Methods (13) as modified by Akimoto (1), wherein the alkalinized sample was acidified with concentrated hydrochloric acid to liberate gaseous hydrogen sulfide. The hydrogen sulfide gas was bubbled through a cadmium chloride solution, trapped as cadmium sulfide and then titrated iodometrically.

FIGURE 7 SEDIMENT TYPES OF SAMPLES TAKEN FROM THE BANANA CREEK AREA



IV. RESULTS

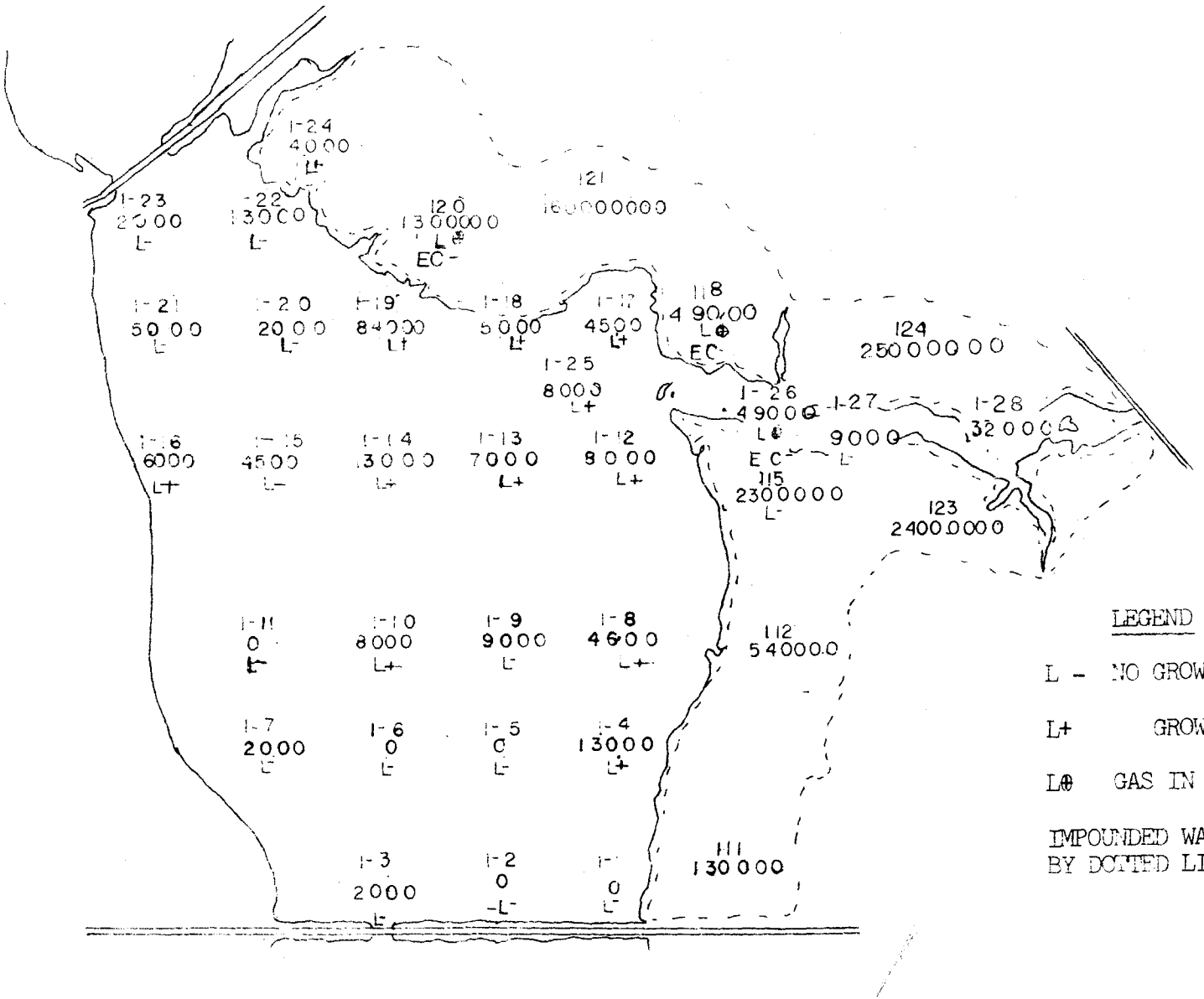
In the lagoonal waters of Area 1, the highest bacterial counts, over 10^4 per 100 ml. of sample, were obtained from the water samples collected at sites within Banana Creek and in the waters west of the mouth of Banana Creek. One other water sample collected at site #1-4 also had an MPN of over 10^4 per 100 ml, as shown in Figure 8. MPN's of less than 10^4 per 100 ml. were obtained from samples collected at all other open water sites in this area. Twelve water samples from mosquito control impoundments located northwest of and adjacent to Banana Creek, had bacterial counts between 4.9×10^4 and greater than 1.6×10^8 per 100 ml. of sample.

As demonstrated in Figure 9, only two water samples from Area 2, at sites #2-1 and #2-19, had MPN's greater than 10^4 per 100 ml. of sample. Again, two samples of the impounded waters, the sites located between the Titusville Causeway and the Florida East Coast railroad bridge, had bacterial counts of 4.6×10^6 and 1.6×10^8 per 100 ml. of sample.

In Area 3, the sample taken from site #3-1, located at the mouth of Max Hoeck Creek, had an MPN of 1.3×10^5, as shown in Figure 10. All other samples collected from the Indian River Lagoon had bacterial counts of 8.0×10^3 or less, whereas the two samples collected from the impounded waters northwest of Max Hoeck Creek, sites #318 and #311, had MPN's of 4.9×10^4 and 7.0×10^5 per 100 ml. of sample, respectively.

As indicated in Figure 11, two samples from sites in Area 4, located north of Cactus Point, had MPN's greater than 10^4 per 100 ml. of sample.

FIGURE 8 GEOGRAPHICAL DISTRIBUTION OF BACTERIAL POPULATIONS (MPN) IN SURFACE WATERS OF AREA I



LEGEND

L - NO GROWTH IN LACTOSE

L+ GROWTH IN LACTOSE

L⊕ GAS IN LACTOSE

IMPOUNDED WATERS INDICATED BY DOTTED LINES

FIGURE 9 GEOGRAPHICAL DISTRIBUTION OF BACTERIAL POPULATIONS (MPN) IN SURFACE WATERS OF AREA II

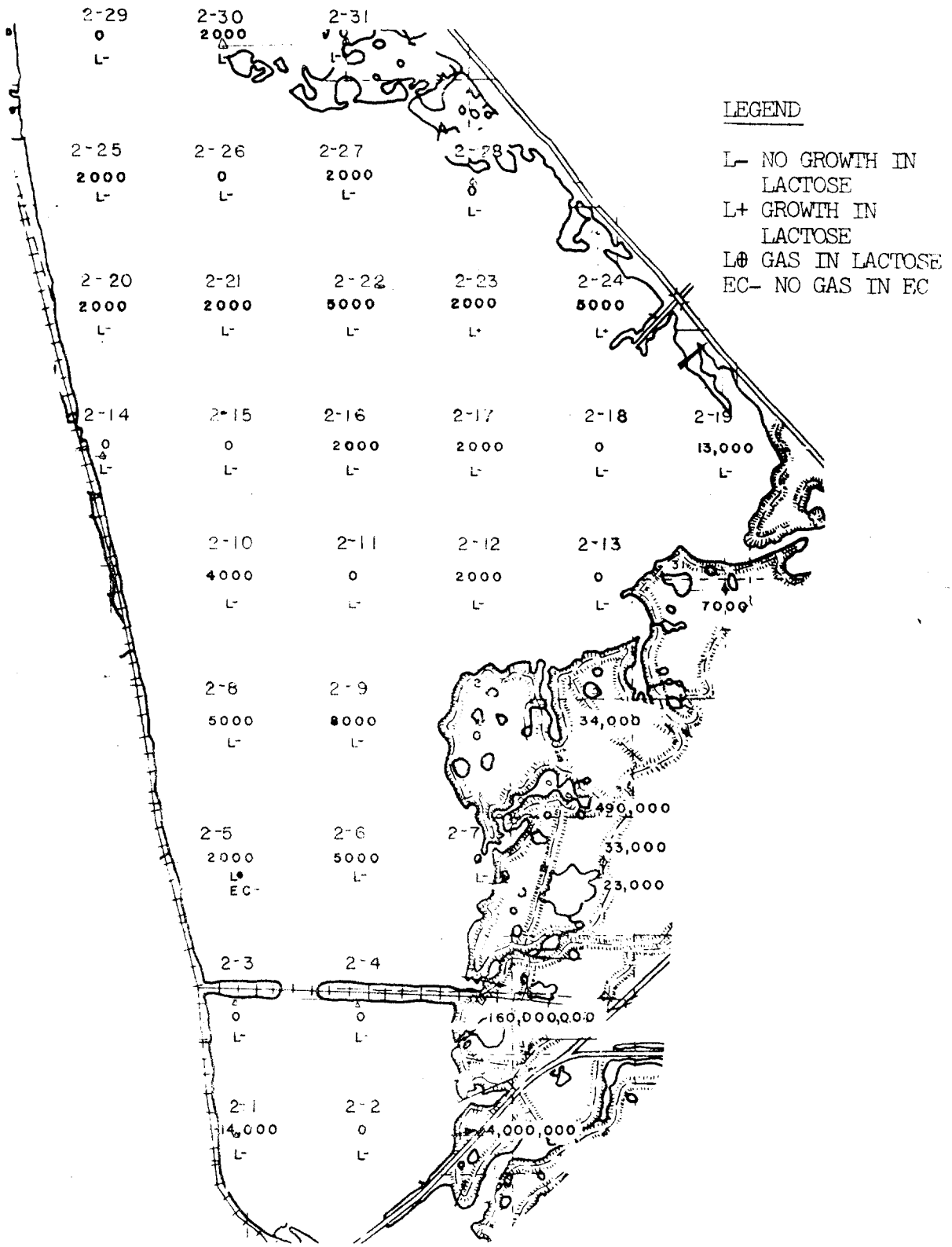
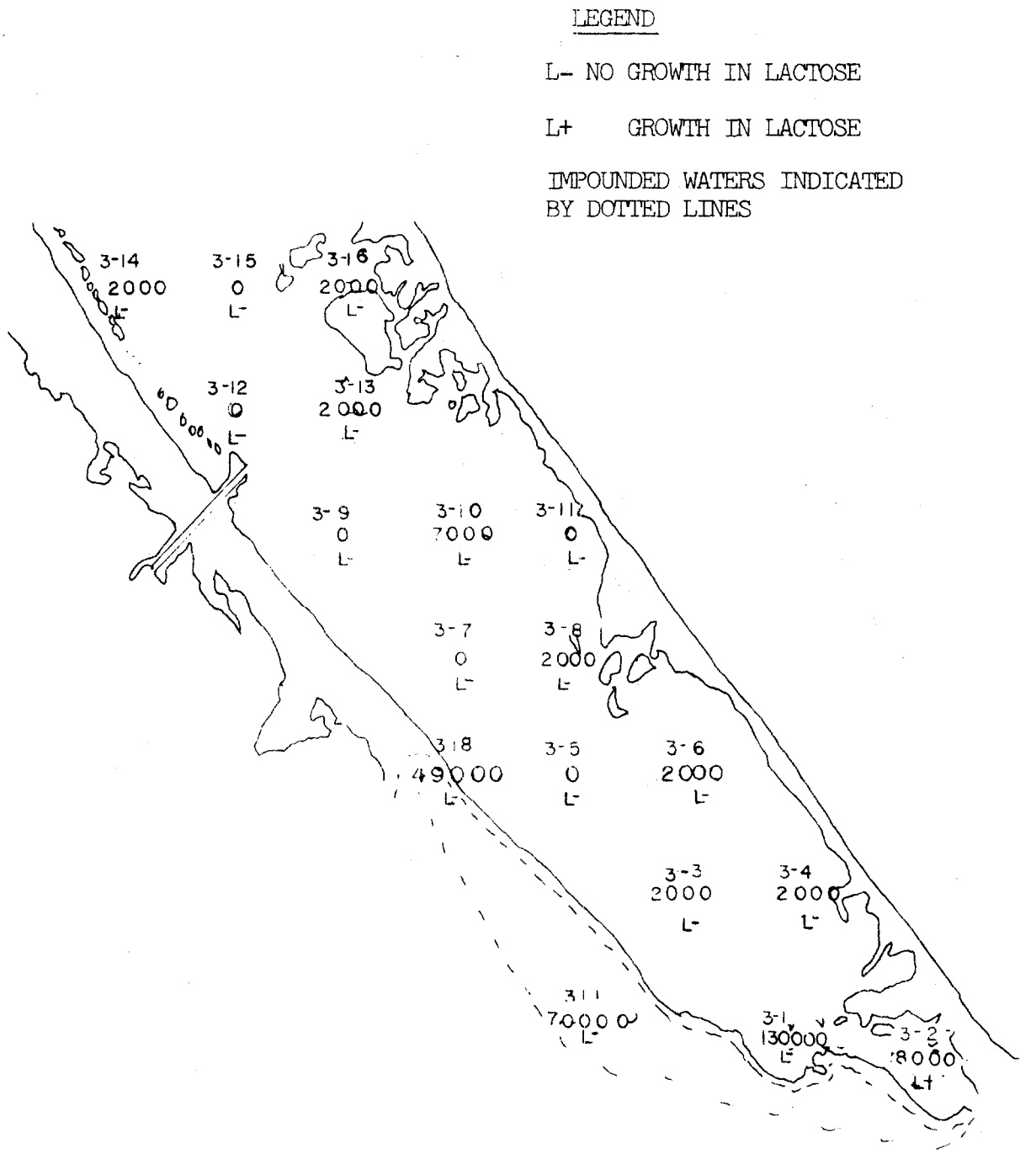


FIGURE 10 GEOGRAPHICAL DISTRIBUTION OF BACTERIAL POPULATIONS (MPN) IN SURFACE WATERS OF AREA III



The sample from site #4-29, located at the west end of the Barge Canal, had an MPN of 3.2×10^4 per 100 ml. of sample, and that sample from site #4-24, located in an impoundment north of the NASA Causeway, had an MPN of 1.7×10^4 per 100 ml. of sample. South of Cactus Point, samples from three sites, #4-9, #4-10, and #4-11, located on an east-west line between Middle Point and a radar installation on the opposite shore, had bacterial counts of 4.6×10^4, 2.3×10^6, and 1.6×10^8 per 100 ml. of sample, respectively. It is notable from Figure 11 that the samples collected from the southern portion of Area 4 had relatively higher bacterial counts than did those from the rest of the area. Samples from sites #4-34 and #4-35, located within the protected waters of the turning basins within Port Canaveral, had MPN's of 1.3×10^4 and 8.4×10^4 per 100 ml. of sample, respectively. The two samples from sites #4-36 and #4-37 also located in quiet waters north of the Bennett Causeway, had MPN's of 2.3×10^4 and 3.2×10^4 per 100 ml. of sample, respectively.

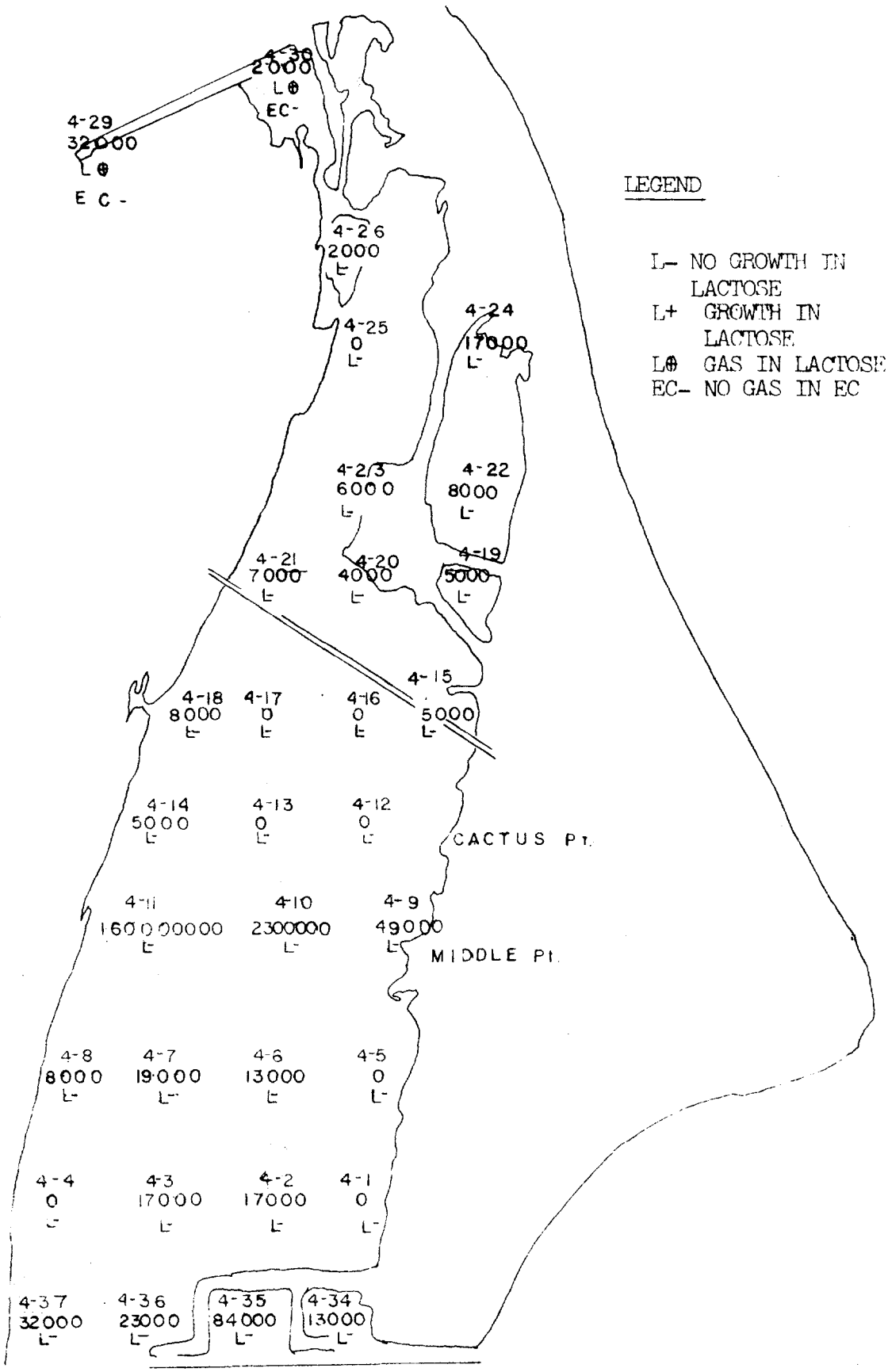
In Area 1, samples of water taken from seven sites in the impoundments northwest of and adjacent to, and one site within Banana Creek yielded presumptive coliform counts between 10^3 and 10^5 per 100 ml. of sample. Similar evidence was obtained from only one sample from Area 2 and three samples from Area 4. No coliforms were cultured from samples collected in Area 3. Escherichia coli was seldom detected and fecal E. coli was never detected in any sample collected from the Kennedy Space Center area.

In general, the highest bacterial counts were obtained from the samples collected in the Banana Creek area. Therefore, a vertical water column study was conducted as described. As may be seen from the site

profiles in Figure 12, sediment samples taken at each site in Banana Creek and at selected sites beneath the waters immediately west of the mouth of Banana Creek had higher bacterial counts than did the water samples taken above them. The highest MPN, 1.6×10^8, was obtained from one gram, wet weight, of the sediment sample collected at site #S-8, located at the mouth of a waste water outfall, east of State Road 3. Coliforms were cultured from the sediments collected at sites #S-8, #S-9, #S-10, and #S-11, located east of State Road 3; sites #1-28, and #1-29, located within Banana Creek; and site #1-8 in the open lagoon. The respective MPN's of coliforms were 10^6, 10^4, 10^3, 10^4, 10^4, 10^5, and 10^3 per gram, wet weight, of sediment sample. The water sample taken from the mouth of the waste water outfall, site #S-8, also had a coliform count of 10^3 per 100 ml. of sample, as shown in Figure 13. No evidence of the presence of E. coli was obtained from any sample collected in the Banana Creek area. Neither were Salmonella and Shigella cultivated from any sample on a medium selective (SS Medium, Difco) for these genera.

When the sediments were grouped according to geological type, regardless of the height of water above the site, those designated as "sulfide muds" generally had bacterial populations an order of magnitude greater than those designated as "fine sands", and two orders of magnitude greater than those designated as "sandy". These data are summarized in Figure 14. Smears were made from the mixed cultures cultivated from the sulfide sediments and stained by Gram's method (5). The predominant organism was a gram-positive, spore-forming rod that was anaerobic in culture. When streaked on thioglycollate agar (1.5 percent) plates, they produced colonies that were irregular, raised, and erose.

FIGURE 11 GEOGRAPHICAL DISTRIBUTION OF BACTERIAL POPULATIONS (MPN) IN SURFACE WATERS OF AREA IV

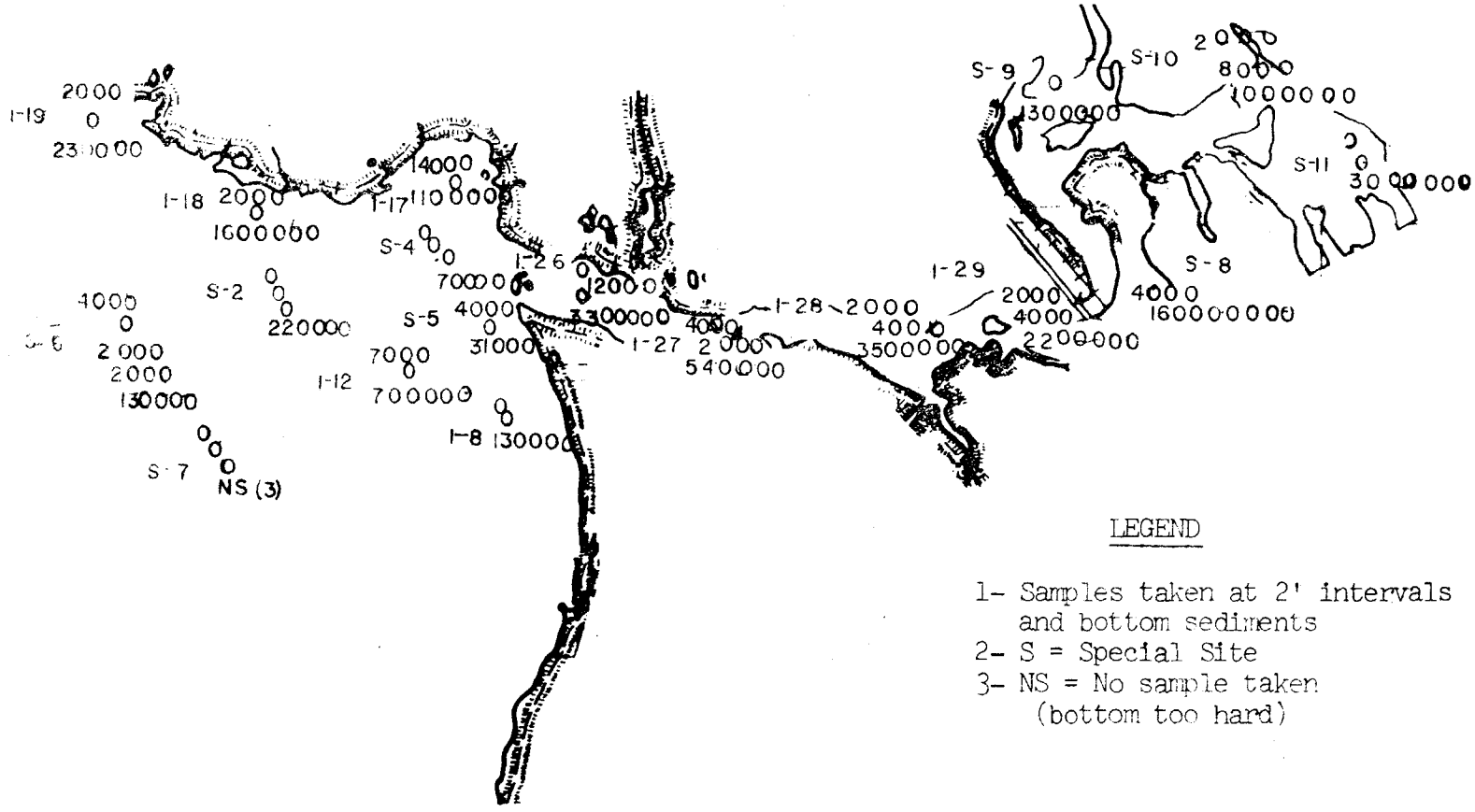


In a related study conducted at Punta Gorda, Florida, the sediment samples also had higher bacterial counts than the water above them, and again the predominant organism was a gram-positive, spore-forming rod. In the Punta Gorda study, as shown in Table 1, the water samples collected from Charlotte Harbor had MPN's of total bacteria between 0 and 3.3×10^4 per 100 ml. of sample, with a median count of 4.5×10^3 per 100 ml. of sample; whereas the sediment samples had bacterial counts between 3.1×10^5 abd 1.6×10^7 per gram, wet weight. Sulfide ion concentrations in the sediments ranged between 0.0 and 7.65 mg. per cent, dry weight (8).

Water samples collected from a canal system not yet connected to Charlotte Harbor had MPN's of total bacteria ranging between 0 and 1.7×10^4 per 100 ml., with a median of 2.0×10^3 per 100 ml. of sample. The bacterial counts of the sediment samples were between 1.7×10^5 and 2.4×10^8 per gram, wet weight, with a median of 1.3×10^7, per gram, wet weight. Only two sediment samples from this area contained detectable sulfide ions, one 6.71 mg. per cent, and the other 16.63 mg. per cent (8). At both sites, the MPN's of total bacteria were less than the median.

Water samples collected from an adjacent canal system recently opened to Charlotte Harbor had bacterial counts between 0 and 7.8×10^3 per 100 ml., with a median of 2.0×10^3 per 100 ml. of sample. The MPN's of the sediment samples ranged between 1.5×10^6 and 2.3×10^7 per gram, wet weight. Again, two sediment samples yielded detectable sulfide ions (6.97 and 17.17 mg. per cent) (8). However, no sulfide was detected in the sample which yielded the highest MPN of total bacteria.

FIGURE 12 WATER COLUMN PROFILE OF BACTERIAL POPULATIONS (MPN) OF BANANA CREEK - TOTAL BACTERIA

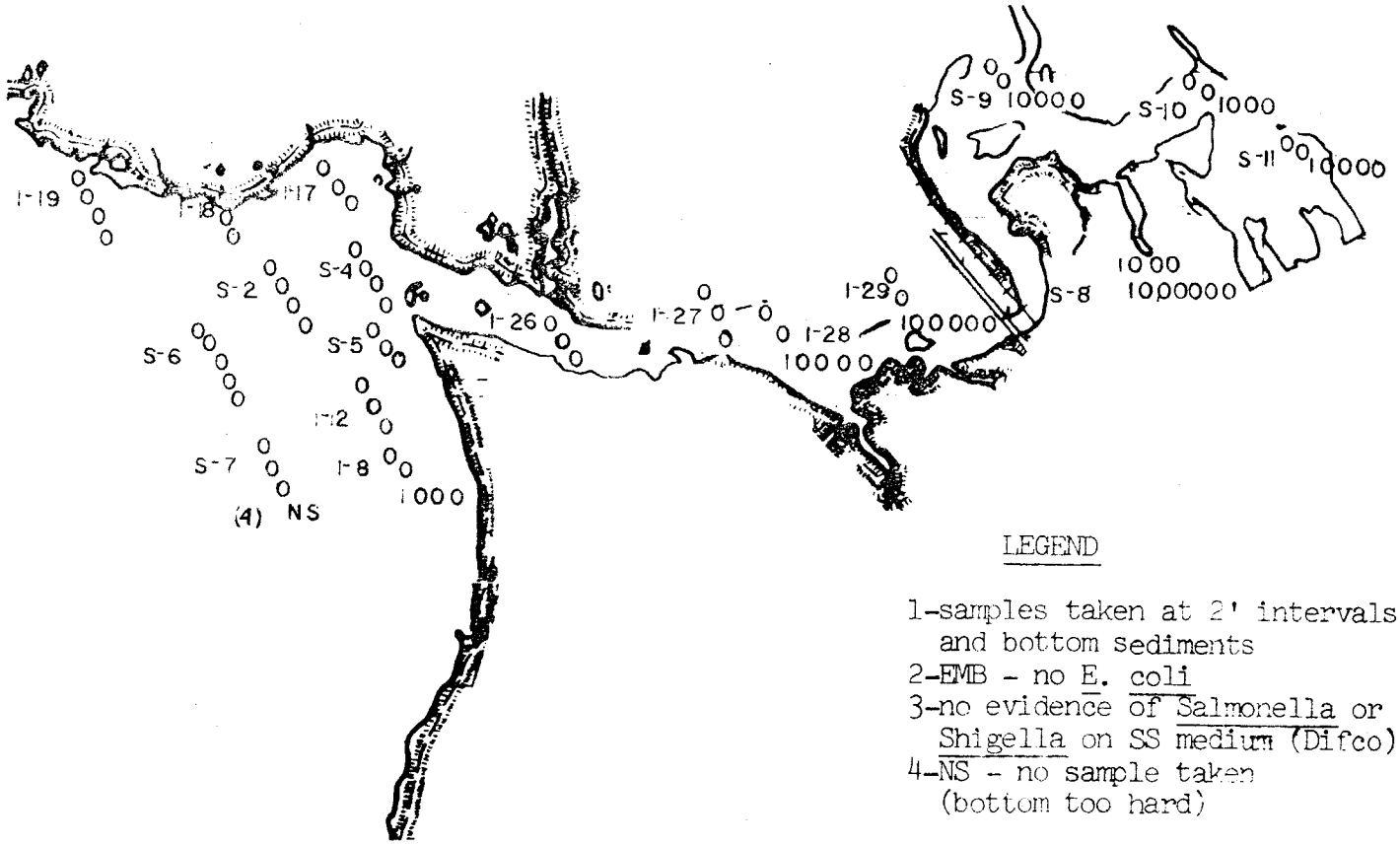


LEGEND

1- Samples taken at 2' intervals and bottom sediments
2- S = Special Site
3- NS = No sample taken (bottom too hard)

FIGURE 13 WATER COLUMN PROFILE OF COLIFORM POPULATIONS (MPN)

OF BANANA CREEK



LEGEND

1-samples taken at 2' intervals and bottom sediments
2-EMB - no E. coli
3-no evidence of Salmonella or Shigella on SS medium (Difco)
4-NS - no sample taken (bottom too hard)

FIGURE 14 BACTERIAL POPULATIONS (MPN) OF SEDIMENT TYPES FROM BANANA CREEK REGARDLESS OF WATER DEPTH

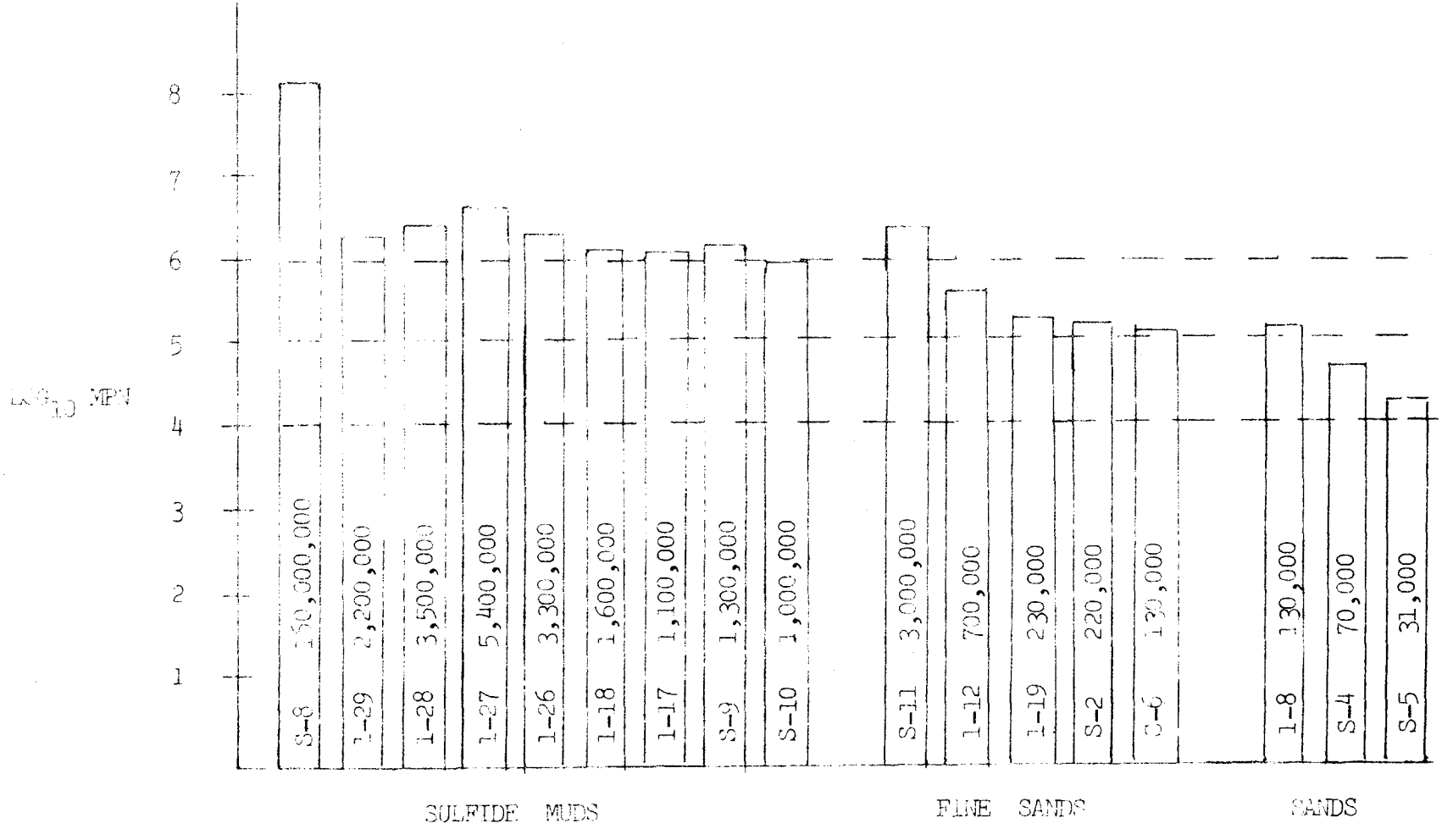


TABLE 1 "RELATIONS OF TOTAL BACTERIAL POPULATIONS (MPN) OF SAMPLES COLLECTED FROM SURFACE, MIDDLE, AND BOTTOM WATERS WITH THOSE COLLECTED FROM THE SEDIMENTS AT PUNTA GORDA"

Area	Total Bacterial Populations (MPN) of Waters		Average Bacterial Populations (MPN) of Water Column ($\times 10^3$)			Average Bacterial Populations (MPN) of Sediments
	Range	Median	Surface	Middle	Bottom	
Open Harbor	$0 - 3.3 \times 10^4$	4.5×10^3	7.1	7.7	12.5	7.07×10^6
New Open Canals	$0 - 7.8 \times 10^3$	2.0×10^3	2.5	2.45	3.25	1.24×10^7
Closed Canals	$0 - 1.7 \times 10^4$	2.0×10^3	5.83	4.05	3.90	4.85×10^7
Old Open Canals	$0 - 1.9 \times 10^4$	7.8×10^3	8.62	4.6	10.95	1.63×10^7

Water samples collected from an established canal system yielded bacterial counts between 0 and 1.9×10^4 per 100 ml. of sample, with a median of 7.8×10^3 per 100 ml. of sample and the sediment samples had MPN's between 2.3×10^6 and 3.3×10^7 per gram, wet weight, of sample. A sulfide ion concentration of 14.15 mg. per cent was found in one sample (8).

In presenting the data, ranges and medians of MPN's of bacteria obtained from the collective water samples were generally used. In addition, the MPN's of total bacteria obtained from the samples of surface, mid-depth, and bottom waters, collected at Punta Gorda, were averaged in order to gain some insight into the general distribution of bacteria throughout the water columns. As shown in Table 1, in three of the four areas the average MPN's of total bacteria yielded by the surface samples were less than those of the bottom water samples. The average MPN of total bacteria obtained from the surface water samples collected from the closed canal system was higher than that of the bottom water samples. It was also noted that the waters of the closed canal system were more saline than the open waters of Charlotte Harbor. Whether the increased salinities of the waters in the closed canal system had any effect on the bacterial populations in these waters was not determined.

Following the study at Punta Gorda, sediment samples were collected at nine sites approximating those sampled by Akimoto (1) at Vero Beach. MPN's of total bacteria revealed that larger numbers of bacteria might be expected from sites in deeper waters. Samples collected at sites which had water depths of six feet of greater, for example, had total bacterial counts between 1.4×10^7 and 2.4×10^8 per gram, wet weight, whereas

samples collected at sites with water depths of less than six feet had bacterial counts between 1.8×10^6 and 1.3×10^7 per gram, wet weight. As demonstrated by Figure 15, MPN's of sulfide producing bacteria, estimated from grown cultures as described, in sediments collected at sites six feet or more below the surface ranged between 4.5×10^3 and 1.3×10^5 per gram, wet weight, with a median of 1.3×10^4 per gram, wet weight. MPN's of sulfide producing bacteria obtained from samples taken from sites with water depths of less than six feet ranged between 2.0×10^3 and 7.0×10^4 per gram, wet weight, with a median of 8.0×10^3 per gram, wet weight, of sample. As indicated in Table 2, similar results were obtained during a study conducted near the Orlando Utilities Commission Power Plant at Delespine, Florida.

Microscopic examination of the smears made from the cultures grown from the sediment samples collected at Vero Beach revealed that the predominant organism was a gram-positive, spore-forming rod similar to those encountered in the other areas studied.

The use of iron wire enabled an apparent correlation to be made between the numbers of sulfide producing bacteria and the occurrence of sulfide ion concentrations in the sediments. However, the applicability of the iron wire for determining the MPN of sulfide producing organisms had to be confirmed.

A sediment sample yielding strong olfactory evidence of hydrogen sulfide was collected from the Indian River near the Florida Institute of Technology Anchorage. The sample was prepared as previously described and used to inoculate three sets of 25 Tube MPN tests concurrently. In one set, iron wire was placed in the tubes; the second had lead acetate paper

FIGURE 15 POPULATIONS (MPN) OF SULFIDE PRODUCING BACTERIA IN THE SEDIMENTS AT VERO BEACH

LEGEND

( ) - DENOTES DEPTH OF WATER IN FEET

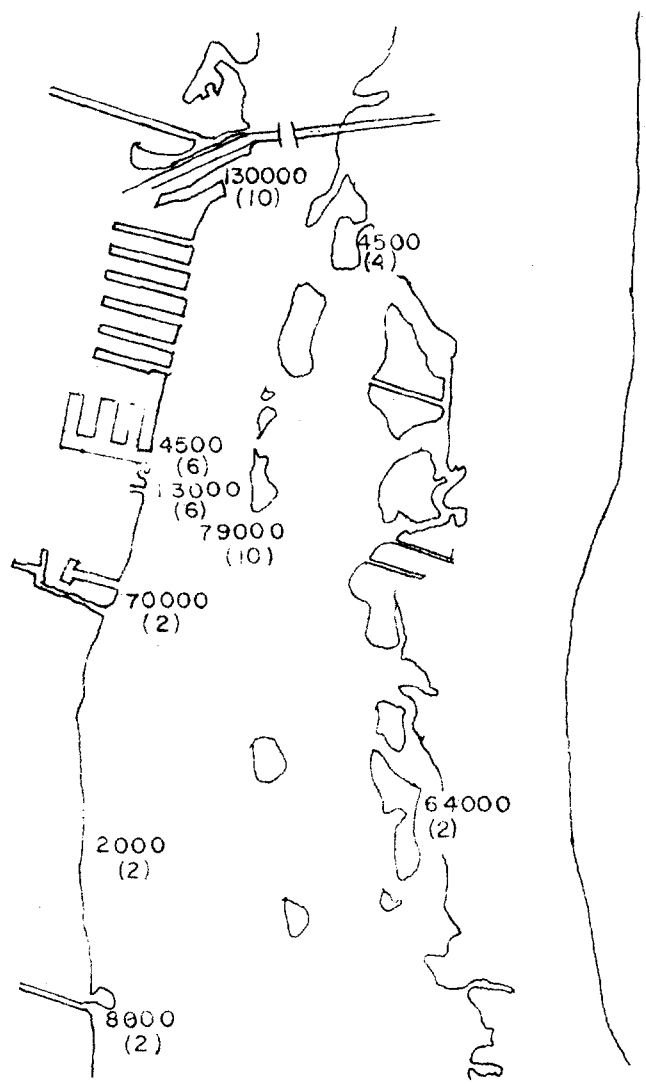


TABLE 2 "RELATIONS OF THE TOTAL BACTERIA (MPN) AND SULFIDE PRODUCING BACTERIA (MPN) WITH WATER DEPTHS OF THE SEDIMENTS COLLECTED NEAR THE ORLANDO UTILITIES COMMISSION POWER PLANT NEAR DELESPINE"

WATER DEPTH (FEET)	TOTAL BACTERIA (MPN) PER GRAM, WET WEIGHT, OF SEDIMENT	H_2S PRODUCING BACTERIA (MPN) PER GRAM, WET WEIGHT, OF SEDIMENT	H_2S PRODUCING / TOTAL BACTERIA
2	4.9×10^4	0	0
2	1.3×10^5	1.1×10^4	.0846
2	7.0×10^5	1.3×10^4	.0186
2	4.9×10^6	2.6×10^4	.0053
2	6.4×10^4	2.1×10^4	.328
2	1.1×10^5	2.0×10^3	.0182
4	1.3×10^5	2.0×10^3	.0154
4	3.3×10^5	4.5×10^3	.0135
8	2.2×10^5	1.7×10^4	.0773
8	1.3×10^6	4.1×10^4	.0316
10	1.4×10^6	4.5×10^4	.0321
10	7.0×10^4	6.8×10^3	.0971
12	2.3×10^6	4.6×10^4	.0200
14	1.1×10^6	2.0×10^4	.0182

strips held in place in each tube by the plastic cap; and the third with no additions served as a control in determining the MPN of total bacteria.

The control test indicated an MPN of total bacteria of 5.4×10^8 per gram, wet weight, of sample; whereas the first test employing iron wire revealed an MPN of total bacteria of 9.2×10^8 per gram, wet weight, of sample. The presence of iron sulfide in the tubes indicated an MPN of sulfide producing bacteria of 1.7×10^8 per gram, wet weight, of sample. The test employing lead acetate paper also indicated a total bacterial count of 5.4×10^8 per gram, wet weight, and the presence of lead sulfide on the paper indicated an MPN of sulfide producing bacteria of 2.1×10^7 per gram, wet weight, of sample. The experiment was repeated three times with the following five weeks and the results are summarized in Table 3.

The mixed cultures were streaked on thioglycollate agar (1.5 per cent) plates and incubated anaerobically at 35°C. for 24 hours. Fourteen strains of gram-positive, spore-forming rods were isolated and used to inoculate fresh tubes of fluid NIH Thioglycollate medium (Difco). The cultures were checked for purity and sent to an independent laboratory for confirmation of identification. Nine of the strains were reported to be members of the genus Clostridium. The remaining five strains were reported as members of the genus Bacillus which were facultative anaerobes.

Sediment samples were once more collected from the Banana Creek area. Both sulfide ion and bacterial analyses were conducted.

These experiments are summarized in Figure 16, where it is evident that the highest concentration of sulfide ions, 13.68 mg. per cent, and the highest total bacterial count, 7.0×10^7 per gram, wet weight, in the

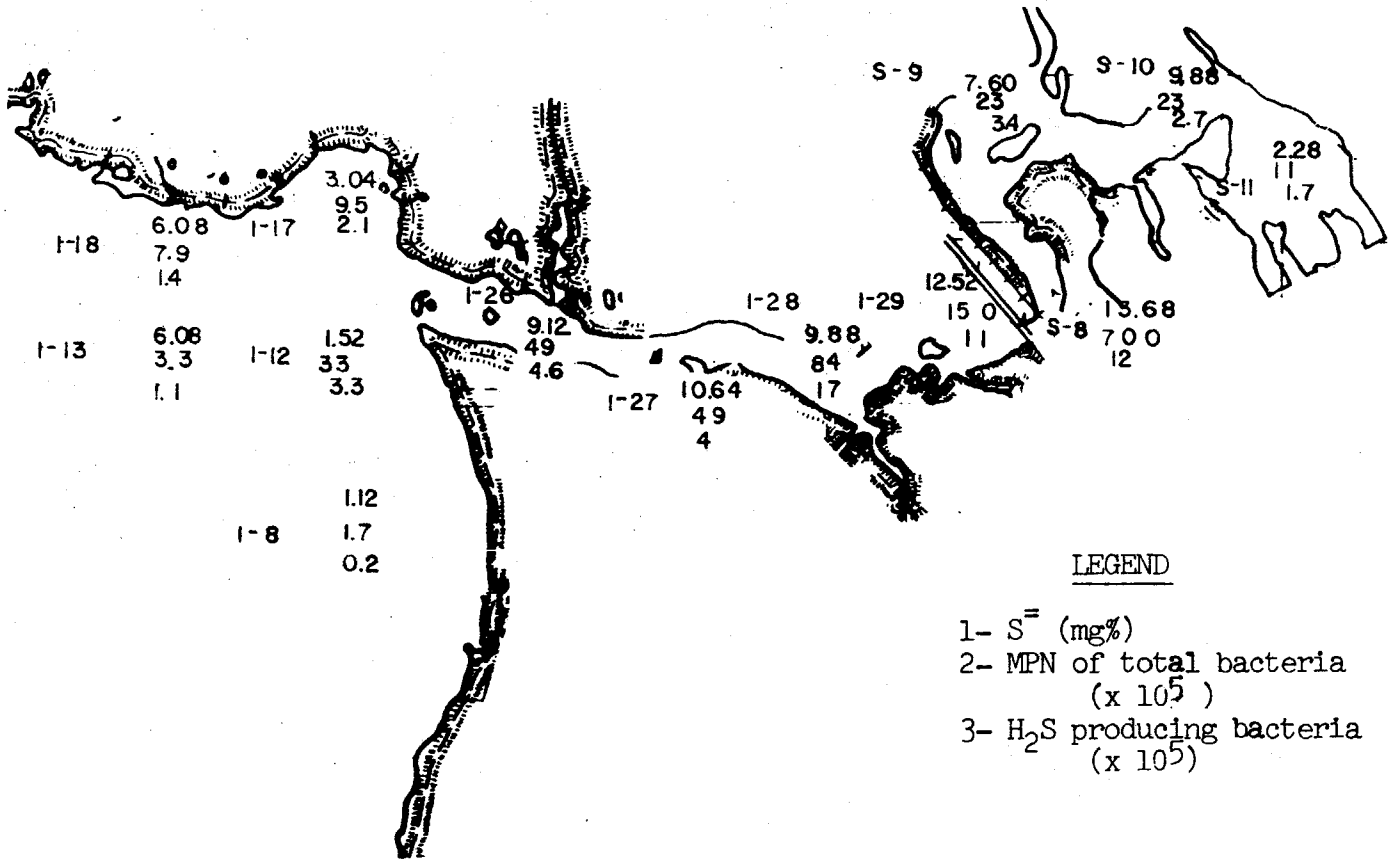
TABLE 3 "COMPARISON OF IRON WIRE AND LEAD ACETATE AS INDICATORS FOR THE DETERMINATIONS OF THE MPN'S OF SULFIDE PRODUCING BACTERIA IN THE SEDIMENTS OF THE INDIAN RIVER"

DATE	IRON WIRE			LEAD ACETATE		
	MPN ($\times 10^6$) Total Bacteria	MPN ($\times 10^6$) H_2S Producers	$\frac{H_2S \text{ Producers}}{\text{Total Bacteria}}$	MPN ($\times 10^6$) Total	MPN ($\times 10^6$) H_2S	$\frac{H_2S}{\text{Total}}$
4-17-73	920	170	.185	540	21	.039
4-24-73	70	33	.471	79	3.2	.041
4-27-73	540	17	.031	540	64	.118
5-24-73	70	3.7	.053	79	3.5	.044

sediment samples were encountered at site #S-8, located at the mouth of the waste water outfall. Both the sulfide ion concentrations and total bacterial MPN's generally decreased with increasing distance in both directions from site #S-8.

However, the MPN's of sulfide producing bacteria did not decrease as the sites increased in distance from site #S-8. The highest MPN of sulfide producing bacteria, 1.7×10^6 per gram, wet weight, of sample, was obtained from the sample collected at the mouth of a tributary draining into Banana Creek.

FIGURE 16 MPN OF TOTAL BACTERIA, MPN OF SULFIDE PRODUCING BACTERIA, AND SULFIDE ION CONCENTRATION (mg %) OF THE SEDIMENTS IN THE BANANA CREEK AREA



V. DISCUSSION

A. Occurrences of bacterial populations and sulfide ion concentrations

Although several samples yielded presumptive evidence of coliforms, fecal strains of E. coli were not detected in any sample collected from sites in or around the Kennedy Space Center. However, the distances between the sample sites and the adverse affects of saline water on coliforms do not preclude the possibility of localized pollution by sewage (15).

The three sample sites on an east-west line in Area 4 were located in close proximity to spoil islands on which birds were observed to roost. The high bacterial populations obtained from the surface water samples collected at these sites are probably due to large amounts of available nutrients from guano and other wastes from the birds. All other surface water samples which had high MPN's of total bacteria were obtained from sites that were located in protected areas or areas of restricted water movement. It was also noted that the sediments of the areas of restricted water movement contained detectable amounts of hydrogen sulfide. Upon further investigation, it appeared that there might be a correlation between the occurrences of high sulfide ion concentration and large bacterial populations in the sediments.

However, from the results obtained from the study at Punta Gorda, there appeared to be no such correlation between the occurrences of sulfide ion concentrations and total bacterial populations in the sediments. It might be possible that the occurrences of large concentrations of sulfide ions in the sediments of certain areas are due to introduced materials containing

sulfur and the activities of sulfide producing bacteria.

The studies conducted at Vero Beach suggested a correlation between sulfide ion concentration (1) and MPN's of sulfide producing bacteria in the sediments with increasing depths of water over the site from which the sample was obtained. Proliferation of the anaerobic bacteria and the formation of anoxic conditions (4) in the sediments under greater water depths, e.g. six feet or more, could possibly be caused by decreased competition for nutrients by non-bacterial benthic organisms, decreased effects from water turbulence induced by wind, and gravitational transport of sulfur containing materials from shallower areas. However, large populations of sulfide producing organisms were also encountered from samples collected from shallow water sites located near the mouths of canals. Therefore, there may be some correlation between the large populations of sulfide producing organisms and the possible occurrences of introduced nutrient materials.

B. Comparison of iron wire and lead acetate paper as indicators for determining the MPN's of sulfide producing materials

One of the proposals of this study was to determine the applicability of using iron wire as an indicator of hydrogen sulfide production in mixed cultures. However, certain problems arose.

In order to save time, the iron wire strips were cleaned as described and placed in the thioglycollate tubes prior to sterilizing in an autoclave. In the haste of cutting the iron, some strips were considerably longer than two inches. As a result, the iron not submersed in the medium rusted during sterilization. This presented a twofold problem. First, the rust settled to the bottom of the tube and appeared dark in color, making differentiation between the dark iron oxide and the black iron sulfide difficult. Secondly, a large amount of rust in the medium could completely oxidize the indicator, making the medium less suitable for anaerobic growth. Therefore, during subsequent experiments, the iron wire was not placed into the tubes until growth had already occurred.

In order to evaluate the applicability of the iron wire, a parallel test was conducted using lead acetate paper as an indicator. Lead acetate paper strips were selected as indicators of hydrogen sulfide production for several reasons. Lead acetate is recommended as a hydrogen sulfide production indicator by the Manual of Microbiological Methods (5). Lead sulfide is very insoluble in water and its black color can be readily recognized. However, precaution must be taken not to accidentally dip the paper into the medium. Lead and its salts, as are the salts of other heavy metals, are toxic to most organisms.

The iron wire did not prove applicable during the final survey of the Banana Creek sediments. As standard practice, the test employing lead acetate paper was run concurrently with the same sample. The MPN's of sulfide producing bacteria as indicated by the presence of iron sulfide did not correlate with those indicated by the presence of lead sulfide. Three of the thirteen samples failed to produce any iron sulfide in culture, whereas the presence of lead sulfide on the paper strips indicated MPN's of sulfide producing organisms of 4.6×10^5, 3.3×10^5, and 1.1×10^5 per gram, wet weight, of sample. The sulfide ion concentrations found in the sediment samples at these sites were 9.12, 1.52, and 6.08 mg. per cent, respectively. At site #1-28, the difference between the two MPN's was on the order of two magnitudes. Therefore, iron wire as used in this study was not applicable as an indicator of hydrogen sulfide production.

C. Hydrogen sulfide producing bacteria

Certain bacteria can cause a reaction between the sulfhydryl group in amino acids with sulfur to produce a disulfide and hydrogen sulfide (14):

$$2\ R - SH + S = R - S - S - R + H_2S$$

Sulfur utilizing bacteria can be found in areas of organic decomposition where hydrogen sulfide is produced. Certain organisms, such as Clostridium nigrificans, employ compounds representing the various oxidative states of sulfur as proton acceptors (3):

$$2\ CH_3 - CHOH - COONa + H_2SO_4 = 2\ CH_3 - COONa + H_2S + 2\ CO_2 + 2\ H_2O$$

(Sodium lactate) (Sodium acetate)

The predominant organisms encountered in the mixed cultures producing hydrogen sulfide obtained from the sediments of the Indian River were gram-positive, spore-forming rod shaped anaerobes. They were identified as members of the genus Clostridium. Similar organisms were also encountered from the sediments collected at Punta Gorda.

During one sampling excursion, the supply of NIH Formula Thioglycollate (Difco) medium was exhausted. Thioglycollate (Difco) medium without indicator or agar was substituted. The MPN's of sulfide producing bacteria obtained per gram, wet weight, of sediment sample were generally several orders of magnitude less than previously recorded. It is probable that the lack of agar facilitated oxygen diffusion throughout the medium.

Since the sulfide producing organisms are obligate anaerobes, the presence of oxygen in the medium would inhibit them. Also, any hydrogen sulfide present would probably be more easily oxidized. It would therefore, be advisable to avoid using medium without anti-diffusion agents, such as agar-agar, in studies similar to these.

D. Hydrogen sulfide producing bacteria as potential indicators of introduced materials to an area

Banana Creek receives much of the natural fresh water runoff from northern Merritt Island as well as waste water from the Kennedy Space Center. As a result, much terrestrial material is introduced into Banana Creek enriching the water and especially the sediments. Since the terrestrial materials may include enrichments, it might be possible to locate the sources of this introduced material by locating areas of increased populations of sulfide producing organisms.

The water currents in Banana Creek were observed to flow from East to West and into the Indian River. The presence of copious amounts of hydrogen sulfide in the sediments located upstream from a few small islands within Banana Creek suggests that these islands impede water movement, causing nutrient material to be deposited. Should there be only one source of introduced materials into Banana Creek, the MPN's of sulfide producing bacteria should be the highest at that location, and the MPN's of sulfide producing bacteria should decrease with increasing distance from it due to dispersion. As is evident in Figure 16, this is generally the case in Banana Creek, but other sources of enrichment are also suggested.

It is notable that at the easternmost site, in Banana Creek, #S-11, the MPN of sulfide producing bacteria found in the sediment sample was relatively small. The samples collected from the other three sites east of State Road 3 revealed increasing MPN's of sulfide producing bacteria with increasing distance downstream from site #S-11. Sites #S-10 and #S-9 are both located at the mouths of small creeks draining into Banana

Creek, whereas site #S-8 is located at the mouth of the waste water outfall. The sample from site #1-29, located west of State Road 3 and downstream of site #S-8, had a lower MPN of sulfide producing bacteria than that from site #S-8. There is no apparent tributary, creek, outfall, or other possible source of introduced materials located between sites #S-8 and #1-29. The sediment sample collected from site #1-28, located at the mouth of a large tributary draining into Banana Creek, had a higher MPN of sulfide producing bacteria than any other sample collected. This might indicate enrichment from both the tributary and the waste water outfall at site #S-8. A slightly higher MPN of sulfide producing bacteria occurred in the sediment at site #1-26, located at the mouth of a small creek. It appears that the MPN's of sulfide producing bacteria in the sediments generally decrease with an increase in distance downstream from a source of introduced materials except where there are additional sources of introduced materials.

Members of the genera Clostridium and Bacillus are gram-positive, rod shaped organisms which characteristically form endospores. The endospore is a dormant cell with a thick protective coating which makes it highly resistant to unfavorable conditions. Activation of spore germination may be initiated by heat or by the presence of certain chemicals, e.g., L-alanine, glucose, or of some reducing agent (3). The anaerobic Clostridium produces spores only in an anaerobic environment. The facultative aerobic members of the genus Bacillus may produce spores either aerobically or anaerobically. Spores may be produced in one area and transported mechanically to another by air or water currents, remaining dormant until they reach an environment suitable for germination.

A question still remains as to whether the sulfide producing bacteria are present in the sediments in their vegetative state or in their spore state. Smears were not made from the sediments themselves and examined microscopically. Further studies in this area should include the preparation of smears of the sediments in order to confirm or deny the presence of spores.

VI. CONCLUSION

The bacteriological survey of the Indian River lagoonal system in and around the Kennedy Space Center indicated no classical bacterial evidence of sewage pollution, however, large bacterial populations were encountered in areas of restricted water movement. Associated with the areas of restricted water movement are the occurrences of large concentrations of sulfide ions in the sediments.

In attempting to estimate the relative numbers of sulfide producing bacteria in mixed cultures from the sediments, it was found that lead acetate paper was more applicable than iron wire for determining hydrogen sulfide production.

The predominant sulfide producing organisms in the sediments appear to be members of the genus Clostridium, with a few members of the genus Bacillus. These or similar organisms are also prevalent in areas other than the Kennedy Space Center. Since these organisms may exist naturally in either the vegetative or spore state, there may be a lack of correlation between the numbers of total bacteria and sulfide producing bacteria. However, the occurrences of large populations of sulfide producing bacteria may indicate sources of introduced materials to an area. This may prove useful in future studies.

APPENDIX

Most probable number of bacteria per 100 ml of water sample (MPN) supplies (per sample)

a. 25 tubes (5 ml/tube) thioglycollate medium (NIH Formulation)
b. 6 Sterile water blanks, 90 ml each capped
c. 7 10 ml pipettes, sterile

Procedure:

a. Use "Sterile technique" throughout
b. Add 10 ml of sample to 90 ml of sterile water. Shake vigorously for 5 minutes.
c. Transfer 10 ml of the 1st dilution to a 2nd blank. Shake vigorously 5 minutes.
d. Using a fresh pipette, add 1 ml of the diluted sample to each of 5 tubes of medium.
e. Use the same pipette to transfer 10 ml of the second dilution to a third water blank.
f. Repeat "d" and "e" until 5 tubes of medium are inoculated with each dilution, from 10^{-2} to 10^{-6}. Be sure to use a fresh pipette for each dilution.
g. Prepare dilutions as follows:

1:10
1:100
1:1000
1:10000
1:100000
1:1000000

h. Label each row of tubes carefully. Incubate 35°C. Observe at 24 hours and 48 hours.

Results:

a. Add the number of tubes of each dilution in which any growth occurred.
b. Determine the MPN from the table on p.p. 100-101, Porter; Bacterial Physiology and Chemistry.

Presumptive Test for Numbers of Coliforms

Supplies:

5 tubes lactose broth (25 ml) with gas collection tubes inserted

6 sterile water blanks, 90 ml each capped

7 10 ml pipettes, sterile

Procedure:

a. Prepare a series dilution of the sample as described for the MPN determination, or use the same preparations

b. Add samples of the diluted specimen to the culture tubes according to the following:

10 ml of 10^{-2} → Tube 1
10 ml of 10^{-3} → Tube 2
10 ml of 10^{-4} → Tube 3
10 ml of 10^{-5} → Tube 4
10 ml of 10^{-6} → Tube 5

c. Carefully label each tube, place in the incubator at 35 C, and examine for growth and gas formation at 24 hours and again at 48 hours.

d. Record any gas formation, or displacement of fluid from the inverted tube, according to the incubation time, and the dilution in which it occurred.

e. Plate gassing cultures on EMB Agar. Incubate, observe at 24 hours for typical E. coli colonies.

f. Gram-stain selected E. coli type colonies and examine at 990K magnification. Small gram-rods in pure culture completes the test.

Reference: Standard Methods for the Examination of Water and Waste-Water. Page: 596

Test for Fecal Coliforms

Supplies:

a. Water bath 45°C

b. Inoculating loop (3mm diameter)

c. Gassing culture in lactose broth from presumptive test

d. 5 ml tubes of E.C. Broth with gas collection tubes

Procedure:

Using sterile technique, transfer 1 loopful of culture from lactose broth to E.C. medium or to Boric Acid broth.

Incubate in water bath for 24 hours.

Gas production in E.C. medium within 24 hours is confirmed test for fecal coliforms.

Reference:

Standard Methods for the Examination of Water and Waste-Water. P.P.:599-600

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Section II, Article 6

The Interaction of Ethion and the Sulfur Cycle Bacteria

Joan C. Sherman

1972

Evidence for the Bacterial Breakdown of Ethion

by

Joan C. Sherman

B.S. in Chem., Northwestern University, 1953

Submitted to the Graduate Faculty
in partial fulfillment of
the requirements for the degree of

Master of Science

in

Oceanography
Environmental Science Option

Florida Institute of Technology

1972

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I. INTRODUCTION

In studies of the persistence of pesticides in the environment, there is little quantitative information concerning the relationships of these chemicals to the microorganisms in oceanic and estuarine environments. Only scattered data are available concerning pesticide persistence in aquatic environments. Microbial processes in the environment regulate chemical balances necessary to the sustenance of all higher life.

From a geobiological point of view, of all microbial processes in the sea, next in importance to photosynthesis is the sulfur cycle . The sulfur cycle describes sulfur metabolism involving both reductive and oxidative processes and their cooperative actions. It is part biological and part chemical. Each phase of the sulfur cycle involves different organisms and different microbial pathways. The cycle has significant effects on pH, Eh and phosphorous solubility in water and sediments. Sulfur functions like carbon in the energy exchange, acting as an electron acceptor. In many plants and bacteria, it is probable that both sulfide and sulfate are directly incorporated into biological materials and both can be considered important nutritionally. In other bacteria, enzymatic data suggest that sulfur in the form of sulfate may be of no direct nutritional significance. Sulfides and elemental sulfur are components of the earths crust; many of these deposits being formed by biological activity. Organic materials can also serve as a source of sulfur by anaerobic degradative processes.

Currently used pesticides are generally organic in nature.

Unlike some of their inorganic predecessors, most organic pesticides are decomposed in the environment by biological and physiochemical processes. One group of organic pesticides are the organophosphorous compounds, so called because of phosphorous content and structural composition. Some of these compounds are largely effective per se while others undergo oxidative conversions in plants or animals.

It is known that soil microorganisms metabolize the organophosphorous compounds fairly rapidly. In general, the higher the moisture content, the more rapid the degradation. Therefore, it follows that microorganisms and microbial processes in the sea can be directly affected by either pesticides per se or their degradation products. In turn, microbial activity is probably directly responsible for decreasing persistence of pesticides in the environment. Microbial attack has been found to oxidize many pesticides; Parathion[a] in the presence of yeast is reduced to the non-toxic aminoparathion in soil.[(1)*]

Some of the organophosphorous pesticides contain sulfur. Since there is history of microbial action on organophosphorous compounds, the interaction of the sulfur containing members of the group and the microorganisms directly involved in the sulfur cycle should be of extreme significance 1) to the balance and equilibrum of the cycle itself, 2) to the problem of pesticide persistence in aquatic environments.

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[a] Parathion is the trade name for o,o-diethyl o-p-nitrophenyl thiophosphate, empirical formula $C_{10}H_{14}NO_5PS$; a product of Shell Chemical Corporation.

*Parenthetical references placed superior to the line of text refer to the bibliography.

This paper describes laboratory experiments on the degradation of the organophosphate pesticide Ethion by bacteria in sediment samples from the Indian River.[b]

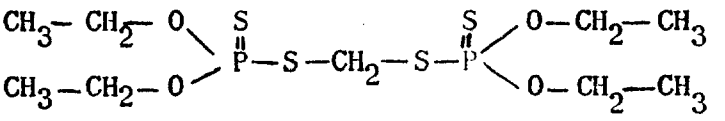
[b] The Indian River is a lagoon, separated from the Atlantic Ocean by a barrier beach. It is saline, with an influx of fresh water and exhibits estaurine characteristics.

II. TECHNICAL ASPECTS

A. Ethion and the Organophosphates

1. Structure

Ethion is o,o,o',o'-tetraethyl-s,s'-methylene- bisphosphorodithioate having the chemical formula:



2. Properties

Ethion belongs to the class of pesticides termed aliphatic organophosphates. All organophosphates undergo similar reactions due to structural similiarities, specific pesticidal action being through the inhibition of the enzyme cholinesterase, which breaks a metabolic chain and permits acetylcholine to accumulate. Potency depends not only on their intrinsic enzyme affinity, but also on anti-cholinesterase properties acquired through invivo metabolism. These compounds can be differentiated on the basis of whether they are largely effective per se or whether they undergo oxidative converstion in plants or animals.(1)

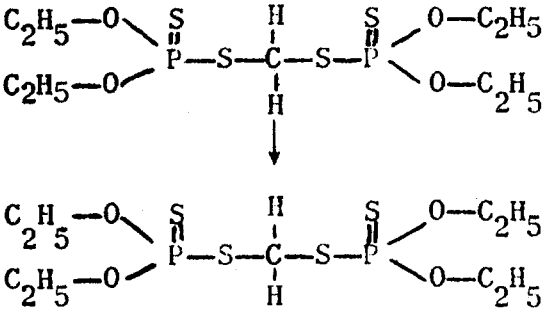
Ethion is soluble in hydrocarbons and ketones; is slightly soluble in water and has been extracted from river water using twenty per cent benzene in hexane.(2)

3. Persistence

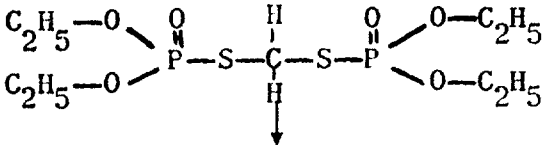
Ethion is slightly soluble in water.(3) In soil, an increase in pH or moisture content increases degradation.(1) Probable degradation

reactions of Ethion are:

a. Oxidation.



b. Degradation of.



to produce acetaldehyde, mercaptans and acidic fragments. Oxidation increases H_2O solubility and anti-cholinesterase activity.(1) The persistence of Ethion in river water after a three week period was studied in a laboratory experiment on water taken from the Little Miami River in Ohio.(2) After a three week period, fifty per cent of the original Ethion was still present in the sample. The organophosphorous compound did not undergo a change when kept in distilled water for this same period.

"Ethion did not undergo changes as rapidly as the other thiophosphate compounds. The relative stability of Ethion may be explained by steric hinderance due to the symmetry of this molecule."(2)

4. Modes of Pesticidal Action

The mode of attack of organophosphate insecticides depends upon their being hydrolyzed or isomerized. The mechanism of hydrolysis involves an attack on the phosphorous by an OH^- group. This is a nucleophilic attack; a negatively charged group attacking a positively charged site.

The more positive the site, the more effective the attack Rate of hydrolysis is dependent on the properties of the group attached to the phosphorous. Electrophylic groups make the phosphorous-oxygen bond more subject to attack. Since =O is more electrophilic than =S, the conversion of =S to =O enhances suspectibility to hydrolysis. This mechanism and the ability to form negative ions by hydrolyzing off a group are important to the stability of the organophosphates and provide a basis for an understanding of their biochemistry. Much is written on the effects of organophosphates on cholinesterase.[5] Organophosphates are effective insecticides because they inhibit cholinesteral activity via a reaction such as: [c]

$$(RO)_2P(O)X + EOH \rightarrow (RO)_2P(O)OE + H^+ + X^-$$

involving a complex of enzyme and inhibitor; a phosphorylation with covalent bond formation.

B. Sulfur Cycle

Sulfur metabolism in nature is the cooperative action of an oxidative and reductive process. The sulfur cycle involves an eight electron change between sulfate and sulfide, with the formation of numerous intermediates. Inorganic sulfur generally enters into biosynthetic pathways at oxidative levels of ($SO_4^=$) sulfate and ($S^=$) sulfide. Other naturally occurring forms of sulfur such as thiosulfate, polythionates, polysulfides and elemental sulfur must either be oxidized to sulfate or reduced to sulfide before becomin available for biosynthetic reaction. This conversion, biologically is a

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[c] In the equation, EOH = enzyme.

reversible process. The overall sulfur cycle may involve different organisms and different enzymatic pathways.

In contrast to animals, plants and bacteria have the ability to reduce sulfate to the level of sulfide as has been indicated by their growth with sulfate as the sole source of sulfur. Animals depend on external sources of sulfur and sulfur containing metabolite as sources for nutrition. It is believed that in plants and bacteria both $SO_4^=$ and $S^=$ are directly incorporated into biological materials. In other bacteria, enzymatic data suggest that sulfur in the form of sulfate may not be metabolized.(5)

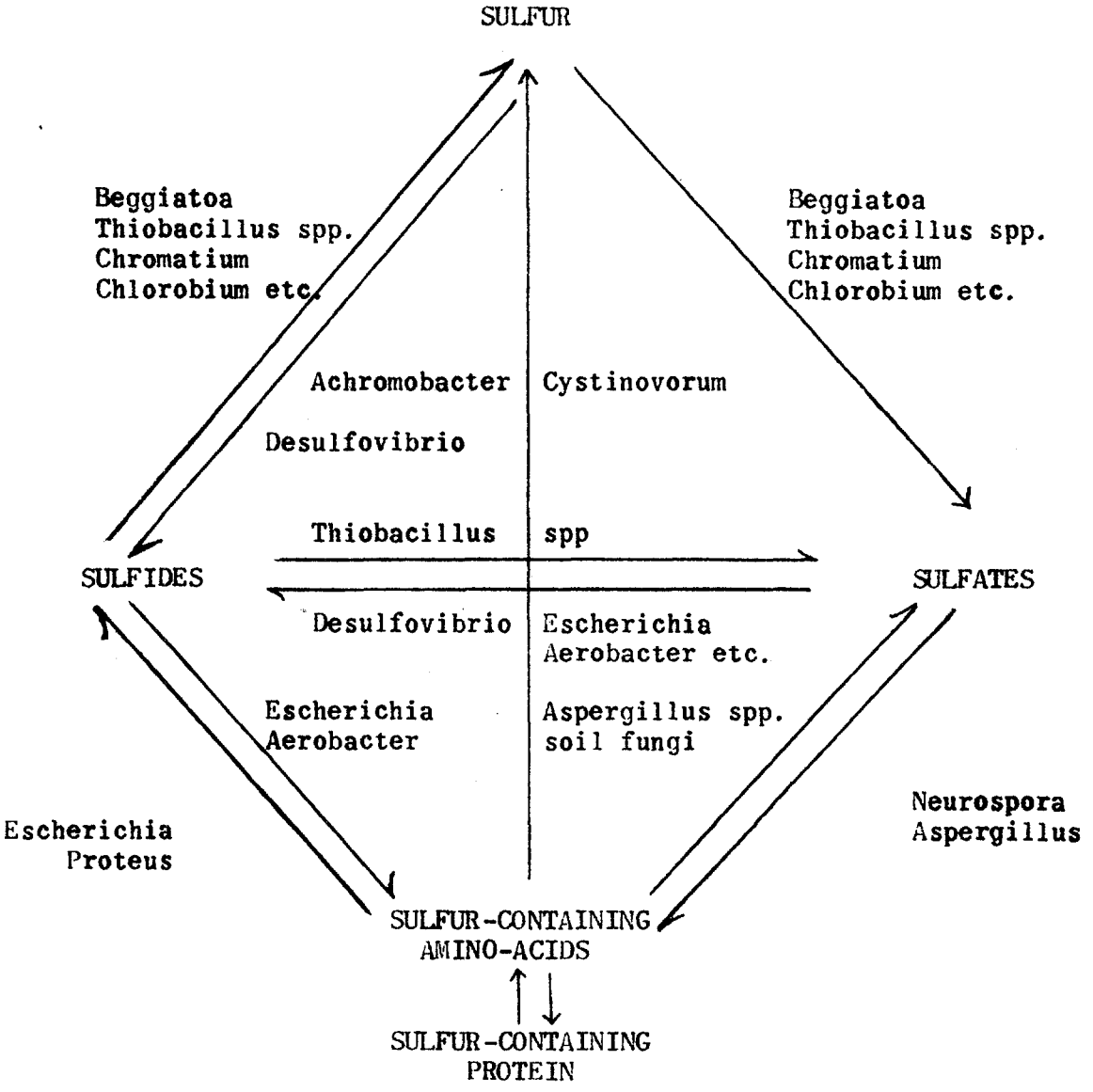
"Sulfate reduction, physiologically characterized by the formation of only enough sulfide to meet nutritional requirements has been termed assimilatory sulfate reduction. This is the only type of sulfate reduction occurring in plants and the most commonly encountered type in bacteria. A small group of anaerobic bacteria, known as the sulfate reducing bacteria, produce massive amounts of sulfide during growth in the presence of sulfate and an electron donor. This process has been identified as dissimilatory or respiratory sulfate reduction in that sulfate serves as the terminal electron acceptor in respiration in much the same manner as oxygen in aerobic respiration."(6)

There are three primary types of physiological reactions in which sulfate can be involved:(6)

1. direct incorporation in organic materials
2. reduction to sulfide for nutritional purposes (assimilatory sulfate reduction)
3. reduction to sulfide during sulfate respiration (dissimilatory sulfate reduction)

In microorganisms reduced inorganic sulfur, such as sulfide, sulfur, and thiosulfate can serve as electron donors for aerobic or anaerobic respiration and photosynthesis with the formation of sulfate and largely acidic conditions.

THE MICROBIAL SULFUR CYCLE



An active sulfate reducing mechanism by Desulfovibrio desulfuricans has been described by Peck [8] and Ishimoto.[9] Peck has investigated Desulfovibrio in detail and has shown that only sulfite is formed if the reduction is carried out at pH 7.75. At pH 6.0, H_2S is the product. The overall system for sulfate reduction to sulfite in Desulfovibrio may be summarized as:[10]

$$H_2 + \text{cyt.} - c_3\ (2\ Fe^{+3}) \rightarrow \text{cyt.} - c_3\ (2FE^{+2}) + 2H^+$$

$$ATP^{-4} + SO_4^{-2} + H^+ \rightarrow APS^{-2} + PP^{-3}$$

$$APS^{-2} + \text{cyt.} - c_3\ (2FE^{++}) \rightarrow AMP^{-2} + SO_3^{-2} + \text{cyt.} - c_3(2Fe^{+3})$$

$$H_2 + ATP^{-4} + SO_4^{-2} \longrightarrow AMP^{-2} + SO_3^{-2} + PP^{-3} + H^+$$

Sulfite formation from sulfate and hydrogen requires ATP, Mg^{++} and cytochrome - C_3. The stoichiometry of the reduction reaction shows that for each mole of hydrogen taken up, one mole of ATP is split to AMP and pyrophosphate and one mole of sulfite is formed.

Reduction of sulfate to sulfite is thermodynamically an unfavorable reaction. The reaction $SO_4^{-2} + H_2 \longrightarrow SO_3^{-2} + H_2O$ has a standard free energy of +14 kcal.[11] As an analogy with carboxyl group reduction in enzymatic systems, it is of significance that sulfate reduction also requires an activation prior to the reduction step. Chemically, esters and anhydrides are more readily reduced than the corresponding anions.

Sulfate reduction by Desulfovibrio has been studied with whole cell suspensions as well as with extracts.[11] Postgate has shown that cytochrome-c_3 is important in sulfite reduction. From free energy data, Postgate [11] showed that sulfite reduction by reduced cytochrome-c_3 is energy yielding.

A number of organisms use thiosulfate as a sulfur source; many systems have been found which reduce $S_2O_3^=$ to equimolar quantities of $SO_3^=$ and H_2S. This system has been found both in Proteus vulgaris and Escherichia coli.

C. The Interaction of Pesticides and Microorganisms and Enrichment

It has been estimated that even though some pesticides do not sustain microbial growth, they can be degraded by microbial action. Other pesticides have chemical composition and structures similar to compounds readily used in the metabolic processes of organisms.

Therefore, there are two mechanisms by which an otherwise recalcitrant molecule can be attacked. Horvath[12] has studied co-metabolism of organic compounds which fail to support bacterial growth but are broken down into other organic molecules. Therefore, co-metabolism although it does not result in complete mineralization to the elements, could be an important mechanism for the breakdown of pesticides in the environment by natural microbial populations. He indicates that microorganisms capable of co-metabolism can be enriched for by repeated applications of the substance or by application of enrichment techniques.

Enrichment techniques can also be used to study biodegradability. Enrichment utilizes natural selection. The mixed microbial population in sediments can be considered to be of many different species and competing metabolic types. The method of enrichment culture provides those selective features which lead to the predominance of a particular species. Therefore, this mechanism can be used to study biodegradability of pesticides in the environment. One type of biodegradability is represented by complete

degradation of the organic molecule to its basic elements. A second type of biodegradability which might be just as significant is the conversion of the organic pesticide to other decomposition products.

III. STATEMENT OF THE PROBLEM

The literature indicates that the amount of work on the toxicity of pesticides on the macroscopic level far exceeds the work on the effects of these chemicals on microbial populations. Several recent papers by Horvath and Eichelberger et. al.[12] have studied microbial degradation of organic compounds in nature. It was proposed to extend this work to a specific pesticide.

In Brevard County, Florida, Ethion is widely used as a pesticide in the orange groves[d] and the Indian River receives run off from these groves. Therefore, the interaction of Ethion and the microbial community of the Indian River is pertinent to the ecology of the area.

Sediment samples from the Indian River were used as the source of microorganisms for the experiments.

Ethion is a sulfur containing compound and conditions in the Indian River indicate the presence of sulfur bacteria. Therefore, the interaction of these two factors, namely the possible biological action of a general group of microorganisms on Ethion, was the overall intent of the study.

There was a twofold approach in the experimental program.

1) a bacteriological approach, utilizing enrichment culture
2) a chemical approach monitoring the sulfate/sulfide ratio

IV. DATA DISCUSSION AND INTERPRETATION

Fourteen sediment samples were taken from the Indian River, ranging from Cape Kennedy to Vero Beach. Selection area of samples was not significant but type was important. Sediments were chosen which had a high probability of containing important members of bacteria involved in the sulfur cycle. Samples were taken from the upper regions of the sediment layer and were refrigerated until enrichment cultures were initiated.

Types of sediments varied, being from large grained sands to black peat-like material (see Table I).

For the initial chemical analyses, samples were centrifuged for twenty minutes at 5000 rpm, and weighed. 2 mls of 6M sodium hydroxide (NaOH) were added to avoid hydrogen sulfide (H_2S) loss. Samples were dried for 24 hours at 110^{0}C and reweighed (Appendix C). Water contents were calculated after weights were corrected for the sodium hydroxide additions.

Table I summarizes the types of sediments and the per cent of water. Three samples which were black and peat-like, (Nos. 3, 9, & 14) had water contents in excess of sixty per cent. The remaining samples had water contents from twenty-three to thirty per cent.

Samples were also analyzed for sulfate by barium sulfate precipitation and sulfide by distillation from an acidic mixture (Appendix C). $SO_4^=/S^=$ ratios were calculated on a dry basis. The sulfide contents of the fourteen samples ranged from 0.45 to 64.7 mg per 100 grams of dry sample. (see Table II)

TABLE I

Sample Description

Sample Number	Type of Sediment	Water Content (per cent)
1	tan sand, gravel	23.4
2	black medium grain	24.7
3	dark, peat-like	66.7
4	tan sand	25.1
5	sand, light brown	23.8
6	sand, light brown	24.9
7	sand, light brown	25.1
8	dark & vegetation	27.4
9	black, peat-like	66.9
10	sand, gravel	23.1
11	sand	28.2
12	grey silty sand	26.5
13	black silt } from impounded waters	30.8
14	black silt } from impounded waters	80.8

TABLE II

Initial Chemical Analyses

Sample	H_2O Content	$S^=$ mg/100g	$SO_4^=$ g/100g	$SO_4^=/S^=$ Weight Ratio
1	23.4	2.50	0.35	0.14
2	24.7	1.71	0.49	0.29
3	66.7	64.7	0.83	0.13
4	25.1	1.10	0.25	0.23
5	23.8	1.54	0.22	0.14
6	24.9	1.32	0.26	0.20
7	25.1	0.88	0.31	0.35
8	27.4	1.15	0.41	0.37
9	66.9	4.82	2.19	0.45
10	23.1	1.07	0.17	0.16
11	28.2	0.45	0.74	0.30
12	26.5	1.20	0.24	0.20
13	30.8	1.40	0.03	0.02
14	80.8	2.50	0.36	0.14

Samples were not fixed with sodium hydroxide directly at the point of collection and, therefore, cannot be taken as indicative of absolute $S^{=}$ concentration in the River, due to possible losses of H_2S before samples were made alkaline. Sulfate was also determined (see Table II). It can be noted that samples No. 3 and No. 9 were high in both sulfate and sulfide, but the sulfate to sulfide ratios were not excessive. All samples had $SO_4^{=}:S^{=}$ ratio from 0.02 to 0.45 indicating a definite $SO_4^{=}:S^{=}$ equilibrium in the sediments.

Sulfate analyses are representative of the actual situation in the river sediments. Refrigeration should not result in sample oxidation. Sulfate concentrations in the sediments ranged from 0.03 to 2.19 grams per 100 grams of dried sediment.

At the time when samples were taken for chemical analyses, enrichment cultures were begun. Each sample was incubated anaerobically and aerobically; one ml of Ethion was added to each portion of the sample. Controls, i.e., samples without Ethion were also incubated both ways (see Appendix C). Samples were stored at room temperature in a dark area for twenty days. Aerobic samples were kept moist by the addition of sterile distilled water.

At the conclusion of the twenty day period, all samples were inoculated into thioglycollate medium (see Appendix C). Four distinct sets of experimental parameters were used:

1) anaerobic sediment enrichment culture, Ethion added

2) anaerobic sediment enrichment culture, No Ethion added

3) aerobic sediment enrichment culture, Ethion added

4) aerobic sediment enrichment culture, No Ethion added

The thioglycollate cultures were incubated at 37°C for 48 hours. All tubes showed evidence of bacterial growth. The same experimental parameters were kept as with the enrichment cultures, i.e., those samples which were in the sediments with Ethion, also were inoculated into thioglycollate tubes with Ethion.

All samples were then inoculated into nutrient agar tubes to which an iron wire had been added. If bacterial degradation of the Ethion occurred, the wire would serve as a source of iron for the production of iron sulfide. The Ethion/no Ethion identity was maintained throughout the experiment. Samples were incubated at 37°C and examined periodically. After twelve hours, production of iron sulfide in five different samples (see Table III) was observed.

Examinations of the culture tubes indicated four different conditions. (See photograph No. 2, page 27.)

1) Inoculated media which had an iron wire and Ethion gave evidence of darkening of the wire but also, and most significant, gave evidence of FeS production at the point of inoculation. After twelve hours of incubation, FeS production at the point of inoculation was

visible. Upon further incubation of the culture, FeS discoloration spread from the inoculation point throughout the culture There was no FeS production along the surface of the slant, nor did the spread of the FeS proceed toward the surface, indicating the reaction was taking place anaerobically. The source of the discoloration of the agar was at the point at which the stab was inserted into the agar, suggesting that it was due to the presence of the microorganism (see Table III).

2) Uninoculated media which had an iron wire and Ethion gave evidence of FeS production by a darkening of the wire. This indicated that there was a chemical reaction of the Ethion with the wire. However, there was no dissipation of the FeS throughout the medium and the reaction remained adjacent to the wire.

3) Inoculated media which had an iron wire but no Ethion gave evidence of growth but not of FeS production. This provides positive evidence that the organism could not produce FeS without the Ethion as a source of sulfur.

4) Uninoculated media which had an iron wire but no Ethion served as the experimental control. There was no growth, indicating no contamination of the experiment and no outside uncontrolled source of sulfur other than Ethion.

Nine samples produced no FeS in either experimental or control tubes. Gram stains of a smear of the culture, when observed under oil immersion at 980 X indicated the presence of a gram positive spore forming rod.

Ethion is a reducing agent. In the presence of a reducing agent, anaerobic bacteria readily grow, utilizing the reducing agent as a source of energy.

TABLE III

Bacteriological Data - FeS Production

1) Colonies which exhibited FeS production when incubated with Ethion but no FeS without Ethion.

Sample Number	FeS with Sulfate	FeS with Ethion
2 anaerobic	+	+
9 anaerobic	+	+
13 aerobic	+	+
14 aerobic	+	+

2) Excess of FeS production produced by colonies to which Ethion was added:

Sample Number	FeS with Sulfate	FeS with Ethion
8 anaerobic	+	+

This data taken from agar slants to which sulfate and iron wire had been added. Colonies were then inoculated on slants with Ethion and iron wire.

3) Gram stain data indicated a gram positive spore forming organism.

Of the five sediment samples which suggested microorganisms reacted with Ethion and iron to produce FeS, four were stored aerobically with Ethion in the sediment samples; one (sample 8) was stored anaerobically. The presence of spores would indicate a method by which this group of microorganisms could exist aerobically but would produce FeS anaerobically from the iron and the Ethion.

A parallel experiment was performed. Sediment samples were stored with Ethion; thioglycollate tubes with no Ethion were inoculated from the sediments; and agar stabs with Na_2SO_4 and Fe wire were inoculated from the thioglycollate. The five samples which degraded the Ethion also produced FeS from the Na_2SO_4 and iron wire.

Nutrient agar plates were streaked and incubated anaerobically for 48 hours. Colonies from the streaks were inoculated into nutrient agar tubes with iron wire and Ethion. FeS was produced. Gram stains again indicated a spore forming gram positive rod.

No effort was made during this study to pursue further the chemical mechanism of the reaction or to evaluate the breakdown products of Ethion. Changes in $SO_4^=$ and $S^=$ composition were utilized as suggestions of Ethion degradation.

After the twenty day enrichment culture period, samples were taken for chemical analyses. Initial methods of sample preparations were repeated and samples were analyzed for sulfate and sulfide composition. The sulfate to sulfide ratio is given in Table IV.

Table V and VI summarize the specific sulfate and sulfide compositions for the five samples which biologically degraded Ethion.

TABLE IV

The Sulfate to Sulfide Relationship

$SO_4^=:S^=$ expressed as grams $SO_4^=$ per mg $S^=$

		Aerobic		Anaerobic	
Sample	Initial	No Ethion	Ethion	No Ethion	Ethion
1	0.14	0.52	0.07	0.13	0.23
2	0.29	0.33	0.06	0.13	0.01
3	0.13	0.05	0.10	1.00	0.52
4	0.23	0.12	0.33	0.21	0.14
5	0.14	0.12	(high)	0.08	0.09
6	0.20	0.34	0.21	0.20	(broken)
7	0.35	0.31	0.11	0.50	0.15
8	0.37	0.39	(broken)	0.13	0.39
9	0.45	0.29	0.28	0.27	0.30
10	0.16	1.80	0.01	1.90	0.17
11	0.30	0.23	0.06	0.04	0.25
12	0.20	0.08	0.08	0.17	0.14
13	0.02	0.10	1.33	0.95	0.12
14	0.14	0.08	0.24	0.11	0.15

TABLE V

Sulfide Content of Positive Samples

mg $S^{=}$ per 100 g sample

Sample	Initial	Aerobic		Anaerobic	
		No Ethion	Ethion	No Ethion	Ethion
2	1.71	1.86	8.00	1.47	9.58
8	1.15	1.45	1.90	1.60	0.95
9	4.82	6.52	8.43	4.66	7.02
13	1.40	2.98	2.93	3.48	3.67
14	2.50	13.7	16.16	11.4	24.6

TABLE VI

Sulfate Content of Positive Samples

g $SO_4^{=}$ per 100 g samples

Sample	Initial	Aerobic		Anaerobic	
		No Ethion	Ethion	No Ethion	Ethion
2	0.49	0.61	0.48	0.22	0.05
8	0.41	0.42	(Lost)	0.22	0.37
9	2.19	1.87	2.37	1.22	2.10
13	0.03	0.35	(Lost)	0.33	0.46
14	0.36	1.17	3.87	1.35	3.77

Prior to chemical analysis the remaining Ethion was extracted out of the enrichment culture with hexane.

In all cases except one (sample 2), the sulfate concentration increased after exposure of the sediments to the Ethion. This change was not accompanied by a corresponding decrease in sulfide concentrations indicating some other source of sulfide, i.e., Ethion.

Final sulfide concentrations increased (compared to initial analyses), again suggesting an addition of sulfur to the cycle. No analytical correlation can be made with the increase in sulfide after Ethion addition, indicating no quantitative measure of biological reactions.

A reagent blank was run each day when sulfide determinations were made. Ethion was added to sterile distilled water in the same concentrations as added to the enrichment cultures. This amount increased the reagent blank by 0.032 milligrams per analysis (1 ml Ethion added per analysis), not significant enough to explain increases in $S^{=}$ content.

The theoretical calculated yield of sulfur per ml of Ethion is 0.406 g of $S^{=}$ per ml which is equivalent to 406 mg of $S^{=}$. The increased $S^{=}$ concentrations in the samples after Ethion did not exceed 10 mg of $S^{=}$. The blank increase did not exceed 0.1 mg; therefore, suggesting other mechanisms affecting chemical compositions in the sediment samples.

Based on sample amount used in each enrichment culture of sediment, there was no correlation between theoretical and actual $S^{=}$ concentrations, as stoichiometry of the biological reactions were not measured.

The analytical chemistry of the project established that there was degradation of the Ethion. The data shows that the samples with no Ethion were generally lower or equal to the initial composition in $SO_4^=$, but increased considerably after Ethion addition, suggesting replenishment from the organic sulfur source. The increase in $S^=$ concentration after Ethion addition showed degradation of the molecule. Evidently the effects of biological and chemical degradation, are additive resulting in no direct correlation in the unexplained observations, only unusually high $S^=$ concentrations.

The bacteriological experiments in the project suggested that more than just a chemical mechanism was involved.

Biological degradation would be significant to the ecology of the area because:

1) microbial degradation of Ethion which had entered into the river as run off, would decrease the persistence of the pesticide, decreasing exposure time to fish and other animal life.

2) biological degradation products would possess different toxicity levels, changing entirely the effects on life in the river.

3) presence of excessive quantities of Ethion and Ethion degradation products could produce emission of high H_2S concentrations[e] due to excessive activity of sulfur cycle bacteria (see chart - The Microbial Sulfur Cycle).

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[e] Excessive quantities of H_2S emitted from the river at specific periods in the year could be partly tracable to pesticide run off.

Pages 26 through 29 omitted.

Colored Photographs of Bacterial Growths.

B. Raw Data

1) Water Content

Water Content of Sediment Samples

Sample Number	Per cent Water[f]
1	23.4
2	24.0; 25.4
3	66.7
4	25.1
5	23.8
6	24.9
7	25.1
8	27.4
9	66.9
10	23.1
11	28.2
12	27.0; 26.0
13	30.8
14	80.8

[f] Per cent by weight of H_2O driven off by drying for 24 hrs at 110°C

2) Sulfide Content

A Comparison of Sulfide Content of All Samples

Sulfides expressed as milligrams $S^{=}$ per 100 gram sample

Sample	Initial	Aerobic		Anaerobic	
		No Ethion	Ethion	No Ethion	Ethion
1	2.50	0.70	4.18	1.92	3.40
2	1.71	1.86	8.00	1.47	9.58
3	64.7	1.84	3.70	0.26	5.21
4	1.09 1.10	0.77	6.45	0.75	1.97
5	1.54	0.65	high not measurable	1.47	3.20
6	1.37 1.27	0.94	0.58	1.61	2.11
7	0.88	0.67	1.43	0.41	1.25
8	1.11 1.19	1.45	1.90	1.60	0.95
9	4.82	6.52	8.43	4.66	7.02
10	1.07	0.18	14.5	0.82	10.70
11	0.45	7.24	13.6	2.83	2.47
12	1.20	2.42 1.65	1.42	2.86	2.34
13	1.40	3.52 3.19	2.93	3.48	3.67
14	2.50	13.7	16.16	11.4	24.6

Initial Sulfide Determinations

Sample	gm Sample	$mgS^{=}$	$mgS^{=}$/100 g Sample
1	29.40	0.730	2.50
2	8.443	0.144	1.71
3	5.018	3.240	64.7
4	7.105	0.080	1.10
	10.987	0.120	1.09
5	8.3028	0.128	1.54
6	10.500	0.144	1.37
	9.463	0.120	1.27
7	10.928	0.096	0.88
	10.123	0.112	1.11
8	8.427	0.100	1.19
9	4.307	0.208	4.82
10	13.509	0.144	1.07
11	8.942	0.041	0.45
12	10.607	0.128	1.20
13	8.870	0.124	1.40
14	1.598	0.040	2.50

Final Sulfide Determination - Aerobic, no Ethion

Sample	gm Sample	mgS$^{=}$	mgS$^{=}$/100 g Sample
1	11.464	00.80	0.70
2	9.474	0.176	1.86
3	8.738	0.160	1.84
4	10.430	0.080	0.77
5	7.399	0.048	0.65
6	8.529	0.080	0.94
7	9.465	0.064	0.67
8	5.400	0.080	1.45
9	2.706	0.170	6.52
10	5.727	0.100	0.18
11	1.988	0.144	7.24
12	5.330	0.101	2.42
	9.124	0.150	1.65
13	5.350	0.192	3.52
	3.271	0.104	3.19
14	3.369	0.464	13.7

Final Sulfide Determination - Aerobic, Ethion

Sample	gm Sample	mgS$^{=}$	mgS$^{=}$/100 g Sample
1	2.8711	0.120	4.18
2	3.572	0.273	8.00
3	7.329	0.271	3.70
4	7.456	0.481	6.45
5	7.120	too high to measure	
6	8.287	0.048	.58
7	8.4069	0.122	1.43
8	6.845	0.131	1.90
9	2.965	0.250	8.43
10	4.745	0.692	14.5
11	8.892	1.21	13.6
12	8.4410	0.121	1.42
13	3.762	0.111	2.93
14	5.723	0.921	16.16

Final Sulfide Determination - Anaerobic, no Et ion

Sample	gm Sample	mgS$^{=}$	mgS$^{=}$/100 g Sample
1	10.421	0.200	1.92
2	3.259	0.048	1.47
3	2.1093	0.056	0.26
4	8.550	0.064	0.75
5	10.327	0.152	1.47
6	10.488	0.168	1.61
7	7.834	0.032	0.41
8	9.935	0.016	1.60
9	2.059	0.096	4.66
10	6.095	0.050	0.82
11	6.226	0.176	2.83
12	6.732	0.192	2.86
13	4.163	0.145	3.48
14	4.497	0.512	11.4

Final Sulfide Determination - Anaerobic, Ethanon

Sample	mg Sample	$mgS^{=}$	$mgS^{=}$/100 g Sample
1	7.751	0.264	3.40
2	3.868	0.368	9.58
3	5.201	0.271	5.21
4	10.625	0.212	1.97
5	10.005	0.320	3.20
6	6.817	0.141	2.11
7	6.406	0.082	1.25
8	7.392	0.073	0.95
9	3.185	0.221	7.02
10	7.474	0.800	10.70
11	6.470	0.164	2.47
12	8.815	2.08	23.4
13	5.238	0.189	3.67
14	8.329	2.060	24.6

3) Sulfate Content

Sulfate Determination Comparison

Sulfate concentration expressed as g.SO_4 = per 100 g. sample

Sample	Initial	Aerobic		Anaerobic	
		No Ethion	Ethion	No Ethion	Ethion
1	0.35	0.36	0.30	0.24	0.78
2	0.49	0.61	0.48	0.22	0.05
3	0.83	0.01	0.38	2.72	2.78
4	0.25	0.09	0.21	0.16	0.28
5	0.22	0.08	0.27	0.12	0.28
6	0.26	0.32	0.12	0.33	[g]
7	0.31	0.21	0.15	0.22	0.19
8	0.41	0.42		0.22	0.37
9	2.19	1.87	2.37	1.22	2.10
10	0.17	0.33	0.15	1.52	0.19
11	0.74	1.82	0.85	0.13	0.63
12	0.24 0.25	0.18 0.25	0.11 0.12	0.50 0.21	0.33
13	0.03	0.35		0.33	0.46
14	0.36	1.17	3.87	1.25	3.77

[g] Sample lost, crucible broke in transport

Initial Sulfate Determinations

Sample	gm Sample	gm $BaSO_4$	gm $SO_4^=$	$\frac{\text{gm } SO_4^=}{\text{100 gm Sample (dry)}}^h$ (per cent)
1	20.000	0.1652	0.0702	0.350
2	9.8599	0.1140	0.0481	0.488
	9.4700	0.0740	0.0312	0.329
3	2.4501	0.2239	0.0940	3.83
4	11.5693	0.0686	0.0290	0.250
5	11.9371	0.0634	0.0267	0.223
6	9.0456	0.0624	0.0263	0.263
7	10.5348	0.0782	0.0320	0.312
8	10.3437	0.1019	0.0428	0.412
9	3.8435	0.2007	0.0841	2.19
10	7.6084	0.0311	0.0131	0.172
11	7.4088	0.1339	0.0565	0.742
12	9.3843	0.0528	0.0222	0.237
	7.5609	0.0452	0.190	0.251
13	5.8946	0.0035	0.0015	0.027
14	1.1550	0.0097	0.0041	0.355

$$\frac{SO_4^{=h}}{BaSO_4} = X \text{ Sample (gm)} \left(\frac{98.06}{233.40} \right) = .421$$

Final Sulfate Determinations (Anaerobic, Ethion)

Sample	gm Sample	gm $BaSO_4$	gm $SO_4^=$	gm $SO_4^=$ / 100 gm Sample (dry) (per cent)
1	17.4305	0.3230	0.1362	.783
2	16.1900	0.0212	0.0087	.054
3	1.8122	0.1217	0.0502	2.78
4	14.6486	0.0956	0.0403	.276
5	10.6854	0.0407	0.0172	.162
6[i]				
7	21.1016	0.0947	0.0398	.188
8	11.1385	0.0969	0.0408	.366
9	1.1611	0.0529	0.0223	2.10
10	5.9786	0.0275	0.0116	.194
11	0.6781	0.0347	0.0147	2.17
	5.4030	0.0813	0.0343	.635
12	4.5900	0.0359	0.0152	.332
13	10.5729	0.1153	0.0486	.460
14	0.7643	0.0679	0.0287	3.77

[i] crucible broken.

Final Sulfate Determination (Anaerobic, No Excision)

Sample	gm Sample	gm $BaSO_4$	gm $SO_4^=$	gm $SO_4^=$ / 100 gm Sample (dry) (per cent)
1	10.5564	0.0609	0.0256	0.243
2	3.3251	0.0176	0.0074	0.222
3	3.2573	0.2100	0.0886	2.72
4	16.1089	0.0605	0.0254	0.158
5	13.0475	0.0359	0.0151	0.116
6	10.7413	0.0845	0.0356	0.332
7	9.5301	0.0501	0.0213	0.223
8	11.1170	0.0580	0.0244	0.219
9	3.2618	0.1180	0.0497	1.52
10	6.2708	0.0185	0.0078	0.125
11	6.7946	0.0811	0.0341	0.502
12	5.9266	0.0289	0.0122	0.206
13	4.1041	0.0321	0.0135	0.329
14	0.5700	0.1690	0.0713	1.25

Final Sulfate Determinations (Aerobic, Ethion)

Sample	gm Sample	gm $BaSO_4$	gm $SO_4^=$	gm $SO_4^=$ / 100 gm Sample (dry) (per cent)
1	15.760	0.1155	0.0470	0.298
2	12.970	0.0700	0.0616	0.476
3	2.102	0.0145	0.0061	0.389
	10.871	0.0374	0.0157	0.145
4	11.969	0.0571	0.0250	0.214
5	5.596	0.0367	0.0154	0.276
6	5.880	0.0162	0.0068	0.116
7	7.679	0.0280	0.0118	0.154
8	9.884 [j]			
9	1.356	0.0761	0.0322	2.37
10	7.379	0.0252	0.0107	0.146
11	2.410	0.0487	0.0205	0.853
12	7.028	0.0173	0.0073	0.104
	7.945	0.0235	0.0098	0.124
13	2.251			
14	0.476	0.0438	0.0185	3.87

[j] crucible broken.

Final Sulfate Determinations (Aerobic, No Ebullition)

Sample	gm Sample	gm $BaSO_4$	gm $SO_4^=$	gm $SO_4^=$ / 100 gm Sample (dry) (per cent)
1	12.7059	0.1076	0.0454	0.357
2	10.7109	0.0148	0.0063	0.0588
3	8.1658	0.0221	0.0093	0.0114
4	10.6254	0.0223	0.0094	0.089
5	6.0493	0.0121	0.0051	0.0843
6	9.3601	0.0717	0.0303	0.324
7	9.4254	0.0470	0.0197	0.208
8	4.2722	0.0421	0.0178	0.417
9	1.6784	0.0744	0.0314	1.87
10	5.6059	0.0434	0.0183	0.326
11	1.7329	0.0747	0.0315	1.82
12	9.8000	0.0425	0.0179	0.183
	9.4271	0.0548	0.0231	0.245
13	6.1625	0.0487	0.0215	0.350
	4.6916	0.0186	0.0078	0.167
14	0.3875	0.0685	0.0289	7.47

Comparison of FeS Production - Samples 1- 14

	FeS Produced			
	Aerobic [k]		Anaerobic [k]	
Sample No.	Ethion	No Ethion	Ethion	No Ethion
2			+	
8			+	
9			+	
13	+			
14	+			

All other samples were negative. The culture was nutrient agar with iron wire. Ethion was added to the test tubes; no Ethion was added to the control tubes.

[k] In sediments

Aerobic Ethion Added to Sediment

Sample	Thioglycollate	Agar Stab					Agar Plates			
		Cloudy	FeS	Surface White	Surface Yellow	Liquified	Microscopic discrete	Microscopic filmy	Microscopic gm pos.	Microscopic gm neg.
1		-	-	- sparce	-	-	-	-		
2		-	-	+	-	-	-	+		rods
3			+					+		rods
4				+			-	-		
5		+	-	-	-	-	-	-		
6			+					+		rods
7		+	-	-	-	-	+		+	
8		+	-	-	-	-	-	-		ellipse
9					+					rods
10		-	-	-	-	-				
11		+	+	-	-	-	+	+	rods	rods
12				+			+			rods
13			+					+		rods
14			+					+	rods	rods
15		-	-	-	-	-		+	rods	rods

Aerobic No Ethion Added to Sediment

Sample	Thioglycollate	Agar Stab					Agar Plates			
		Cloudy	FeS	Surface White	Surface Yellow	Liquified	Microscopic discrete	Microscopic filmy	Microscopic gm pos.	Microscopic gm neg.
1			+				-	-		
2			+			+		+		rods
3			+				-	-		
4			+				-	-		
5				+			+	+	cocci	
6			discolored				-	-		
7			discolored						cocci	
8			+			+		+		rods
9				+			-	-		
10				+				+	rods	
11			+					+		ellipse
12			+	+			-	-		
13				+			-	-		
14									globular +	rods
15				-						

Anaerobic Ethion Added to Sediment

Sample	Thioglycollate	Agar Stab					Agar Plates			
		Cloudy	FeS	Surface White	Surface Yellow	Liquified	Microscopic Discrete	Microscopic filmy	Microscopic gm pos.	Microscopic gm neg.
1				+				+		rods
2			+	+			+	+	rods	rods
3				+				+	ellipse	rods
4		+					-	-	-	-
5		+					+		+ rods ellipse	
6			+	+		+	+	+	rods	rods
7			+			+	-	-	-	-
8			++			+	+		ellipse	rods
9			+				+	+	ellipse	rods
10				+	+			+		rods
11			+	+			+	+	rods	rods
12				+	+		+		+ rods	few rods
13			+		+		yel. globules			rods
14			+				-	-	-	-

Anaerobic No Ethion Added to Sediment

Sample	Thioglycollate	Agar Stab				Agar Plates			
		Cloudy	FeS	Surface Colored	Liquified	Microscopic		Microscopic	
						Discrete	Filmy	gm pos.	gm neg.
1		-	-	-	-	-	-		
2		-	-	-	-	-	-		
3			+	+			+		rods
4			+				+		rods
5				+		+		+	
6			+	+	+	Splotchy		ellipse	
7			+			+	+	rods	
8			+	+	+	+	+	rods	rods
9				+		+		spores rods	
10				+			+		rods
11			+	yel.		raised+	+	ellipse	rods
12				+		raised+	+	rods	rods
13			+	+	+			rods	
14			+			+		rods	

Bacteriological Data - Alternate Procedure

FeS Production at 37° for 24 Hours

	Aerobic[1]		Anaerobic[1]	
Sample	Ethion	No Ethion	Ethion	No Ethion
1	-	-	-	-
2	+	-	-	-
3	-	-	-	-
4	-	-	-	-
5	-	-	-	-
6	-	-	-	-
7	-	-	-	-
8	-	-	-	-
9	+	-	-	-
10	-	-	-	-
11	-	-	-	-
12	-	-	-	-
13	+	-	+	-
14	-	-	+	-

[1] Refers to status of the enrichment culture.

C. Procedures

1. Outline of Processes

a. Sample Preparation.

All sediment samples were prepared for chemical analytical determinations according to the following procedure:

1) Samples were centrifuged at 5000 rpm for 20 minutes.
2) Weighed centrifuged samples to which 2.0 ml of 6N NaOH was added, were dried at 110°C for 24 hours.
3) Cooled dried samples were ground with a mortar and pestle.
4) Approximately 10 gram samples were then accurately weighed and used for sulfate and sulfide determination.

b. Water Determination.

All samples were analyzed for water content in order to provide a base line for calculations:

1) Samples were centrifuged for 20 minutes at 5000 rpm.
2) Weighed amounts were transferred to weighed evaporating dishes; Dishes plus samples were weighed.
3) Samples were dried 24 hours in an air oven at 110°C.
4) Samples plus dishes were reweighed.
5) Per cent H_2O was calculated: Per cent $H_2O = 100 \left(\frac{C-B}{A} \right)$

c. Ethion Extraction.

Prior to analysis, samples to which pesticide had been added were extracted to eliminate Ethion

1) Sediment samples were transferred to 100 ml. graduated cylinders
2) Twenty mls of pesticide grade hexane were added to the cylinder.
3) The samples were shaken with the hexane for one minute and then allowed to settle.
4) The hexane soluble Ethion was then drawn off the top with a pipet.
5) The extraction was then repeated and the hexane-Ethion mixture discarded.

d. Sulfide Determination.

The method used to determine sulfide in the sediment samples was essentially that described in Standard Methods for the Examination of Water and Waste Water; 12th Edition; 1965, Page 426. The procedure was modified to allow a more accurate determination of low sulfide concentrations (solution concentrations were decreased).

1) Reagents
   a) N_2 generator
   b) Zinc acetate solution 2N. Dissolved 220 g $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ in 870 ml of water.

c Concentrated hydrochloric acid

d) Iodine solution, 0.01 N - dissolved 12-15 grams of potassium iodide, KI, in a little distilled water and added 1.270 g. iodine. After the iodine had dissolved diluted it to 1 liter and standardized against 0.01 N sodium thiosulfate, using a starch indicator.

e) Sodium thiosulfate, 0.01 N - Dissolved 2.48 grams $Na_2S_2O_3 \cdot 5H_2O$ in boiled and cooled distilled water and diluted to one liter. Prepared 0.01 N $S_2O_3^{=}$, could also have been used.

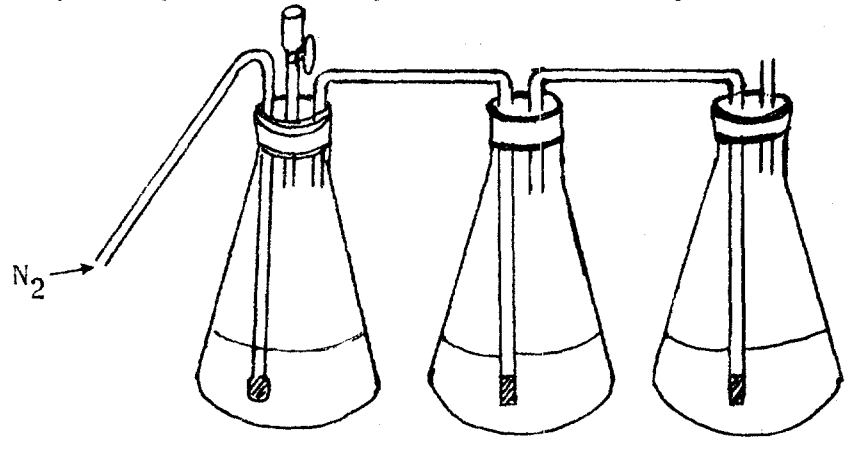
f) Starch Solution - Prepared an emulsion of 5 grams of soluble starch in distilled water. Poured this emulsion into 1 liter of boiling water. Cooled.

2) Equipment

a) Connected 3 - 250 ml flasks in series as per the following drawing.

b) Set up the first flask with a fritted gas dispersion tube.

c) Connected the three flasks so N_2 could be bubbled into the first cylinder and would carry vapor over into each subsequent cylinder at a point below the liquid level.



3) Procedure

a) To the first flask, added a weighed prepared sediment sample plus 100 ml of distilled water.

b) Added 5 ml of zinc acetate solution and 100 ml distilled water to each of the other two flasks.

c) Connected the three flasks and purge with nitrogen.

d) Without disturbing the closed system, added 10 ml concentrated HCl to the first flask.

e) Bubbled N_2 through the system for one hour.

f) Combined both flasks[m] and added iodine solution in excess of the amount necessary to react with the collected sulfide.

g) Added 10 ml concentrated HCl, stoppered and mixed well.

h) Back titrated the excess iodine with the 0.01N $Na_2S_2O_3$, using a starch indicator.

i) Ran a blank on the reagents.

4) Calculation

One ml of I_2 solution = 0.16 mg $S^=$. The differences in the mls of I_2 and $S_2O_3^=$ used in the titration were the mls used by the sample. Therefore, the mg $S^=$ per sample was equal to

$$0.16 \text{ mg } S^= / \text{ml} \left(\text{ml } I_2 - \text{ml } S_2O_3^= \right)$$

---

[m] Flask number 2 and 3.

e. Sulfate Determination.

Sulfate was determined gravimetrically by precipitating the sulfate as barium sulfate filtering out the precipitate and weighing it. The method is described in Soil Mechanics for Road Engineers:[14]

1) Reagents

a) Concentrated hydrochloric acid

b) 5 per cent by weight solution of barium chlorine ($BaCl_2$)

2) Equipment

a) Electric muffle furnace

b) Analytical balance

c) Bunsen burner

d) Porcelain crucibles

e) Miscellaneous glassware

f) Whatman No. 44 filter paper

3) Procedure

a) Weighed amounts of prepared sediment samples[n] were transferred to Erlenmeyer flasks.

b) Approximately 150 ml of H_2O was added and then samples were shaken for one hour.

c) Samples were allowed to set for twenty-four hours.

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[n] Refers to procedure a, page

d) The soil suspensions were then filtered using Whatman 44 filter paper.[o]

e) The residues were washed with twenty-five mls of H_2O.

f) The extract was acidified with a few drops of HCl and brought to boiling.

g) Barium chloride was slowly added to the hot liquid until no further precipitation occurred.

h) The precipitate was filtered using Whatman 44 filter paper and washed until a negative chloride test[p] was given with silver nitrate.

i) The filter paper was then folded into a crucible which had previously been brought to constant weight.[q]

j) The crucible was warmed to char the filter paper.

k) The crucible was then placed in a muffle furnace at 700°C for 10 hours.

l) The crucibles were cooled and weighed.

4) Calculations

a) Weight $BaSO_4$ equals weight of filled crucible minus weight of empty crucible.

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[o] A high retentive, low ash filter paper.

[p] A negative chloride test gave no white precipitate when one drop of silver nitrate ($AgNO_3$) was added to the wash water.

[q] Process of ashing at 700° for 5 hrs., weighing and comparing weight with previous weighing.

$$\text{b)}\quad \frac{\text{gm } SO_4^{=}}{100 \text{ gm}} = \frac{\text{gm precipitate}\left(\frac{98.06}{233.4}\right)(10^{})}{\text{gm sample}}$$

$$= \frac{\text{gm precipitate } (0.421)(100)}{\text{gm sample}}$$

f. Bacteriological Procedures.

1) Enrichment Cultures - anaerobic and aerobic Enrichment culture techniques were applied to the samples.

a) Centrifuged sediment samples were divided into four parts, two parts were placed into two petri dishes and the other two portions were placed into two jars with screw cap lids.

b) Two mls of Ethion were added to one of the petri dishes and to one of the jars.

c) All samples were covered with supernatant H_2O from the centrifuging process. When there was not sufficient supernatant sterile distilled water was used.

d) The two jars were equipped with a lighted candle. The jar was shut tightly and the candle was checked to ensure that it did not continue to burn.

e) Samples were allowed to stand at room temperature for twenty days. They were kept in a storage area where light could enter.

f) When liquid evaporated from the aerobic samples in the petri dishes, sterile distilled water was added to keep the samples moist.

2) Culture Media - composition per liter

a) Thioglycollate medium (fluid)

Bacto-casitone 15 g

Bacto-Yeast Extract 5 g

Bacto-Dextrose 5.5 g

Sodium chloride 2.5 g

L-cystine 0.5 g

Sodium Thioglycollate 0.5 g

Bacto-agar 0.75 g

Resazurin 0.001 g

b) Agar Slants

Bacto beef extract 3 g

Bacto peptone 5 g

Bacto agar 15 g

To each tube was added one inch of iron wire and 1 ml of Ethion (equivalent to .0033 moles).

c) Agar Plates

Bacto beef extract 3 g

Bacto peptone 5 g

Bacto agar 15 g

3) Procedure

a) Thioglycollate media was inoculated with supernatant from enrichment cultures of all samples (2 tubes/sample). Inoculated tubes were incubated for one week at 37°C.

b) After the one week period, agar slants were prepared with .01M Na_2SO_4 and a one half inch piece of iron wire. Iron wire had been cleaned with diluted HCl. Stabs were made from all thioglycollate tubes. Stabs were incubated at 37°C for 48 hours.

c) After the 48 hr. incubation period, agar plates were streaked with samples from each slant, which had a positive FeS test. These plates were then kept anaerobically at 35°C for 48 hrs.

d) Gram stains were made from the agar streak.

e) Data was reviewed for cultures which produced FeS with Ethion but did not produce it without Ethion.

f) Colonies from these plates were inoculated into agar slants with iron wires. Those cultures which had received Ethion in the original sediment enrichment cultures were inoculated into slants with 1 ml of Ethion. The control samples were inoculated into tubes with no Ethion.

g) FeS production was observed.

h) Gram stains were made.

4) Procedure Revision

A check of the bacteriological procedures was run.

a) Cultures from the original thioglycolate tubes were inoculated into fresh thioglycolate media. Samples previously treated with Ethion were inoculated into tubes to which Ethion had been added. Control samples received no Ethion.

b) After forty-eight hours of incubation at 37°C, organisms were inoculated into stabs, again maintaining controls with no Ethion.

c) Cultures were incubated at 37°C for twenty-four hours and reviewed for FeS production.

5) Ethion dosage which was added to each agar stab was calculated on a sulfur per ml. basis.

Density = 1.22 g/ml

Molecular weight = 384

$$\text{grams S per ml} = \frac{128}{384}(1.22)$$

$$= 0.406 \text{ g Sulfur/ml}$$

6) Ethion Sterilization

Prior to addition to the cultures, Ethion was sterilized by passing through a 0.45 micron millipore filter. Millipore equipment was sterilized via autoclaving prior to usage.

2. Verification of Analytical Procedures

a) Sulfide Analysis

The accuracy of the procedure for the determination of sulfide was verified by the usage of known sulfide concentrations. The recovery of the system was also determined. A solution of sodium sulfide ($Na_2S \cdot 9H_2O$) was accurately prepared to contain 0.571 mg $S^{=}$ per ml of solution.

1) Trial runs were made by adding known amounts of sulfide ion to the system and titrating them. Results were:

Trial	mg $S^{=}$ Added	mg$S^{=}$ Determined	Per cent accuracy
1	0.571	0.550	96.6 per cent
2	0.290	0.290	100.0
3	0.294	0.288	98.0

2) Known amounts of sulfide ion were then added to a pre-

b) Sulfate Analysis

Precision of the procedure was determined by analyzing duplicate samples. Results were (g $SO_4^=$/ 1 g sample) :

Sample	Trial 1	Trial 2	Trial 3	Average
12 AE[r]	.0024	.0029		.0027
12 AN[s]	.0043	.0058	.0042	.0048
2 AE	.0014	.0019		.0016

c) Sulfide Blank

1) A reagent blank was run daily on chemicals used in the sulfide analysis.

2) A check was performed on possible sulfide contamination by incomplete Ethion extraction. One half ml of Ethion produced less than 0.016 mg of $S^=$. Two mls of Ethion were added to samples and extracted. Since 0.016 mg was produced by one half ml, it was determined that error due to insufficient extraction was insignificant in the deter mination.

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[r] Aerobic

[s] Anaerobic

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Section II, Article 7

The Utilization of Sulfur Compounds by Indigenous Halophiles in the Indian-Banana River

Wendell L. Blevins

1974

THE UTILIZATION OF SULFUR COMPOUNDS BY INDIGENOUS HALOPHILES IN THE INDIAN-BANANA RIVER LAGOONAL SYSTEM

by

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Abstract

Enrichment culture technique was used to study the utilization of sulfur compounds by mixed bacterial flora in the Indian-Banana River lagoonal system. A pathway separate from the traditional oxidative sulfur cycle was observed. An organic, iodometrically titratable material, was found to be produced in large quantities by the bacterial population upon enrichment. Partial identification of this material, and its possible function are presented.

Acknowledgements

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The author gratefully acknowledges the assistance of Dr. Thomas A. Nevin in the preparation of this thesis. Appreciation is also expressed to Dr. J. Lasater and Dr. R. Jones for their assistance in preparing this work. A special thanks is expressed to P.G. Dallemagne at Jensen Beach, and to Jim Jones, Tom Shell, and Bill Carmen at the Kennedy Space Center for their assistance in analytical instrumentation.

Introduction

Sulfur is a structural component of all complete proteins, and is therefore an element essential to all life on this planet. It also serves as a key element in many biochemical reactions because of its bond versatility. It has the capacity to form multiple bonds, thus contributing to the thermodynamics of energy transfer and storage. The ability to form up to six covalent bonds greatly increases the variety and extent of energy changes which may occur. It allows a wide range of possibilities for resonance among precursors and products of exchange reactions. The relatively wide spacing and weakness of sulfide bonds, together with the tendency to add an electron pair in the unoccupied third orbital of each atom contributes to the reactivity of its compounds with other molecules thus promoting electron exchange reactions (Wald, 1969). These properties of sulfur are readily summarized in the concept of a natural cycle.

The sulfur cycle aids in explaining the mineralization of organic materials, as well as the synthesis of the numerous intermediate compounds which enable recycling throughout the marine, aquatic, and terrestrial systems. Included in it are many biochemical reactions involving a variety of organisms. The bacteria mediated reactions of the cycle are well known. The most important of these are shown in Figure 1 (Peck, 1962).

Sulfur Cycle

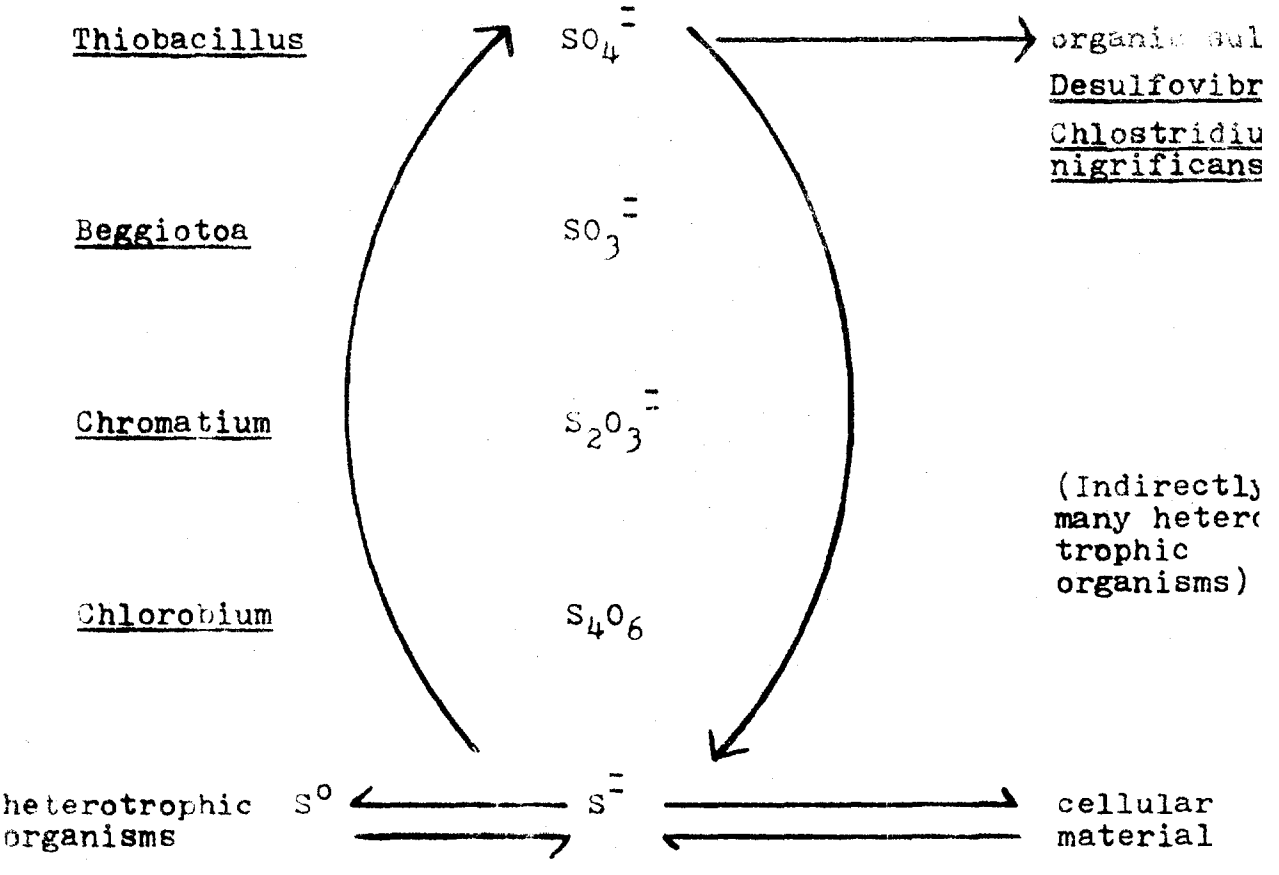
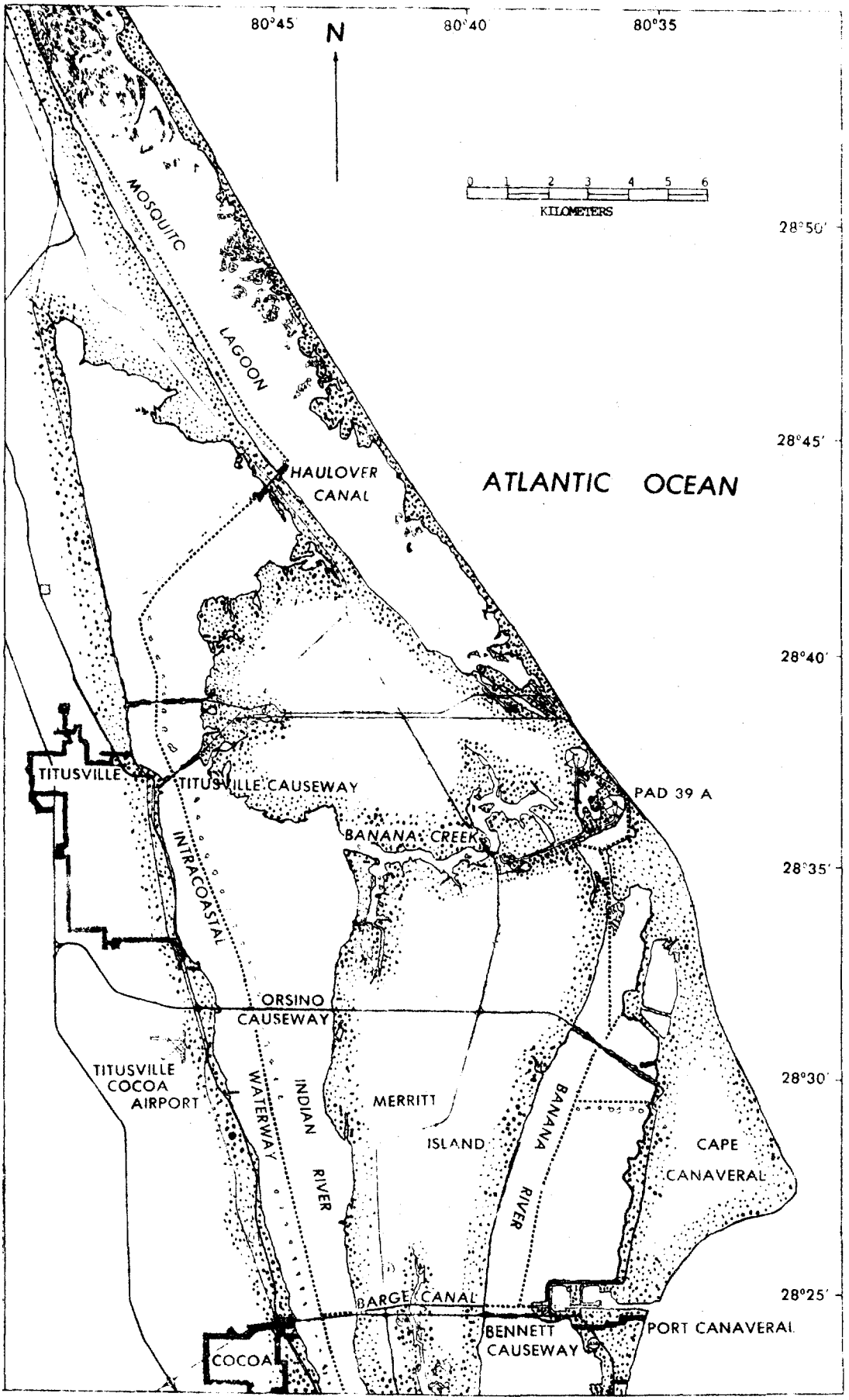


Figure 1. Simplified diagram of the sulfur cycle. The major microorganisms that participate in the reduction of sulfur are listed on the right hand side; those that take part in the oxidation of elemental sulfur and sulfide to sulfate are listed on the left (Peck, 1962).

Two phases of the sulfur cycle can be discerned; a reductive phase in which sulfate is reduced to sulfide, and its oxidative counterpart in which sulfide is oxidized to sulfate. Many of the biochemical reactions and organisms involved in this oxidative phase are not fully understood, and an acceptable intermediate has not been clearly identified.

Experimentation was conducted in Banana Creek, (Figure 2) which is an estuarine sub-system that drains the northern part of Merritt Island and empties into the Indian River. The presence of beds of sulfide muds among the sediments underlying the waters of this saline lagoon was established by Akimoto (1971),and extended to Banana Creek by Beazley (1974). Beazley demonstrated a relationship between the mud beds, transport of nutrients and certain anaerobic bacteria. In the present work, preliminary observations indicated the disappearance of hydrogen sulfide from the water column just above the muds, but no measurable increase in sulfur oxides could be demonstrated. The probable fate of the hydrogen sulfide produced in the muds is the subject of this thesis.

FIGURE 2


80°45
N
80°40
80°35
0 1 2 3 4 5 6
KILOMETERS
28°50'
28°45'
28°40'
28°35'
28°30'
28°25'
MOSQUITO LAGOON
HAULOVER CANAL
ATLANTIC OCEAN
TITUSVILLE
TITUSVILLE CAUSEWAY
BANANA CREEK
PAD 39 A
INTRACOASTAL WATERWAY
ORSINO CAUSEWAY
TITUSVILLE COCOA AIRPORT
INDIAN RIVER
MERRITT ISLAND
BANANA RIVER
CAPE CANAVERAL
BARGE CANAL
BENNETT CAUSEWAY
PORT CANAVERAL
COCOA

Methods

The primary method used for eliciting bacterial response was the well recognized enrichment culture technique (Pelczar, 1957). In practice lagoonal water was collected in sterile 500 ml glass bottles. Aliquots of water samples were transferred to sterile 125 ml Nalgene ® bottles containing an enrichment of one ml of nutrient broth (Difco) to each 10 ml of water sample. The medium was prepared to label strength with lagoonal water and sterilized before use.

Parallel enrichment cultures were incubated at 37°C for 48 hours under both aerobic and anaerobic conditions. A disposable gas pack (BBL) equipped with a hydrogen and carbon dioxide generator envelope was used to achieve anaerobic conditions.

These experiments were designed so that initial (pre-incubation), final (post-incubation), and control bottles of enriched lagoonal water were included. The control consisted of water enriched after filter sterilization using a pre-sterilized Millipore ® apparatus containing a 0.4μ membrane filter (Millipore Corp.). The control in all cases was incubated at the same temperature as the final bottle. Precent transmittance, sulfide, sulfite, and sulfate ion concentrations were determined both initially and finally on all samples including the control.

Optical measurements were made using a Bausch-Lomb Spectronic 20 set at 460μ after which the cell crop was harvested by centrifugation (International Centrifuge Model HT with head number 856) at 9,000 rpm for five to six minutes.

Sulfide as hydrogen sulfide was determined by iodometric titration of the sample after acid liberated hydrogen sulfide gas was trapped in cadmium chloride at pH 1-2 (Akimoto, 1971). Sulfite ion was also determined iodometrically in an acidified sample (Standard Methods, 1971) and corrected for sulfide concentration by difference. Sulfate ions were determined by barium precipitation (Standard Methods, 1971). A photometric standard curve for a range of 0 to 3 g/l was used for turbidimetric sulfate ion determination.

Qualitative spot tests used regularly were: the malachite green test for sulfite ions (sulfite decolorizes malachite green); the mercuric chloride and litmus paper test for thiosulfate (two percent mercuric chloride added to a sample of thiosulfate followed by a small amount of KCL turns blue litmus red); and, the iodine-azide test for reduced sulfur (Feigl, 1958).

A test for total thiols was performed with an alkaline solution of cupric chloride and hydroxylamine hydrochloride (Feigl and Anger, 1966). A test for determination of primary and secondary thiols (Feigl and Anger,

1966) was also performed. The sample was added to concentrated ammonia and heated in boiling water. A positive test was indicated by blackening of lead acetate paper on the mouth of the sample tube.

Ether extractions were performed by shaking approximately 100 ml of ether with 300 ml of "cell free" culture medium vigorously for about 10 minutes. The water layer was then decanted and the ether layer transfered into a clean beaker. The ether was allowed to evaporate, leaving a residue in a small amount of water. This material was treated with approximately 2.5 ml of a 50% (v/v) solution of mercuric nitrate (Karchmer, 1966; Rayland and Tamele, 1970). A yellow precipitate resulted, which was washed twice with 25 ml aliquots of distilled water and desiccated overnight. The resulting powder was analyzed with an infrared spectrophotometer (Perkin-Elmer). Additional instrumentation methods for identification of the thiol were conducted by the micro-chemistry laboratory at the Kennedy Space Center.

Results

The initial experiments employed samples enriched with nutrient borth (Difco), which were incubated aerobically and anaerobically (BBL disposable gas pack) at 37°C, 23°C, and 9°C to detect variations in hydrogen sulfide production. Hydrogen sulfide was determined by the blackening of lead acetate paper at the mouth of the sample test tubes (Pelczar, 1957). Hydrogen sulfide production was noted in samples incubated at 37°C whether aerobically or anaerobically. Hydrogen sulfide production at 23°C under aerobic conditions was slight, whereas under anaerobic conditions it was quite strong. No growth occured at 9°C, indicating that lagoonal psychrophilic bacteria had no definable role in hydrogen sulfide production in these experiments. (See Table VI in the appendix for raw data). It is acknowledged that the enrichmen used may not have supported growth of some indigenous organisms

Attention was then directed toward the establishment of baseline values for sulfide, sulfite, and sulfate ions in enriched cultures before and after incubation under aerobic and anaerobic conditions. These values are presented in Table I.

Remarkably large amounts of sulfate disappeared under aerobic conditions, and to a lesser extent under anaerobic conditions. This probably represents the utilization of sulfate as a hydrogen acceptor by various members of the mixed flora. Sulfate production was noted

Table I

Changes in sulfide, sulfite, and sulfate (mg/l) levels in samples of lagoonal water enriched with nutrient broth (Difco) after 48 hours incubation at 37°C under aerobic and anaerobic conditions. (See Table VII in appendix for raw data)

	$S^{=}$	$SO_3^{=}$	$SO_4^{=}$
Aerobic			
Surface Water	+0.004	+5.00	-440
Bottom Water	-0.016	+7.25	-540
Anaerobic			
Surface Water	+0.02	+16.75	-350
Bottom Water	+0.002	+18.30	-240

only when inorganic phosphate (KH_2PO_4) was added to 48 hour cultures and incubated for twelve additional hours. The addition of 40 mg/l inorganic phosphate resulted in an increase of 100 mg/l of sulfate ion.

Sulfide production was not greatly evident under aerobic conditions, but did occur under anaerobic conditions although the amounts recovered were not large. These data, in addition to the results of the preliminary experiments do, in fact establish that the production of hydrogen sulfide under aerobic conditions continues to be unusual. Sulfide ions, however, may be incorporated into other sulfur compounds.

The amounts of iodometrically titratable materials, which were then thought to be sulfite, increased markedly under both conditions of incubation, and were three times greater in surface water samples incubated under anaerobic conditions than in those incubated under aerobic conditions. The bottom water samples (collected three to six inches above the sediments) yielded similar differences. Both yielded greater amounts than did the surface water samples. The anaerobic culture, however, yielded about 2.5 times more than the aerobic culture. More concise identification of the iodometrically titratable material was then undertaken.

A suspension of bacterial cells was obtained by enriching several liters of lagoonal water, incubating

anaerobically for 48 hours, then harvesting by centrifugation. The cells were washed once in sterile lagoonal water, then suspended in 50 ml thereof. The suspension was divided between two dialysis bags, one of which was then heated to 100°C for 15 minutes to kill the cells. Each bag was then placed into a container of sterile lagoonal water to which a measured amount of sodium sulfite had been added. Sulfite and sulfate levels were determined immediately after introduction of the dialysis bags, and again after four hours of incubation at 37°C. Thereupon the bags were opened, the cells separated by centrifugation and sulfate and sulfite levels determined.

The initial level of sulfate 2.5 g/l was about that which is usually encountered in lagoonal water samples throughout the Indian-Banana River lagoonal system. About the same amount of sulfate disappeared from both containers, thus in this experiment no immediately useful purposes were served by this ion. Sulfite ions, however, migrated into the dialysis bags and seemed to be retained. The calculations, however, indicated much greater amounts of sulfite in the bag containing live cells; an increase of 6.9 mg/l over that which could be explained by the amount added. This value was established by adding the final sulfite concentration in the tank and the sac, and from this value subtracting the concentration of the tank initially. The resulting figure represented the

amount of sulfite produced. A small increase is also evident in the bag containing the killed cells, but may only reflect a residue of incompletely deactivated enzyems. These data are summarized in Table II.

These data support the possibility that the substance formed was not sulfite. Consequently qualitative tests were carried out in order to gain some idea of the material(s) nature. The iodine-azide reaction for sulfur present as sulfhydryl, disulfide or thiosulfate was positive. The qualitative tests for sulfide, metabisulfite, bisulfite and thiosulfate were negative. Since is was reasonably evident that the material was not a simple sulfur compound, the probability of an organic compound was considered. The iodine-azide test was also positive when cystine and cysteine were studied, therefore these amino acids were used as additions to enrichment cultures. Methionine was also used as a matter of interest. The results indicated that these materials were used by the mixed bacterial flora to produce additional iodometrically titratable material. The data are presented in Table III.

Since it had been noted that hydrogen sulfide disappeared from the water a few inches above the sulfide muds in the lagoon, sodium sulfide was added with nutrient broth enrichment, and also served as a precursor for the iodometrically titratable material. These data are

Table II

Changes in sulfite (mg/l) levels as effected by "resting" bacterial suspensions* in dialysis sacs. Incubated for four hours at 37°C.

	Initial (tank)	Final tank	Final sac	net change in sac
Live Cells				
$SO_3^=$	7.50	2.20	12.20	+6.90**
Killed Cells				
$SO_3^=$	9.50	3.80	6.70	+1.00

* in sterile river water with added Na_2SO_3

** final(tank) + final(sac) - initial(tank)

Table III

Increase in iodometrically titratable material upon addition of sulfur containing compounds (mg/l).

amino acid enrichments*	initial	final	net increase**
cysteine	11.0	23.0	7.0
cystine	11.0	21.0	6.0
methionine	11.0	24.0	8.0
control	11.0	16.0	

* The nutrients were added to cultures that had been incubated at 37°C for 48 hours. The same incubation conditions were maintained for another 12 hours. At this time the experiment was terminated.

** net increase = final - control final

Table IV

inorganic enrichment*	initial	final	net increase
control	2.0	3.9	1.9
Na_2S and nutrient broth	2.0	19.7	15.8
nutrient broth	1.7	12.0	8.1
Na_2S by difference			7.7

* The inorganic enrichments were added to cultures initially and incubated for 48 hours at 37°C.

summarized in Table IV.

The amino acids were used to increase the amount of iodometrically titratable material produced, therefore it seemed unlikely that these could also be the material(s) produced. Qualitative tests for other reactive compounds were then conducted, and were positive for primary and secondary thiols. In addition, amino acids are generally insoluble in ether, whereas thiols are soluble (Weast, 1973), thus ruling out cysteine as the thiol. A summary of the precursor compounds in thiol synthesis is presented in Figure 3.

Thin layer chromotography was used for further purification and identification of the thiol. Ether extraction followed by precipitation with mercuric nitrate yielded a material which could be partially identified by infrared analysis. An expanded infrared curve is presented as Figure 4. Strong peaks at 1600 cm^{-1} and 450 cm^{-1} indicated a benzene ring. Meta substitution on the ring is evidenced by peaks at 680 cm^{-1} and 450cm^{-1}. The -SH group is identified by weak peaks at 2550 cm^{-1} and 900 cm^{-1} as are $-CH_3-C$ and $-CH_2-$ groups by strong peaks at 2910 cm^{-1}, 2850 cm^{-1}, 1375 cm^{-1} and 1525 cm^{-1}. The significant groups on the scan are identified and presented in Table V as taken from Dyer (1965) with their ranges.

The data presented in Table V indicates that one of the following is the most probable structure of the thiol.

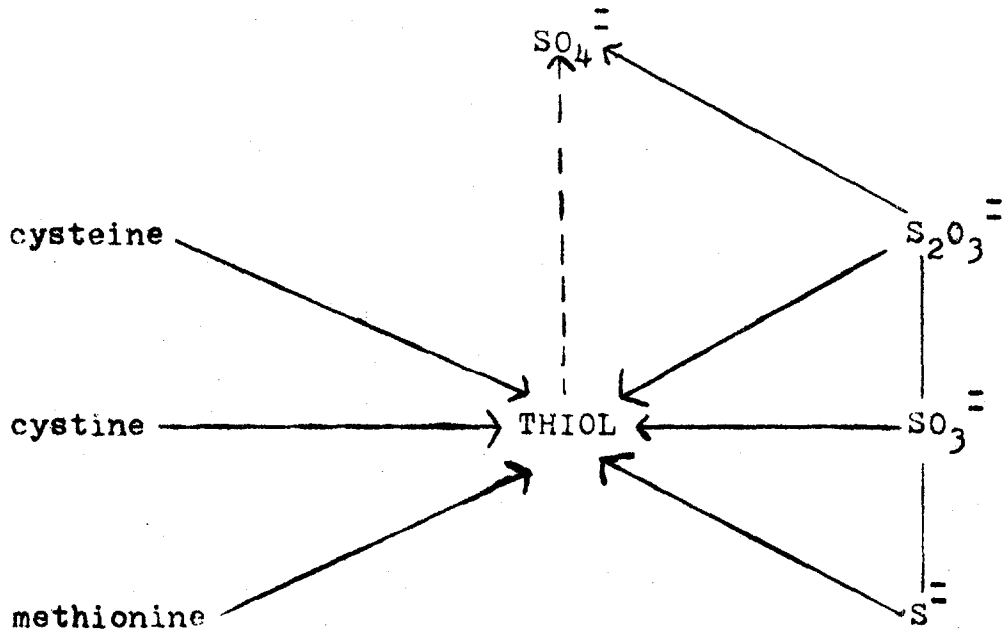


Figure 3. The compounds shown are known to be metabolized to the thiol. The oxidation of the thiol to sulfate is uncertain.

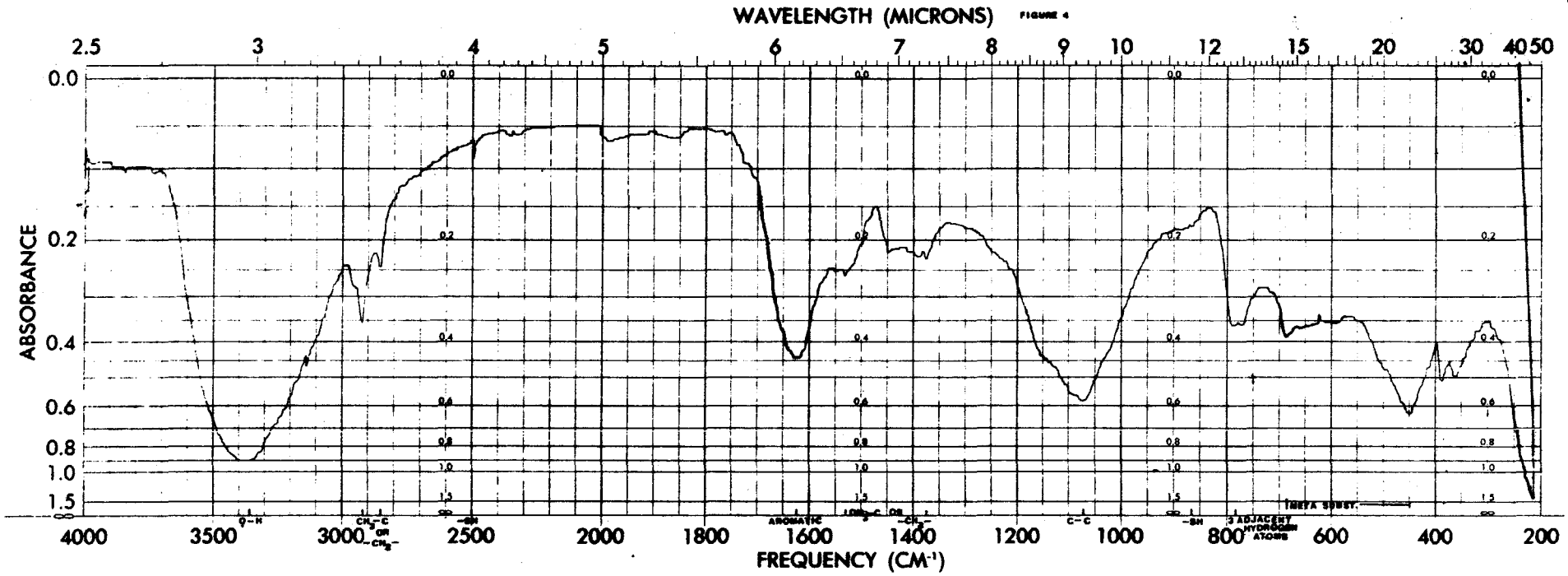
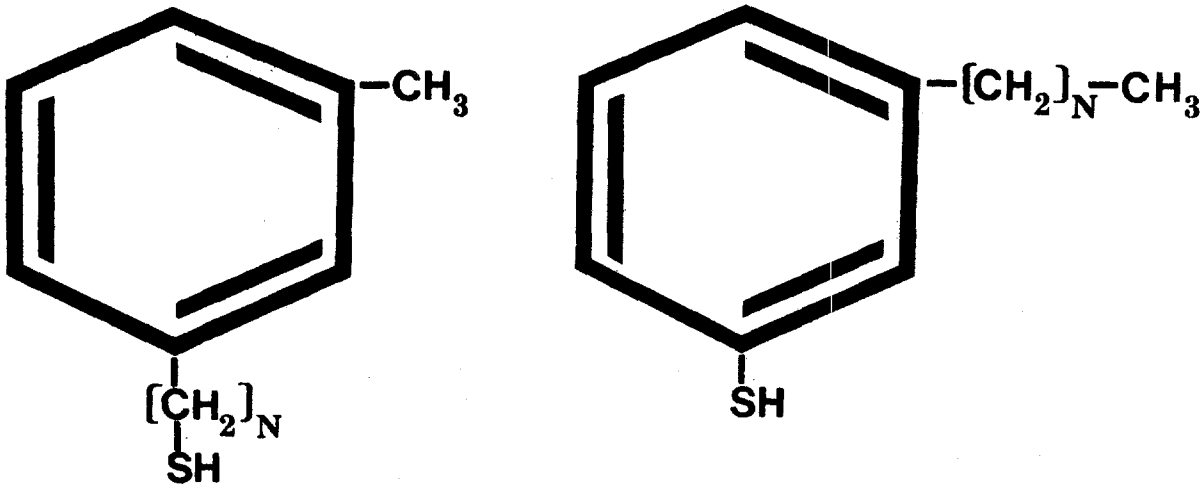
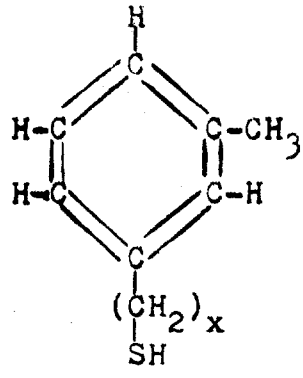

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
50
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)
AROMATIC
C-C
3 ADJACENT HYDROGEN ATOMS

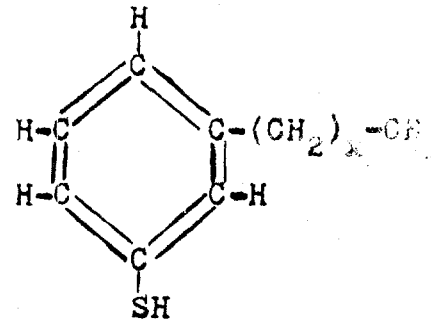
Table V

Group	range cm^{-1}	intensity
aromatic substitution:		
three adjacent hydrogen atoms	780	medium
-SH	2660-2550	weak
-SH	940-820	weak
<u>meta</u> substitution	740-680 and 500-400	weak weak
OH stretching	3400-3200	strong
aromatic	1600 and 1450	strong
C-C stretch	1200-800	strong
CH_3-C or -CH_2-	3000-2825 1400-1350 and 1490-1425	strong strong strong

(Dyer, 1965)


CH3
[CH2]N
SH
[CH2]N–CH3
SH





The scan indicates that a sulfhydryl and a methyl group are in the meta position with respect to each other on the benzene ring. The position of the methylene group(s) could not be established. It is most likely that these group(s) are located subterminally on either of the meta positioned side chains described since no third substitution is indicated.

Discussion

Previous authors (Peck, 1962; Jocelyn, 1972; Lees, 1960) have suggested that organic intermediates might occur in the oxidative sulfur cycle, but the identification and function of such intermediates has not been described. Various proposals have been made to explain how the intermediates are formed. Peck (1962) has suggested that at some oxidative level, the inorganic sulfur is incorporated into an organic molecule. Lees (1960), however, believes that an organic acceptor strips the -SH groups from the sulfur compounds in the medium. Voger's (1942) work, however indicated that Thiobacillus thiooxidans was synthesizing an organic storage product from CO_2 during sulfur oxidation. In the present work, an iodometrically titratable material was produced by a mixed bacterial flora which developed in enrichment cultures. Production of the material was augumented by the addition of any of a variety of sulfur compounds to the enrichment.

Identification of the compound(s) was undertaken by means of established methods. The "cell free" supernatant of freshly grown enrichments were known to react with iodine. The supernatant also produced (N_2) when mixed with iodine-azide reagent, a highly sensitive test for sulfur present as sulfhydryl, disulfide or thiosulfate groups (Feigl, 1958). Dithionate and polythionates do not react with iodine (Karchmer, 1970; Starkey, 1934) and could be ruled

out. The malachite green test for sulfite, bisulfite and metabisulfite groups,and the mercuric chloride test for thiosulfate (Feigl, 1958) were negative, ruling out these compounds as well.

Having eliminated the probable inorganic sulfur compounds as the iodometrically titratable material, attention was directed toward the more common organic sulfur compounds. Cystine and cysteine, both reacted in the iodine-azide test, but methionine did not. Thus suggesting either a sulfhydryl (-SH) group or a disulfide (-S-S) group.

Upon reaction with mercuric nitrate ($Hg(NO_3)_2$) (Karchmer, 1970), the bacterial product yielded a black precipitate. Upon testing cystine, cysteine, and methionine, only cysteine formed a similar black precipitate, increasing the probability of a thiol (-SH) group being the compound. Thiols are also known to react with iodine (Karchmer, 1966; Rayland and Tamele, 1970). Qualitative tests of the sample for a thiol group, using an alkaline solution of cupric chloride and hydroxylamine (Feigl and Anger, 1966) were strongly positive as was the alkaline decomposition test for primary and secondary thiols. Further analysis as indicated in the results, resulted in two possible structures of the compound. Either of the most probable chemical structures of the thiol is remarkably similar to

meta-thioanisole, and may eventually prove to be a close analogue. The benzene moiety in the structure may be derived from tannin and lignin which accmulates in the waters following plant tissue degradation. It is possible then, that thiol synthesis serves two purposes, a storage depot for reduced sulfur since the amount produced under anaerobic conditions is about double that found under aerobic conditions as well as a means of detoxifying the unusually bactericidal natural phenolics.

The probability of thiol formation in nature is furthered by the failure to demonstrate hydrogen sulfide in the water column, particularly above sulfide muds. Small amounts (1-2 mg/l) of thiol are, however, ordinarily encountered. Following storms and periods of high winds, the noticable stench particularly along the shore lines attest to the rapid increase in amount and subsequent volatilization of the thiol. The increase is best explained as a result of the turnover of the water column, disturbance of the bottom muds, and a concomitant increase in the precursor nutrients in the water, in effect an enrichment, the volatile thiol is then formed by bacterial action.

The thiol was produced whenever previously established inorganic compounds of the sulfur cycle (Peck, 1962) were added to enrichment cultures. The addition of sulfate, however, did not affect thiol production. It is a reason-

able assumption then, that sulfate ions are not significantly involved in this phase of the sulfur cycle. It is also reasonable to suggest that the reductions leading to thiol production are mediated by heterotrophic organisms since the methods used were selective for heterotrophs, whereas those leading to sulfate production are probably mediated by autotrophic organisms (Peck, 1962; Trudinger, 1965).

Evidence presented by Roy and Trudinger (1968) indicates that the metabolism of tetrathionate and trithionate, both aerobically and anaerobically by the facultative Thiobacillus neopolitanus, is very sensitive to thiol-binding reagents while the oxidation of these compounds is inhibited by 100% oxygen (Trudinger, 1964a+b). It was suggested that thiol groups are necessary for polythionate oxidation, and that reduced oxygen tension was associated with the generation of thiol groups. The works of several authors (Lees, 1960; Peck, 1962; Jocelyn, 1972; Trudinger, 1965) suggest that the oxidation of polythionates takes place at the outer surface of the cell membrane.

Jocelyn (1972) observed that oxidation of thiols can drive the phosphorylation of ADP to ATP when inorganic phosphate is supplied. In the present work also, the addition of phosphate to enrichment cultures yielded a significant increase (approximately 100 mg/l) in sulfate

ions, suggesting a reaction parallel to that described by Jocelyn. However, there was no concomitant change in thiol accumulation. Previous work (Peck, 1962) also demonstrated that sulfate can not be formed from thiosulfate or tetrathionate without added inorganic phosphate.

The phosphate requirement for sulfate production has been well established by several authors (Santer, 1959; Margulies and Santer, 1958; Trudinger, 1965) and appears to involve mainly the autotrophic genus Thiobacillus. Although most members of this genus are obligate aerobes several are faculative anaerobes and their combined activities may have been observed when sulfate synthesis was noted in the present report. Especially since Peck (1962) suggest that there is a gradation in the ability of various Thiobacillus species to oxidize reduced sulfur compounds; the facultative anaerobes being less efficient than the obligate aerobes.

The inorganic phosphate dependent reaction sequence described in thiobacilli involved the oxidation of thiosulfate or tetrathionate to sulfate (Santer et. al. 1960; Santer, 1959; Peck and Fisher, 1961). Tetrathionate may be an intermediate in the oxidation of thiosulfate. In the absence of inorganic phosphate, in cells suspended in tris (hydroxymethyl)aminomethane buffer (0.3 M., pH 7.2) oxygen consumption was approximately 70% of the theoretical amount required to oxidize thiosulfate to sulfate (Santer

et.al, 1960).

Phosphate catalyzes the oxidation of the thiosulfate to sulfate. In some cases arsenate has been substituted for phosphate (Santer et.al, 1960), and may also catalyze the reaction or it may replace the phosphate in intracellular compounds (Peck, 1962). It has been demonstrated (Margulies and Santer, 1958) that the oxidation of radioactive thiosulfate in the absence of phosphate yielded unidentified intermediates. This was confirmed by Santer (1959) who used phosphate labelled with radioactive oxygen (O^{18}). Upon incubating with thiosulfate the resulting sulfate contained the O^{18} labelled oxygen.

The literature presented in the discussion and the results described in the present work open several areas for further research. Some of these areas are:

1. Radioactive tracing of the oxidative sulfur cycle to confirm the reactions as they are presently understood.
2. Final isolation and identification of the thiol with complete instrumentation including nuclear magnetic resonance (NMR), gas-liquid chromotography (GLC), and liquid chromotography.
3. Final identification of the several bacterial species in the mixed cultures that are involved in the oxidative sulfur cycle.
4. Confirmation of the chemical linkage of -SH

groups to tannins and lignins as a detoxifying reaction.

5. Determine the fate of excess thiol in the water column.
6. A broad study of the occurrence, and concentration of thiols in the Indian-Banana River lagoonal system as related to changing meterological conditions.

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APPENDIX

Key for Appendix

ae ---------- aerobic

ana --------- anaerobic

grow -------- growth

sul --------- sulfide production

sur --------- surface

bot --------- bottom (3 to 6 inches form the bottom)

2/1/74

TABLE VI

sample site	depth	sulfate mg/l	Incubation at 37°C				Incubation at 23°C				Incubation at 9°C			
			ae		ana		ae		ana		ae		ana	
			grow	sul	grow	sul	grow	sul	grow	sul	grow	sul	grow	sul
1-26	surface	1880	+	+	+	+	+	+	+	+	-	-	-	-
1-26	bottom	1910	+	+	+	+	+	-	+	+	-	-	-	-
1-27	surface	1950	+	+	+	+	+	-	+	+	-	-	-	-
1-27	bottom	1950	+	+	+	+	+	+	+	+	-	-	-	-
1-28	surface	1900	+	+	+	+	+	-	+	+	-	-	-	-
1-28	bottom	1480	+	+	+	+	+	-	+	+	-	-	-	-
1-29	surface	1700	+	+	+	+	+	-	+	+	-	-	-	-
1-29	bottom	1400	+	+	+	+	+	-	+	+	-	-	-	-
BS8	surface	2150	+	+	+	+	+	+	+	+	-	-	-	-
BS8	bottom	2100	+	+	+	+	+	+	+	-	-	-	-	-

Table VII

SAMPLE SITE + date (all 1974)	DEPTH + aerobic or anaerobic	mg/l SULFIDE (S^{--})			mg/l SULFATE (SO_4)			mg/l THIOL			% TRANSMITTANCE		
		initial	final	control	initial	final	control	initial	final	control	initial	final	control
1-28 3/8	sur ae	0	0	-	1700	1950	1900	3.5	5.5	2.0	82.8	67.5	-
1-28 "	bot ae	0	0	-	1900	2050	1900	2.0	8.0	2.0	85.0	65.5	-
1-29 "	sur ae	.035	0	-	1650	1950	1950	1.0	6.5	1.0	85.0	69.0	-
1-29 "	bot ae	.112	0	-	1800	2000	1650	1.0	9.0	1.0	83.0	67.5	-
BS8 "	sur ae	.008	0	-	1400	2050	1600	1.5	9.0	1.0	88.5	77.0	-
BS8 "	bot ae	.104	0	-	1700	2050	1500	1.0	7.5	1.0	85.0	68.0	-
3-9 3/26	sur ae	.120	.024	-	2550	2000	3100	1.0	9.0	3.0	71.0	39.0	-
3-9 "	bot ae	.130	.004	-	2700	1550	2900	2.0	7.0	2.0	78.0	44.5	-
3-10 "	sur ae	.032	.024	-	2300	-	2700	1.0	4.0	2.0	64.0	22.0	-
3-10 "	bot ae	.104	.028	-	2200	-	3200	2.0	3.0	2.0	70.0	41.0	-
3-11 "	sur ae	.040	.032	-	1900	-	3100	1.0	6.0	2.0	67.0	40.0	-
3-11 "	bot ae	.088	.016	-	2100	-	3300	2.0	4.0	2.0	61.0	28.0	-
1-25 3/24	sur ae	.008	.032	-	1100	2100	2250	2.8	5.0	2.0	62.0	55.5	-
1-25 "	bot ae	.028	0	-	1600	2150	2400	2.0	6.0	3.0	74.0	27.0	-
1-26 "	sur ae	.006	.024	-	1250	1550	2200	2.0	6.0	2.0	84.0	23.0	-
1-26 "	bot ae	-	.032	-	1700	1900	3000	3.0	5.0	2.0	82.0	33.0	-
1-27 "	sur ae	.072	.032	-	9000	2100	3100	2.0	10.0	3.0	76.0	44.0	-
1-27 "	bot ae	.280	.020	-	1700	-	2600	1.0	9.0	2.0	65.0	30.0	-
1-28 "	sur ae	.080	.032	-	2250	1900	2250	2.0	3.0	2.0	75.0	80.0	-
1-28 "	bot ae	.096	.024	-	1700	2050	2800	2.0	8.0	3.0	76.0	35.0	-
1-29 "	sur ae	.064	.016	-	1100	1700	1400	3.0	6.0	2.0	80.0	25.0	-
1-29 "	bot ae	.008	0	-	1750	1900	2450	2.0	5.0	3.0	70.0	55.0	-
BS8 "	sur ae	0	0	-	1550	1700	2250	1.0	2.0	2.0	87.0	60.0	-
BS8 "	bot ae	.008	.036	-	1330	1330	1700	2.0	12.0	3.0	76.0	35.0	-
1-28 4/30	sur ae	0	0	0	800	2100	2100	2.0	5.0	2.0	44.0	36.0	43.0

Table VII (Continued)

SAMPLE SITE + date (all 1974)	DEPTH + aerobic or anaerobic	mg/l SULFIDE (S^{--})			mg/l SULFATE (SO_4^{--})			mg/l THIOL			% TRANSMITANCE		
		initial	final	control	initial	final	control	initial	final	control	initial	final	control
1-28 4/30	bot ae	0	0	0	800	2000	2350	2.0	11.0	2.0	88.0	69.5	78.0
1-29 "	sur ae	0	0	0	900	2050	2250	1.0	5.0	2.0	58.0	44.0	57.0
1-29 "	bot ae	0	0	0	2000	2000	-	2.0	10.0	-	50.0	20.0	-
1-28 "	sur ana	0	0	0	800	2100	2350	2.0	20.0	2.0	88.0	80.0	78.0
1-28 "	bot ana	0	0	0	800	2100	2350	2.0	19.0	2.0	88.0	90.0	78.0
1-29 "	sur ana	0	0	0	900	1700	2250	1.0	17.0	2.0	58.0	-	60.0
1-29 "	bot ana	0	0	0	2000	2000	-	2.0	17.0	2.0	70.0	50.0	-
1-28 5/23	sur ae	.016	.004	.016	2650	2500	2100	1.0	15.0	3.0	65.0	40.0	70.0
1-28 "	bot ae	0	0	.016	2650	4000	4200	2.0	8.0	3.0	63.0	38.0	31.0
1-29 "	sur ae	.016	0	.016	2100	4100	4200	1.0	5.0	4.0	64.0	16.0	73.0
1-29 "	bot ae	.008	0	.024	2050	3750	3900	2.0	10.0	4.0	69.0	35.0	29.5
1-28 "	sur ana	.016	.004	.008	2650	3700	4400	1.0	18.0	3.0	65.0	42.0	78.0
1-28 "	bot ana	.012	.008	.008	2650	4250	4450	2.0	20.0	2.0	63.0	38.0	71.5
1-29 "	sur ana	.016	.016	0	2100	4500	5100	1.0	22.0	3.0	64.0	32.0	47.5
1-29 "	bot ana	.008	0	0	2050	4400	4900	2.0	27.0	4.0	69.0	30.0	49.0
1-29 7/4	sur ae	0	0	0	1200	1200	1300	1.0	9.9	2.0	70.0	36.0	75.2
1-29 "	bot ae	0	0	0	1300	1150	1050	1.2	9.7	2.0	72.0	24.0	72.0
1-29 7/29	sur ae	.015	.015	.028	1325	1300	1300	5.0	22.5	4.5	72.0	36.0	75.0
1-29 "	bot ae												
40 mg/l PO_4	added	.015	.011	.012	1325	1400	1300	5.0	21.0	4.5	72.0	36.0	75.0
1-29 8/1	sur ae	-	-	-	780	925	950	1.5	32.2	9.2	56.0	14.0	37.0
1-29 "	bot ana	-	-	-	780	1200	1200	1.5	26.7	7.5	56.0	34.0	12.0
1-29 8/3	sur ae	0	.008	-	600	675	-	1.7	12.0	-	74.0	37.5	84.0
1-29 "	sur ae												
40 mg/l Na_2S	added	4.8	.8	4.6	750	820	750	2.0	19.7	3.9	77.0	46.5	84.0

Section III, Article 8

Chemical Characterization of Shallow Groundwater at the Kennedy Space Center, Florida

Glenn Craig Woodsum

1974

CHEMICAL CHARACTERIZATION OF SHALLOW GROUNDWATER AT THE KENNEDY SPACE CENTER, FLORIDA

by

Glenn Craig Woodsum

B.S. in Zoology, University of Michigan, 1969

Submitted to the Graduate Faculty
in partial fulfillment of
the requirements for the degree of
Master of Science
in
Bio-environmental Oceanography

Florida Institute of Technology
1974

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I. INTRODUCTION

The Kennedy Space Center is located on the northern section of Merritt Island in Brevard County, Florida, which is on the Atlantic coast of Florida about midway between Miami and the northern Florida border (Figure 1). Merritt Island is part of the barrier island system that occurs along much of Florida's east coast. It is bounded on the west by the Indian River, on the north by Mosquito Lagoon, and on the east by the Banana River and Atlantic Ocean (Figure 2).

A shallow aquifer under nonartesian conditions underlies the entire island (Brown and Hyde, 1964). Thickness of this aquifer varies from 15 feet to over 70 feet and depth to the water table ranges from land surface to about 20 feet below land surface. An artesian aquifer occurs below the nonartesian aquifer at depths from 120 to 80 feet below mean sea level. The aquifers are separated by relatively impermeable beds of fine sand, silt, shells, and clay.

Shallow groundwater interacts rather directly with nearby surface water bodies, climatic factors such as rainfall and evaporation, surface vegetation, and many of the surface activities of man (Ward, 1967). For these reasons it was thought that a chemical study of the shallow groundwater of northern Merritt Island would provide useful information as a portion of an ecological baseline study.

Brodsky and Popov (1959) have stated that the results of chemical analyses should indicate general characteristics of regional groundwater quality, principles regarding chemical change (areally and in time), and the suitability of groundwaters for practical use. The present study has considered some aspects of the first two of these approaches. If information is desired regarding potential consumptive use of the groundwater, Walton (1970) or McKee and Wolf (1963) may be consulted.

Regional groundwater quality was investigated by the drilling of bore holes that penetrated the upper part of the saturated zone. Analyses for the major ionic constituents (except silica) as defined by Davis and DeWiest (1966) were performed in order to permit identification and classification of the major types of shallow groundwater.

Principles concerning temporal and areal change in groundwater quality were investigated by means of insertion and periodic sampling of shallow observation wells. The wells were located near surface water bodies (described in detail in a later section) so as to provide information on the nature of the interaction between surface water and shallow groundwater. Water level records were kept and rainfall data obtained to help explain the effects of precipitation and evapotranspiration on ionic concentration.

The primary objective of this study was to provide baseline chemical data on conditions in the shallow aquifer. Secondarily, the influence of some processes such as saline intrusion, rainfall, and evaporation were examined. Naturally occurring minor constituents and artificial contaminants such as pesticides were beyond the scope of this project.

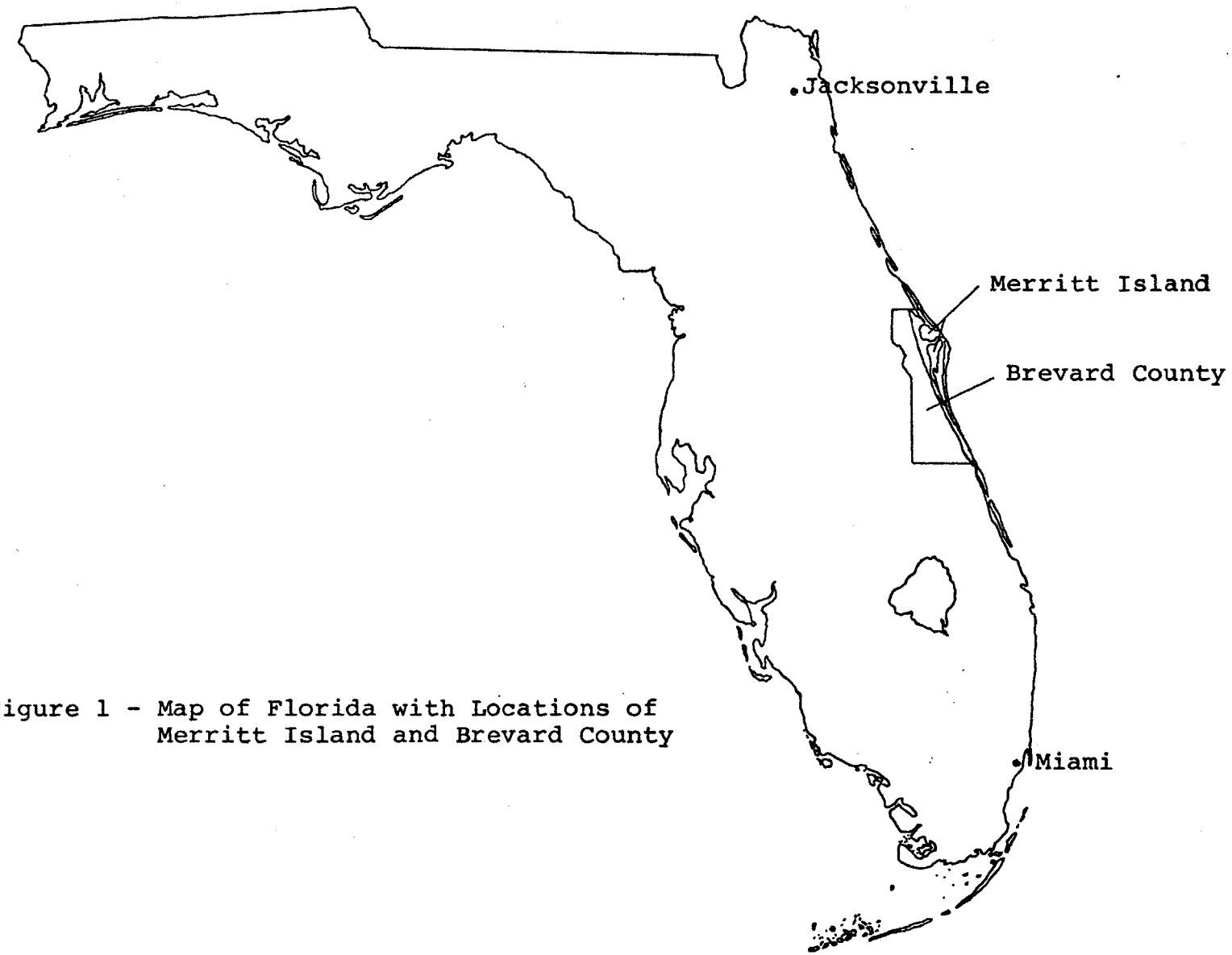


Figure 1 - Map of Florida with Locations of Merritt Island and Brevard County

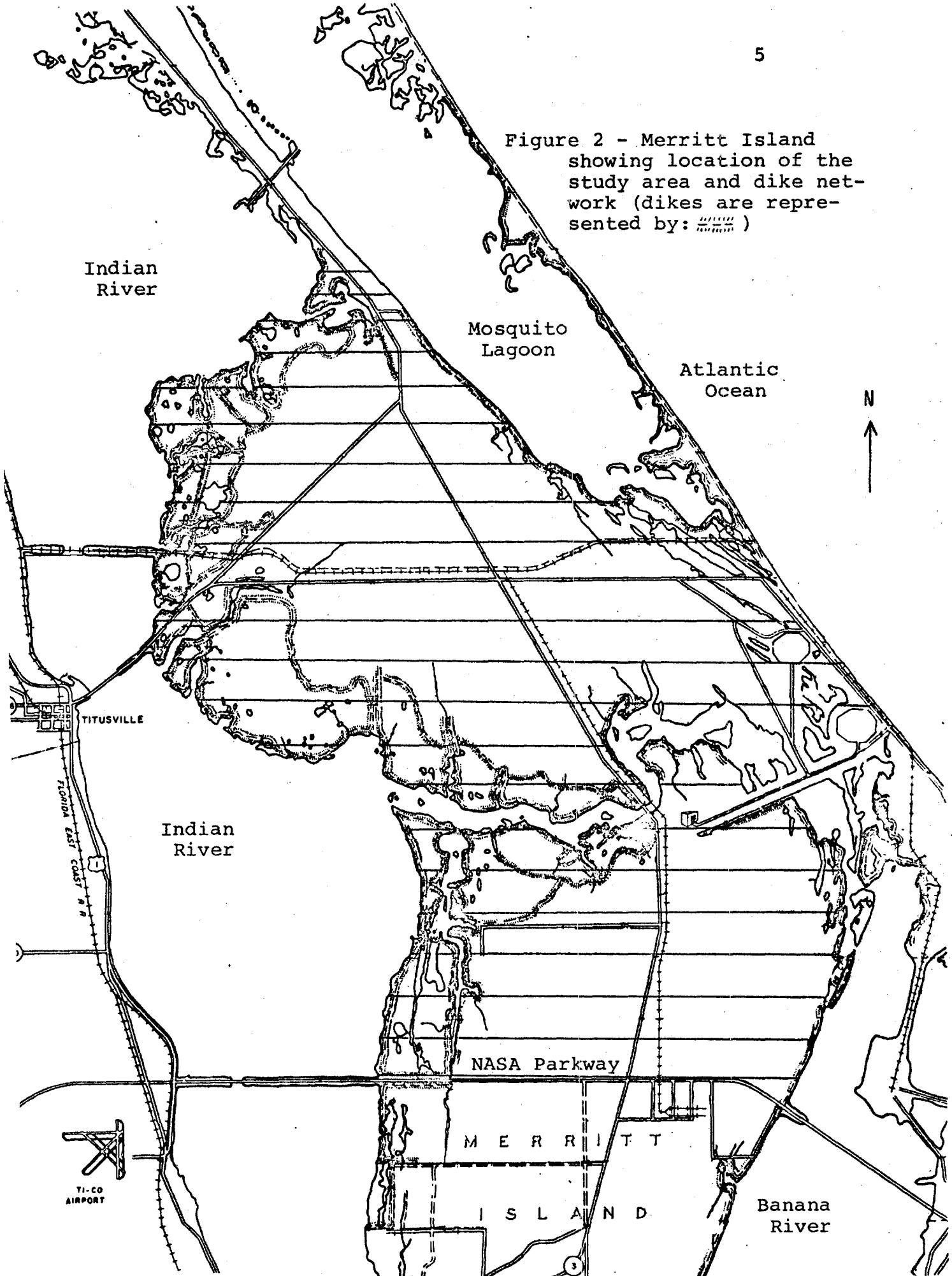


Figure 2 - Merritt Island showing location of the study area and dike network (dikes are represented by: //////)

II. BACKGROUND

A. The Groundwater Regime

Only a very small fraction of the water involved in the global hydrologic cycle occurs as water in the pore spaces of rocks and soils of the earth's crust (Odum, 1971). Water reaches the earth surface generally as precipitation in the form of rain or snow. A portion of the precipitation infiltrates the soil and serves to recharge the volume of soil water (groundwater). Once in the ground, water may be evaporated (if close to the surface), transpired by plants, or begin movement toward ultimate points of discharge, generally rivers, streams, lakes, and the sea. Movement through rock and soil is very slow, rarely more than three feet per day (Meinzer, 1942).

Since virtually all of the material in the earth's crust is at least slightly soluble in water (Kuenen, 1963), water reaching the soil begins to dissolve the material with which it is in contact. The rate and degree to which dissolution proceeds is influenced by a number of processes and physicochemical principles. Among these are initial solute concentrations of the source water, solubility of crustal minerals, temperature, pressure, pH, adsorption, ion-exchange (Carroll, 1959), the action of clays as semi-permeable membranes (Bredehoeft, et. al., 1963), climate, amount and type of vegetational cover, activity of soil microorganisms, and the influence of man (Hem, 1970).

The ultimate chemical composition of a body of groundwater is therefore a reflection of the manner in which chemical reactions, physical processes, and environment have combined in a given region. The nature of the interactions can be very complex and variable in time and space, thereby making cause and effect relationships in groundwater chemistry difficult to establish (Hem, 1970).

B. The Merritt Island Area

The area included in the present study consisted of Merritt Island north of the NASA Parkway (Figure 2). The region has been included in previous studies. Brown and Hyde (1964) of the U.S. Geological Survey conducted a study of the nonartesian aquifer for the purpose of evaluating the possible fate of radioactive materials accidentally released in the vicinity. Brown and others (1962) compiled a report on water resources of Brevard County with special emphasis on the artesian aquifer. This aquifer was not investigated during the present study.

Brown and Hyde provided much information on the physical characteristics of the nonartesian aquifer. The following discussion is adapted from their findings.

The deposits of the nonartesian aquifer consist of unconsolidated sands of Pleistocene and Recent age

with some shells, silt, clay, and coquina. The relative amounts of silt, clay, and shells in a given deposit were found by Brown and Hyde to create a large variability in the permeability of nonartesian soils. They reported coefficients of permeability ranging from 0.04 to 280 gallons per day per square foot. The porosity of nonartesian sediments ranged from 34.2 to 58.5 per cent. Rate of horizontal water movement in the aquifer was roughly computed at about three inches per day. The predominance of sand in the nonartesian aquifer resulted in low ion-exchange capacities. The highest reported value was 11.6 milliequivalents per 100 grams for a "grayish blue clay." Most of the values were between 1 and 2 milliequivalents per 100 grams, and were reported for clean sands with some silt or shells.

The geological deposition of Merritt Island proceeded generally from west to east. An originally undulating surface on the western side has been flattened by erosional activity. Hence much of the western side of the island is a low marshy area with many creeks draining into the river. With the exception of the beach ridges the highest land and water table levels are attained in the central section of the island.

In the 1950's and early 1960's a system of dikes (Figure 2) was constructed by the Brevard County Mosquito Control District. The dikes created a series of impoundments

(Figure 2) which served to control the breeding of the salt marsh mosquito, but also restricted the free exchange of water between the marshes, creeks, and the river. Nevin, et. al. (1973) have shown that impoundments which formerly connected to the river have shallow sediment profiles more characteristic of the river than of terrestrial ponds and marshes. Water level in the impoundments is generally controlled by natural processes of rainfall and evaporation, but during periods of low water levels river water may be pumped into the impoundments to supplement natural sources (Salmella, 1973).

The climate of the Merritt Island area is humid subtropical (Brown and Hyde, 1964). Average annual temperature is about 72°F, with monthly averages ranging from 62.4°F in January to 81.6°F in August. Average annual rainfall is about 50 inches, most of which is received during the "rainy season" from June through October. During this period, intense rainfall of short duration is common (Brown and Hyde, 1964).

III. MATERIALS AND METHODS

A. Bore Holes

For survey information concerning shallow groundwater over the entire study area twenty bore holes were drilled at the locations shown in Figure 3. A total of five holes were drilled at site one at distances of 10, 30, 50, 75, and 100 feet from the shore of impoundment T-10-D. Construction and sampling of water from the bore holes was conducted over the three day period July 24-26, 1973.

The bore holes were started with a shovel by digging a hole about two feet deep. A hand auger was then used to drill deeper. Drilling with the auger was continued until water filled the bottom of the hole. The depth to which the hole was bored to obtain water did not necessarily represent the depth to the water table. In a few cases the water level was rising at the time of sampling, thus making it impossible to determine the level which water would obtain in a well.

As the holes were drilled, records were kept of the layers encountered. These included measurement of depth and extent of each layer along with a visual description of the color and nature of the material comprising the layer. Sulfide odors were also noted. Resistant layers were encountered during construction of some bore

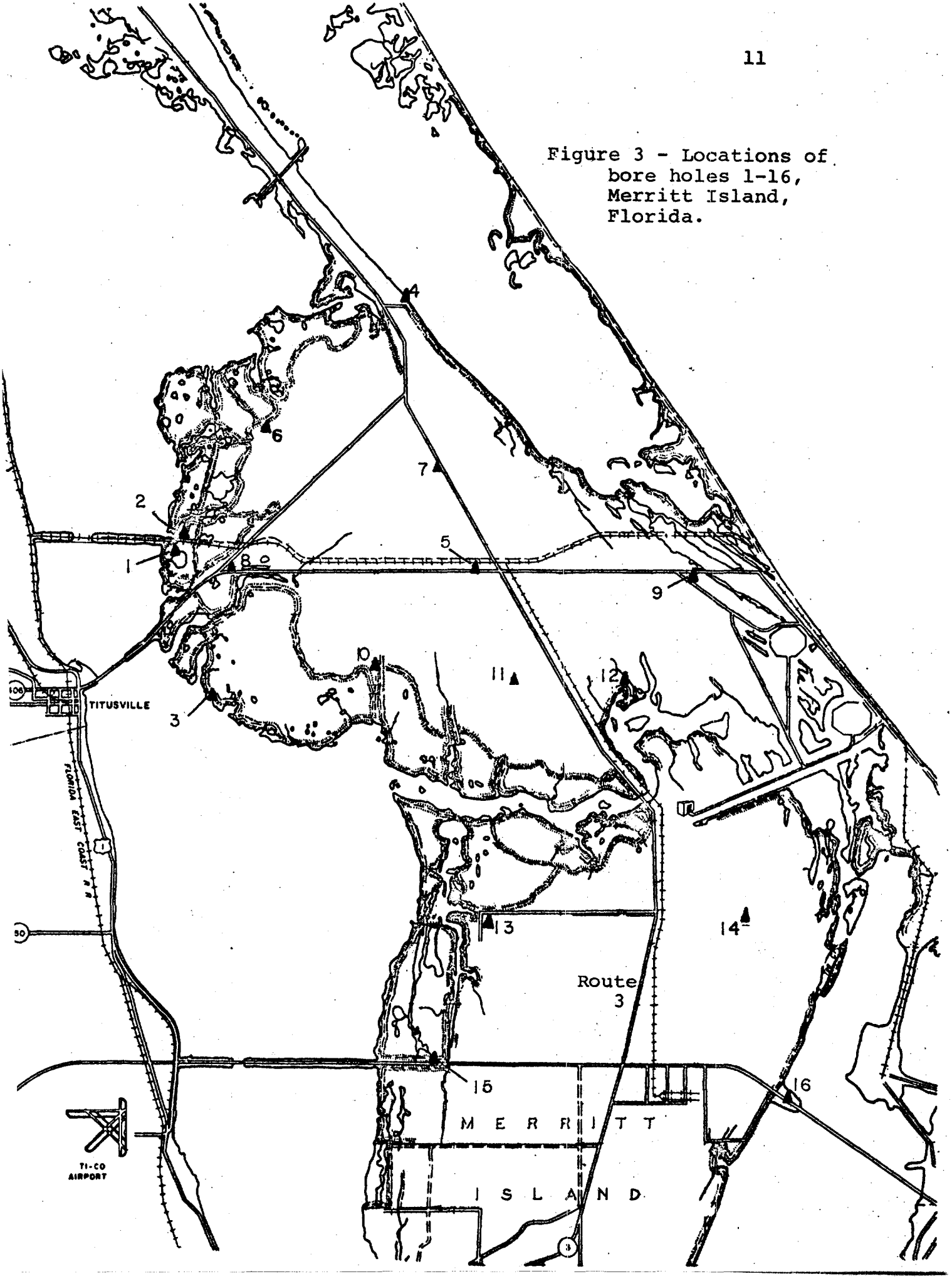


Figure 3 - Locations of bore holes 1-16, Merritt Island, Florida.

holes. Most notable of these were layers at sites five and fourteen that appeared to be compacted layers of fine black silty sand.

Samples of water were obtained by dipping a small polyethylene bottle secured to the end of a six foot wooden rod into the bottom of the bore hole. When the bottle filled it was retrieved and the contents poured into a larger bottle. This was repeated several times, until a total sample volume of about one liter was collected. The temperature was then recorded and the pH determined with a battery operated field pH meter (Orion Research, Ionalyzer model 404) equipped with a Corning glass electrode (Corning cat. no. 476024). The meter was calibrated with a recently prepared buffer solution of pH 7.03 prior to each reading.

An aliquot (10-25 ml) of the sample was filtered through medium filter paper in preparation for an alkalinity titration. The mixed bromcresol green-methyl red indicator method was used (Standard Methods, 1971). Alkalinity measurements were completed within 15 minutes of the time the water was removed from the ground.

When all samples for the day had been collected they were returned to the laboratory. When the entire series of bore hole samples had been collected they were analyzed for chloride, sodium, calcium, magnesium, sulfate, and dissolved solids according to procedures outlined

below in the laboratory section. Analyses were completed 13 days after the initial samples were taken.

B. Wells

Five locations in the study area were chosen as well sites (Figure 4). Four of these were at or near the island margin and one was centrally located in the island interior. Sites were selected in order to sample a variety of the situations that exist where the island meets surface water bodies. Figures five through nine show the land and surface water relationships, land surface profile, and well locations and depths for each site.

All wells were inserted by the jetting method. The method employed the use of a three horsepower gas-powered centrifugal pump to draw water from the nearest body of surface water and force it through a section of one inch diameter PVC pipe. The stream of water emitted from the pipe was directed into the surface sediments. For most wells this was sufficient to scour a hole to the desired depth, although resistant layers were encountered at sites one and five. The most effective way of penetrating these layers was found to involve alternating use of the water jet with a steel well point joined to a section of galvanized steel pipe. The well point was driven against the resistant layer several times and removed,

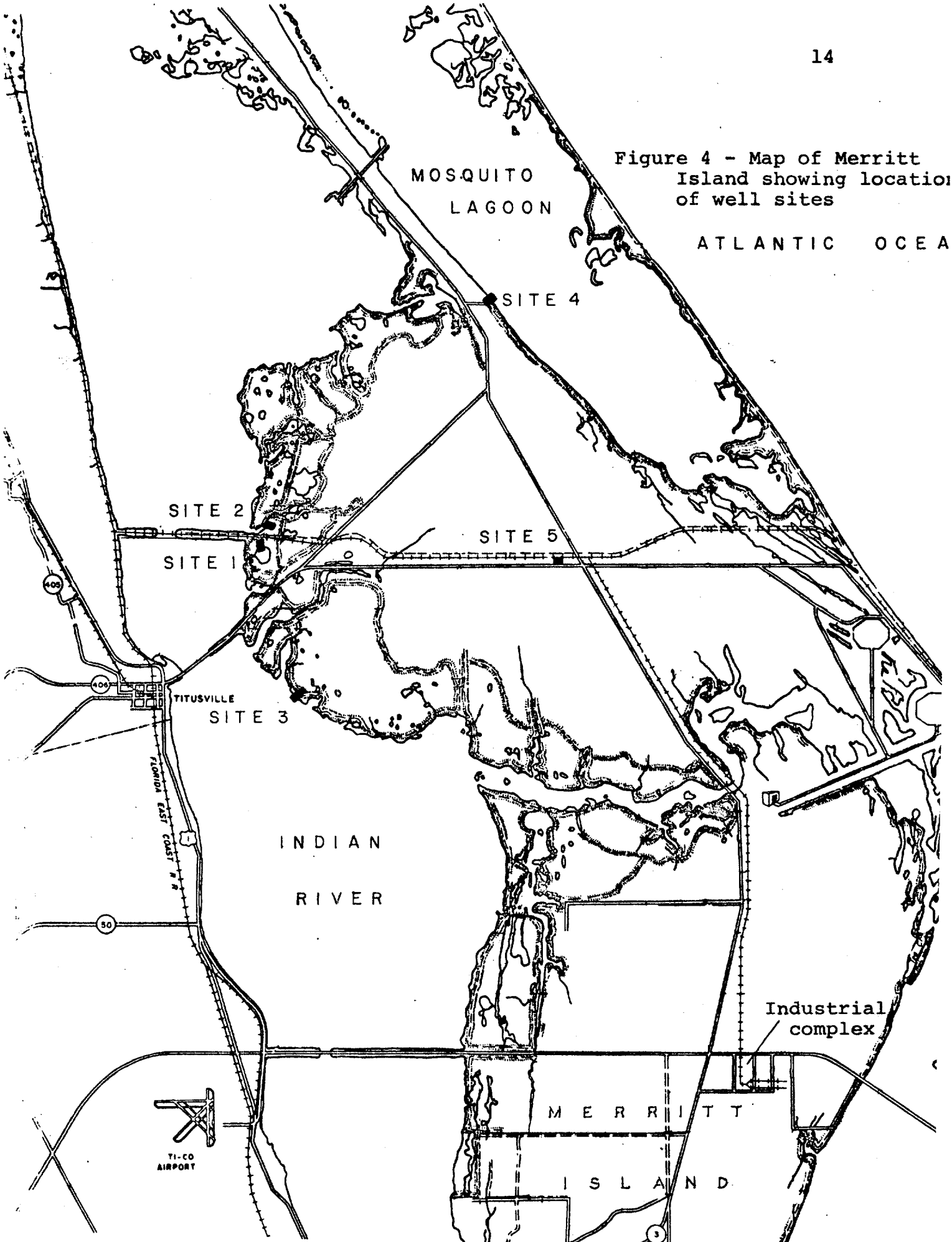
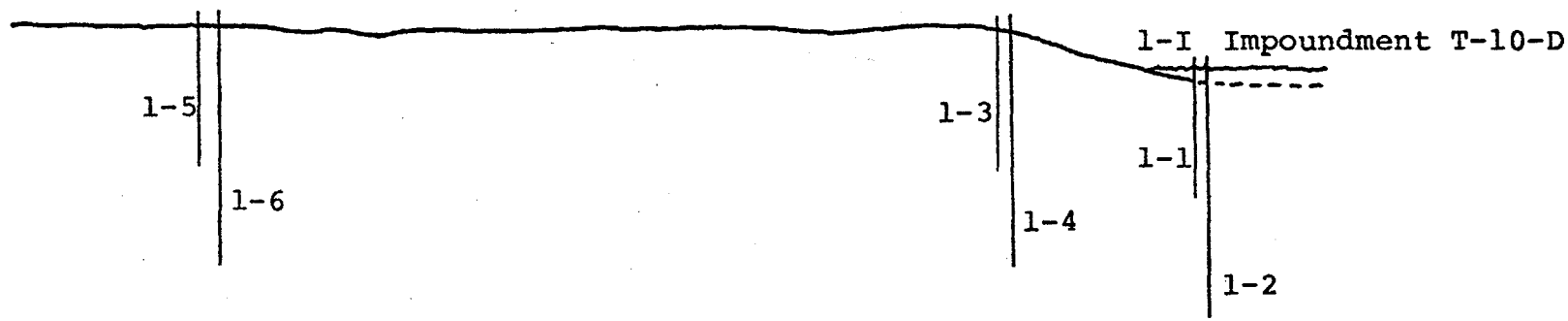


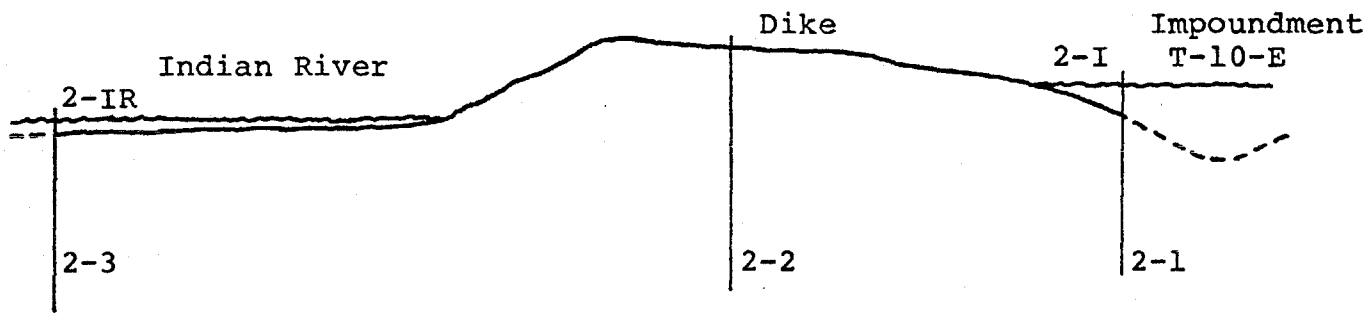
Figure 4 - Map of Merritt Island showing location of well sites



Well	Depth (ft.)
1-1	5
1-2	10
1-3	6
1-4	10
1-5	6
1-6	10

Scale: one inch = 8 feet

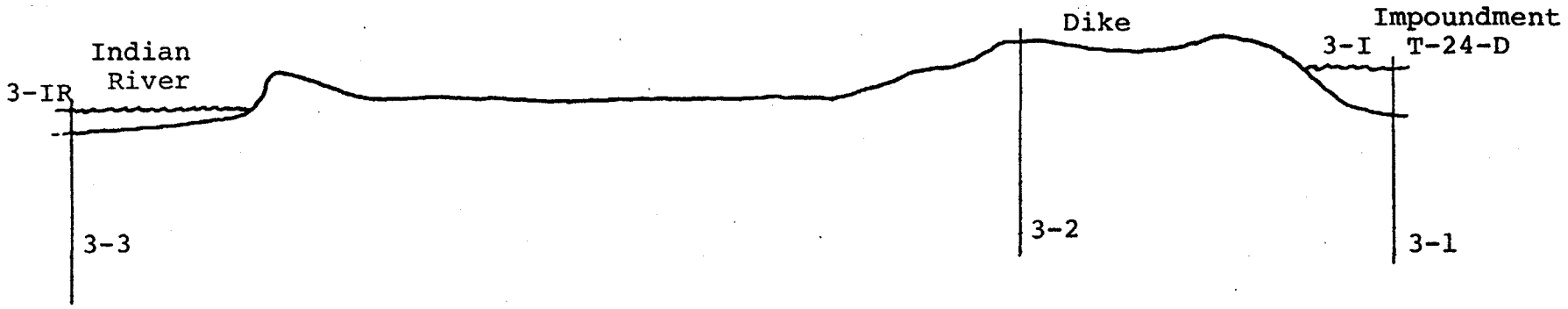
Figure 5 - Land, Surface Water, and Well Relationships at Site One



Well	Depth (ft.)
2-1	6.5
2-2	10
2-3	7

Scale: one inch = 8 feet

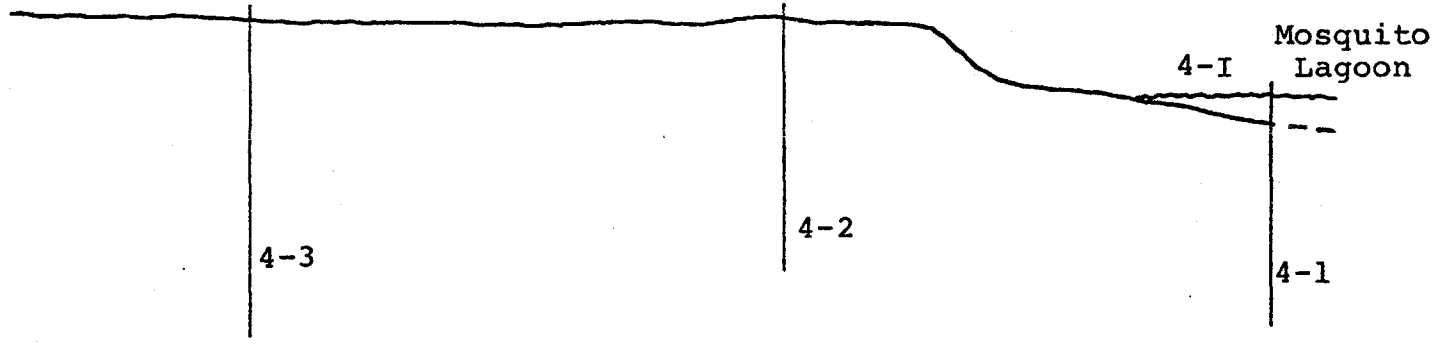
Figure 6 - Land, Surface Water, and Well Relationships at Site Two



Well	Depth (ft.)
3-1	7
3-2	10
3-3	8

Scale: one inch = 8 feet

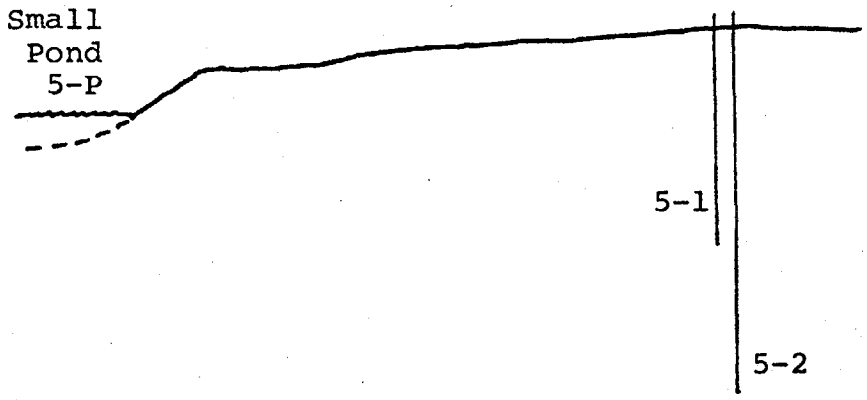
Figure 7 - Land, Surface Water, and Well Relationships at Site 3



Well	Depth (ft.)
4-1	8.5
4-2	10.5
4-3	13

Scale: one inch = 8 feet

Figure 8 - Land, Surface Water, and Well Relationships at Site Four



Well	Depth (ft.)
5-1	9
5-2	15

scale: one inch = 8 feet

Figure 9 - Land, Surface Water, and Well Relationships at Site Five

followed by insertion of the water jet to remove material loosed by the well point. Repeated application of this procedure was enough to penetrate even the most resistant layers. From the nature of the material carried upward out of the hole by the jetting water, these layers appeared to consist mostly of shells and shell fragments. Sand layers were penetrated with the least effort.

When the jetting pipe was inserted to the desired depth it was disconnected from the discharge hose of the pump, capped, and left in place as a well casing. Because the hole was larger than the pipe diameter, sediments that had accumulated at the surface were replaced around the casing and packed. Since the jetting pipe was also to function as the well casing the bottom one foot had been previously drilled with about 200 holes of 1/16 inch diameter.

The six wells and impoundment T-10-D at site one were sampled nine times between March 28 and July 3 of 1973. The wells and surface water bodies at sites two through five were sampled three times at two-week intervals between June 4 and July 3 of 1973.

The initial part of the procedure consisted of recording the water level in each well. The device for this purpose incorporated a length of speaker wire, voltmeter, transistor radio battery, and lead fishing sinker. One end of the wire was split into two leads and secured

to the sinker. The other end was split and connected to the voltmeter and battery in such a way that completion of the circuit at the sinker end would cause the needle of the voltmeter to jump. Field procedure consisted of lowering the sinker down the well casing until water was reached, at which time the voltmeter would register. The length of wire lowered into the casing was recorded. Measuring the distance from the ground surface to the top of the casing allowed calculation of water level depth below ground surface.

In addition to the water level in wells a record was kept of the level in impoundment T-10-D at site one. This was done by recording the water level reading at the Brevard County Mosquito Control District water control structure at the southern end of the impoundment. These readings cannot be interpreted as exact water levels at the well site because of the influence of wind action operating over the distance between the well site and the water control structure. However, the readings provide a good record of water level changes occuring in the impoundment as a whole.

Water samples from the wells were obtained with a section of PVC pipe 3/4 inch in diameter. The sampling pipe was lowered inside the well casing allowing well water to rise in the sampling pipe. The upper (open) end of the pipe was sealed with a cupped hand, after which

the pipe was withdrawn from the casing. The water which remained in the sampling pipe after withdrawal was drained into a clean polyethylene bottle. This procedure was repeated until a suitable volume was obtained, usually 300-400 milliliters.

After collection of the sample, the water temperature and pH were measured. When all samples had been collected they were returned to the laboratory for chemical analysis. Analyses were usually completed within three days of the time of collection and at no time did the period of storage exceed 19 days. Analyses were conducted for chloride, calcium, magnesium, phosphate, and sulfate (July 3 samples only) according to procedures described below.

C. Laboratory

Accepted procedures and techniques of analytical chemistry were followed as closely as possible. These include such things as the use of clean glassware and sample bottles, reagent grade chemicals, careful measurement of weights and volumes, standardization of reagents prior to use, and treatment for interfering substances where significant. The reference methods of analysis were modified in certain instances and will be noted where appropriate.

The argentometric method (Standard Methods) was used for the determination of chloride ion. The method includes any amounts of iodide, bromide, and cyanide (Standard Methods). As a wide range of chloride concentrations were encountered, a concentrated silver nitrate titrant solution (Martin, 1968) was used for the samples with high chloride levels.

Interference was caused by color and sulfide in some of the samples. The interference by color was minimized by the process of dilution of small volumes of sample. Sulfide interfered by the formation of a brown precipitate so these samples were shaken and allowed to stand until further titration indicated that the interference was no longer present.

Calcium and magnesium ion concentrations were determined with a modification of the EDTA titrimetric method given in Standard Methods. The method is presented by Katz and Navone (1964) and enables determination of calcium and magnesium in the same water sample.

The end points of the titration were found to be somewhat gradual. Therefore titration was continued until addition of titrant caused no further color change. Such problems cause difficulty in studies where highly accurate measurements are required. In his study of ionic ratios in the Indian River, Hutchinson (1973) found gravimeter methods more suitable.

Several metal ions interfere with the calcium/magnesium determination (Standard Methods). The addition of an inhibitor (hydroxylamine hydrochloride) minimized effects of some of these (aluminum, copper, iron, and manganese) although others are included in the titrated values. These include barium, cadmium, lead, and strontium. The first three of these are present in very low amounts in natural water (Hem, 1970), although strontium can be significant. Data on trace constituents (presented later) indicate that as much as 10 mg/l strontium may be included in a few of the calcium values.

Sulfate ion concentration was determined with a turbidimetric method (Standard Methods) utilizing a Bausch and Lomb spectrophotometer (Spectronic 20). Color interfered with some samples so these samples were diluted until the color problem was minimized.

Orthophosphate concentration was measured using the Hach Chemical Company Phos Ver III method. It is a spectrophotometric method with color development proportional to phosphate concentration. Some samples contained little or no phosphate and had such high transmittances that those reported values serve only to indicate very low phosphate concentrations.

The concentration of sodium ion was measured with a gravimetric method (Standard Methods). Interferences

suggested in Standard Methods as possibly affecting the procedure were not believed to be present in significant amounts. Precipitation of silica may have occurred but the effects of this on calculated sodium are small (Standard Methods).

The Standard Methods procedure for filtrable residue was used for the determination of dissolved solids. All samples were filtered first through medium filter paper (Scientific Products, F2402-125), then through Millipore filter papers of successively smaller pore sizes. The pore diameter for the last of the filtrations was 0.45 micron. After filtration 50 or 100 ml. portions of the sample were placed in weighed flasks, evaporated, and dried for 24 hours at 178-180°C. Results are therefore reported as filtrable residue on drying at 179°C.

IV. RESULTS

A. Data Obtained from Bore Holes

1. Soil Profiles

The nature of the soil structure at each bore hole location was described as the bore holes were drilled. The descriptions of soil profile at each location are included as Table 2 of Appendix A.

The data show that while fine sand is the predominant material comprising the shallow soils of the study area, there is considerable variation in the occurrence of peat, shells, silt, and clay. Color banding in sediment layers was observed at every location. Shades of gray, brown, and black were the dominant colors. Layers would often contain two or more colors resulting in a mottled appearance. The darker colors (especially black) were usually associated with finer sediments and/or the presence of decomposing plant material. Hydrogen sulfide odor was detected in several bore holes, including all of those drilled on the edge of the island bordering the Indian River. The five bore holes drilled at site one indicate that soil profiles may vary considerably even over relatively short distances.

2. Chemical Analyses

The results of chemical tests performed on the bore hole samples are shown in Table 1. The data indicate that shallow groundwater on Merritt Island is highly variable with regards to concentrations of the major ionic constituents.

As shown in Table 1, the pH of shallow groundwater was very low at two sites (about 4.5 at site B14 and 5.0 at site B12). Hem (1970) states that most groundwaters in the United States have pH values from 6.0 to 8.5. Most of the samples in this study were in the pH range 6.1 to 7.0. The samples with very low pH occurred in an area of the island described by Brown and Hyde as containing "acid" groundwaters.

Concentration of sodium ion ranged from 14 mg/l at site B16 to 5,840 mg/l at site B1. Six sites had concentrations over 1,000 mg/l while seven sites contained less than 100 mg/l sodium. Calcium concentration was lowest at site B14 (17 mg/l) and highest at site B1 (384 mg/l). Six sites contained calcium in amounts less than 70 mg/l and six sites were in the range 100-200 mg/l. Magnesium ranged from 5 mg/l at site B14 to 715 mg/l at site B1. Most sites contained less than 100 mg/l magnesium. The highest magnesium values seemed to be associated with the highest calcium values.

TABLE 1 - RESULTS OF CHEMICAL ANALYSES OF SAMPLES OBTAINED FROM BOREHOLES (RESULTS IN MILLIGRAMS PER LITER (mg/l) EXCEPT FOR TEMPERATURE AND pH.)

SITE	DEPTH APPROX (ft.)	TEMP °C	pH	Na^+	Ca^{++}	Mg^{++}	Cl^-	$SO_4^=$	HCO_3^-	FILTRABLE DISSOLVED SOLIDS
B1	4.4	27.7	7.02	5,840	348	715	10,490	710	1,200	20,700
B2	5.4	27.4	6.28	4,130	235	505	7,480	657	785	15,300
B3	6.6	26.6	6.70	1,430	35	86	2,160	27	572	4,700
B4	5.6	28.8	6.76	185	59	73	139	72	751	1,020
B5	5.4	27.4	5.80	69	50	7.6	95	1.0	162	534
B6	4.4	28.0	6.97	1,650	176	127	2,430	240	808	5,610
B7	3.1	26.5	6.50	54	129	7.9	156	9.5	434	528
B8	4.0	28.1	6.76	24	108	26	55	7.5	387	470
B9	4.7	27.2	6.50	840	70	155	1,450	121	609	3,460
B10	2.3	28.2	6.60	500	204	56	955	2.6	662	2,540
B11	1.7	27.0	6.60	19	111	5.3	70	4.4	281	470
B12	5.1	29.0	5.02	25	40	5.3	105	2.2	101	272
B13	5.2	27.4	6.86	1,550	110	151	2,490	282	275	5,390
B14	7.0	26.8	4.51	33	17	50	111	16	-	350
B15	2.5	28.3	6.10	2,390	238	222	4,110	55	677	8,570
B16	3.2	29.2	6.88	14	127	9.2	91	124	252	487
B1(30)	3	-	-	-	562	1,210	18,800	781	-	-
B1(50)	2.5	-	-	-	460	1,010	12,200	1,300	-	-
B1(75)	6.9	-	-	-	304	581	8,580	1,180	-	-
B1(100)	3.0	-	-	-	194	77	624	678	-	-

The anions chloride, sulfate, and bicarbonate also had wide concentration ranges. Chloride ranged from 55 mg/l at site B8 to 10, 490 mg/l at site B1. Sulfate was highest at site B1 (710 mg/l) and lowest at site B5 (1 mg/l). Site B1 also had the highest bicarbonate concentration (1,220 mg/l) while site B12 had the lowest (101 mg/l). Alkalinity was not measured at site B14, however (presence of color and fine suspended matter interfered with the field procedure). Based on considerations of pH and the dissociation of dissolved carbon dioxide species (Hem, 1970) the low pH at site B14 (4.5) probably indicates that this site was actually the lowest in terms of bicarbonate concentration.

The distribution of dissolved solids in the study area appears similar to that for the major ionic constituents. Site B1 had the highest concentration (20,700 mg/l) while site B12 had the lowest (272 mg/l). As with the ionic components this represents a considerable range of concentration. The areal distribution of dissolved solids is shown in Figure 10. It is clear that the sites with greater than 1,000 mg/l dissolved solids occur at or near the edges of the island while the sites containing less than 1,000 mg/l are more centrally located. A line separating these two regions includes virtually all of the impounded areas as well as some of the island interior. The line cannot be taken to indicate that all of the groundwater

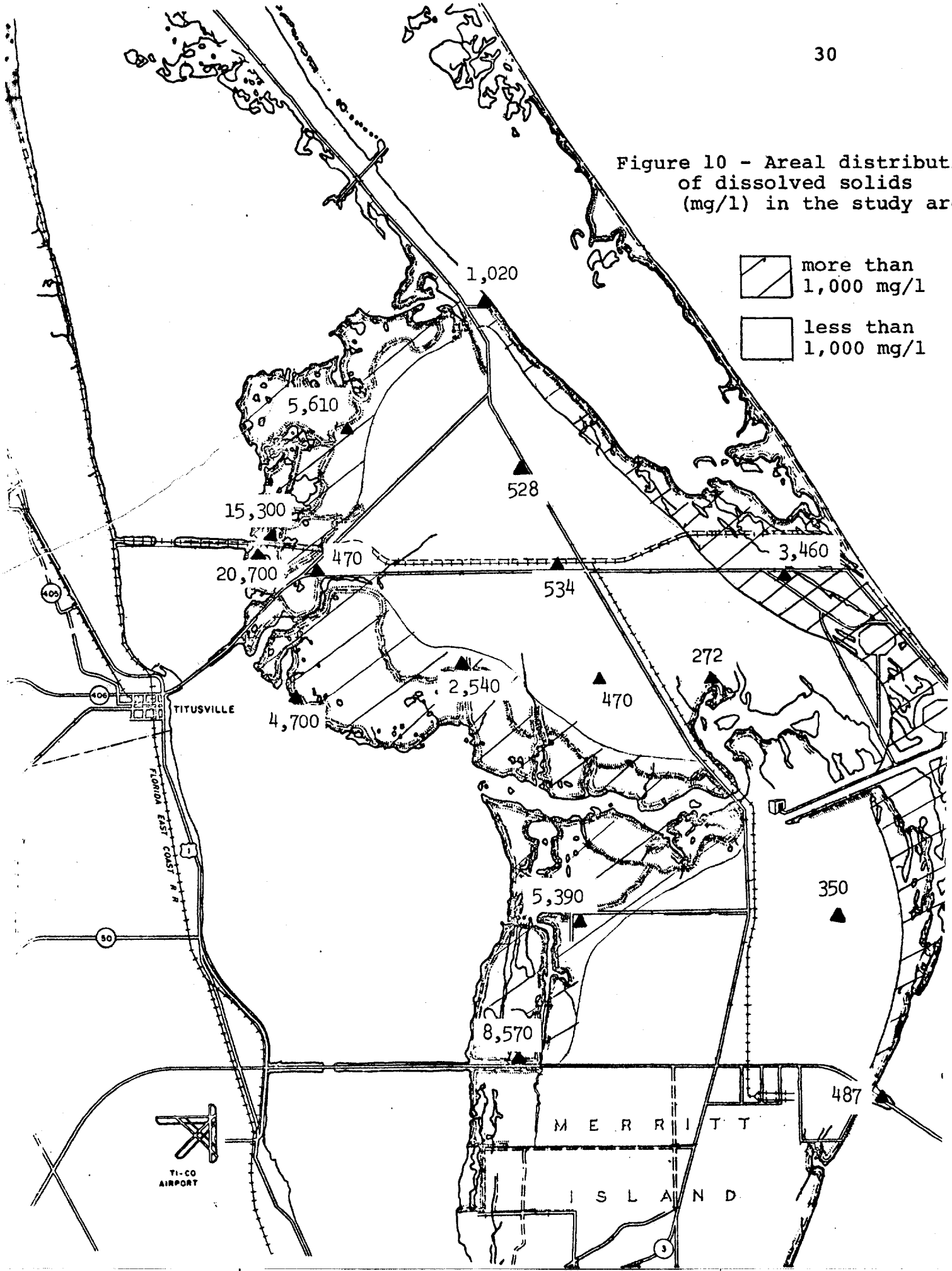


Figure 10 - Areal distributi
of dissolved solids
(mg/l) in the study are

within the cross-hatched area contains over 1,000 mg/l dissolved solids. It does indicate the area of the island where groundwater of high concentration may be expected.

B. Data Obtained from the Well Sites

1. Site one

Results of the analyses performed on samples obtained from wells and surface water bodies are given in Table 2. When the results from site 1 are displayed with time, the resulting hydrographs (Figures 11-17) permit easier visualization of the data. The following presentation is based on the hydrographs.

The first hydrograph (Figure 11) depicts chloride concentration during the study period. In the impoundment (1-I) chloride initially decreased then increased steadily until a maximum concentration of 21.5 grams/liter was reached on May 21. This was followed by a steady decrease until June 20 and a rise during the final sampling period. The difference between highest and lowest observed concentrations was about 7 grams/liter. The difference could be greater than (but not less than) 7 grams/liter because the sampling procedure allows measurement only of net changes during a sampling interval. This must be remembered when considered data from any of the hydrographs.

TABLE 2 - CHEMICAL ANALYSES OF WATER FROM SHALLOW WELLS AND SURFACE-WATER BODIES ON MERRITT ISLAND

Analyses in milligrams per liter except temperature and pH.

LOCATION	DATE OF COLLECTION	TEMPERATURE	pH	CHLORIDE (Cl)	CALCIUM (Ca)	MAGNESIUM (Mg)	PHOSPHATE (PO_4)	SULFATE (SO_4)
1 - 1	3/28/73	23.0	-	18,800	-	-	-	-
1 - 2	"	22.2	-	14,530	-	-	-	-
1 - 3	"	22.8	-	10,400	-	-	-	-
1 - 4	"	22.3	-	14,840	-	-	-	-
1 - 5	"	21.5	-	15,480	-	-	-	-
1 - 6	"	22.1	-	15,060	-	-	-	-
1 - I	"	25.0	-	14,890	-	-	-	-
1 - 1	4/06/73	24.0	7.09	18,140	-	-	-	-
1 - 2	"	23.7	6.88	15,290	-	-	-	-
1 - 3	"	24.0	6.61	-	-	-	-	-
1 - 4	"	24.1	6.90	14,770	-	-	-	-
1 - 5	"	23.2	7.11	15,480	-	-	-	-
1 - 6	"	23.8	6.85	14,550	-	-	-	-
1 - I	"	25.8	7.63	14,480	-	-	-	-
1 - 1	4/13/73	24.0	7.24	17,920	550	1,210	-	-
1 - 2	"	23.8	7.17	15,350	660	1,100	-	-
1 - 3	"	23.1	6.90	10,050	390	690	-	-
1 - 4	"	23.8	7.12	14,830	700	1,060	-	-
1 - 5	"	22.9	7.43	15,440	530	1,130	-	-
1 - 6	"	23.4	7.21	14,580	600	1,070	-	-
1 - I	"	24.0	7.63	15,170	420	1,000	-	-
1 - 1	4/23/73	23.6	7.18	18,900	540	1,220	0.7	-
1 - 2	"	22.5	7.11	16,080	630	1,140	2.9	-
1 - 3	"	23.2	6.85	10,700	380	720	4.2	-
1 - 4	"	22.9	7.15	15,210	720	1,040	4.6	-

Table 2 (cont.)

LOCATION	DATE OF COLLECTION	TEMPERATURE	pH	CHLORIDE (Cl)	CALCIUM (Ca)	MAGNESIUM (Mg)	PHOSPHATE (PO_4)	SULFATE (SO_4)
1 - 5	4/23/73	23.3	7.31	16,000	520	1,140	8.0	-
1 - 6	"	22.9	7.34	15,000	580	1,070	3.4	-
1 - I	"	28.8	7.82	17,030	450	1,080	0.2	-
1 - 1	5/07/73	23.3	7.44	18,500	530	1,270	3.1	-
1 - 2	"	22.8	7.55	15,890	650	1,160	4.4	-
1 - 3	"	22.5	7.18	11,200	390	790	6.5	-
1 - 4	"	22.9	7.43	15,160	670	1,110	5.2	-
1 - 5	"	23.0	7.61	15,580	540	1,140	6.1	-
1 - 6	"	22.7	7.68	14,720	560	1,110	6.3	-
1 - I	"	24.4	8.03	10,060	490	1,280	2.3	-
1 - 1	5/21/73	26.8	6.93	18,830	530	1,220	2.4	-
1 - 2	"	25.7	7.10	15,830	650	1,120	1.7	-
1 - 3	"	26.5	6.79	11,380	390	800	1.5	-
1 - 4	"	26.8	7.19	15,310	660	1,090	2.1	-
1 - 5	"	27.1	7.10	14,630	510	1,090	10.3	-
1 - 6	"	25.8	7.36	14,930	570	1,100	2.4	-
1 - I	"	32.6	7.03	21,510	550	1,410	0.2	-
1 - 1	6/04/73	26.0	6.87	18,340	500	1,200	1.5	-
1 - 2	"	25.0	7.03	16,000	650	1,130	1.8	-
1 - 3	"	25.5	6.74	11,120	380	780	1.4	-
1 - 4	"	24.8	6.95	15,330	670	1,100	-	-
1 - 5	"	25.2	7.15	15,360	520	1,100	8.0	-
1 - 6	"	24.8	7.06	15,430	620	1,180	2.2	-
1 - I	"	26.0	6.68	19,720	500	1,290	0.5	-
2 - 1	6/04/73	26.7	7.61	9,130	280	480	1.0	-
2 - 2	"	25.2	6.88	9.110	280	480	2.2	-
2 - 3	"	27.8	6.90	10,060	320	530	2.0	-
2 - I	"	25.9	8.40	9,020	260	470	0.8	-
2 - IR	"	27.9	7.42	16,770	430	910	0.5	-

Table 2 (cont.)

LOCATION	COLLECTION	TEMPERATURE	pH	CHLORIDE (Cl)	CALCIUM (Ca)	MAGNESIUM (Mg)	PHOSPHATE (PO_4)	SULFATE (SO_4)
3 - 1	6/04/73	25.7	7.02	780	38	34	0.5	-
3 - 2	"	25.5	7.10	920	26	29	1.7	-
3 - 3	"	27.7	6.73	14,500	370	79	1.4	-
3 - I	"	27.4	7.35	730	34	34	0.5	-
3 - IR	"	29.5	7.56	16,240	39	830	0.3	-
4 - 1	"	27.0	6.92	18,500	42	1,000	2.2	-
4 - 2	"	26.1	7.35	17,350	410	940	3.2	-
4 - 3	"	27.0	7.71	17,500	400	950	1.0	-
4 - ML	"	29.1	7.81	17,520	400	970	0.3	-
5 - 1	6/04/73	28.9	6.93	210	85	13	1.0	-
5 - 2	"	24.5	7.55	120	90	11	0.4	-
5 - P	"	30.6	6.94	110	92	9	0.8	-
1 - 1	6/20/73	26.7	6.98	19,970	550	1,320	0.6	-
1 - 2	"	25.6	7.13	16,110	650	1,140	1.7	-
1 - 3	"	26.8	6.70	10,930	390	770	2.4	-
1 - 4	"	25.9	6.94	15,490	700	1,110	2.7	-
1 - 5	"	26.2	7.06	15,650	570	1,100	5.5	-
1 - 6	"	26.7	7.02	15,540	650	1,160	1.9	-
1 - I	"	30.4	6.71	18,000	460	1,170	0.2	-
2 - 1	6/20/73	27.1	7.71	8,320	260	530	0.1	-
2 - 2	"	26.6	7.11	9,360	260	610	1.0	-
2 - 3	"	27.2	7.42	9,800	300	620	0.0	-
2 - I	"	29.0	7.78	8,330	250	510	0.0	-
2 - IR	"	29.3	7.52	14,090	390	910	0.0	-
3 - 1	"	25.9	7.27	730	30	36	0.5	-
3 - 2	"	26.3	7.16	840	22	34	2.9	-
3 - 3	"	28.2	7.74	3,870	110	230	3.2	-

Table 2 (cont.)

LOCATION	COLLECTION	TEMPERATURE	pH	CHLORIDE (Cl)	CALCIUM (Ca)	MAGNESIUM (Mg)	PHOSPHATE (PO_4)	SULFATE (SO_4)
3 - I	6/20/73	30.1	7.05	680	28	32	6.5	-
3 - IR	"	30.0	7.66	13,870	340	890	0.0	-
4 - 1	"	26.6	7.15	18,970	460	1,240	3.7	-
4 - 2	"	25.8	7.42	14,910	400	960	5.0	-
4 - 3	"	26.7	7.46	17,310	410	1,110	0.4	-
4 - ML	"	30.1	7.84	17,020	400	1,090	0.3	-
5 - 1	"	27.7	7.46	210	94	11	0.4	-
5 - 2	"	27.3	7.49	120	87	8.7	1.3	-
5 - P	"	30.2	7.17	160	87	7.6	5.2	-
1 - 1	7/03/73	28.2	7.13	20,830	560	1,350	0.8	2,800
1 - 2	"	27.8	7.21	16,670	620	1,150	0.7	2,450
1 - 3	"	28.5	6.90	11,070	380	770	1.1	1,280
1 - 4	"	26.8	7.15	15,370	680	1,090	2.3	2,310
1 - 5	"	27.6	7.30	15,570	560	1,100	4.6	1,610
1 - 6	"	26.0	7.29	15,480	640	1,130	1.7	2,430
1 - I	"	29.4	6.65	19,620	490	1,270	0.6	2,690
2 - 1	"	29.0	7.23	8,510	280	540	0.5	890
2 - 2	"	26.9	7.35	9,140	290	570	1.3	810
2 - 3	"	29.2	7.40	9,850	320	610	1.3	730
2 - I	"	29.8	7.92	9,370	280	550	0.6	950
2 - IR	"	31.0	7.43	15,920	430	1,020	0.3	2,330
3 - 1	"	30.5	7.41	670	27	34	0.6	36
3 - 2	"	29.0	7.37	980	28	47	5.0	58
3 - 3	"	31.0	7.28	1,210	35	59	11.3	58
3 - I	"	33.0	7.84	680	27	33	0.5	16
3 - IR	"	33.5	6.72	14,850	370	950	0.7	2,320

Table 2 (cont.)

LOCATION	COLLECTION	TEMPERATURE	pH	CHLORIDE (Cl)	CALCIUM (Ca)	MAGNESIUM (Mg)	PHOSPHATE (PO_4)	SULFATE (SO_4)
4 - 1	7/03/73	28.9	7.69	17,580	440	1,130	4.2	2,570
4 - 2	"	-	-	-	-	-	-	-
4 - 3	"	29.0	7.37	17,310	410	1,100	9.0	2,540
4 - ML	"	31.8	7.51	18,560	420	1,190	8.2	2,720
5 - 1	"	29.0	7.86	110	95	9.9	5.2	28
5 - 2	"	26.1	7.90	120	96	8.6	0.7	61
5 - P	"	33.2	7.30	120	93	9.0	6.1	71

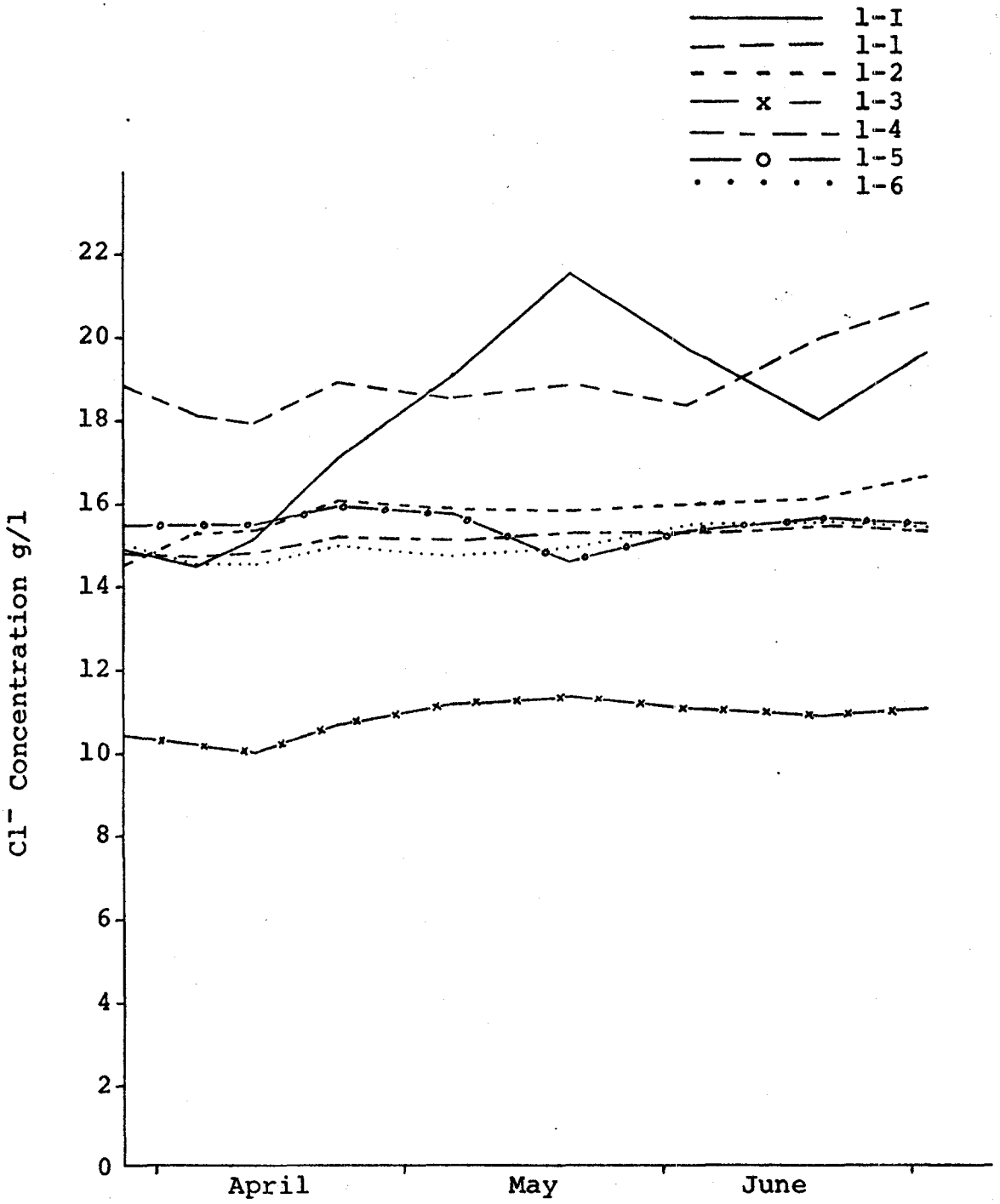


Figure 11 - Hydrograph of Chloride Concentration at site 1 for three months during 1973

It is clear from Figure 11 that all of the wells were more constant in chloride content than the impoundment. There was considerable variation from one well to another, but for any single well the chloride composition remained relatively constant with time. Well 1-1 had the highest concentration of any well. It is also located closer to the impoundment than any other well. Wells 1-2, 1-4, 1-5, and 1-6 were all very similar in chloride content, with concentrations about midway between those of well 1-1 and well 1-3, which had the lowest concentrations. Wells 1-1 and 1-3 are physically quite close to one another (Figure 5), but have a large difference in chloride concentration. This suggests the presence of some sort of unusual circumstance in this region (i.e. at the edge of the impoundment).

Well 1-3 appears to be unusual in another respect. It appears to be the only well in which concentration changes reflected the concentration changes that occurred in the impoundment during the same sampling interval.

The hydrograph for calcium concentration (Figure 12) shows many of the same relationships. Over the same time period as that for chloride, calcium concentration in the impoundment experienced similar increases and decreases, with the maximum concentration observed on May 21. Calcium composition was also more constant through time in the wells than in the impoundment. Well 1-3 again had the

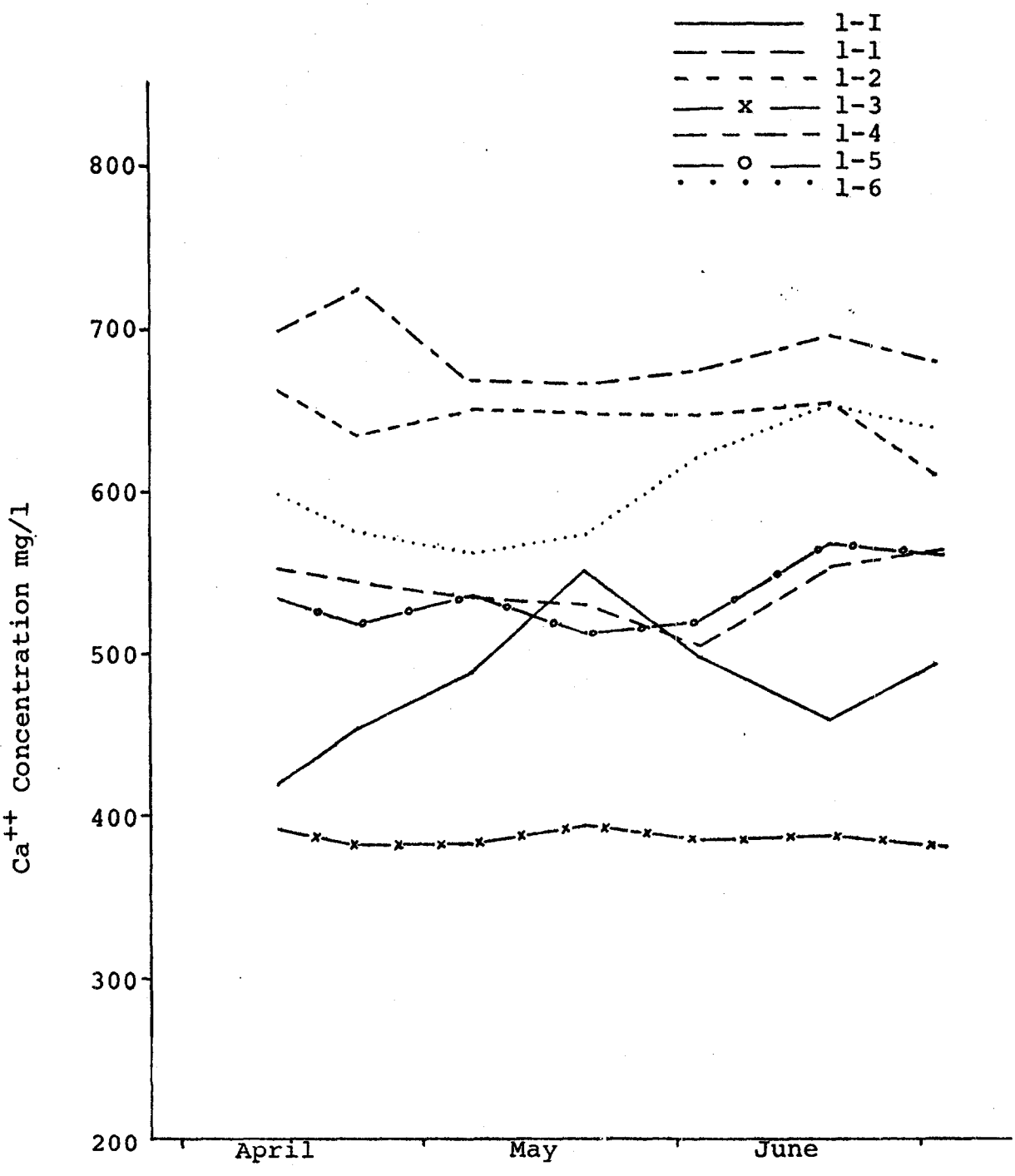


Figure 12 - Hydrograph of calcium concentration at site 1 for three months during 1973

lowest concentration and was the only well to exhibit a peak concentration at the same time as the impoundment.

The calcium hydrograph shows that most of the wells had generally higher calcium concentrations than the impoundment. This was not true for chloride. Furthermore, the highest calcium concentrations were found in the deeper wells (1-2, 1-4, and 1-6).

As with chloride, concentration increases or decreases in one well were not necessarily accompanied by similar increases or decreases in other wells. Thus there does not appear to be any process that influences these concentrations that acts uniformly in all wells at the same time.

The hydrograph for magnesium (Figure 13) appears most similar to that for chloride. The impoundment had the highest recorded concentration (again on May 21), well 1-1 had the highest of the wells, well 1-3 the lowest, while wells 1-2, 1-4, 1-5, and 1-6 were very similar in concentration. All wells were more constant through time than the impoundment. Changes in magnesium concentration in one well were not associated with similar changes in other wells. Well 1-3 was again the only well to show general increase and decrease in conjunction with increase and decrease in the impoundment.

It should be noted that the values reported for magnesium on June 4 were calculated after averaging the

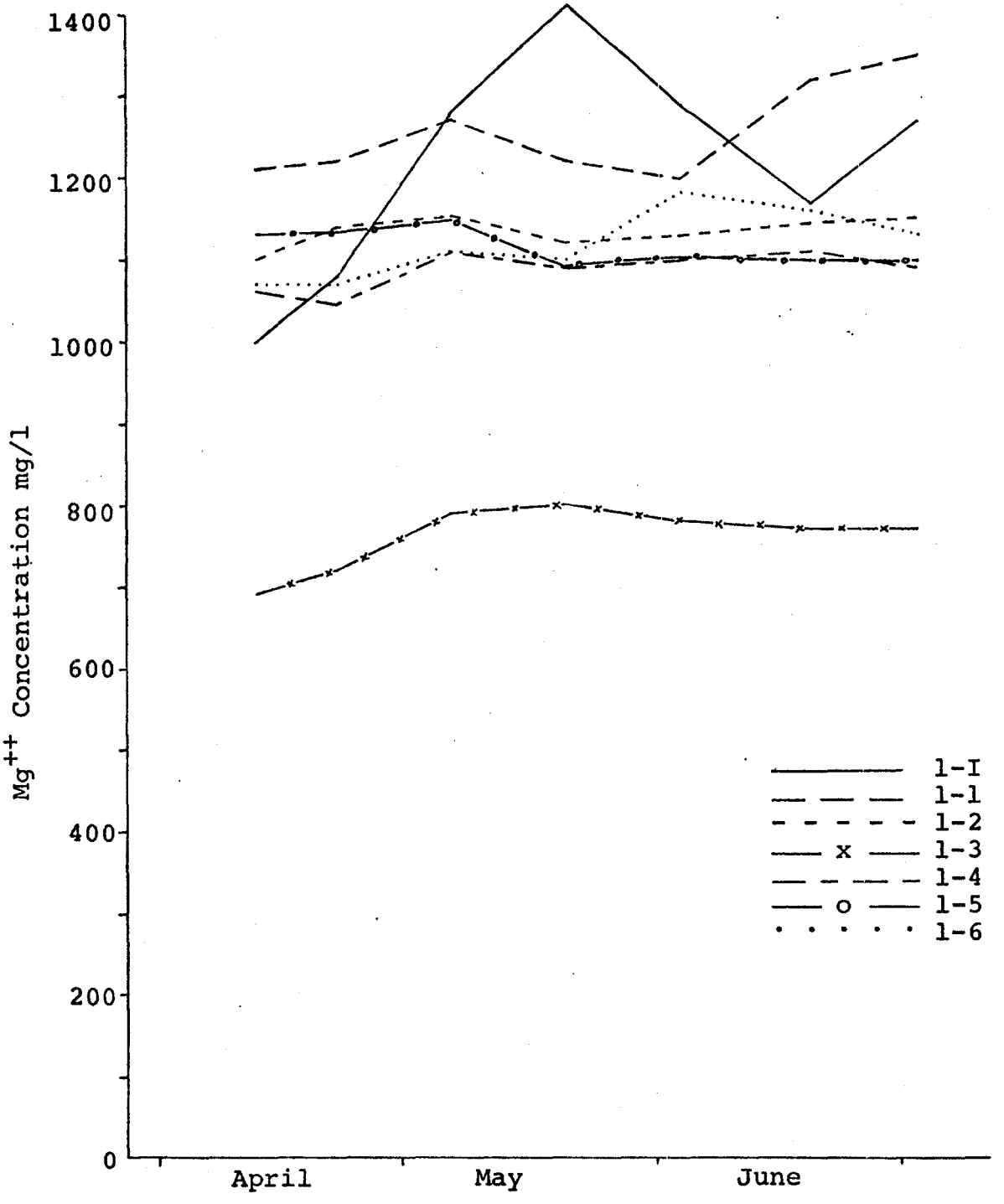


Figure 13 - Hydrograph of Magnesium Concentration at Site 1 for Three Months During 1973

amounts of titrant needed to titrate a standard magnesium solution for the other sampling dates. An error was discovered in the magnesium standardization for the June 4 samples, necessitating the above recovery procedure.

The hydrograph for phosphate concentration (Figure 14) appears quite different from the others presented. The impoundment in this case had the lowest concentrations. Excluding well 1-5 for the moment, it appears significant that the increase in early May followed by a sharp decline and leveling at low concentrations occurred uniformly, i.e. in all wells at the same time. This was not observed for any of the constituents previously discussed.

Well 1-5 did not follow the pattern set by other wells although its hydrograph may indicate a lag of about two weeks for some process that had earlier affected the other wells. Another explanation is favored, however, and involves the difficulty encountered when sampling this well. The level of water in well 1-5 was only a few inches above the bottom of the well where sediment had moved through the holes in the well casing and accumulated. In the process of removing water from this well the sediments were necessarily disturbed. According to Standard Methods (p. 521) agitation such as this could cause desorption of orthophosphate from suspended particles, leading to anomalous results.

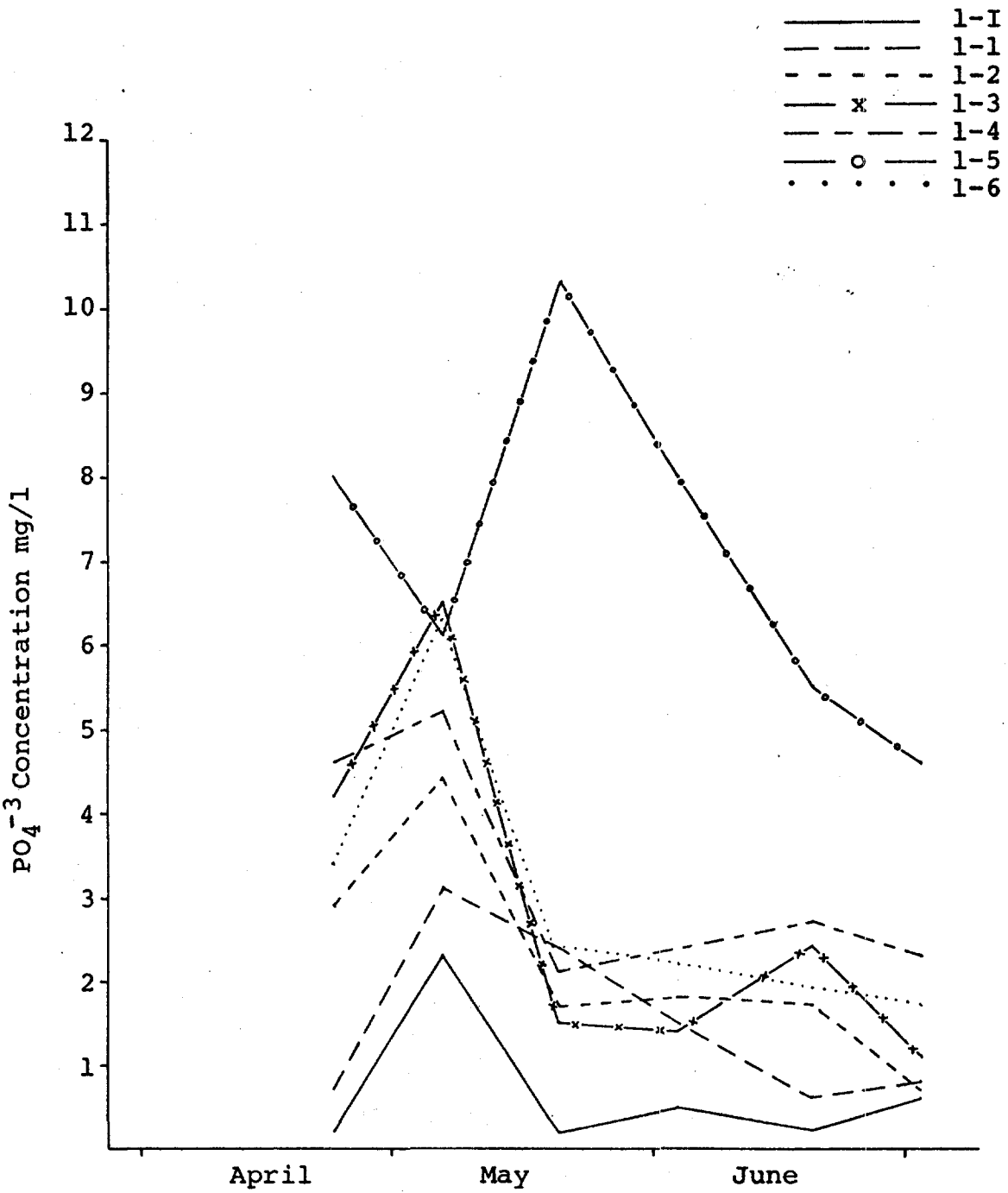


Figure 14 - Hydrograph of Phosphate Concentration at Site 1 for Three Months During 1973

Mean and standard deviation, along with standard deviation expressed as per cent of the mean, are shown in Table 3 for all measured ionic constituents at site one. The higher variability of the impoundment, relative constancy of groundwater concentrations in a given well and extreme variability of phosphate concentrations are all indicated by these data.

Groundwater temperatures during the study period (Figure 15) ranged from a low of 21.5°C (well 1-5) on March 28 to 28.5°C on July 3 (well 1-3). The temperature hydrograph shows that most of this general increase occurred during the interval May 7 - May 21. This rather sharp increase consisted of a three to four degree (°C) rise in all wells. Temperature changes in the wells were uniform in that increase or decrease in groundwater temperature occurred simultaneously in all wells. As with ionic concentrations the impoundment was more variable than groundwater. Impoundment temperature was consistently higher than that of adjacent groundwaters.

The hydrograph for pH at site one (Figure 16) indicates that changes in pH were also generally uniform. The range of pH encountered at site one was from 6.6 (well 1-3) to about 7.5 (well 1-6). The pH rose early in the study period (until May 7), after which a relatively sharp decrease occurred (May 7 - May 21). The pH remained about the same for a month (May 21 - June 20) then began to rise

TABLE 3 - MEAN, STANDARD DEVIATION, AND STANDARD DEVIATION AS PERCENT OF MEAN FOR IONS AT SITE 1 DURING THE STUDY PERIOD

Cl^- g/l				Mg^{++} mg/l			
SAMPLE	MEAN	STANDARD DEVIATION	AS % OF MEAN	SAMPLE	MEAN	STANDARD DEVIATION	AS % OF MEAN
1 - 1	18.91	0.93	4.9	1 - 1	1,256	59	4.7
1 - 2	15.75	0.62	3.9	1 - 2	1,134	19.9	1.8
1 - 3	10.86	0.45	4.1	1 - 3	760	40	5.3
1 - 4	15.15	0.27	1.8	1 - 4	1,086	26.4	2.4
1 - 5	15.47	0.36	2.3	1 - 5	1,114	21.5	1.9
1 - 6	15.03	0.38	2.5	1 - 6	1,117	42.3	3.8
1 - I	17.72	2.48	14.0	1 - I	1,214	140	11.5

Ca^{++} mg/l				$PO4^{-3}$ mg/l			
SAMPLE	MEAN	STANDARD DEVIATION	AS % OF MEAN	SAMPLE	MEAN	STANDARD DEVIATION	AS % OF MEAN
1 - 1	537	19.8	3.7	1 - 1	1.52	1.03	67.8
1 - 2	644	14.0	2.2	1 - 2	2.20	0.61	27.6
1 - 3	386	5.3	1.4	1 - 3	2.85	2.11	74.1
1 - 4	686	21.5	3.1	1 - 4	3.38	1.42	42.0
1 - 5	536	22.3	4.2	1 - 5	7.08	2.08	29.4
1 - 6	603	35.0	5.8	1 - 6	2.98	1.73	58.0
1 - I	483	47.5	9.8	1 - I	0.67	0.82	122.

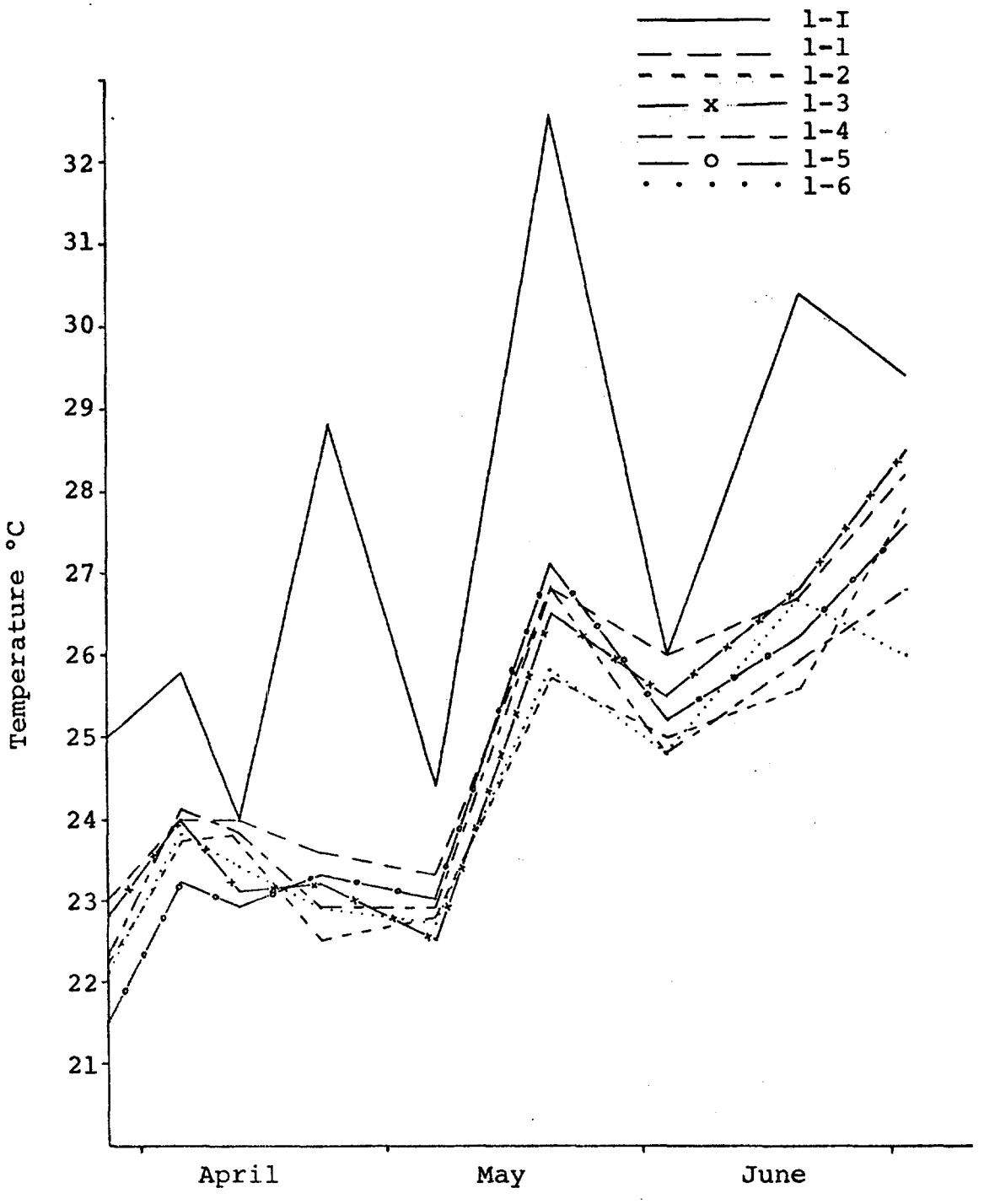


Figure 15 - Hydrograph of Temperature at Site One For Three Months During 1973

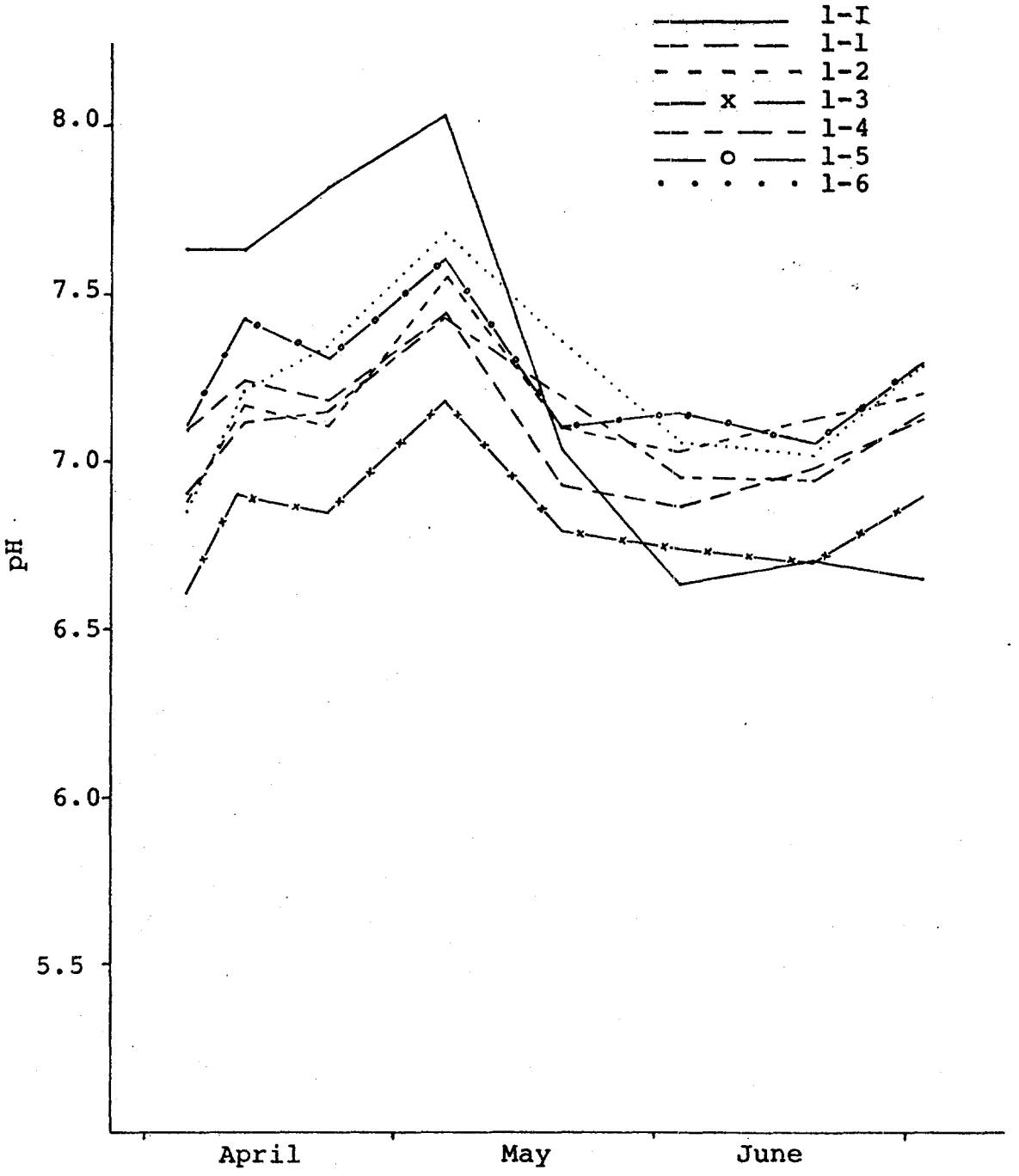


Figure 16 - Hydrograph of pH at Site 1 for Three Months During 1973

during the final sampling interval. The impoundment was again more variable than the groundwater and had a pH range from 6.7 to 8.0.

The hydrograph of depth to water in wells (Figure 17) shows a steady decline in water levels until May 21. Water level then rose until June 20, after which the level declined during the final sampling interval. Water levels were found to be generally higher in the deeper wells although the level in shallow wells could temporarily rise above that of deeper wells (June 20).

Because the effects of rainfall and evaporation were thought to be important influences on water levels and ionic concentrations, daily rainfall measurements were obtained from the Space Flight Meteorology Group of the National Weather Service at Kennedy Space Center. These data are presented in Table 4. The rain gage for these measurements was located at the Space Center Industrial Complex (Figure 4). Since the rainfall data were recorded several miles from the well site, the data do not indicate exact rainfall at the site. Data for the months prior to the study period were obtained for reasons to be explored later.

Some of the effects of rainfall and evaporation are suggested in Figure 18. Daily rainfall appears as a bar graph at the bottom of the figure, while water level and chloride concentration of the impoundment at site 1 are shown as hydrographs. It may be seen that early May

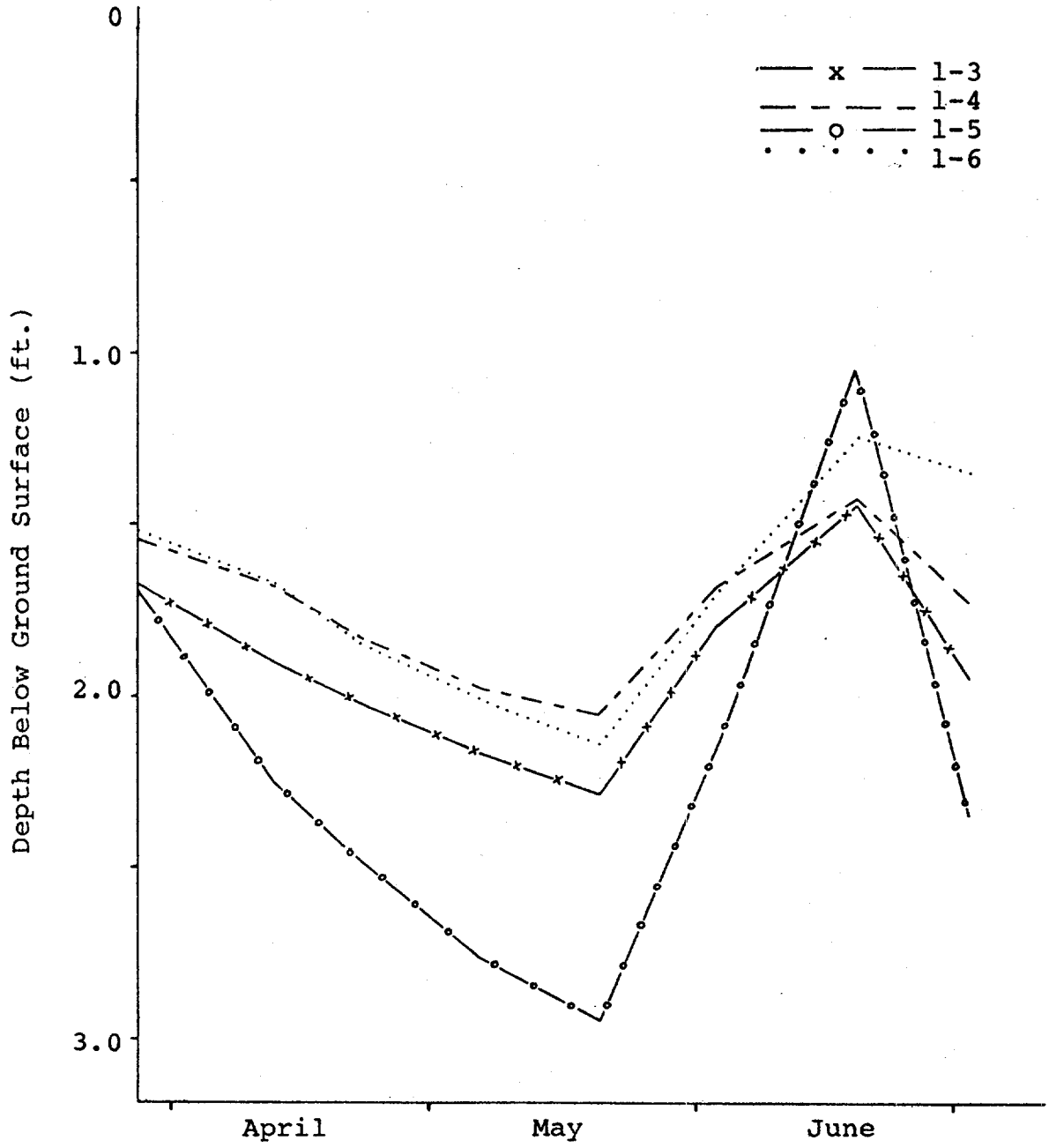


Figure 17 - Hydrograph of Depth to Water in Wells at Site 1

TABLE 4 - RAINFALL IN INCHES AS RECORDED BY THE NATIONAL WEATHER SERVICE AT KENNEDY SPACE CENTER.

Those days not listed had either no rain or less than .01 inches. Monthly totals are in parentheses.

DATE	AMOUNT		DATE	AMOUNT	
1/10/73	.32		3/29/73	.48	(3.92)
1/11/73	.88				
1/12/73	1.42		4/01/73	.13	
1/22/73	.50		4/04/73	.50	
1/23/73	2.10		4/08/73	.37	
1/24/73	.08		4/26/73	.42	(1.42)
1/27/73	.18				
1/28/73	.40		5/08/73	.08	
1/29/73	.02		5/09/73	.06	
1/30/73	.01	(5.91)	5/24/73	.02	
			5/25/73	.35	
2/02/73	.32		5/29/73	.49	
2/03/73	.04		5/30/73	.60	(1.60)
2/09/73	.55				
2/10/73	.17		6/07/73	.55	
2/15/73	.07		6/08/73	2.23	
2/18/73	.25		6/14/73	.15	
2/19/73	.03	(1.33)	6/15/73	.20	
			6/18/73	.71	
3/02/73	.05		6/21/73	.10	
3/09/73	.65		6/30/73	1.50	(5.44)
3/17/73	.37				
3/20/73	.24		7/06/73	.03	
3/25/73	2.10		7/09/73	.50	
3/26/73	.03				

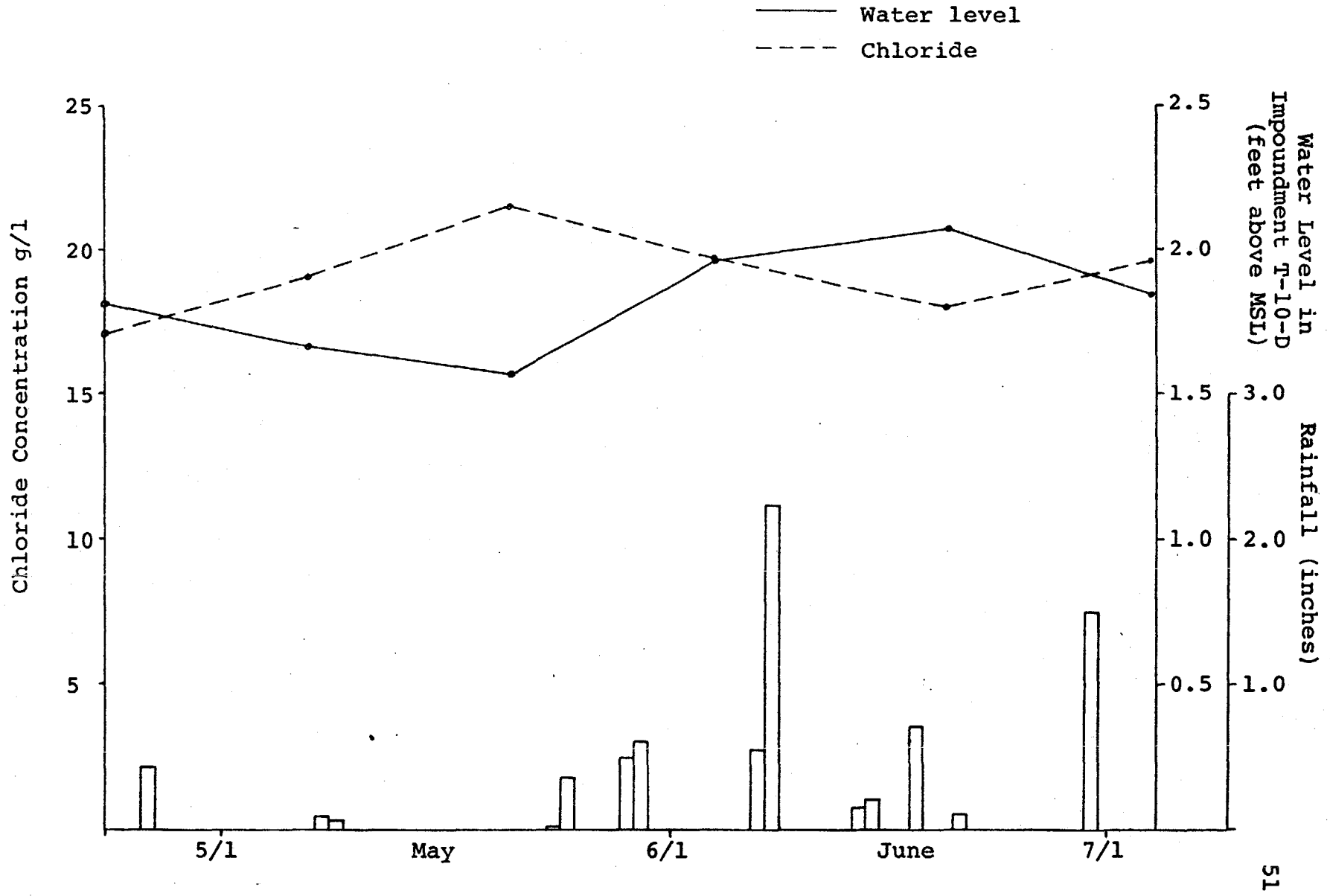


Figure 18 - Hydrographs of Chloride Concentration, Water Level and Rainfall at Impoundment T-10-D (Site 1)

was a relatively dry period and was associated with dropping water level and increasing chloride concentration. The rains of late May and June were associated with rising water levels and declining chloride concentration. The decrease in water level during the last sampling interval seems to indicate that the heavy rainfall (1.5 inches) on June 30 was not received at the well site.

2. Wells and Surface Bodies at Sites Two Through Five

The results of analyses from sites two through five are listed in Table 2. Since there is insufficient data to describe temporal relationships at these sites, the following sections will outline the results from a single sampling run (July 3, 1973).

3. Site Two

The three wells at site two (Figure 6) were along a transect that cut across a mosquito control dike. The dike separated an impoundment (T-10-E) from the Indian River.

On July 3, 1973 chloride concentration in the impoundment was 9.37 g/l. Calcium concentration was 280 mg/l, magnesium 550 mg/l, phosphate 0.6 mg/l, and sulfate 950 mg/l. Concentrations in the Indian River were generally much higher than those in the impoundment. Chloride concentration was 15.92 g/l, calcium 430 mg/l, magnesium 1,020 mg/l, phosphate 0.3 mg/l, and sulfate 2,330 mg/l.

Ionic concentrations in the groundwater in the area of the dike were similar to those of the impoundment. Moving across the dike from the impoundment to the river chloride ion increased from 8.51 g/l (well 2-1) to 9.85 g/l (well 2-3). Calcium increased from 280 to 320 mg/l, magnesium increased from 540 to 610 mg/l, and phosphate increased from 0.5 to 1.3 mg/l. Sulfate ion was the only constituent measured that did not increase in this direction across the dike. Sulfate concentration decreased from 890 to 730 mg/l.

The similarity in groundwater and impoundment concentrations seems to indicate that impoundment water migrates through (or under) the dike in the direction of the Indian River. Well 2-3 was located 16 feet out from the edge of the river (Figure 6) yet contained water with concentrations similar to those of the impoundment. Groundwater flow in this direction was probably initiated by pressure differences due to the higher water level in the impoundment (Figure 6).

4. Site Three

Site three was similar to site two in that the three wells were along a transect across a mosquito control dike that separated an impoundment (T-24-D) from the Indian River. The total distance involved was greater at site three (Figure 7).

Chloride concentration in the impoundment on July 3 was 680 mg/l (much lower than the two sites previously considered). Calcium concentration was 27 mg/l, magnesium 33 mg/l, phosphate 0.5 mg/l, and sulfate 16 mg/l. River concentrations were much higher (phosphate the only exception). Chloride concentration was 14.85 g/l, calcium 370 mg/l, magnesium 950 mg/l, phosphate 0.7 mg/l, and sulfate 2,320 mg/l.

As with site two groundwater concentrations under the dike and the river edge were much closer to those of the impoundment. Moving across the dike in the direction of the river chloride concentration increased from 670 mg/l (well 3-1) to 1,210 mg/l (well 3-3). Calcium concentration increased from 27 to 35 mg/l, magnesium from 34 to 59 mg/l, and phosphate from 0.6 to 11.3 mg/l. Sulfate ion did not decrease through the dike as it had at site two. At site three it increased from 36 to 58 mg/l (sensitivity of the sulfate test at these low concentrations is questionable, however).

These data also show the similarity of groundwater concentrations to those of the impoundment. A pressure gradient flow may also exist (at least during part of the year) at this site due to higher water levels in the impoundment (Figure 7).

5. Site Four

The series of three wells at site four extended from Mosquito Lagoon to the inland distance of about 36 feet (Figure 8). The results presented from this site are those of June 20 because by July 3 the casing of well 4-2 had been removed (probably vandalism).

A surface water sample from Mosquito Lagoon on June 20 had a chloride concentration of 17.02 g/l. Calcium concentration was 400 mg/l, magnesium 1,090 mg/l, and phosphate 0.3 mg/l. Groundwater concentrations at this site were generally similar to those of the river. At well 4-3 chloride concentration was 17.31 g/l, calcium 410 mg/l, magnesium 1,110 mg/l, and phosphate 0.4 mg/l.

Concentrations were lower in well 4-2 (except for phosphate). This well was slightly shallower than the others at site four (Figure 8) and was located near the edge of the lagoon. The situation was similar to that for well 1-3 at site one, which also had lower concentrations.

Groundwater levels at site four were low (3.41 feet below ground surface in well 4-3 on July 3), at about the same level as the water in the lagoon. Thus in the absence of a pressure differential (such as that at sites two and three) groundwater flow (or possibly ionic migration by diffusion) appeared to be directed inland during the study period. Presumably the lack of a persistent

pressure differential also accounted for the occurrence of highly saline water inland at site one. Groundwater levels at site one were also about the same as the level in the impoundment.

6. Site Five

Site five was located in about the middle of Merritt Island (Figure 4), well removed from saline surface water bodies. The two wells at this site were about 24 feet inland from a small fresh water pond (Figure 9).

On July 3 there was little difference in concentrations of chloride, calcium, and magnesium between the pond and the two wells. As an example, the chloride concentration in the pond was 120 mg/l while it was 110 mg/l and 120 mg/l in wells 5-1 and 5-2, respectively. Phosphate, however, was 6.1 mg/l in the pond, 5.2 mg/l in well 5-1, and 0.7 mg/l in well 5-2. Sulfate was also lower in wells than in the pond. Pond concentration was 71 mg/l while it was 28 mg/l in well 5-1 and 61 mg/l in well 5-2.

Groundwater levels at site five were also about the same as the level in the surface water body, in this case the pond. On July 3 depth to water in well 5-1 was 3.76 feet while it was 3.89 feet in well 5-2. Thus at site five there was little (if any) pressure difference that could generate groundwater flow.

7. Trace Constituents

Sample aliquots from all wells and surface water bodies from the June 4 sampling run were delivered to the Bendix Chemical Analysis Laboratory at Kennedy Space Center for atomic absorption and flame spectrophotometric analysis on many minor constituents of groundwater. The results of these analyses are given in Table 1 of Appendix A. The following discussion briefly summarizes these results.

Copper, vanadium, and aluminum were never detected in amounts as high as 0.1 parts per million (ppm). Mercury had a maximum concentration of .026 ppm (well 4-3) but was generally less than .01 ppm. Manganese was almost always less than 0.1 ppm and reached a maximum of 0.11 ppm in wells 1-1 and 2-3.

Iron concentrations were less than 0.16 ppm in all wells and surface water bodies except well 4-1, where the concentration measured was 0.31 ppm. Zinc reached a maximum concentration of 0.28 ppm in the Indian River at site three (3-IR) but concentrations were generally between 0.1 and 0.2 ppm. Nickel achieved a maximum concentration of 0.31 ppm in well 4-2 although it was usually present in amounts less than 0.1 ppm. Strontium was present in higher quantities with the maximum at site one (10.5 ppm in well 1-4). Strontium averaged about 6 ppm at site two, 3 ppm at site three, 7 ppm at site four, and 1 ppm at site five.

Concentrations of these minor constituents were always in the lowest amounts at site five. As a general statement it seems that the highest concentrations of the trace constituents were associated with ground and surface waters with high chloride concentrations.

V. DISCUSSION

A. General Chemical Character of the Shallow Groundwaters of Merritt Island

The results presented for the analyses of samples obtained from bore holes indicate that a wide range of ionic concentrations is encountered in the shallow groundwaters of Merritt Island. A simple classification scheme used by Davis and DeWiest (1966), based on concentration of dissolved solids, when applied to the current data indicates that the groundwater ranges from fresh (less than 1,000 ppm) to salty (over 10,000 ppm). Many sites contained water of brackish character (1,000 - 10,000 ppm). It was shown in Figure 10 that the brackish and salty waters occurred at the island margin and extended some distance landward.

Other classification systems require data in the form of milliequivalents per liter. Accordingly, the data from bore holes has been converted to this form (Table 5) using conversion factors presented by Hem (1970). These data may now be used in a classification based on the dominant ions present (Davis and DeWiest, 1966). The Piper trilinear diagram (Figure 19) has been used for this purpose. In this diagram the per cent of total milliequivalents per liter of the cations and anions are presented

in the triangular forms at the bottom of the figure. The central diamond-shaped form includes all ions.

It can be seen from Figure 19 that the two most common forms of the water may be classed as "sodium chloride" water and "calcium bicarbonate" water. The sodium chloride waters appear as a group near the right hand corner of the diamond shaped figure. Sea water plots at this apex (Hem, 1970). The sites included in this group were classified as brackish or salty under the previous system. It thus appears that much of the groundwater of Merritt Island has an affinity for the composition of sea water, although diluted to some degree.

The fresh waters of the island were dominated by the calcium and bicarbonate ions, although sodium and chloride were also significant in some of these samples. As the sediments of the nonartesian aquifer were deposited under marine conditions and shell material is common (Brown and Hyde, 1964) the prevalence of calcium and carbonate species in the fresher waters might be expected.

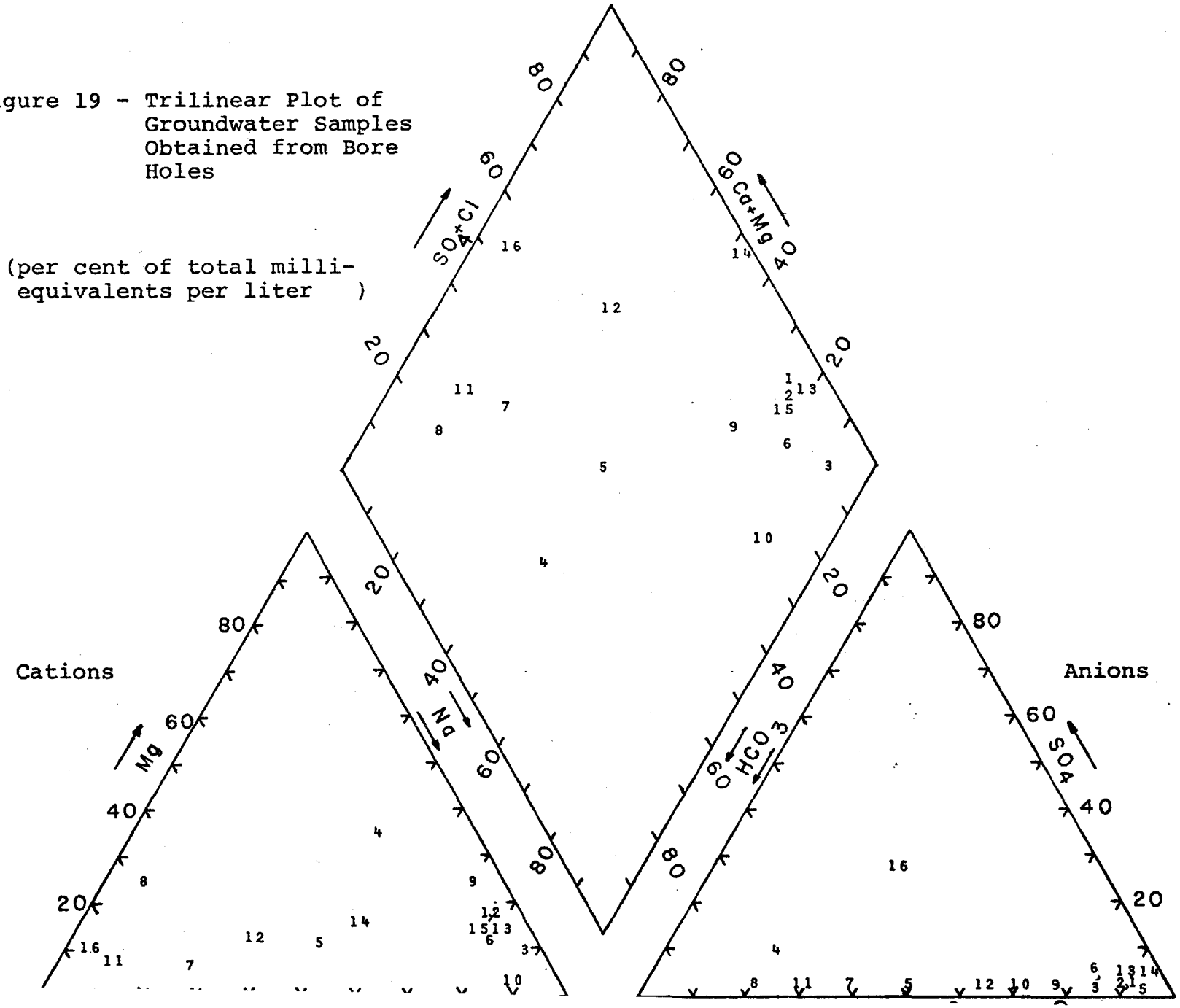
1. The Influence of Surface Water Bodies

It is reasonable at this point to consider a possible source of the salts that occur in much of the island's groundwater. The Indian River is a lagoonal system with salinities commonly in the range 20-30 parts per thousand (Nevin, et. al., 1973). As mentioned previously,

TABLE 5 - RESULTS OF CHEMICAL ANALYSES OF BORE HOLE SAMPLES EXPRESSED AS MILLIEQUIVALENTS PER LITER

LOCATION	Na^+	Ca^{++}	Mg^{++}	Cl^-	$SO_4^=$	HCO_3^-	$\sum$ CATIONS	$\sum$ ANIONS
B1	254	17.4	58.8	296	14.8	20.0	330.2	330.8
B2	180	11.7	41.5	211	13.7	12.9	233.2	237.6
B3	62.2	1.7	7.1	60.9	0.6	9.4	71.0	70.9
B4	8.05	2.9	6.0	3.9	1.5	12.3	16.95	17.7
B5	3.0	2.5	0.6	2.68	0.02	2.66	6.1	5.36
B6	71.8	8.8	10.4	68.6	5.0	13.2	91.0	86.8
B7	2.3	6.4	0.6	4.4	0.20	7.1	9.3	11.7
B8	1.0	5.4	2.1	1.6	0.16	6.3	8.5	8.1
B9	36.5	3.5	12.7	40.9	2.5	10.0	52.7	53.4
B10	21.8	10.2	4.6	26.9	0.05	10.9	36.6	37.8
B11	0.83	5.5	0.4	2.0	0.09	4.6	6.73	6.69
B12	1.1	2.0	0.4	3.0	0.05	1.7	3.5	4.7
B13	67.4	5.5	12.4	70.2	5.9	4.5	85.3	80.6
B14	1.4	0.85	0.4	3.1	0.33	0	2.65	3.43
B15	104	11.9	18.3	116	1.1	11.1	134.2	128.2
B16	0.61	6.3	0.8	2.6	2.6	4.1	7.71	9.3

Figure 19 - Trilinear Plot of Groundwater Samples Obtained from Bore Holes



Brown and Hyde (1964) noted that much of the low-lying western section of the island consisted of creeks and marshes with water exchange with the river. It is thus likely that a significant portion of that area came into contact with saline river water as an adjacent surface water body.

It has been shown by this study that groundwaters in proximity to surface water bodies have chemical characteristics very similar to those of the surface water bodies (for at least part of the year). Actual flow is probably responsible for this at sites two and three (due to water level differences across the dikes) although no such assumption can be made for sites one, four, and five. Low water table levels were observed at these sites, however, so flow cannot be neglected as a possibility. In any case the mechanisms that accounted for similar chemical characteristics in the present study, if operative in past geological times, could account for relatively high salt concentrations in those areas of the island once in proximity to saline surface water bodies.

Further evidence for the "marine" origin of the salts is obtained through examination of the chloride-bicarbonate ratio, as suggested by Revelle (1941). He stated that an increased ratio can be indicative of the presence of sea water. The chloride-bicarbonate ratios are presented in Figure 20 as the upper figure in each pair.

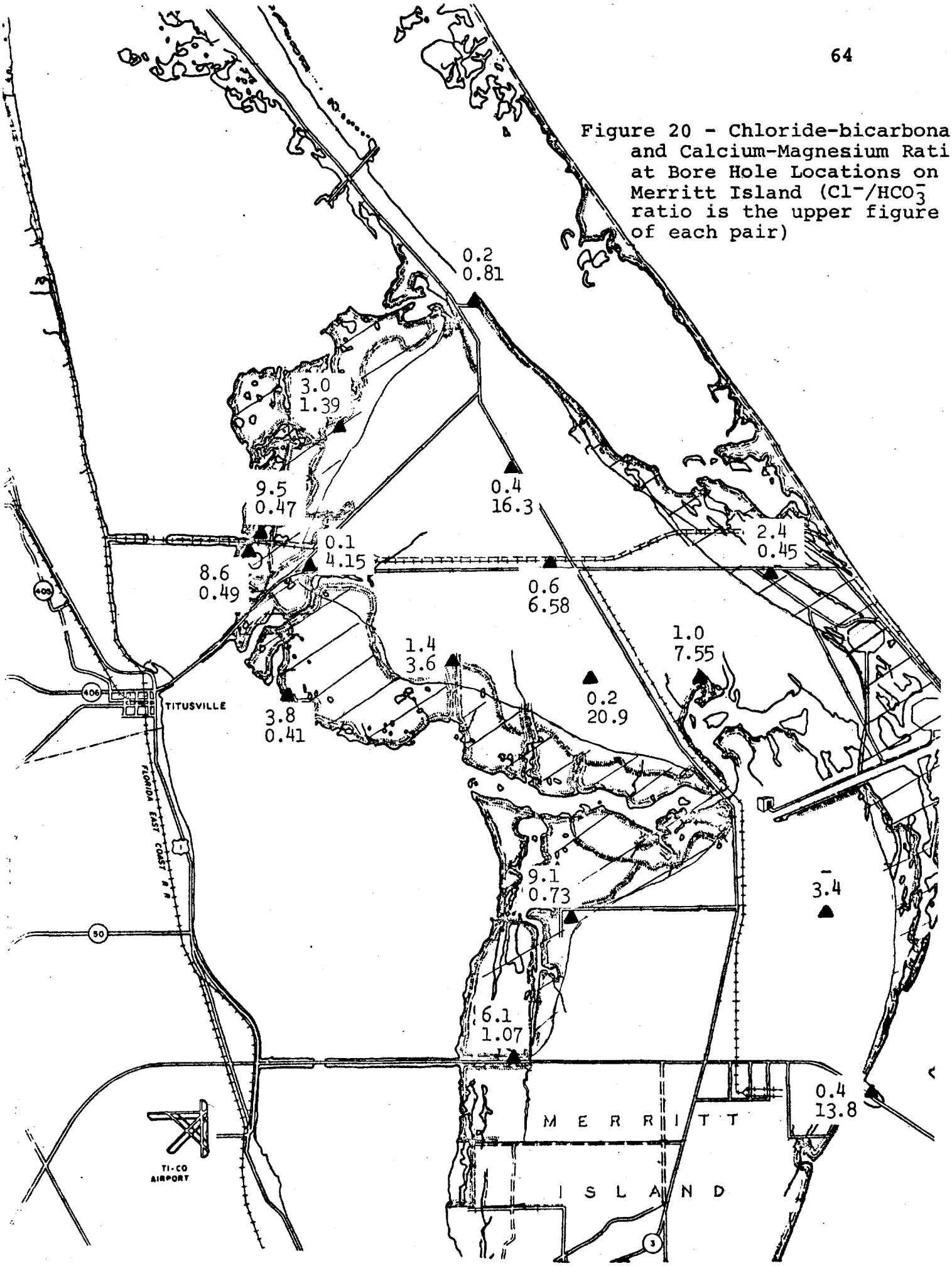


Figure 20 - Chloride-bicarbona and Calcium-Magnesium Rati at Bore Hole Locations on Merritt Island (Cl^-/HCO_3^- ratio is the upper figure of each pair)

Higher ratios are found near the island margin, covering an area roughly the same as the area with dissolved solids of greater than 1,000 mg/l (Figure 10). Calcium-magnesium ratios are included in Figure 20 as they show an opposite relationship, with lower ratios in the more salty waters. These data suggest that a comparison of the chloride-bicarbonate ratio with the calcium-magnesium ratio might prove to be a useful index. A combined ratio yields a value greater than one for salty waters and less than one for the fresher waters.

B. The Variation In Chemical Characteristics With Time

The hydrographs depicting chloride, calcium and magnesium at site one (Figures 11-13) were shown to indicate that while ionic concentrations varied considerably in the surface water body, concentrations remained relatively constant in the wells. Although there was a definite difference in concentrations from one well to another, for any single well the concentrations did not vary much with time.

The variations that did occur were not consistent from one well to another. That is, an increase or decrease in one well was not necessarily associated with an increase or decrease, respectively, in other wells. Such was not the case for phosphate, temperature, and pH values. For

each of these three parameters fairly uniform changes took place (in time) in all wells. It appears important, therefore, to try and account for those changes, especially since they were not observed for any of the measured major ionic constituents.

The generally increasing trend in groundwater temperatures (Figure 15) was probably due to a seasonal increase in air temperatures and coincident increased insolation of the soil as time passed from spring into summer. Rainfall, or the lack of rainfall, may have been important in determining the manner in which a seasonal temperature increase was manifested in temperature increase of the groundwater. The sharp temperature increase from May 7 to May 21 was accompanied by very low rainfall (Table 4), while the decline after May 21 may have been due to cooling effects of heavy rains in late May (Table 4).

The changes of pH in time were also remarkably consistent (Figure 16). The sharp decline that occurred in mid-May coincided with the dramatic rise in groundwater temperatures. Although pH varies with temperature it does not seem likely that the temperature increase could have accounted for the observed magnitude of pH decrease. Published data (Chemical Rubber Company, Handbook of Chemistry and Physics, 53rd ed., 1972) for some phosphate buffer compounds indicate that a ten degree (°C) rise in temperature accounts for a pH decrease of only .03 pH unit. In

this study the temperature rise was 3-4°C while the pH decrease ranged from 0.4 to 1.0 pH units.

Phosphate concentrations (with the exception of well 1-5) also exhibited an abrupt decrease during the May 7 - May 21 sampling interval. It is unlikely that this was due to a solubility dependence on pH because phosphate compounds become more soluble under acid conditions (Handbook of Chemistry and Physics). Thus from solubility considerations the lower pH should have resulted in higher phosphate concentrations, but the opposite (lower phosphates) was observed.

From the preceding it is difficult to explain the observed changes in pH and phosphate based on physical factors alone. Since phosphate is an important biological nutrient material and may serve as a limiting factor in many situations (Odum, 1971) a biological approach was considered, which might account for the results.

While a temperature rise of 3-4°C is small when considering physical effects, such an increase could assume great importance biologically based on the effects of temperature on biochemical reaction rates (Lehninger, 1970). As an assumption, if a ten degree rise can be said to double reaction rates (Lehninger, 1970) then a 3-4°C rise could increase rates as much as 30 to 40 per cent. If the increased rates increased plant growth (which requires phosphate as a nutrient) then a possible

mechanism for explanation of reduced phosphate levels would be at hand.

A biological approach also offers an explanation for the decline in pH values that accompanied the temperature increase. If the temperature rise stimulated rates of bacterial metabolic activity then an increased flux of carbon dioxide released into the groundwater might be expected. According to Skirrow (1965), carbon dioxide takes part in an equilibrium in aqueous solution depicted by the following:

$$H_2O + CO_2 \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons CO_3^{2-} + 2H^+.$$

An increase in carbon dioxide drives the reactions toward the right, thereby increasing the hydrogen ion concentration and reducing the pH (Skirrow, 1965). Equilibrium concepts in the carbon dioxide system are quite complex (Skirrow, 1965) so a more specific statement would not be practical.

Following the period of rising temperature and declining phosphate and pH values, an increase in the amount of algae at the shore of impoundment T-10-D was apparent (personal observation). When sampling the impoundment on June 4 algae had to be pushed aside in order to fill the sample bottle, whereas this had not been necessary on previous dates. Unfortunately the algae was not identified nor were relative amounts present quantified.

Most algal species require inorganic nutrients and certain organic compounds for growth (Jackson, 1968). It is possible that the relatively high rainfall of late May (Table 4) was responsible for draining the soil at the edge of the impoundment of nutrient substances, which in turn promoted the increased algal growth.

The preceding has necessarily been of a speculative nature because the data are incomplete and therefore inconclusive. No biological influences can be proved. The data are only suggestive of such an influence, as alternative hypotheses appear even less adequate in attempts to account for the observations. The nature of the problem is not insignificant, however, for at hand may be mechanisms involved in certain types of "algae blooms." For this reason it is the opinion of this investigator that further study into these problems is warranted. Important considerations in this area include the response of groundwater temperature to seasonal temperature change and rainfall distribution in time, the response of soil bacteria to temperature change in their environment, and the response of algae and other plants to changes in temperature and bacterial activity.

C. The Influence of Rainfall on Ionic Concentrations

The basic influence of rainfall (and evaporation) was indicated earlier in Figure 18. Periods of high

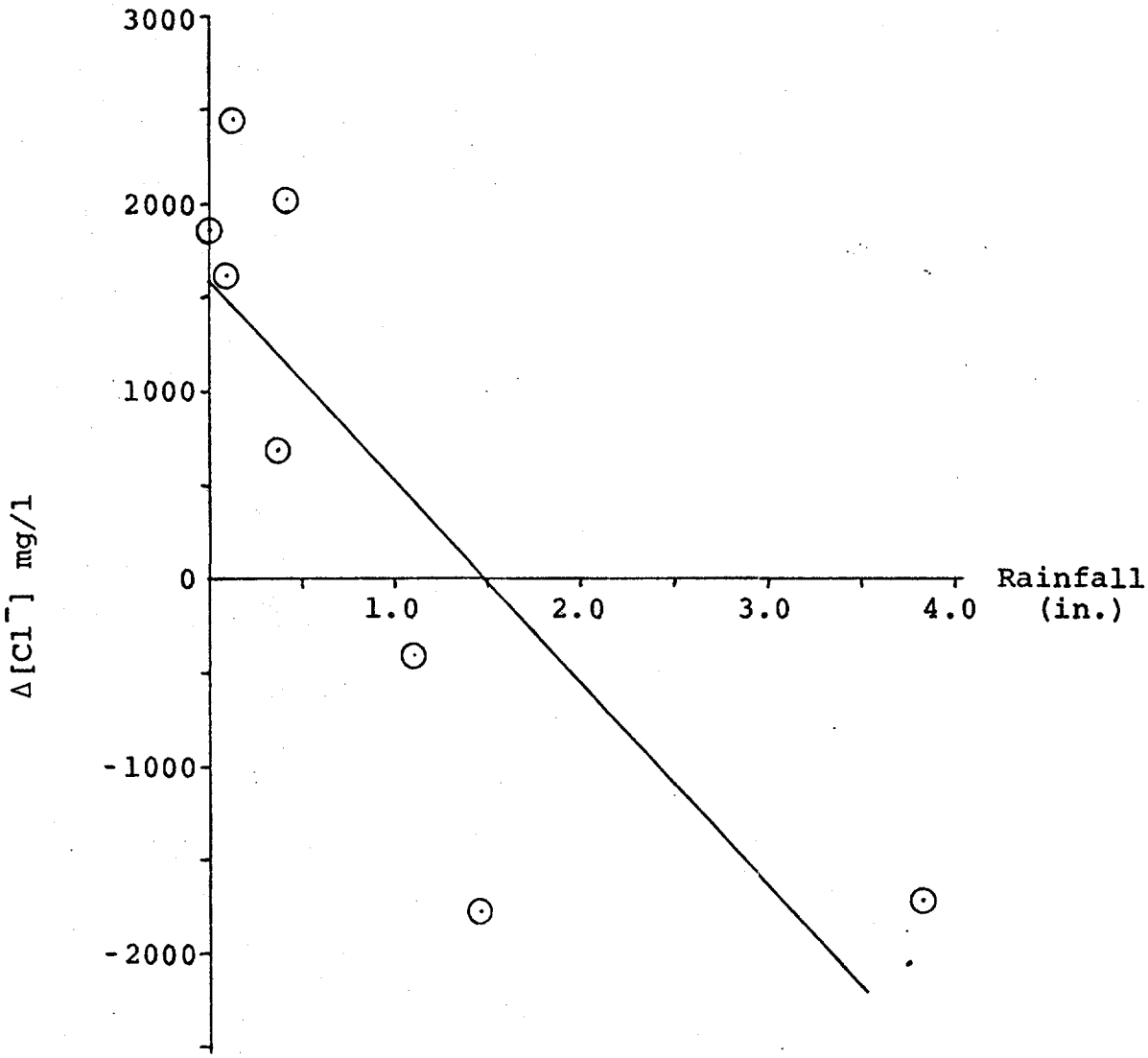
rainfall (rainfall exceeding evaporation) were associated with declining ionic concentrations while periods of low rainfall (evaporation exceeding rainfall) were associated with increasing concentrations. This section will treat the problem more rigorously and discuss an additional feature as well.

In order to more precisely determine the nature of the influence of rainfall a correlation of rainfall during a sampling interval with change in chloride concentration during the interval was performed for impoundment T-10-D. The data used for this correlation are given in Table 6.

Table 6 - Total Rainfall and Chloride Concentration Changes During Study Period Sampling Intervals

Sampling Interval	$\Delta [Cl^-]$ mg/l	Rainfall (in.)
3/28 - 4/5	-410	1.11
4/6 - 4/12	+690	0.37
4/13 - 4/22	+1860	0
4/23 - 5/6	+2030	0.42
5/7 - 5/20	+2450	0.14
5/21 - 6/3	-1790	1.46
6/4 - 6/19	-1720	3.84
6/20 - 7/3	+1620	0.10

The results of the correlation are shown in Figure 21, which has a correlation coefficient (r) equal to -0.82 ($r^2 = 0.66$). The intercept of the regression line (obtained by least squares method for small sample sizes) with the axis for rainfall indicates that about one and a half inches of rain in a sampling interval are required for the concentration to remain stable (i.e. $\Delta[Cl^-] = 0$).



r = -0.82

Figure 21 - Correlation of Rainfall with Change in Chloride Concentration in Impoundment T-10-D at Site One

Similar results were obtained when rainfall was correlated with the changes in calcium and magnesium concentrations during a sampling interval (Figure 22). The intercepts of these regression lines also indicate that about 1½ inches of rain are required every 1-2 weeks for stable concentrations.

When the preceding correlations were examined it was observed that a stronger correlation would be obtained if it were assumed that the rainfall of 2.23 inches on June 8 as recorded at the weather station was not received at the well site. A correlation was then performed that excluded this amount (Figure 23). The correlation coefficient in this instance was much stronger ($r = -0.95$, $r^2 = 0.91$). This is admittedly a dangerous technique (especially when so few sample points are involved) but the results are interesting and there is some evidence that rainfall in the Merritt Island area is unevenly distributed (as will be shown later).

The effects of rainfall on concentrations in the groundwater were harder to discern. This was presumably because the wells at site one penetrated the saturated zone to a depth below that at which highly saline water was encountered. Rain percolating through the soil at this site would be inhibited in downward movement when it reached the denser salt water, thereby delaying (or perhaps eliminating) observation of dilution effects of rainfall.

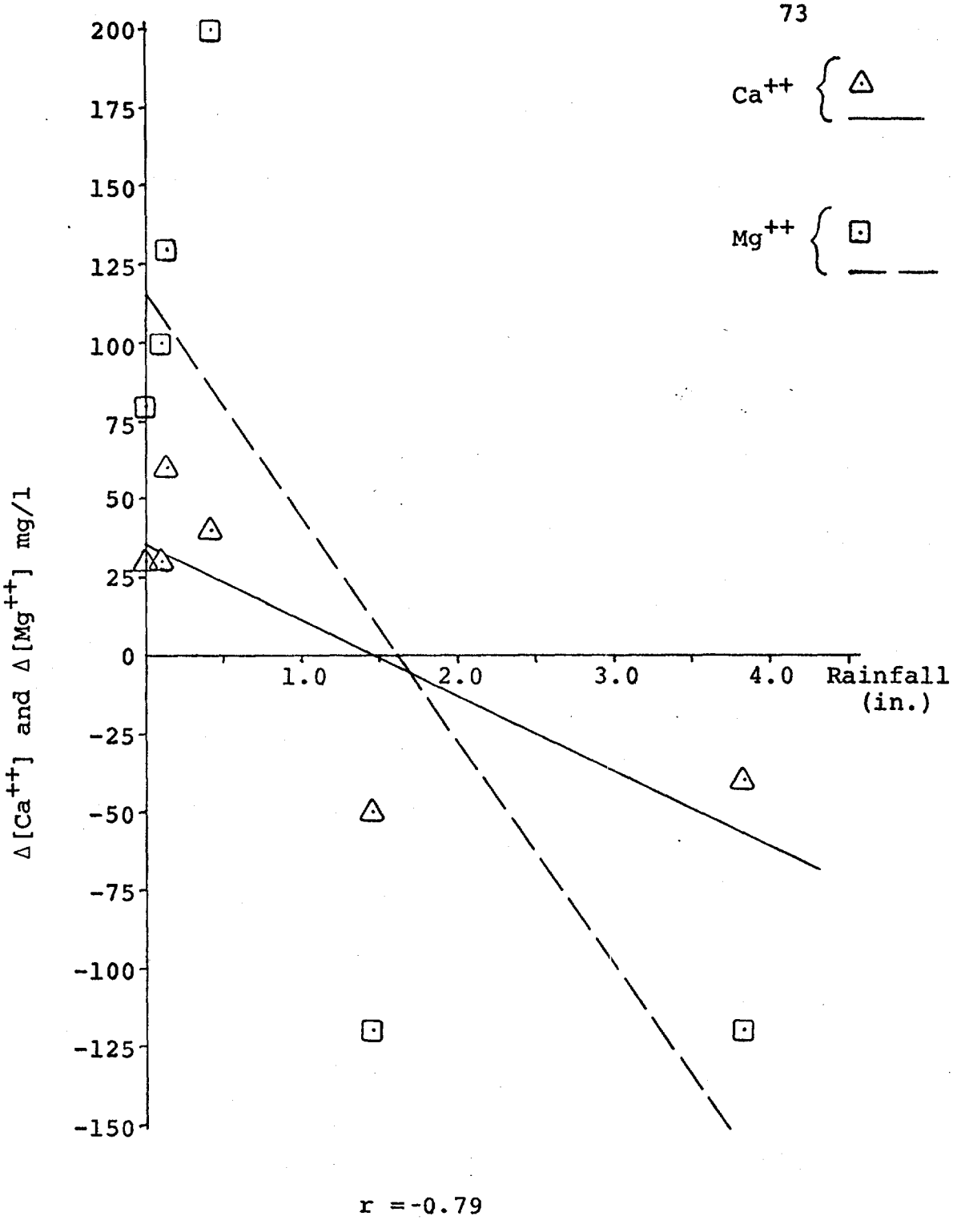


Figure 22 - Correlation of Rainfall with Change in Concentration of Calcium and Magnesium in Impoundment T-10-D

To investigate this problem the change in chloride concentration in well 1-1 during a sampling interval was correlated with rainfall recorded during a corresponding interval 60 days earlier. The figure of 60 days was selected because the hydrographs for chloride, calcium, and magnesium (Figures 11-13) show an increase for well 1-1 that follows the increase in the impoundment by 60 days.

Following the above procedure the correlation presented as Figure 24 was obtained. The correlation coefficient ($r = -0.51$, $r^2 = 0.26$) in this case is weaker than that obtained from the previous correlations, but the influence of a single major rain storm is much more evident. A second correlation (Figure 25) was performed and did not include the rainfall of 2.1 inches on March 25 that was received at the weather station. The correlation coefficient ($r = -0.85$, $r^2 = 0.72$) indicates a much stronger relationship when the assumption is made.

It has been shown in the preceding discussion that stronger correlations of rainfall and concentration changes are obtained when it is assumed that a large rainfall received at the weather station was not received at the well site. Two questions immediately arise from this. First, what is the validity of the assumption? Secondly, what are the implications?

There is good evidence that at least one major rainfall occurred at the weather station and not at the

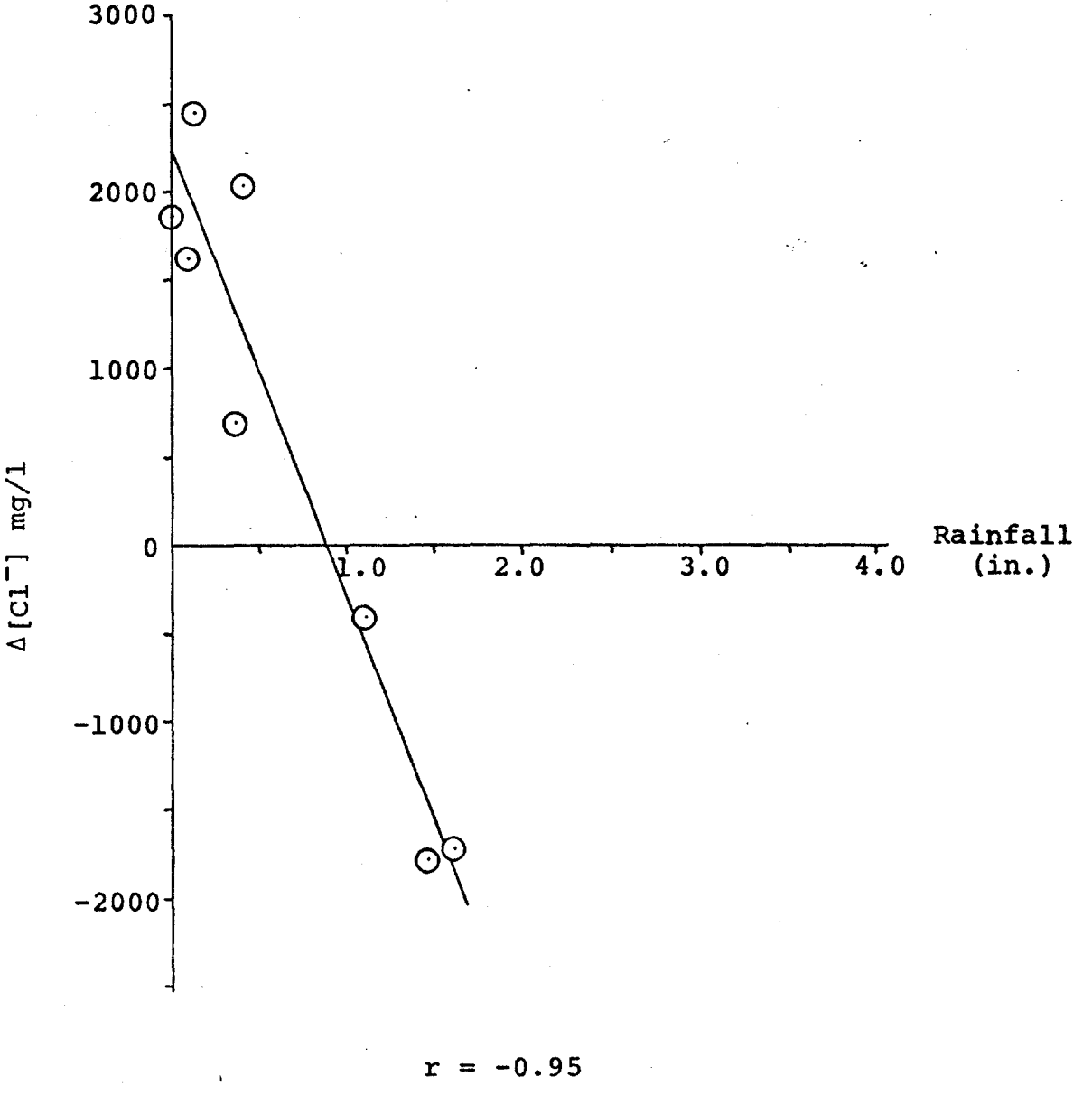
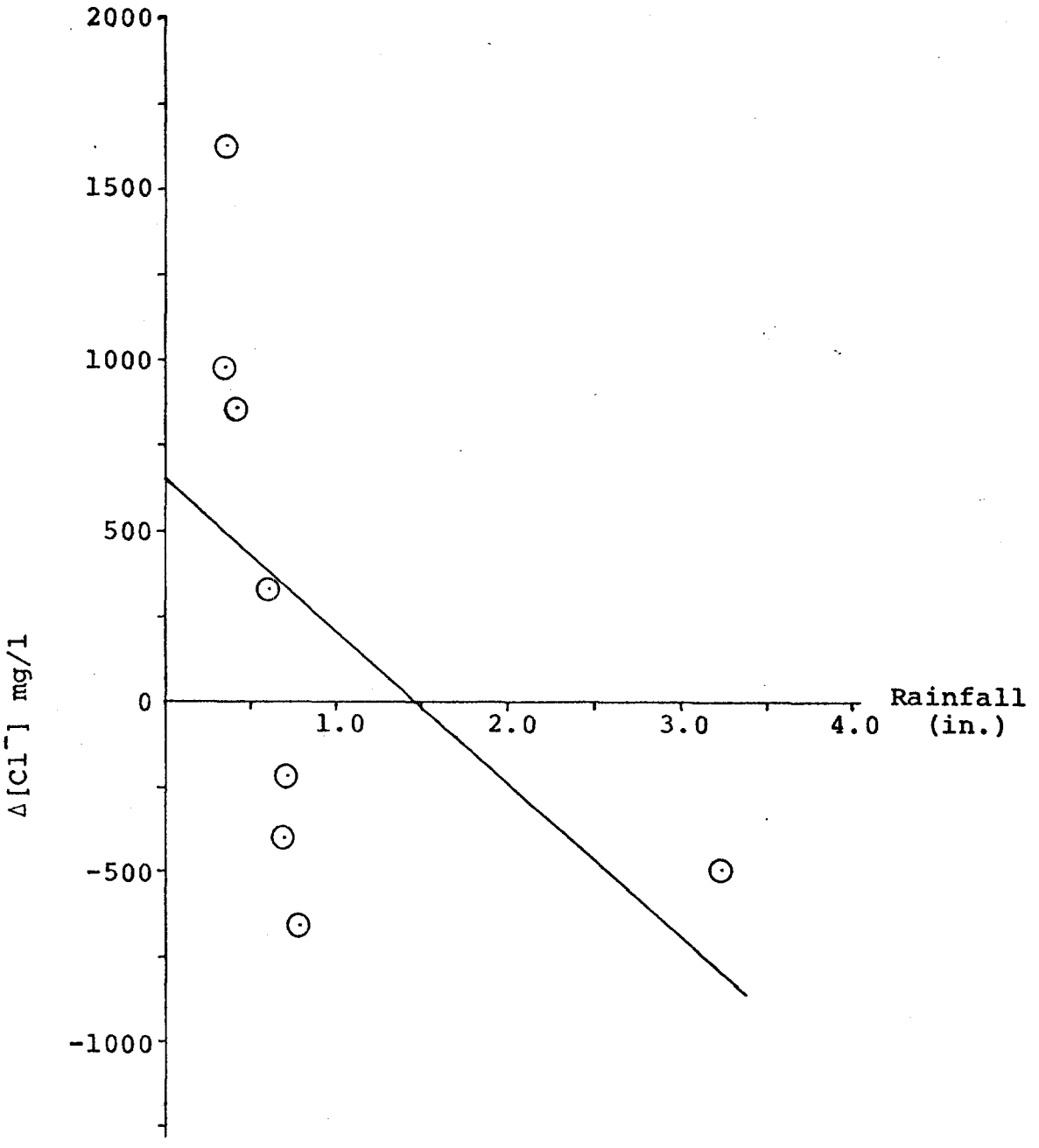


Figure 23 - Correlation of Rainfall with Change in Chloride Concentration of Impoundment T-10-D, Excluding the Heavy Rain on June 8, 1973



r = -0.51

Figure 24 - Correlation of Chloride Concentration Change in well 1-1 with Rainfall Received 60 Days Prior to Observed Changes

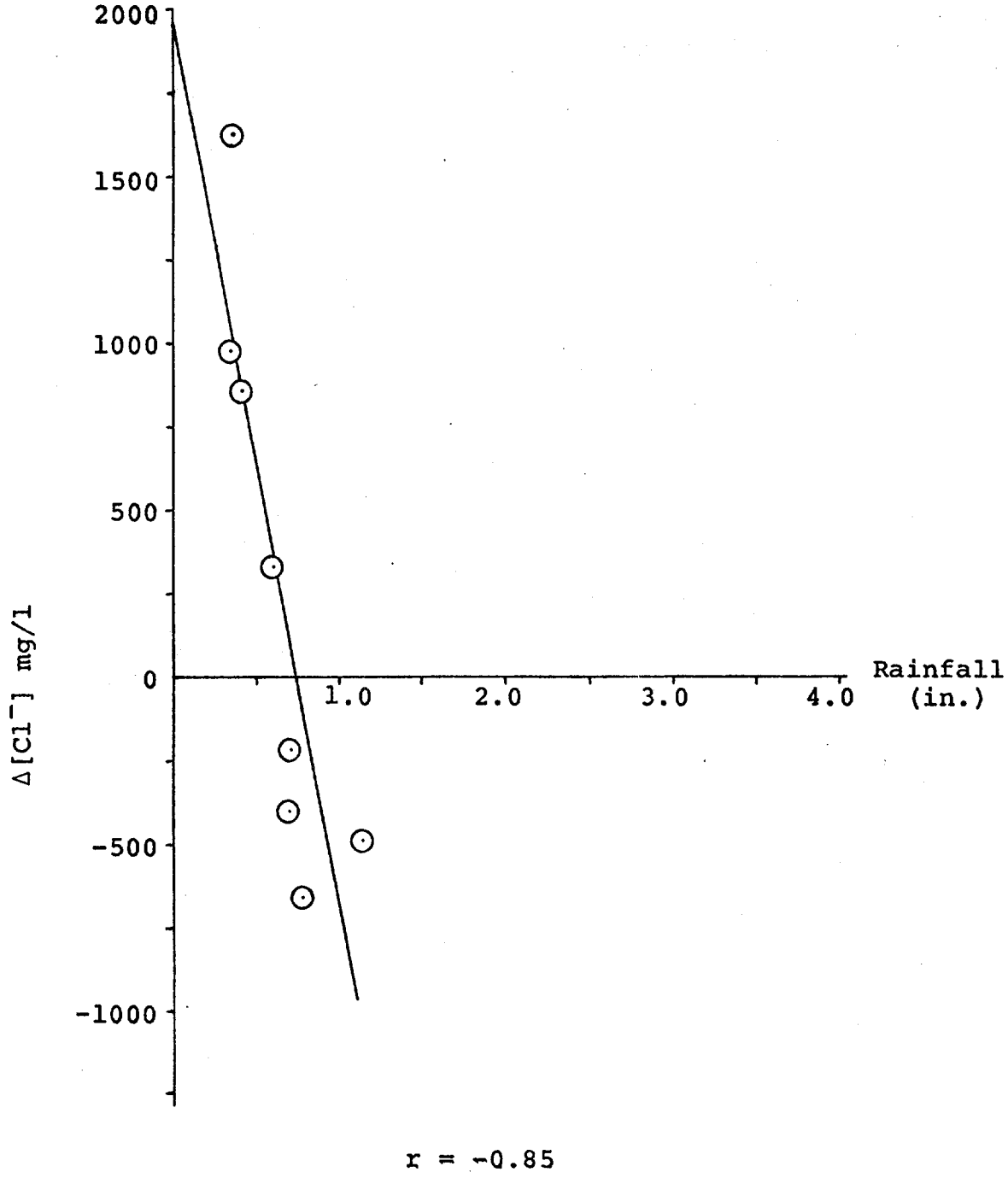


Figure 25 - Correlation of Chloride Change in Well 1-1 With Rainfall Received 60 Days Prior to Change, Excluding the Heavy Rain of March 25, 1973.

well site. It was noted in the discussion of Figure 18 that a rainfall of 1.5 inches on June 30 was accompanied by declining water level and increasing chloride concentration in the impoundment. The correlations presented in this section have indicated that a rainfall of at most 1.5 inches is required for stable concentrations. Thus if the rainfall of June 30 had actually occurred at the well site there should have been little or no concentration change. This is contrary to observation. The chloride increase during the interval in question was 1620 mg/l, very close to an expected change if no rainfall had occurred (Figure 21).

That the weather station at the Space Center receives higher quantities of rainfall than surrounding areas is also supported by data obtained from two other rain gages located farther south on the barrier island. A comparison of rainfall amounts from the Space Center weather station, Pan American weather station at Cape Canaveral City, and the weather station at Patrick Air Force Base is shown in Table 7. For each of the three dates of questionable rainfall (March 25, June 8, and June 30) the highest rainfall was recorded at the Space Center weather station. The probability of this occurring (assuming random rainfall distribution) is one chance in twenty-seven.

Table 7 - Rainfall Measurements at Three Weather Stations in the Area of Merritt Island for Three Selected Days of 1973 (Rainfall in Inches)

Date	Kennedy Space Center Industrial Complex	Pan Am Station Cape Canaveral, Fla.	Patrick Air Force Base
3/25	2.10	1.0	0.95
6/8	2.23	1.68	1.12
6/30	1.50	0.90	0.32

Thus it appears that there is some validity in excluding rainfall on the above dates from the correlations. While total exclusion may not be most accurate (based on Table 7 the rain storms on the dates in question must have been fairly widespread) a significant reduction in amounts used for correlation does seem to be indicated.

The implications of the assumption involving exclusion of rainfall on certain dates lie in the apparent nonrandom distribution of rainfall over the area. It appears that the weather station at Kennedy Space Center receives greater amounts of rainfall than nearby areas. The problem then involves a mechanism which would account for this.

The industrial complex at the space center contains many concrete buildings and paved roads and parking lots. The concentration of concrete in the vicinity likely has characteristics of heat absorption and back radiation that are different from those of surrounding areas of vegetation. Thus it is conceivable that the industrial

complex has an effect on local weather conditions, possibly analogous to the "heat island" effect observed for cities.

A possibly related phenomenon was observed while sampling from bore hole number 14 (Figure 3). A heavy rainstorm was observed approaching from the northwest and it was feared the sampling effort would soon be rained out. The storm passed to the west, however, and moved to the south following a course that roughly coincided with route 3 (a four-lane highway). Personal communication with a local worker revealed that such movement of rainstorms is not uncommon.

The above are indications that localized concentrations of concrete and pavement may influence the pattern of rainfall distribution in the study area. If such is the case, then these areas are undoubtedly important from an ecological viewpoint. The abundance and areal distribution of rainfall is particularly important to various forms of vegetation (Odum, 1971). Further study of rainfall distribution over the Merritt Island area would most likely provide very useful information.

VI. CONCLUSIONS

1. Most sediments consist of fine sand although variable amounts of peat, clay, silt and shells are common. Profiles appear generally banded with shades of gray and brown. Hydrogen-sulfide odors may occur, and are mostly observed on the western side of island.

2. Concentrations of major ionic constituents are quite variable on Merritt Island. Highest concentrations are found in low-lying areas in proximity to surrounding surface water bodies. Lower concentrations are found at higher elevations toward the center of the island.

3. Groundwater concentrations are subject to less variation (in time) than those of surface water bodies.

4. Surface water bodies do influence immediately adjacent groundwater concentration. Presumably this effect will vary seasonally according to water levels, but during the present study groundwater concentrations close to a surface water body were more similar to those of the surface water body than groundwater elsewhere on the island.

5. Differential water levels on either side of mosquito control dikes (lower in the river during this study)

creates groundwater flow through the dike directed toward the river. Groundwater concentrations in wells beneath the river contained water more similar in chemical character to that of the impoundment located across the dike than the water of the river.

6. Ionic concentrations in wells may vary with depth and distance from surface water bodies. Concentration changes in time are variable even among wells closely positioned to one another, indicating slow groundwater movement and relatively small zones with water of a given concentration. Temperature and pH changes occur rather uniformly in shallow groundwater.

7. Evidence was obtained with the Piper trilinear diagram and an examination of chloride-bicarbonate ratios that shallow groundwater near the island margin has an ionic composition closer to that of sea water than of typical fresh water. The calcium-magnesium ratio also proved useful in this regard.

8. Rather uniform changes of pH and phosphate levels in shallow wells are difficult to explain based on physical considerations. A biological approach offers a reasonable (although highly speculative) explanation. The nature of the problem, however, is such that further research should be considered.

9. Ionic concentrations in surface water bodies (based on data from impoundment T-10-D) respond to relative amounts of precipitation and evaporation. When predipitation exceeds evaporation concentrations decrease while concentrations increase with evaporation exceeding precipitation. Correlations indicate that in spring and early summer about 1½ inches of rain are required every two weeks in order to just balance evaporation and water loss out of an impoundment due to groundwater flow (when impoundment water levels are relatively high).

10. When shallow groundwater contains high levels of dissolved material, rainfall that percolates through the soil appears to be inhibited in downward movements and probably serves to dilute only the uppermost region of the saturated zone.

VII. RECOMMENDATIONS

1. The importance of groundwater as a water source for vegetation, when combined with the disturbance of natural flow conditions caused by digging of drainage ditches and impoundment of certain areas for mosquito control, stresses the need for a more comprehensive understanding of the Merritt Island groundwater. Of primary importance in this regard are the seasonal patterns exhibited in groundwater quality. A longer-term study would provide useful information for detection of possible future alterations in the groundwater.

2. A study of the minor groundwater constituents and contaminants such as pesticides would certainly provide additional (and possibly quite important) information.

3. The hypothesis that a rapid rise in groundwater temperature triggered a series of events leading to increased algal growth in a surface water body requires testing. With adequate preparation (and cooperation from the forces of Nature) it is felt that the events could be accurately described and a causal relationship (if it exists) could be shown.

4. A question also remains as to the areal distribution of rainfall in the area. If the natural situation has in fact been modified by the activities of man, then

the long-term consequences could be serious (at least to the presently existing plant associations). A study of areal rainfall distribution presents some problems, but if they were overcome the results of such a study could be extremely important.

TABLE 1 - RESULTS OF MINOR CONSTITUENTS ANALYSES ON WELL SAMPLES OBTAINED JUNE 4, 1973 (ANALYSES PERFORMED BY THE BENDIX LABORATORY, KENNEDY SPACE CENTER, RESULTS REPORTED IN PARTS PER MILLION)

SITE	TEMP	pH	Cu	Hg	Ni	K	V	Zn	Fe	Al	Sr	Ca	Mg	Na	Mn
1-1	26.0	6.87	<0.1	.003	0.17	560	<1ppm	0.16	0.12	<1	9.1	600	1300	10,400	0.11
1-2	25.0	7.03	<0.1	.009	0.14	510	"	0.12	0.13	<1	10.4	780	1200	9,000	<0.1
1-3	25.5	6.74	<0.1	.004	0.16	510	"	0.15	<0.1	<1	8.2	470	840	7,000	<0.1
1-4	24.8	6.95	<0.1	.003	0.14	270	"	0.20	0.10	<1	10.5	760	1200	8,400	0.10
1-5	25.2	7.15	<0.1	.004	<0.1	290	"	0.18	0.13	<1	9.6	600	1100	8,400	<0.1
1-6	24.8	7.06	<0.1	.013	0.17	850	"	0.15	<0.1	<1	10.0	660	1100	8,400	<0.1
1-I	26.0	6.68	<0.1	.002	<0.1	370	"	0.15	0.12	<1	9.0	640	1300	10,600	<0.1
2-1	26.7	7.61	<0.1	.014	<0.1	160	"	0.19	0.15	<1	6.0	330	570	5,000	<0.1
2-2	25.2	6.88	<0.1	.006	<0.1	160	"	0.11	0.13	<1	6.0	340	570	5,000	<0.1
2-3	27.8	6.90	<0.1	.004	<0.1	186	"	0.11	0.10	<1	6.6	360	650	5,800	0.11
2-I	25.9	8.40	<0.1	.009	<0.1	177	"	0.15	0.10	<1	5.9	310	600	5,200	<0.1
2-IR	27.9	7.42	<0.1	.006	<0.1	380	"	0.15	0.13	<1	8.1	490	1100	8,900	<0.1
3-1	25.7	7.20	<0.1	.007	<0.1	11	"	<0.1	<0.1	<1	0.9	27	66	460	<0.1
3-2	25.5	7.10	<0.1	.004	<0.1	27	"	0.10	<0.1	<1	0.6	14	88	570	<0.1
3-3	27.7	6.73	<0.1	.004	0.16	311	"	0.18	0.13	<1	7.6	410	970	7,900	<0.1
3-I	27.4	7.35	<0.1	.008	<0.1	10	"	0.11	0.12	<1	0.9	30	81	430	<0.1
3-IR	29.5	7.56	<0.1	.004	<0.1	342	"	0.28	0.13	<1	7.8	440	1100	8,400	<0.1
4-1	27.0	6.92	<0.1	.003	0.15	516	"	0.12	0.31	<1	7.4	413	1207	10,000	<0.1
4-2	26.1	7.35	<0.1	.005	0.31	452	"	0.13	0.13	<1	7.2	413	1117	9,194	<0.1
4-3	27.0	7.71	<0.1	.026	0.18	474	"	0.15	0.13	<1	7.5	413	1128	9,140	<0.1
4-ML	29.1	7.81	<0.1	.003	0.18	477	"	0.20	<0.1	<1	7.5	413	1184	9,140	<0.1
5-1	28.9	6.93	<0.1	.005	<0.1	9	"	<0.1	<0.1	<1	0.9	94	7	50	<0.1
5-2	24.5	7.55	<0.1	.001	<0.1	7	"	<0.1	<0.1	<1	1.1	110	7	45	<0.1
5-P	30.6	6.94	<0.1	.002	<0.1	6	"	<0.1	<0.1	<1	1.1	96	7	49	<0.1

TABLE 2: DESCRIPTIONS OF SOIL PROFILE FROM SHALLOW BORE HOLES DRILLED AT THE KENNEDY SPACE CENTER DURING JULY, 1973

LOCATION	DEPTH (inches)	DESCRIPTION COLOR	GRAINS	REMARKS
B1	surface			short grasses and shrubs
(10 feet from edge	0 - ½	black	silt	humus
of impoundment)	½ - 8	light gray	fine sand	
	8 - 22	dark gray	fine sand	
	22 - 32	dark gray	fine sand	strong H_2S odor
	32 - 35	black	peat	H_2S
	40 - 53	dark gray	fine sand	some decaying plant matter
B2	surface			short grasses
	0 - 1	very dark gray	fine sand	some organic matter
	1 - 20	mottled light and dark gray	fine sand	
	20 - 26	very dark gray	fine sand	H_2S, at 23" a layer of decomposing stems and roots
	26 - 38	medium to dark gray	fine sand	H_2S
	38 - 44	black	peat	H_2S
	44 - 55	black	clayey sand	some plant matter
	55 - 65	black	fine sand	
B3	surface			short grasses
	0 - 9	dark gray, brown and dark brown	fine sand	
	9 - 16	gray	fine sand	H_2S
	16 - 37	very dark gray	fine sand	H_2S
	37 - 47	dark brown	silty sand with peat	stems and roots not much decomposed, H_2S

Table 2 (cont.)

LOCATION	DEPTH (inches)	DESCRIPTION COLOR	GRAINS	REMARKS
	47 - 59	black	silty sand	many roots, H_2S
	59 - 64	black	clayey sand	some plant matter
	64 - 79+	very dark gray	fine sand	
B4	surface			short grasses and shrubs, cabbage palms nearby
	0 - 6	dark brown	fine sand	with shell fragments
	6 - 9	light brown	fine sand	with shell fragments
	9 - 11½	light gray	fine sand	shell fragments
	11½ - 15	very dark brown	fine sand	shell fragments
	15 - 16	light gray	fine sand	many shell fragments
	16 - 50	black	silty fine sand	few plant fragments, no shells
	50 - 67+	very dark brown	fine sand	no plant or shells
B5	surface			short grasses, palms nearby
	0 - 6	very dark brown	fine sand	a few shells and plant roots
	6 - 10	mottled gray and brown	fine sand	
	10 - 15	brown and black	fine sand	
	15 - 27	gray	fine sand	
	27 - 31	dark gray-brown	fine sand	
	31 - 37	black	fine sand	much decayed plant matter
	37 - 49	very dark reddish brown	clayey sand	plant matter
	49 - 51	black	fine sand	black "concretions"

Table 2 (cont.)

LOCATION	DEPTH (inches)	DESCRIPTION COLOR	GRAINS	REMARKS
	51 - 54	dark gray	fine sand	
	54 - 67	black	fine sand	some organic matter
	67 - 70	dark reddish brown	fine sand	mild H_2S
B6	surface			grasses, close to pines and cabbage palm
	0 - 7	light gray-brown	fine sand	roots and shell fragments
	7 - 16	black	silty sand	plant matter
	16 - 20	gray	fine sand	no shells or plant matter
	20 - 25	dark brown	fine sand	
	25 - 43	very light gray	fine sand	a few shell fragments
	43 - 53+	gray	fine sand	
B7	surface			Australian pines, palmettoes and grasses nearby
	0 - 32	dark gray	fine sand	many shells and fragments, roots, and decaying plant matter
	32 - 37	dark gray	fine sand	copious shelllayer
	37 - ?	yellow brown and gray	sand and clayey sand	shells
B8	surface			grasses adjacent to marsh
	0 - 1	very dark brown	humus	root zone
	1 - 13	dark brown	fine sand	some shell fragments
	13 - 19	black	fine sand	decaying plant matter
	19 - 45	dark brown and gray	fine sand	large shells and fragments
	45 - 48	black	fine sand	few shells or plant matter
	48 - ?	brown	fine sand	no shells

Table 2 (cont.)

LOCATION	DEPTH (inches)	DESCRIPTION COLOR	GRAINS	REMARKS
B9	surface			tall grass and cattails
	0 - 8	very dark brown	fine sane	some roots
	8 - 17	brown	fine sand	many roots
	17 - 48	black	fine sand	decaying vegetation
	48 - 56+	dark brown	fine sand	
B10	surface			short grasses
	0 - 2	gray and brown	fine sand	copious shells and fragments
	2 - 27	very dark gray	fine sand	some shell fragments
	27 - ?	gray brown		very hard layer of shell and sand concretions (couldn't penetrate with auger)
B11	surface			tall grasses
	0 - 11	dark brown	fine sand	roots and other organic matter
	11 - 21	light gray	fine sand	many shells and concretions
B12	surface			short grass, trees and shrubs nearby
	0 - 12	light brown	fine sand	some shell fragments, many roots
	12 - 30	very light gray with some dark gray	fine sand	few plant fragments
	30 - 61+	light brown	fine sane	some decaying plant matter
B13	surface			short grass and dead shrubs
	0 - 2½	light brown	fine sand	some shell fragments
	2½ - 32	black	silty sand	many decaying plant roots and stems
	32 - 39	very dark brown	fine sand with some silt	mild H_2S
	39 - 45	dark brown	silty sand	

Table 2 (cont.)

LOCATION	DEPTH (inches)	DESCRIPTION COLOR	GRAINS	REMARKS
	45 - 56	brown	fine sand	
	56 - 63+	gray	fine sand	
B14	surface			short grasses, relatively open field
	0 - 6	brown	fine sand	root zone, some shell fragments
	6 - 12	gray	fine sand	some roots
	12 - 34	light gray	fine sand	large plant fragments
	34 - 64	light gray and brown	fine sand	
	64 - 66	very dark brown	fine sand	
	66 - 84+	black	silty sand	some organic matter, strange odor
B15	surface			short grass, very close to swamp with cattails, cabbage palm and sawgrass
	0 - 25	very dark gray	fine sand	some shell fragments, many decomposing roots and stems
	25 - 30+	black	fine sand	decayed plant matter, H_2S
B16	surface			short grasses
	0 - 25	light brown	fine sand	many shells and shell fragments
	25 - 39	gray	fine sand	many shells and fragments
B1	0 - 8	light gray	fine sand	
(30 feet from edge of impoundment)	8 - 21	dark gray	fine sand	
	21 - 31	dark gray	fine sand	H_2S
	31 - 34	black	peat	H_2S
	34 - 39	black	fine sand	H_2S
	39 - 45	dark gray	fine sand	H_2S
B1	0 - 7	brown	fine sand	
(50 feet inland)	7 - 30	gray	fine sand	many tiny shell fragments, mild H_2S

Table 2 (cont.)

LOCATION	DEPTH (inches)	DESCRIPTION COLOR	GRAINS	REMARKS
B1 (75 feet inland)	0 - ½	very dark gray	fine sand	
	½ - 17	gray and brown (mottled)	fine sand	shells and shell fragments
	17 - 50	very dark gray to black	fine sand (some peat)	strong H_2S from peat layers
	50 - 65	very dark brown	fine sand	some plant matter, H_2S
	65 - 83	dark gray	fine sand	a few shell fragments
B1 (100 feet inland)	0 - 5	light and dark brown (mottled)	fine sand	shell fragments
	5 - 8	gray	fine sand	
	8 - 12	very dark brown	fine sand	
	12 - 36	gray	fine sand	some shell fragments

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Section III, Article 9

The Analysis of Five Major Ions and the Validity of Salinity Measurements in the Indian and Banana Rivers

Jay Bryson, Hutchison, Jr.

1973

THE ANALYSIS OF FIVE MAJOR IONS AND THE VALIDITY OF SALINITY MEASUREMENTS IN THE INDIAN AND BANANA RIVERS

By

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ABSTRACT

The major ion to chlorinity ratios of the oceans must be relatively constant for chlorinity titrations and conductivity measurements of salinity to be valid. Variations in the major ion to chlorinity ratios, in estuaries of appreciable salinity, are usually not detectable.

The Indian and Banana Rivers are a lagoonal system located on the east, central coast of Florida. Seven water sites were chosen, four in the Indian River, one in the Banana River, and two in the Atlantic Ocean.

Sodium, potassium, calcium, magnesium, and sulfate, were analyzed using Standard Methods as a guide. Calcium and magnesium were also both analyzed using a simultaneous EDTA complexone titration. Conductivity measurements were made on an induction salinometer and chlorinity was analyzed by the Knudsen titration. Refractive index determinations were made on a Spencer refractometer and a hand held refractometer.

The only ion in the river system that did not conform to reported ion concentrations in the oceans was calcium. The calcium levels were consistently high. Calcium was probably present as dissolved and, to a lesser extent, colloidal calcium carbonate.

The other ions showed some regional variability, which was associated with fresh water run-off and river water to river bottom interactions. The sodium and potassium concentrations

were both slightly lower than the Atlantic samples. The magnesium and sulfate levels both corresponded to the reported concentrations for the oceans. The sulfate variability could possibily be associated with the sulfur cycle.

The examination of ionic equivalence indicated that the river system was in a dynamic state attributable to the calcium ion input exceeding the precipitation time necessary to bring the system to equilibrium.

The determinations of salinity by the chlorinity titrations and conductivity measurements were good approximations, with conductivity giving the results with greater accuracy. Both determinations resulted in low river salinity values for neither method could completely compensate for increased calcium levels. Refractive index determinations gave approximations of the salinity that were less accurate than both of the above.

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I. INTRODUCTION

Marcet proposed in 1819 that the composition of sea water around the world appeared relatively constant, and that only the total salinity varied regionally. Some variability appeared to exist in the specific ionic composition of sea water samples through 1966, though in most instances the variability was within analytical error (Riley, 1965). Analytical investigations by Culkin (1966) on sodium, potassium, calcium, magnesium, and strontium, demonstrated that very little variability existed in the ionic composition of the world oceans when the samples were analyzed by a single investigative team (Table 13).

Salinities were originally determined by evaporating sea water to dryness and then weighing the sample. The organic matter was eventually oxidized, as the sample was heated and evaporated. The precipitated magnesium chloride was decomposed into salts of uncertain composition and hydrogen chloride was liberated. The results were difficult to reproduce depending on the method of treatment and analysis (Riley, 1965).

A definition of salinity was developed in the early 1900's. The definition stated:

> Salinity is defined as the weight in grammes of the dissolved inorganic matter in 1 kg of sea water after all the bromide and iodide have been replaced by the equivalent amount of chloride, and all the carbonate converted to oxide. (Riley, 1965)

Dittmar, in the late 1800's, suggested that because the major ion concentrations appeared constant (Table 1), a single ion could be analyzed and related by arithmetic formula to the total salinity of the sample. Knudsen used silver nitrate to precipitate the halogens in sea water and helped to develop the concept of chlorinity, which was defined to be:

> The chlorinity is the mass in grammes of pure silver necessary to precipitate the halogens in 328.5233 grammes of sea water. (Riley, 1965)

An arithmetic expression was developed by Knudsen relating the chlorinity to salinity as follows:

$$S\ o/oo = 1.8050\ Cl\ o/oo + 0.030.$$
(Wooster, 1970)

The above expression was based on just nine saline samples and the constant, 0.030, apparently varied with locality (Martin, 1968). The formula has since been modified to be:

$$S\ o/oo = 1.80655\ Cl\ o/oo.$$
(Wooster, 1970)

Thus, chlorinity can strictly be used in the computation of the salinity and density of sea water only if the major ion to chlorinity ratios are constant (Riley, 1971).

Within the last 30 years, conductivity has become a rapid method of determining the salinity of sea water samples. Hydrographic tables, using standard sea water dilutions and based on the Knudsen equation, have been developed that relate conductivity ratios with specific salinities. Investigations by F. Culkin,

TABLE 1

The Ionic Concentrations, Ion/Chlorinity Ratios, Residence Times, and Principle Species in 35 o/oo Sea Water

Constituent*	Concentration* gm/kg	Ion/Cl Ratio	Residence** Time (Years)	Principle** Species
Cl	19.353	———	———	Cl^-
Na	10.76	0.5555	2.6×10^8	Na^+
SO_4	2.712	0.1400	———	SO_4^{2-}
Mg	1.294	0.0668	4.5×10^7	Mg^{2+}, $MgSO_4$
Ca	0.413	0.0213	8.0×10^6	Ca^{2+}, $CaSO_4$
K	0.387	0.0200	1.1×10^7	K^+
HCO_3	0.142	0.0073	———	HCO_3^-, H_2CO_3 CO_3^{2-}
Br	0.067	0.0035	———	Br^-
Sr	0.008	0.0004	1.0×10^7	Sr^{2+}, $SrSO_4$
B	0.004	0.0002	———	$B(OH)_3$, $B(OH)_4^-$
I	0.001	0.00005	———	IO_3^-, I^-

* Riley, 1965

** Horne, 1969

R. A. Cox, and J. P. Riley, have resulted in a new set of tables, the International Oceanographic Tables, that compare conductivity ratios to salinity by the new definition. The tables include conductivity ratios ranging from 0.85000 to 1.17999 and salinities from 29.196 o/oo to 42.168 o/oo (Wooster, 1970).

Modern conductivity instruments, with temperature compensating electrical bridges, can measure the salinity to 0.001 o/oo (Riley, 1965). Agreement between conductimetric salinity measurements and those calculated from chlorinity titrations is dependent on the constancy of the relative composition of sea water (Riley, 1971).

Refractive index is also used to determine the salinity and the constancy of composition must hold to obtain valid salinity values. Standard sea water dilutions were used by several investigators to obtain tables relating refractive index to salinity.

The major ion concentrations are constant because they are conservative in the saline medium. Table 2 was taken from Horne (1969) and shows the expected cation and anion interactions in sea water of 19 o/oo chlorinity and for a temperature of 25°C. It was assumed that the interactions between the major ions resulted only in the formation of ion pairs. Sodium, potassium, and chloride are represented as 99 percent dissociated. Calcium and magnesium ions each exist associated to a slight degree with the

TABLE 2

Species Distribution of Some Major
Sea Water Constituents
(Horne, 1969)

Ion	Molality	Free Ion, %	With Sulfate, %	With Bicarbonate, %	With Carbonate, %
Ca	0.0104	91	8	1	0.2
Mg	0.0540	87	11	1	0.3
Na	0.4752	99	1.2	0.01	—
K	0.0100	99	1	—	—

			With Ca, %	With Mg, %	With Na, %	With K, %
SO_4	0.0284	54	3	21.5	21	0.5
HCO_3	0.00238	69	4	19	8	—
CO_3	0.000269	9	7	67	17	—

sulfate ion. The major ions generally exhibit long residence times allowing them time to come to a steady state equilibrium (Table 1).

The total anion and cation equivalences were calculated from the major ion concentrations listed in Table 1. Table 3 lists the major ions with their projected equivalences calculated from 35 °/oo sea water. The total equivalence of the cations is equal to 0.6057 and the total of the anions is 0.6056. The two values are close to agreement and an ionic equilibrium is indicated.

The major ion to chlorinity ratios must be relatively constant for modern techniques to be valid measurements of salinity. The validity of the chlorinity titrations, conductivities, and refractive indices become questionable analyses for the determination of salinity where extreme dilutions of sea water occur. However, variations in the concentration ratios in estuarine water of appreciable salinity are usually not detectable (Riley, 1971).

The Indian and Banana River lagoonal system provides an excellent diluted sea water environment to test the validity of the above measurements. This thesis was proposed to evaluate the concentrations of sodium, potassium, calcium, magnesium, and sulfate to determine if the ionic composition was similar to sea water and if the chlorinity titration and conductivity and refractive index measurements could be utilized to determine river salinities.

TABLE 3

The Ionic Equivalence of 35 o/oo Sea Water

Ion	Ionic Equivalence
Cl	0.5459
Na	0.4680
SO_4	0.0565
Mg	0.1064
Ca	0.0206
K	0.0099
HCO_3	0.0023
Br	0.0008
Sr	0.0002
B	0.0007
I	0.0001

II. METHODS AND MATERIALS

A. Sampling Sites

The Indian and Banana River lagoonal system is located on the east central coast of Florida. The most noted landmark in the region is Kennedy Space Center located on Merritt Island (Figures 1 and 2).

Seven sample sites were chosen, four in the Indian River, one in the Banana River, and two in the Atlantic Ocean. The Indian River sites were:

Site 1	Titusville Causeway, Titusville
Site 2	Bennett Causeway, State Road 528
Site 4	Eau Gallie Causeway, Eau Gallie
Site 5	State Road 510 Causeway, Wabasso

Site 3 was located on the Bennett Causeway (State Road 528) in the Banana River.

Site 6A was located off of the Indialantic Beach for two sampling excursions. Site 6B was located off of the Fort Pierce Inlet. This sample served as a sea water substandard. Samples from Sites 6, A and B, were analyzed with the other samples to insure the validity of the ion analyses used.

Site 1 is located in the northern region of the Indian River. The Banana Creek is located four miles south of the causeway and no other major creeks are in the vicinity.

Site 2 and Site 3 are approximately 17 miles below Site 1 and are connected by a Barge Canal bisecting Merritt Island. Sykes

FIGURE 1

Florida

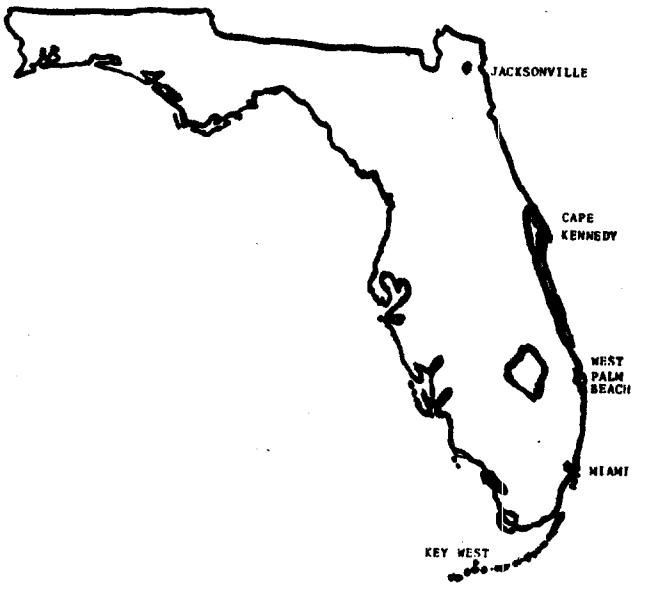
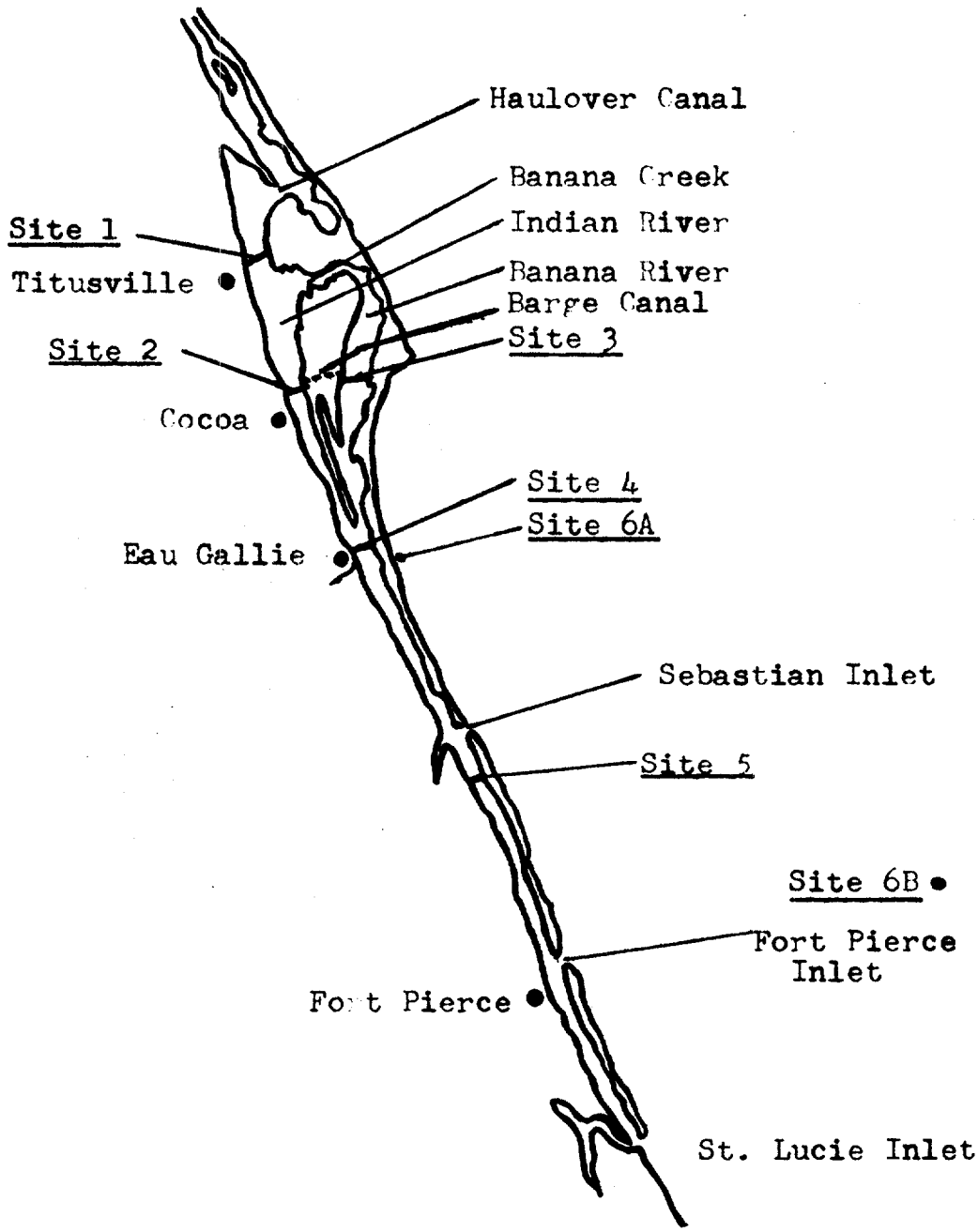


FIGURE 2

Sample Site Locations



Creek opens directly into the Barge Canal. The Banana Creek is approximately 13 miles north of Site 2.

Site 4 is approximately 20 miles south of Site 2 near the mouth of the Eau Gallie River, located less than one mile south of the causeway (Figure 2).

Site 5 is 31 miles south of Site 4 and 7 miles south of the Sebastian Inlet, a direct opening to the Atlantic Ocean. The Sebastian Creek is 7 miles north of the 510 causeway (Figure 2).

B. Sampling Procedure

The samples were taken by rope and bucket from the specified river localities at depths between three to five feet and transferred to two quart low density polyethylene containers.

All samples were returned to the chemical laboratory, filtered through 1.2 micron Millipore cellulose acetate filter paper, and stored in 500 milliliter (ml) high density polyethylene containers. The samples were generally analyzed within a three day time period.

C. Conductivity

Conductivities were measured on a Portable Induction Salinometer, Beckman Model RS-7B, according to the instructions provided with the instrument (Instruction Manual for Model RS-7B Portable Induction Salinometer, Beckman Instruments, Inc., 1965).

The salinities were determined from the measured conductivity ratio using the hydrographic tables, based on the Knudsen equation, supplied in the manual. The salinities were corrected for machine drift and temperature, the chlorinity was calculated from the Knudsen equation, and the new salinity definition was applied to obtain a corrected salinity.

D. Refractive Index

Refractive index was measured on a Spencer Refractometer, Model 819, using a constant temperature water bath and a sodium D line light source (5890 Å, 5896 Å). A hand held optical refractometer, the AO T/C Refractometer was also used. Both instruments were operated according to their instruction manuals (Directions for the Operation and Care of the Spencer Refractometer, American Optical Company, 1947, and Instructions for the Use and Care of the TS Meter and T/C Refractometer, American Optical Company, 1964).

Table 48B, Appendix B, was used to determine refractive indices for 30°C and 32°C, by extrapolating from a semilogarithmic plot of the data.

The extrapolated refractive indices, Table 49B, Appendix B, were used to calculate salinities for the Spencer refractometer data.

E. Chemical Methods

The chemical procedures for the major ions were taken from

Standard Methods of Fresh Water and Waste Water Analysis, American Public Health Association, Vol. 13, 1971.

Silica	pp. 301-303
Sodium	pp. 320-323
Potassium	pp. 285-286
Calcium (EDTA)	pp. 84-86
Calcium(Gravimetric)	pp. 80-82
Magnesium	pp. 201-203
Sulfate	pp. 331-333

The procedures for the chlorinity determination (Martin, 1968) and for the "Simultaneous Determination of Calcium and Magnesium," Katz (1964), are located in Appendix A.

1. Chlorinity

The chlorinity was determined by the precipitation of the halides from river water samples with silver nitrate. Potassium chromate was used as the endpoint indicator.

$$X = Cl^-, Br^-, I^-$$

$$Ag^+ + X^- \rightarrow AgX$$

$$\underset{\text{(Excess)}}{Ag^+} + \underset{\text{(Yellow)}}{CrO_4^{2-}} \rightarrow \underset{\text{(Pink)}}{Ag_2CrO_4} \quad \text{(Martin, 1968)}$$

2. Silica

The silicates were separated by the evaporation of the

saline sample to dryness in the presence of concentrated hydrochloric acid. The silicates were separated as $SiO_2 \cdot xH_2O$ (Koltoff, 1969). Dilute hydrochloric acid was added to redissolve the soluble salts, the insoluble silicates were filtered, ignited in an electric furnace at 2,000°F, and weighed. The procedure was carried out in borosilicate glassware. The determination of silica concentrations was necessary to insure that the silicates were below interference levels.

3. Sodium

Sodium was precipitated using zinc uranyl acetate reagent. The product, sodium zinc uranyl acetate was collected after one hour in Corning fritted glass crucibles, medium porosity, washed with ethanol and ether, and then weighed.

$$Zn(C_2H_3O_2)_2 \cdot 3U(C_2H_3O_2)_3^- + Na^+ + 6H_2O \rightarrow$$

$$Na(C_2H_3O_2) \cdot Zn(C_2H_3O_2) \cdot 3U(C_2H_3O_2)_3 \cdot 6H_2O$$

4. Potassium

Trisodium cobaltinitrite was used to precipitate potassium from sea water. A known volume of standard potassium dichromate was added to the carefully washed dipotassium sodium cobaltinitrite precipitate followed by 5 ml of concentrated sulfuric acid. The excess dichromate was measured colorimetrically using a Bausch and

Lomb Spectronic 20. The concentration of potassium was determined from a standard curve.

$$Na_3Co(NO_2)6 + 2K^+ \rightarrow K_2NaCo(NO_2)_6 + 2Na^+$$

5. Calcium

Three methods were used in the determination of calcium. The ethylenediamine tetracetic acid (EDTA) analysis (Standard Methods, 1971) was initially used, then the "Simultaneous Determination of Calcium and Magnesium" with EDTA by Katz (1964), and finally the precipitation of calcium as the oxalate was used.

The titration of calcium utilizing EDTA was a complexone reaction. Strontium was also analyzed in this procedure because of its similarity to the calcium ion. The Standard Methods analysis and Katz analysis both followed the same basic procedure. Magnesium hydroxide was precipitated from the sample by the addition of enough sodium hydroxide to increase the pH of the sample to between 12 and 13. An organic indicator, either Murexide or Eriochrome Blue S.E., was added to the sample. The sample was titrated with EDTA which has a greater affinity for the calcium and strontium than the indicator. When an excess of EDTA was added, it complexed with the dissociated indicator to produce a color change from blue to red.

$Y = Ca^{2+}, Sr^{2+}$

I = Indicator

$Y + I \rightarrow Y - I$

$Y - I + EDTA \rightarrow Y - EDTA + I$

$EDTA + I \rightarrow EDTA - I$ (Martin, 1968)
(Blue) (Red)

Calcium and strontium were also determined gravimetrically. The two ions were precipitated from an acidified medium containing ammonium oxalate as the solution was neutralized with ammonium hydroxide. The precipitate was filtered, ignited in an electric furnace at 2,000°F, and weighed.

$$Ca^{2+} + C_2O_4^{2-} + H_2O \rightarrow CaC_2O_4 \cdot H_2O$$

$$CaC_2O_4 \cdot H_2O \xrightarrow{\text{heat}} CaO + CO + CO_2 + H_2O \quad \text{(Koltoff, 1969)}$$

6. Magnesium

Magnesium was determined by the simultaneous EDTA method described above. After the analysis of calcium and strontium, the magnesium hydroxide precipitate was dissolved with dilute hydrochloric acid, and then the solution was buffered to a pH of 10.1. A new indicator, Eriochrome Black T, was added and the sample titrated with EDTA. The magnesium concentration was determined from the additional EDTA necessary to titrate to the indicator endpoint.

The precipitation of magnesium as magnesium ammonium phosphate was also used. Calcium and strontium were first removed by the gravimetric method described above. The precipitation of magnesium from an acidic solution containing dihydrogen ammonium phosphate resulted when the solution was neutralized with ammonium hydroxide. The precipitate was dissolved with dilute hydrochloric acid and reprecipitated with additional ammonium phosphate and ammonium hydroxide. The magnesium ammonium phosphate was ignited to magnesium pyrophosphate at 2,000°F in an electric furnace and weighed.

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O$$

$$2MgNH_4PO_4 \cdot 6H_2O \xrightarrow{\text{heat}} Mg_2P_2O_7 + 12\ H_2O$$

(Koltoff, 1969)

7. Sulfate

Sulfate ions were precipitated with dilute barium chloride solution from a hot, acidified solution following a gravimetric procedure. The precipitate was filtered, ignited at 1,616°F in an electric furnace and weighed.

$$BaCl_2 + SO_4^{2-} \rightarrow BaSO_4 + 2Cl^-$$

III. RESULTS

A. Ionic Ratios and Concentrations

Table 1 shows the projected ionic concentrations for the eleven major ions. The chlorinity of 35.00 °/oo sea water was calculated to be 19.37 °/oo, from the Knudsen equation. The major ion to chlorinity ratios were then calculated and added to Table 1.

Table 4 shows the gravimetric silica values. The site 1, site 2, site 3, and site 6, samples all contained silica levels less than 1 mg/l; the samples from site 4 and site 5 contained silica concentrations slightly greater than 1 mg/l, 1.2 mg/l and 1.1 mg/l, respectively, all of which were below interference levels.

The results from which the ion ratios and concentrations were calculated are located in Appendix B. Table 5 and Table 6 were compiled from the chlorinity titration and conductivity measurement data located in Table 43B to Table 46B, Appendix B.

All ion concentrations were corrected to 35 °/oo sea water to compensate for salinity variations between sites and allow comparisons of the ionic concentrations to be made by the following formula:

$$C = \frac{A \cdot 35.00\ ^{\circ}/_{oo}}{B}$$

A = measured ion concentration

B = site mean salinity

C = concentration for 35 °/oo sea water

TABLE 4

Silica

Site	Concentration (g/l)
1	0.0003
2	0.0006
3	0.0006
4	0.0012
5	0.0011
6	0.0007

TABLE 5

The Mean Ion/Chlorinity Ratios

Site	Na/Cl (S.D.)	K/Cl (S.D.)	EDTA Ca-Sr/Cl (S.D.)	Ca-Sr/Cl (S.D.)	EDTA Mg/Cl (S.D.)	Mg/Cl (S.D.)	SO_4/Cl (S^4D.)
1	0.5538 (0.0069)	0.0200 (0.0017)	0.0235 (0.0013)	0.0249 (0.0019)	0.0698 (0.0038)	0.0656 (0.0012)	0.1392 (0.0068)
2	0.5504 (0.0069)	0.0190 (0.0020)	0.0246 (0.0022)	0.0257 (0.0011)	0.0687 (0.0025)	0.0664 (0.0011)	0.1397 (0.0057)
3	0.5546 (0.0118)	0.0190 (0.0020)	0.0255 (0.0007)	0.0270 (0.0010)	0.0692 (0.0031)	0.0663 (0.0010)	0.1413 (0.0031)
4	0.5534 (0.0100)	0.0198 (0.0010)	0.0254 (0.0019)	0.0256 (0.0005)	0.0674 (0.0020)	0.0664 (0.0025)	0.1383 (0.0039)
5	0.5533 (0.0068)	0.0197 (0.0023)	0.0216 (0.0010)	0.0222 (0.0017)	0.0663 (0.0023)	0.0660 (0.0009)	0.1405 (0.0035)
6	0.5541 (0.0069)	0.0197 (0.0011)	0.0210 (0.0002)	0.0210 (0.0024)	0.0674 (0.0009)	0.0656 (0.0008)	0.1411 (0.0045)
7*	0.5555	0.0200	0.0217	0.0217	0.0668	0.0668	0.1400

* Expected Ratio for 35 o/oo Sea Water

TABLE 6

The Mean Ion Concentrations in 35 o/oo Sea Water

Site	Na g/kg (S.D.)	K g/kg (S.D.)	EDTA Ca-Sr g/kg (S.D.)	Ca-Sr g/kg (S.D.)	EDTA Mg g/kg (S.D.)	Mg g/kg (S.D.)	SO_4 g/kg (S.D.)
1	10.73 (0.13)	0.386 (0.033)	0.440 (0.025)	0.475 (0.036)	1.352 (0.074)	1.270 (0.023)	2.695 (0.132)
2	10.66 (0.13)	0.368 (0.039)	0.468 (0.042)	0.490 (0.021)	1.331 (0.048)	1.286 (0.021)	2.707 (0.110)
3	10.75 (0.23)	0.367 (0.039)	0.487 (0.013)	0.514 (0.019)	1.340 (0.060)	1.283 (0.019)	2.737 (0.072)
4	10.72 (0.19)	0.383 (0.019)	0.484 (0.036)	0.489 (0.010)	1.306 (0.039)	1.285 (0.048)	2.679 (0.076)
5	10.72 (0.13)	0.380 (0.045)	0.411 (0.019)	0.423 (0.032)	1.284 (0.045)	1.278 (0.017)	2.721 (0.069)
6	10.73 (0.13)	0.380 (0.021)	0.401 (0.004)	0.401 (0.046)	1.306 (0.017)	1.270 (0.016)	2.734 (0.087)
7*	10.76	0.387	0.414	0.414	1.294	1.294	2.712

* Expected Ion Concentration in 35 o/oo Sea Water

Each ion, from the above tables, was considered individually in the presentation of the results. The projected ionic ratios and concentrations were taken from Table 1. Each mean value is followed by its standard deviation in parentheses.

1. Sodium

The mean sodium concentrations and ratios for the samples at all sites were below the projected 10.76 g/kg and 0.5555. The sample at site 2 was the lowest value having a concentration of 10.66 g/kg (0.13) and a ratio of 0.5504 (0.0069). Samples from the other sites were all within 0.04 g/kg and 0.0022 of the projected concentration and ratio. The standard deviations for the determination were relatively low, generally on the order of one to two percent.

2. Potassium

All of the mean potassium concentrations and ratios were equal to or below the projected 0.387 g/kg and 0.0200. The lowest values were found in the samples at site 2 and site 3. The samples from all sites were within 0.020 g/kg and 0.0010 of the projected values. The standard deviations were high, approximately 10 percent.

3. EDTA and Gravimetric Calcium-Strontium

The mean EDTA calcium-strontium sample concentrations

increased from site 1 to site 3 and were between 0.026 g/kg and 0.073 g/kg greater than the projected o.414 g/kg. The site 4 sample concentration was slightly lower than that of site 3. Samples from site 5 and site 6 were lower than and within 0.013 g/kg of the projected value.

The mean ratios for the samples from site 1, site 2, site 3, and site 4, followed the same pattern described above and were higher than the 0.0200 projected ratio by 0.0018 and 0.0038. The sample ratios at site 5 and site 6 were within 0.0007 of the projected value.

The standard deviations were high for the determination, on the order of 10 percent.

The gravimetric calcium-strontium determination followed the pattern described above. The mean sample concentrations for site 1, site 2, and site 3, were 0.030 g/kg to 0.040 g/kg greater than the EDTA levels. The site 4 sample concentration was similar to the EDTA site 4 value. The samples from site 5 and site 6 were within 0.013 g/kg of the projected 0.414 g/kg.

The mean ratios for the samples from site 1, site 2 and site 3, were approximately 0.0015 greater than the EDTA ratios. The site 4 gravimetric and EDTA value were similar. The samples from site 5 and site 6 were within 0.0007 of the 0.0200 projected ratio.

The standard deviations were generally lower than the

EDTA determination, between three to seven percent.

4. EDTA and Gravimetric Magnesium

The mean magnesium concentrations, for the EDTA determination, were high, between 0.037 g/kg to 0.058 g/kg, in the samples from site 1, site 2, and site 3. The samples from the other sites were within 0.012 g/kg of the 1.294 g/kg projected concentration.

The mean ratios followed the pattern described above. The site 1, site 2, and site 3, sample values were between 0.0019 to 0.0030 greater than and the samples from the other sites were within 0.0006 of the 0.0668 projected ratio.

The standard deviations were low, generally between one to three percent.

The gravimetric determination resulted in mean concentrations and ratios that were lower, within 0.024 g/kg and 0.0012, than the projected values for all of the samples from the river sites. The sample from site 6 had a concentration of 1.270 g/kg (0.016) and a ratio of 0.0656 (0.0008).

The standard deviations were low, approximately one percent.

5. The Mean Calcium and Magnesium Values

Table 7 shows the values obtained by taking the mean of the EDTA and gravimetric values for both calcium and magnesium. The same trends still hold for calcium that were noted in Section 3.

The mean magnesium values show better agreement with the projected 1.294 g/kg concentration and 0.0668 ratio. The site 1, site 2, and site 3, sample concentrations and ratios were slightly higher, within 0.018 g/kg and 0.0010, and the samples from the other sites were lower, within 0.015 g/kg and 0.0006, than the projected values.

6. Sulfate

All mean sample values were within 0.033 g/kg and 0.0017 of the projected 2.712 g/kg concentration and 0.1400 ratio. The samples from site 2, site 3, and site 6, were high, within 0.025 g/kg and 0.0013, and the samples from the other sites were low, within 0.017 g/kg and 0.0017, of the projected values.

The standard deviations were low, between two to five percent.

TABLE 7

Mean Calcium-Strontium and Magnesium Ratios and Concentrations

Site	Ca-Sr/Cl (S.D.)	Ca (g/kg) (S.D.)	Mg/Cl (S.D.)	Mg (g/kg) (S.D.)
1	0.0242 (0.0016)	0.458 (0.031)	0.0677 (0.0025)	1.311 (0.049)
2	0.0251 (0.0017)	0.479 (0.032)	0.0676 (0.0018)	1.309 (0.035)
3	0.0263 (0.0009)	0.501 (0.016)	0.0678 (0.0020)	1.312 (0.040)
4	0.0255 (0.0012)	0.487 (0.023)	0.0669 (0.0023)	1.296 (0.044)
5	0.0219 (0.0014)	0.417 (0.026)	0.0662 (0.0016)	1.281 (0.031)
6	0.0210 (0.0013)	0.401 (0.025)	0.0665 (0.0009)	1.288 (0.017)
7	0.0217	0.414	0.0668	1.294

B. Ionic Equivalence, Chlorinity, Salinity, and Refractive Index

1. Ionic Equivalence

Table 8 examines the ionic equivalence of each major ion concentration adjusted to 35 °/oo sea water for the last four analyses. The calcium and magnesium concentrations were both taken from Table 7. The samples from site 1, site 2, site 3, and site 4, had total measured cation equivalences that were greater than the total measured anionic equivalences. The samples from site 5 and site 6 had total measured cation equivalences that were less than the total measured anionic equivalences.

It was assumed that the bromide, iodide, boron, and bicarbonate equivalences were the same as in Table 3. These equivalences were added to the measured equivalences to obtain the total anion and cation equivalences, which follow the same pattern described above.

2. Chlorinity

Table 9 shows the statistical analysis of the chlorinities calculated from the chlorinity titration and conductivity determination, for the last four analyses. The t-test for the examination of the similarity of two means was used (Mendenhall, 1971). Sixteen out of 22 values were within the acceptance region for a 95 percent

TABLE 8

Ionic Equivalence

Ion	Site 1	2	3	4	5	6
Cl	0.5459	0.5459	0.5460	0.5459	0.5459	0.5460
Na	0.4667	0.4637	0.4676	0.4663	0.4663	0.4667
K	0.0099	0.0094	0.0094	0.0098	0.0097	0.0097
Ca-Sr	0.0224	0.0239	0.0250	0.0243	0.0208	0.0200
Mg	0.1079	0.1077	0.1080	0.1067	0.1054	0.1060
SO_4	0.0561	0.0564	0.0570	0.0558	0.0567	0.0569
Total Measured Cations	0.6069	0.6047	0.6100	0.6071	0.6022	0.6029
Total Measured Anions	0.6020	0.6023	0.6030	0.6017	0.6026	0.6031
Total Cations	0.6076	0.6054	0.6107	0.6078	0.6029	0.6031
Total Anions	0.6034	0.6037	0.6044	0.6051	0.6040	0.6043

TABLE 9

The Statistical Analysis of Chlorinity

Analysis Date	Analysis	Site 1	2	3	4	5	6
4-17-73	Chlorinity Cl	14.80 (0.03)	13.19 (0.03)	12.57 (0.03)	12.39 (0.03)	17.33 (0.03)	19.92 (0.03)
	Conductivity Cl	14.81 (0.005)	13.19 (0.005)	12.60 (0.005)	12.51 (0.005)	17.39 (0.005)	19.90 (0.005)
	t-Test	0.2857	0.0000	0.8571	3.714	1.714	0.5714
4-23-73	Chlorinity Cl	15.13 (0.03)	13.09 (0.03)	12.76 (0.04)	12.50 (0.03)	18.14 (0.04)	
	Conductivity Cl	15.09 (0.005)	13.05 (0.005)	12.79 (0.005)	12.79 (0.005)	18.45 (0.005)	
	t-Test	1.143	1.143	0.6383	8.256	6.596	
5-1-73	Chlorinity Cl	15.05 (0.05)	13.27 (0.04)	12.95 (0.03)	12.71 (0.03)	18.83 (0.03)	
	Conductivity Cl	15.12 (0.005)	13.40 (0.005)	13.08 (0.005)	12.85 (0.005)	18.91 (0.005)	
	t-Test	1.207	2.766	3.714	4.000	2.286	
5-3-73	Chlorinity Cl	14.95 (0.03)	13.15 (0.03)	13.08 (0.03)	13.00 (0.03)	19.20 (0.03)	20.08 (0.03)
	Conductivity Cl	14.99 (0.005)	13.16 (0.005)	13.11 (0.005)	13.01 (0.005)	19.20 (0.005)	20.09 (0.005)
	t-Test	1.143	0.2857	0.8571	0.2857	0.0000	0.2857

confidence interval. The rejection region was t greater than 2.353. Seventeen of the 22 chlorinities determined by the conductivity measurement were greater than the chlorinities determined by the chlorinity titration.

3. Salinity and Refractive Index

Table 10 shows the relationship between chlorinity titration and conductivity determination salinities and the salinities determined by the Spencer refractometer and hand held refractometer. The mean of the difference between the Spencer refractometer salinities and conductivity and chlorinity salinities was 0.8 °/oo. The mean of the difference for the hand refractometer was 1.2 °/oo.

TABLE 10

Chlorinity, Conductivity, and Refractive Index Salinities

Analysis Date	Analysis	Site 1	2	3	4	5	6
4-17-73	Chlorinity	26.74	23.82	22.71	22.38	31.31	36.00
	Conductivity	26.75	23.83	22.76	22.60	31.42	35.96
	Spencer	26.7	24.4	23.3	23.1	34.3	36.3
	Hand Held	25.5	22.5	21.5	21.0	30.5	34.5
4-23-73	Chlorinity	27.34	23.65	23.06	22.59	32.77	
	Conductivity	27.26	23.57	23.11	23.11	33.33	
	Spencer	27.5	23.9	22.8	24.4	35.4	
	Hand Held	26.0	22.5	22.0	22.0	36.0	
5-1-73	Chlorinity	27.19	23.98	23.30	22.96	34.01	
	Conductivity	27.32	24.21	23.62	23.22	34.16	
	Spencer	29.2	25.0	25.0	24.4	36.3	
	Hand Held	26.0	23.0	22.5	22.0	36.0	
5-3-73	Chlorinity	27.00	23.75	23.62	23.49	34.68	36.28
	Conductivity	27.07	23.78	23.68	23.50	34.68	36.29
	Spencer	27.5	25.0	24.4	23.9	34.3	35.0

IV. DISCUSSION

A. Ionic Ratios and Concentrations

1. Sodium

The mean sodium ratios and concentrations were consistently low. The concentrations were found to be within 0.04 g/kg of the projected concentration of 10.76 g/kg, except for the sample at site 2 at which the lowest concentration, 10.66 g/kg, was found.

The sample ratio of 0.5546 from site 3 was the only value within the reported range of the Atlantic Ocean of 0.5544 to 0.5567 (Table II). The Atlantic sample's ratio and concentration were determined to be 0.5541 and 10.73 g/kg, which could indicate that complete precipitation in the analysis was not obtained. The ratio does correspond to reported values (Table 12) and it is only 0.0003 lower than the reported range.

The most recent ion analyses by Culkin (1966), resulted in a mean ocean ratio of 0.5555 (Table 13). The only ratio that corresponded to any of the results in this paper was from the North Sea sample.

Sodium is one of the most difficult ions to analyze quantitatively (Horne, 1969). The major difficulty with the determination results from the relatively high solubility of the sodium zinc uranyl acetate precipitate, 5.85 g/100 ml of solution (Riley, 1965), giving

the precipitate a tendency to form supersaturated solutions (Standard Methods, 1971). A large volume of concentrated reagent was added to a small volume of sample to attempt to compensate for the solubility effect (Koltoff, 1969),but the low results were still noted.

The samples from site 1 and site 3 were similar in concentration to the Atlantic sample and the samples from site 2, site 4, and site 5, were slightly low. It was evident that the sodium levels obtained in the river samples were probably variable.

The highest salinity values were found in the samples from site 1 and site 5. The greatest degree of dilution occurred in the samples from site 2, site 3, and site 4 (Table 10). There did not seem to be a correlation between the degree of dilution and a decrease in sodium levels. The sample at site 5 was reported to have the highest river salinity but its ratio was comparable to the sample at site 4 where the greatest dilution was noted. The site 3 sample tended to have lower salinity values than the sample at site 1, yet the sodium values noted were the highest.

The sodium levels in the Indian and Banana Rivers were similar to those found for the Atlantic Ocean sample, however, some regional variability was found to exist.

2. Potassium

The mean potassium values, except for the sample at site 1,

TABLE 11

Major Constituent Concentration-to-Chlorinity Ratios
for Various Oceans and Seas
(Riley, 1965)

Oceans and Seas	Na / o/oo Cl	Mg / o/oo Cl	K / o/oo Cl	Ca / o/oo Cl	Sr / o/oo Cl	SO_4 / o/oo Cl	Br / o/oo Cl
N. Atlantic	—	—	0.02026	—	—	—	0.00337-0.00341
Atlantic	0.5544-0.5567	0.0667	0.01953-0.0263	0.02122-0.02126	0.000420	0.1393	
N. Pacific	0.5553	0.06632-0.06695	0.02096	0.02154	—	0.1396-0.1397	0.00348
W. Pacific	0.5497-0.5561	0.06627-0.0676	0.02125	0.02058-0.02128	0.000413-0.000420	0.1399	0.0033
Indian	—	—	—	0.02099	0.000445	0.1399	0.0038
Mediterranean	0.5310-0.5528	0.06785	0.02008	—	—	0.1396	0.0034-0.0038
Baltic	0.5536	0.06693	—	0.02156	—	0.1415	0.00316-0.00344
Black	0.55184	—	0.0210	—	—	—	—
Irish	0.5573	—	—	—	—	0.1397	0.0033
Puget Sound	0.5495	—	0.0191	—	—	—	—
Siberian	0.5484	—	0.0211	—	—	—	—
Antarctic	—	—	—	0.02120	0.000467	—	0.00347
Tokyo Bay	—	0.0676	—	0.02130	—	0.1394	—
Barents	—	0.06742	—	0.02085	—	—	—
Artic	—	—	—	—	0.000424	—	—
Red	—	—	—	—	—	0.1395	0.0043
Japan	—	—	—	—	—	—	0.00327-0.00347
Bering	—	—	—	—	—	—	0.00341
Adriatic	—	—	—	—	—	—	0.00341

TABLE 12

Principle Determinations of Sodium in Sea Water
(Riley, 1965)

Reference	Ocean etc.	Na(g/kg) for S = 35 o/oo	$\frac{Na(g/kg)}{Cl\ o/oo}$
Morton and Thorpe(1871)	Irish	10.797	0.5573
Schmidt(1878)	Baltic and White	10.725	0.5536
Schmelck(1882)	Atlantic	10.663	0.5544
Forsberg(1883)	Siberian	10.625	0.5584
Dittmar(1884)	Various	10.683	0.5514
Natterer(1892, 1893, 1894)	Mediterranean	10.288	0.5310
Kolotoff(1893)	Black	10.691	0.5518
Makin(1898)	Atlantic	10.609	0.5476
Schloesing(1906)	Atlantic and Mediterranean	10.710	0.5528
Wheeler(1910)	Atlantic	10.786	0.5567
Steiger(1910)	Atlantic	10.786	0.5567
Anderson and Thompson(1932)	Puget Sound	10.646	0.5495
Webb(1939)	Firth of Clyde	10.751	0.5549
Miyake(1939)	W. Pacific	10.650	0.5497
Knapman and Robinson(1941)	Puget Sound Pacific	10.776 10.751	0.5562 0.5549
Fukai and Shiokawa(1955)	W. Pacific N. Pacific	10.774 10.759	0.5561 0.5553
F. Culkin(unpublished work)		10.762	0.5555

TABLE 13

The Analyses of Culkin, 1966

Ocean etc.	Na(g/kg) / Cl o/oo	K(g/kg) / Cl o/oo	Mg(g/kg) / Cl o/oo	Ca(g/kg) / Cl o/oo	Sr(mg/kg) / Cl o/oo
N. Pacific	0.5556 (5)	0.0206 (8)	0.06670 (10)	0.02128 (10)	0.40 (10)
S. Pacific	0.5554 (6)	0.0206 (6)	0.06691 (8)	0.02128 (8)	0.40 (6)
N. Atlantic	0.5552 (7)	0.0206 (7)	0.06691 (9)	0.02128 (9)	0.40 (6)
S. Atlantic	---	---	0.06692 (1)	0.02120 (1)	0.38 (1)
Northern Seas	0.5553 (5)	0.0205 (5)	0.06690 (7)	0.02121 (7)	0.39 (6)
Eastern Ocean	0.5567 (2)	0.0206 (2)	0.06691 (3)	0.02130 (3)	0.40 (3)
Indian Ocean	0.5554 (6)	0.0207 (6)	0.06696 (10)	0.02124 (10)	0.40 (10)
Mediterranean Sea	0.5557 (11)	0.0206 (11)	0.06685 (11)	0.02131 (11)	0.39 (9)
Red Sea	0.5563 (3)	0.0206 (3)	0.06685 (3)	0.02115 (3)	0.38 (3)
Persian Gulf	0.5557 (1)	0.0208 (1)	0.06695 (1)	0.02123 (1)	0.38 (1)
North Sea	0.5541 (2)	0.0206 (2)	0.06703 (2)	0.02118 (2)	0.40 (2)
Baltic Sea	0.5554 (1)	0.0205 (1)	0.06694 (1)	0.02127 (1)	0.38 (1)
All	0.5555 (49)	0.0206 (54)	0.06692 (66)	0.02126 (66)	0.40 (58)
Standard (Batch P33)	0.5562	0.0205	0.06690	0.02122	0.39

(Number of Samples in Brackets)

were lower than the projected 0.387 g/kg concentration and 0.0200 ratio. The site 1 sample was equal to the projected levels.

Table 14 lists the principle determinations of the potassium ion since 1882. The sample from the Atlantic Ocean was similar to the reported range of the Atlantic of 0.01953 to 0.0263 (Table 11). The samples from site 2 and site 3 tend to be the only low results.

Culkin (1966) reported a mean potassium ratio for the oceans to be 0.0205 and found no ocean ratio to be lower (Table 13). The potassium levels for the river system and Atlantic samples tend to be low when the modern determinations are taken into consideration.

The samples from site 1, site 4, and site 5, all have values comparable to the sample from site 6. The site 1 and site 5 sample salinities were greater than the salinities at the other river sites. The site 2 and site 3 samples exhibit low salinities indicating that fresh water dilution could cause low potassium concentrations. The Banana Creek, Sykes Creek, and Barge Canal could exert a predominate effect on the potassium concentrations in the northern Indian and Banana Rivers. The reduced potassium levels were not noted in the samples at site 4 at which the lowest salinities were found.

It was difficult to obtain consistent results with the colorimetric determination, which was indicated by the high standard deviations. Potassium's extreme solubility makes it one of the most difficult ions to analyze in saline water (Horne, 1969).

The mean potassium concentrations and ratios in the Indian

TABLE 14

Principle Determinations of Potassium in Sea Water
(Riley, 1965)

Reference	Ocean etc.	K(g/kg) for S = 35 o/oo	$\frac{K(g/kg)}{Cl\ o/oo}$
Schmelck(1882)	N. Atlantic	0.3925	0.02026
Forsberg(1883)	Siberian	0.4088	0.0211
Dittmar(1884)	Various	0.3931	0.02029
Natterer(1892, 1893, 1894)	Mediterranean	0.3890	0.02008
Kolotoff(1893)	Black	0.4069	0.0210
Makin(1898)	Atlantic	0.3945	0.02036
Macallum(1903)	Atlantic	0.3923	0.02025
Schloesing(1906)	Atlantic and Mediterranean	0.3784	0.01953
Wheeler(1910)	Atlantic	0.5095	0.0263
Steiger(1910)	Atlantic	0.3852	0.01988
Anderson and Thompson(1932)	Puget Sound	0.3700	0.0191
Webb(1939)	Atlantic	0.3892	0.02009
Miyake(1939)	Pacific	0.3700	0.0191
Fukai and Shiokawa(1955)	W. Pacific N. Pacific	0.4117 0.4061	0.02125 0.02096
Jentoft and Robinson(1956)	Atlantic and Pacific	0.3921	0.02023
Sporek(1956)	Copenhagen Standard Sea Water	0.4033	0.0208
	English Channel	0.4010	0.0207

and Banana Rivers were found to be similar to those reported for the Atlantic Ocean, however, some regional variability was evident.

3. Calcium-Strontium

A definite trend in the calcium-strontium levels could be noted in Table 5 and Table 6. The same effect was noted in both the EDTA and gravimetric determination.

The calcium-strontium mean concentrations increased in the samples from site 1 to site 3 (Table 7). The sample concentration at site 4 was similar to the sample at site 2. The above samples contained calcium-strontium levels that were as much as 0.100 g/kg greater than the site 5 and site 6 samples. The site 5 sample concentration was slightly greater than the sample at site 6.

The mean sample ratio at site 5 was in agreement with the range reported for the Atlantic Ocean of 0.02164 to 0.02168 (Table 11 and Table 15) and to the value determined by Culkin (1966) for the South Atlantic (Table 13). 0.0042 was added to the reported calcium levels to compensate for strontium. The site 6 EDTA and gravimetric analyses both resulted in a concentration and ratio that were low.

There was a correlation between the increase in calcium-strontium concentration and a decrease in salinity in the river system. The samples at site 2, site 3, and site 4, contained the greatest calcium-strontium levels and the lowest salinities. The sample salinities at site 1 were greater and the calcium-strontium content

TABLE 15

Principle Determinations of Calcium in Sea Water
(Riley, 1965)

Reference	Ocean etc.	Ca(g/kg) for S = 35 o/oo	$\frac{Ca(g/kg)}{Cl\ o/oo}$
Dittmar(1884)	Various	0.4123	0.02128
Thompson and Wright(1930)	Pacific	0.4098	0.02115
Miyake(1939)	Pacific	0.4107	0.02120
Matida and Yamauchi(1950)	Tokyo Bay	0.4127	0.02130
Fukai and Shiokawa(1955)	W. Pacific	0.4123	0.02128
	N. Pacific	0.4173	0.02154
Carpenter(1957)	Atlantic	0.4119	0.02126
Kirk and Moberg(1933)	Pacific	0.4136	0.02135
Gripenberg(1937)	Baltic	0.4177	0.02156
Chow and Thompson(1955)	Pacific	0.4241	0.02189
Kawasaki and Sugawara(1958)	W. Pacific	0.4028	0.02079
	W. Pacific	0.3987	0.02058
	Indian	0.4067	0.02099
	Antarctic	0.4107	0.02120
Pate and Robinson(1958)	Pacific	0.4134	0.02134
Voipio(1959)	Barents	0.4039	0.02085
Carpenter(1957)	Atlantic	0.4111	0.02122

lower than the sites above. The highest river salinities were found in the samples at site 5 at which the lowest concentrations were determined.

A salt water wedge flowing south from the northern Indian River region, specifically from the Haulover Canal and Mosquito Lagoon, results in site 1 samples with higher salinities (Lasater, 1972) and possibly lower calcium-strontium levels. The southern flow could reduce the dilution influence of the Banana Creek. The site 2 and site 3 concentrations illustrate that the Banana Creek and Sykes Creek apparently exert a predominate influence on river water characteristics. Site 4 samples exhibited high calcium-strontium values which were probably influenced by run-off from the Eau Gallie River. The site 5 sample concentrations were slightly higher than the samples at site 6 indicating that some fresh water influence could be exerted by the Sebastian River, however, the calcium-strontium levels were apparently reduced by daily Atlantic tidal flushing through the Sebastian Inlet.

The high site 1, site 2, site 3, and site 4 calcium-strontium sample concentrations could result from the dissolution of calcareous soils and sediments in the river region. Calcium is probably introduced into the river system as dissolved and, to a lesser extent, colloidal calcium carbonate through land drainage and river water to river bottom interactions. The regional sedimentary structure is composed of large amounts of calcareous shells and shell fragments.

The theoretical saturation of calcium as the carbonate in sea water could be calculated to be 70 mg/l using the solubility product constant of 5.0×10^{-9}, the measured saturation levels range from 100 mg/l to 480 mg/l, and the concentration of the element in sea water is 400 mg/l (Horne, 1969). The measured values are higher because metal ions apparently engage in complex or ion-pair formations (Riley, 1965).

It is evident that calcium-strontium concentrations are higher in the Indian and Banana Rivers than in the Atlantic Ocean and they are not similar to the reported Atlantic values. It is not unusual for calcium carbonate to be present at saturated and supersaturated levels in ocean waters (Horne, 1969). The northern river system is probably supersaturated with respect to calcium carbonate in the remaining concentration would be present in colloidal form to a lesser extent.

4. Magnesium

The mean EDTA magnesium levels for the samples from site 1, site 2, and site 3, tend to be higher than the Atlantic value of 0.0667 (Table 11 and Table 16). The site 4, site 5, and site 6, samples show similarities to the Atlantic value listed above and to the value reported by Culkin (1966) for the South Atlantic of 0.06692 (Table 13).

The mean results from the gravimetric determination of magnesium were all lower than the reported values. The samples from

site 4, site 5, and site 6, were similar to the EDTA values for those sites. The site 1, site 2, and site 3, sample concentrations were lower than the values reported for the EDTA determination.

The simultaneous EDTA analysis by Katz (1964) is used in the fresh water determination of both calcium and magnesium. To this investigator's knowledge, the analysis has not been used on saline samples. The similarity of both the calcium and magnesium EDTA and gravimetric analyses indicates that the Katz determination can be used in saline water.

The means of the EDTA and gravimetric magnesium values (Table 7) concur with the values reported by other investigators (Table 11 and Table 16).

Lower salinities appear to be related to higher magnesium concentrations. The site 2 and site 3 samples exhibit magnesium levels that are greater than the Atlantic sample. The salinities of the samples at site 1 were greater than the salinities at the above sites, but the magnesium concentrations were also high. The low salinity sample at site 4 was similar to and the site 5 sample was slightly lower in concentration than the Atlantic sample. The correlation in the northern river region which was found for calcium was not as definite, however, the Banana Creek and Sykes Creek again appeared to exhibit some effect on river water characteristics.

Magnesium would probably be introduced into the river system as magnesium carbonate through land drainage and river water to

river bottom interactions.

The magnesium concentrations and ratios for the river were similar to the values reported for the oceans by other investigators. The magnesium levels in the northern river region were greater than the Atlantic sample indicating that some magnesium variability due to fresh water dilution was present.

5. Sulfate

The mean sample ratio from site 6 was considerably higher than the reported value of 0.1393 for the Atlantic Ocean (Table 11). The sample ratio at site 4 was the lowest, below the reported levels, indicating a possible dilution effect from the Eau Gallie River The other values found for the sulfates did concur with the values found for other oceans (Table 11 and Table 17).

The localized river sulfate variability could be associated with the generation of hydrogen sulfide by the bacterial reduction of sulfate in the river bottom sediments. The evolved sulfide would be subsequently either lost to the atmosphere or oxidized to sulfate by bacterial action. The result would be regions of high or low sulfate concentration.

No correlation appeared to exist between salinity and the sulfate concentration.

The sulfate determination is subject to many positive and negative interferences that can produce high or low results, however,

the interferences generally tend to balance (Standard Methods, 1971). Co-precipitation can cause high standard deviations (Koltoff, 1969).

It was concluded that the sulfate ion concentrations were consistent with known ocean concentrations, though localized variability did exist.

TABLE 16

Principle Determinations of Magnesium in Sea Water
(Riley, 1965)

Reference	Ocean etc.	Mg(g/kg) for S = 35 o/oo	$\frac{Mg(g/kg)}{Cl,\ o/oo}$
Ellis and Matthews (1928)	E. Mediterranean	1.315	0.06785
	Gulf of Aden	1.320	0.06814
Dittmar(1884)	Various	1.318	0.06801
Thompson and Wright(1930)	N. Pacific	1.297	0.06695
Miyake(1939)	N.E. Pacific	1.296	0.0669
	W. Pacific	1.310	0.0676
Matida and Yamauchi(1951)	Tokyo Bay	1.297	0.06697
Fukai and Shiokawa(1955)	W. Pacific	1.284	0.06627
	N. Pacific	1.285	0.06632
Voipio(1957)	Baltic	1.297	0.06693
Voipio(1959)	Barents	1.306	0.06742
Pate and Robinson(1961)	Pacific	1.296	0.06689
F. Culkin (unpublished work)	Various	1.294	0.06680
Carpenter(1957)	Atlantic	1.292	0.0667

TABLE 17

Principle Determinations of Sulfate in Sea Water
(Riley, 1965)

Reference	Oceans etc.	SO_4 (g/kg) for S = 35 o/oo	$\frac{SO_4 (g/kg)}{Cl\ o/oo}$
Morton and Thorpe(1871)	Irish	2.707	0.1397
Dittmar(1884)	Various	2.689	0.1388
Anderson et.al.(1927)	N. Pacific	2.705	0.1396
Johnson et.al.(1931)	Atlantic	2.699	0.1393
	Pacific	2.701	0.1394
	Mediterranean	2.705	0.1396
	Red	2.703	0.1395
	Indian	2.710	0.1399
	Baltic	2.739	0.1414
Miyake(1939)	W. Pacific	2.707	0.1397
Maeda et.al.(1939)	Pacific and Atlantic	2.751	0.1420
Matida(1951)	Tokyo Bay	2.701	0.1394
Bather and Riley(1954)	Irish	2.710	0.1399
Fukai and Shiokawa(1955)	W. Pacific	2.710	0.1399
	N. Pacific	2.707	0.1397
J. P. Riley (unpublished work)	Various	2.712	0.1400

B. Ionic Equivalence and Salinity

1. Ionic Equivalence

The total anion equivalences for each site were similar (Table 8). The total cation equivalences were greater than the total anion equivalences in the samples from site 1, site 2, site 3, and site 4. The total anion equivalences were greater than the total cation equivalences in the samples from site 5 and site 6. The consistently high calcium-strontium concentrations found in the northern river system apparently contributes to the excess cation equivalence.

The river system appears to be in a dynamic situation in which calcium, and to a lesser extent, magnesium, concentrations are constantly kept high by fresh water run-off and river water to river bottom interactions. The calcium influxes must be greater than the precipitation time necessary to bring the river system to equilibrium.

The site 5 and site 6 sample equivalences were almost equal indicating that the ionic levels at these points were at equilibrium, as would be expected. The low cation equivalences found at these sites apparently results from the low sodium concentrations.

2. Chlorinity, Salinity, and Refractive Index

Agreement was found between the chlorinities calculated

from both the chlorinity titration and conductivity determination for 16 of the 22 measurements. The conductivity determination chlorinity values were greater than the chlorinity titration values for 17 of the 22 measurements.

The chlorinity titration determines the total halide content of the saline sample and an empirical formula relates the halide content to the total salinity. Any increased cation and anion levels, other than the halides, would not be detectable and low salinity values would normally be recorded.

The conductivity determination is a measure of the ability of a solution to conduct an electrical current and is dependent on the ionic strength of the solution. Assuming that the major ions in 35 °/oo sea water are all strong electrolytes and completely dissociated, the relative contribution of the ions to the total conductivity could be estimated to be: Cl^-, 64%; Na^+, 29%; Mg^{2+}, 3%, SO_4^{2-}, 2%; with each of the remaining constituents contributing less than one percent (Horne, 1969). Thus, the major contributors to the conductivity of sea water are the chloride and sodium ions.

The increased calcium content of the river waters would not appreciably increase the total conductivity of the solution and the salinities calculated from the conductivity determination would generally be slightly greater than those calculated from the chlorinity titration. Both determinations would result in low river salinities, for neither analysis could completely compensate for the

increased calcium levels, though conductivity would give the most accurate result.

The refractive index methods used were not extremely accurate. Temperature control and the lack of sufficient decimal place readability for the Spencer refractometer were a definite problem. A refractometer with good temperature control must be readable to 0.00001 to obtain salinities to within 0.05 °/oo (Riley, 1965). The Spencer was readable to only 0.0001, giving an accuracy of 0.5 °/oo. The instrument proved to be slightly less accurate, 0.8 °/oo, probably because of inadequate temperature control.

The hand held refractometer appeared to be slightly less accurate than the 1 °/oo accuracy claimed in the instruction manual. The instrument had been subjected to extensive field use and had a calculated accuracy of 1.2 o/oo.

V. CONCLUSIONS

The sodium concentrations in the Indian and Banana Rivers were generally low and showed some degree of regional variability. There was no correlation between the concentration of the sodium ion and the degree of fresh water dilution.

The potassium concentrations were low regionally. The northern river regions exhibited a correlation between low salinities and low potassium concentrations.

Calcium tended to be the major ion that exhibited the greatest variability from the reported ocean concentrations. Calcium was probably present in the form of dissolved and, to a lesser extent, colloidal calcium carbonate. A correlation existed between the increased calcium levels and decreased river salinities.

Magnesium levels corresponded to the analyzed Atlantic sample and were slightly variable. The northern river regions contained greater magnesium concentrations which corresponded to lower salinities.

Sulfate concentrations varied regionally but were similar to the reported ocean values. The river system sulfates could be affected by bacterial generation and utilization of the sulfate ion. No correlation appeared to exist between salinity and the sulfate concentration.

The examination of ionic equivalence indicated that the river system was in a dynamic state attributable to the calcium ion input

exceeding the precipitation time necessary to bring the system to equilibrium.

Salinity determinations by the chlorinity titrations and conductivity measurements could only be used as good approximations of the salinity, with conductivity giving the most accurate results. Neither determination could completely compensate for increased calcium levels and the reported salinities would be low.

Refractive index measurements were slightly less accurate than their theoretical accuracies.

APPENDIX A

PROCEDURES

I. CHLORINITY

(Martin, 1968)

A. Reagents

1. Potassium Chromate Indicator

Eight grams of reagent grade potassium chromate was dissolved in 100 ml of deionized, distilled water and stored in a clean dropping bottle.

2. Silver Nitrate Solution

37.11 grams of silver nitrate was dissolved in one liter of deionized, distilled water and stored in a brown, stoppered polyethylene bottle.

3. Standard and Substandard Sea Water

Standard Copenhagen sea water (P-52, 18-19/10, 1969) was used to standardize a five gallon container of Atlantic Ocean water taken off of the Fort Pierce Inlet. The sea water was standardized with the Beckman induction salinometer. The substandard sea water was subsequently used to standardize both the induction salinometer and the chlorinity determination before each series of analyses.

B. Procedure

The silver nitrate was standardized against substandard sea water at the beginning of each titration series. 10.00 milliliters of substandard sea water was pipetted into a 250 ml erlenmeyer flask and diluted to 100 ml with chloride free deionized, distilled water. Silver nitrate solution was transferred by funnel to a calibrated and acid washed 50 ml buret.

A magnetic stirring rod was carefully added to the sample flask and the flask was placed on a magnetic stirrer below the buret. The buret tip was lowered into the neck of the flask and the stirrer turned on. The stirring speed was adjusted to the maximum rate before any splashing of the sample occurred.

Three drops of potassium chromate indicator were added and the sample was titrated to the first stable color change from yellow to pink. The sides of the flask were washed with distilled water as the endpoint was approached and the silver nitrate solution was added in one half and one quarter drops until the endpoint was reached.

The volume of silver nitrate used was recorded to the hundredth place and the procedure repeated three times on new substandard samples. A chlorinity equivalent was calculated as follows:

$$\text{Cl } ^{o}/_{oo} \text{ equivalent/ml } AgNO_3 = \frac{s_1 \cdot t}{s_2}$$

where:

s_1 = substandard chlorinity, °/oo

s_2 = ml of substandard

t = ml of $AgNO_3$ titrant

The same procedure was used to titrate 10.00 ml of sample diluted to 100 ml. The chlorinity of the sample was calculated by:

ml $AgNO_3$ · Cl °/oo equivalent = Cl °/oo of sample

II. "METHOD FOR SIMULTANEOUS DETERMINATION OF CALCIUM AND MAGNESIUM" (Katz, 1964)

A. Reagents

1. EDTA Titrant, 0.01 M

The EDTA titrant was prepared as described in Standard Methods, 1971.

2. Buffer Solution

Add, with stirring, 55 ml concentrated hydrochloric acid to 400 ml of distilled water. Add slowly, with stirring, 310 ml 2-aminoethanol to this acidified solution. Add 100 mg of the magnesium salt of EDTA and, when it is dissolved, bring the solution to one liter with distilled water.

3. Eriochrome Black T Indicator

Dissolve 0.5 g of the dye in 100 g of triethanolamine. Keep the solution in a dark-colored bottle.

4. Eriochrome Blue S.E. Indicator

Dissolve 100 mg of the dye in 100 ml of distilled water containing 0.25 g of hydroxylamine hydrochloride. Keep the solution in a dark-colored bottle.

5. Sodium Hydroxide Solution, 1.0 N, Carbonate Free

6. Hydrochloric Acid, 1.0 N

B. Procedure

1. Measure 50.0 ml of sample or an aliquot diluted to 50 ml with distilled water into a porcelain or other suitable vessel.
2. Add 3.0 ml of 1.0 N sodium hydroxide and stir. The pH of the solution should be 12 to 13. The magnesium ions present will precipitate out as magnesium hydroxide.
3. Add three or four drops of Eriochrome Blue S.E. and, while stirring the solution continuously, titrate with EDTA to a definite color change. The color change at the calcium is from wine-red to violet. Record the volume of titrant used. When the proper endpoint is reached, several additional drops of titrant should cause no further color change. The excess of titrant added will be considered as part of the magnesium titration that follows.
4. Add 3.2 ml of 1.0 N hydrochloric acid to the above solution and stir for one minute. The pH of the solution should now be about four and the magnesium hydroxide precipitate should be completely dissolved. Incomplete solution of the precipitate results in a premature and fading magnesium endpoint.
5. Add five ml of buffer solution and one drop of Eriochrome Black

T and stir. The pH of the solution should now be 10.1. While stirring continuously, titrate with EDTA to a definite blue endpoint. This is the magnesium endpoint.

C. Calculations

At the calcium endpoint:

$$\text{mg/l Ca} = \frac{A \cdot f_1 \cdot 1{,}000}{\text{ml sample}}$$

in which A is the milliliters of EDTA used to the calcium endpoint; and f_1 is the milligrams of calcium equivalent to one milliliter of standard EDTA titrant.

At the magnesium endpoint:

$$\text{mg/l Mg} = \frac{B \cdot f_2 \cdot 1{,}000}{\text{ml sample}}$$

in which B is the millililiters of EDTA used in the titration from the calcium endpoint to the magnesium endpoint; and f_2 is the milligrams of magnesium equivalent to one milliliter of standard EDTA titrant.

TABLE 1B

SITE 1 - SODIUM

	Chlorinity					Conductivity				
Date	S o/oo (Cl)*	g/kg	mean g/kg	Na/Cl	Na/Cl mean (S.D.)**	S o/oo (Cl)	g/kg	mean g/kg	Na/Cl	Na/Cl mean (S.D.)
4-17-73	26.74 (14.80)	8.121	8.196	0.5487	0.5544 (0.0067)	26.747 (14.805)	8.113	8.195	0.5480	0.5531 (0.0071)
4-24	27.34 (15.13)	8.469		0.5598		27.264 (15.092)	8.469		0.5612	
4-30	27.19 (15.05)	8.398 8.285		0.5580 0.5505		27.320 (15.123)	8.398 8.285		0.5553 0.5478	
5-4	27.00 (14.95)	8.312 8.104		0.5560 0.5421		27.074 (14.986)	8.312 8.104		0.5547 0.5408	
5-6		8.413 8.234 8.381		0.5627 0.5508 0.5606			8.413 8.234 8.381		0.5614 0.5495 0.5593	

* Chlorinity o/oo
** Standard Deviation

TABLE 2B

SITE 2 - SODIUM

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	Na/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	Na/Cl	mean (S.D.)
4-17-73	23.82 (13.19)	7.395	7.192	0.5607	0.5508 (0.0067)	23.828 (13.190)	7.395	7.195	0.5607	0.5500 (0.0071)
4-24	23.65 (13.09)	7.121		0.5440		23.574 (13.049)	7.121		0.5457	
4-30	23.97 (13.27)	7.382 7.359		0.5563 0.5546		24.211 (13.402)	7.390 7.366		0.5514 0.5496	
5-4	23.75 (13.15)	7.163 7.132		0.5447 0.5424		23.779 (13.162)	7.163 7.132		0.5442 0.5419	
5-6		7.357 7.287 7.198 7.187		0.5595 0.5514 0.5474 0.5465			7.357 7.287 7.206 7.194		0.5590 0.5536 0.5475 0.5466	

TABLE 3B

SITE 3 - SODIUM

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	Na/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	Na/Cl	mean (S.D.)
4-17-73	22.71	7.147	7.161	0.5686	0.5555	22.763	7.147	7.164	0.5672	0.5537
	(12.57)	6.774		0.5389	(0.0115)	(12.600)	6.774		0.5376	(0.0120)
4-24	23.06	7.114		0.5575		23.114	7.110		0.5560	
	(12.76)	6.804		0.5332		(12.794)	6.800		0.5318	
4-30	23.39	7.158		0.5527		23.621	7.158		0.5475	
	(12.95)	7.157		0.5527		(13.075)	7.157		0.5474	
5-6	23.62	7.322		0.5598		23.685	7.329		0.5590	
	(13.08)	7.235		0.5531		(13.110)	7.242		0.5524	
		7.409		0.5664			7.416		0.5657	
		7.494		0.5729			7.502		0.5722	

TABLE 4B

SITE 4 - SODIUM

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	Na/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	Na/Cl	mean (S.D.)
4-21-73	22.38 (12.391	6.847	7.105	0.5526	0.5560 (0.0105)	22.657 (12.542)	6.847	7.100	0.5459	0.5508 (0.0095)
4-25	22.60 (12.51)	6.861 6.988		0.5484 0.5586		23.106 (12.790)	6.861 6.988		0.5364 0.5464	
5-2	22.96 (12.71)	7.331		0.5768		23.221 (12.853)	7.323		0.5698	
5-8	23.49 (13.00)	7.425 7.382 7.407 7.391		0.5553 0.5509 0.5528 0.5529		23.504 (13.010)	7.418 7.375 7.400 7.384		0.5543 0.5499 0.5519 0.5518	

TABLE 5B

SITE 5 - SODIUM

Date	Chlorinity S o/oo (Cl)	g/kg	mean	Na/Cl	mean (S.D.)	Conductivity S o/oo (Cl)	g/kg	mean	Na/Cl	mean (S.D.)
4-25-73	32.75	10.14	10.21	0.5594	0.5549	33.330	10.14	10.21	0.5497	0.5517
	(18.13)	10.06		0.5549	(0.0076)	(18.449)	10.06		0.5453	(0.0059)
5-2	34.01	10.27		0.5455		34.156	10.27		0.5433	
	(18.83)	10.44		0.5544		(18.906)	10.44		0.5522	
5-8	34.68	10.66		0.5548		34.684	10.66		0.5551	
	(19.20)	10.71		0.5573		(19.199)	10.71		0.5576	
		10.72		0.5582			10.72		0.5585	

TABLE 6B

SITE 6 - SODIUM

		Chlorinity					Conductivity				
Site	Date	S o/oo (Cl)	g/kg	mean	Na/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	Na/Cl	mean (S.D.)
A	4-21-73	36.00 (19.92)	11.12	11.06	0.5581	0.5545 (0.0072)	35.958 (19.903)	11.12	11.06	0.5586	0.5536 (0.0068)
D	4-25						36.230 (20.054)	11.25		0.5611	
D	5-2						36.230 (20.054)	11.21 10.92 11.01 11.03		0.5590 0.5447 0.5490 0.5501	
D	5-8	36.28 (20.08)	11.07 11.33 11.12 10.95		0.5513 0.5643 0.5536 0.5453		36.288 (20.086)	11.07 11.33 11.12 10.95		0.5511 0.5641 0.5535 0.5451	

TABLE 7B

SITE 1 - POTASSIUM

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	K/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	K/Cl	mean (S.D.)
4-20-73	26.74 (14.80)	0.263 0.271	0.297	0.0178 0.0183	0.0200 (0.0017)	26.747 (14.805)	0.263 0.271	0.297	0.0178 0.0183	0.0199 (0.0017)
4-26	27.31 (15.13)	0.299 0.299		0.0198 0.0198		27.264 (15.092)	0.299 0.299		0.0198 0.0198	
5-1	27.19 (15.05)	0.339 0.319		0.0225 0.0212		27.320 (15.123)	0.339 0.319		0.0225 0.0211	
5-6	27.00 (14.95)	0.326 0.291 0.326 0.291 0.252 0.309		0.0218 0.0195 0.0218 0.0195 0.0169 0.0207		27.074 (14.986)	0.326 0.291 0.326 0.291 0.252 0.309		0.0218 0.0194 0.0218 0.0194 0.0168 0.0206	

TABLE 8B

STIE 2 - POTASSIUM

Date	Chlorinity S o/oo (Cl)	g/kg	mean	K/Cl	mean (S.D.)	Conductivity S o/oo (Cl)	g/kg	mean	K/Cl	mean (S.D.)
4-20-73	23.82 (13.19)	0.233 0.228	0.251	0.0177 0.0173	0.0190 (0.0020)	23.828 (13.190)	0.233 0.228	0.251	0.0177 0.0173	0.0190 (0.0020)
4-26	23.65 (13.09)	0.237 0.281		0.0181 0.0215		23.574 (13.049)	0.237 0.281		0.0182 0.0215	
5-1	23.97 (13.27)	0.278 0.288		0.0210 0.0217		24.211 (13.402)	0.278 0.288		0.0207 0.0215	
5-6	23.75 (13.15)	0.284 0.243 0.205 0.214 0.273 0.252 0.272 0.254 0.214 0.257 0.223 0.260		0.0216 0.0185 0.0156 0.0163 0.0208 0.0192 0.0209 0.0193 0.0163 0.0195 0.0170 0.0198		23.779 (13.162)	0.284 0.243 0.205 0.214 0.273 0.252 0.272 0.254 0.214 0.257 0.223 0.260		0.0216 0.0185 0.0156 0.0163 0.0207 0.0192 0.0207 0.0193 0.0163 0.0195 0.0169 0.0198	

TABLE 9B

SITE 3 - POTASSIUM

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	K/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	K/Cl	mean (S.D.)
4-20-73	22.71	0.224	0.245	0.0178	0.0190	22.763	0.224	0.245	0.0178	0.0189
	(12.57)	0.240		0.0191	(0.0020)	(12.600)	0.240		0.0191	(0.0020)
4-26	23.06	0.245		0.0192		23.114,	0.245		0.0192	
	(12.76)	0.210		0.0165		(12.794)	0.210		0.0164	
		0.255		0.0200			0.255		0.0199	
5-2	23.39	0.266		0.0205		23.621	0.266		0.0203	
	(12.95)	0.281		0.0217		(13.075)	0.281		0.0215	
5-8	23.62	0.206		0.0158		23.685	0.206		0.0157	
	(13.08)	0.291		0.0222		(13.110)	0.291		0.0222	
		0.223		0.0171			0.223		0.0170	
		0.260		0.0199			0.260		0.0198	
		0.260		0.0199			0.260		0.0198	
		0.228		0.0174			0.228		0.0174	

TABLE 10B

SITE 4 - POTASSIUM

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	K/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	K/Cl	mean (S.D.)
4-21-73	22.38 (12.39)	0.245 0.261	0.253	0.0198 0.0211	0.0199 (0.0010)	22.657 (12.542)	0.245 0.261	0.253	0.0195 0.0208	0.0197 (0.0009)
4-26	22.60 (12.51)	0.259 0.250		0.0207 0.0200		23.106 (12.790)	0.259 0.250		0.0203 0.0196	
5-2	22.96 (12.71)	0.273 0.259		0.0215 0.0204		23.221 (12.853)	0.273 0.259		0.0212 0.0202	
5-8	23.49 (13.00)	0.251 0.246 0.253 0.264 0.237 0.240		0.0193 0.0189 0.0195 0.0203 0.0182 0.0185		23.504 (13.010)	0.251 0.246 0.253 0.264 0.237 0.240		0.0193 0.0189 0.0195 0.0203 0.0182 0.0185	

TABLE 11B

SITE 5 - POTASSIUM

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	K/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	K/Cl	mean (S.D.)
4-21-73	31.31 (17.33)	0.360	0.369	0.0208	0.0197 (0.0023)	31.483 (17.427)	0.360	0.369	0.0207	0.0196 (0.0023)
4-26	32.75 (18.13)	0.297 0.443		0.0164 0.0244		33.330 (18.449)	0.297 0.443		0.0161 0.0240	
5-2	34.01 (18.83)	0.395 0.372		0.0210 0.0198		34.156 (18.906)	0.395 0.372		0.0209 0.0197	
5-8	34.68 (19.20)	0.385 0.364 0.399 0.312 0.381 0.354		0.0200 0.0190 0.0208 0.0162 0.0198 0.0184		34.684 (19.199)	0.385 0.364 0.399 0.312 0.381 0.354		0.0201 0.0190 0.0209 0.0163 0.0199 0.0184	

TABLE 12B

SITE 6 - POTASSIUM

		Chlorinity					Conductivity				
Site	Date	S o/oo (Cl)	g/kg	mean	K/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	K/Cl	mean (S.D.)
A	4-21-73	36.00 (19.92)	0.412 0.371	0.390	0.0207 0.0186	0.0195 (0.0010)	35.958 (19.903)	0.412 0.371	0.395	0.0207 0.0186	0.0198 (0.0011)
A	4-26	36.00 (19.92)	0.380 0.397 0.378 0.396		0.0191 0.0199 0.0190 0.0199		35.958 (19.903)	0.380 0.397 0.378 0.396		0.0191 0.0200 0.0190 0.0199	
B	4-26						36.230 (20.054)	0.412 0.387		0.0206 0.0193	
B	5-2						36.230 (20.054)	0.431 0.418		0.0215 0.0208	
B	5-8	36.28 (20.08)	0.390 0.363 0.407 0.367 0.441 0.381 0.390		0.0194 0.0181 0.0203 0.0183 0.0220 0.0190 0.0194		36.288 (20.086)	0.390 0.363 0.407 0.367 0.441 0.381 0.390		0.0194 0.0181 0.0203 0.0183 0.0220 0.0190 0.0194	

TABLE 13B

SITE 1 - EDTA CALCIUM

		Chlorinity					Conductivity				
	Date	S o/oo (Cl)	g/kg	mean	Ca/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	Ca/Cl	mean (S.D.)
*	11-22-72	30.21 (16.73)	0.3790	0.3474	0.0227	0.0235 (0.0013)	30.459 (16.870)	0.3790	0.3674	0.0225	0.0234 (0.0013)
			0.3778		0.0226			0.3778		0.0224	
			0.3887		0.0232			0.3887		0.0230	
			0.3828		0.0229			0.3828		0.0227	
			0.3714		0.0226			0.3714		0.0224	
			0.3770		0.0225			0.3770		0.0224	
*	12-20	30.03 (16.63)	0.3969		0.0239		30.025 (16.614)	0.3969		0.0239	
			0.3905		0.0235			0.3905		0.0235	
			0.3905		0.0235			0.3905		0.0235	
*	12-30	29.52 (16.35)	0.3769		0.0228		29.525 (16.398)	0.3769		0.0227	
			0.3725		0.0231			0.3725		0.0230	
			0.3729		0.0228			0.3729		0.0227	
*	1-5-73	29.04 (16.09)	0.3529		0.0219		29.161 (16.151)	0.3529		0.0219	
			0.3517		0.0219			0.3517		0.0218	
			0.3572		0.0222			0.3572		0.0221	
**	1-31	29.05 (16.08)	0.3699		0.0230		29.258 (16.195)	0.3699		0.0228	
			0.3595		0.0224			0.3595		0.0222	
**	2-7	25.91 (14.34)	0.3662		0.0255		26.203 (14.504)	0.3662		0.0253	
			0.3742		0.0261			0.3742		0.0258	
			0.3781		0.0264			0.3781		0.0261	
			0.3837		0.0268			0.3837		0.0265	
**	2-13	25.98 (14.38)	0.3415		0.0238		26.203 (14.504)	0.3415		0.0236	
			0.3423		0.0238			0.3423		0.0236	
			0.3511		0.0244			0.3511		0.0242	
			0.3543		0.0246			0.3543		0.0244	
**	2-26	26.69 (14.77)	0.3410		0.0231		26.872 (14.874)	0.3410		0.0230	
			0.3402		0.0230			0.3402		0.0229	
			0.3405		0.0231			0.3405		0.0229	

* Standard Methods
** Katz (1964)

TABLE 14B

SITE 2 - EDTA CALCIUM

	Date	Chlorinity S o/oo (Cl)	g/kg	mean	Ca/Cl	mean (S.D.)	Conductivity S o/oo (Cl)	g/kg	mean	Ca/Cl	mean (S.D.)
*	11-22-72	27.01 (14.96)	0.3664	0.3634	0.0245	0.0246 (0.0022)	26.557 (14.709)	0.3664	0.3634	0.0249	0.0245 (0.0022)
			0.3625		0.0242			0.3625		0.0247	
			0.3664		0.0245			0.3664		0.0249	
			0.3625		0.0242			0.3625		0.0247	
			0.3625		0.0242			0.3625		0.0247	
*	12-20	28.58 (15.83)	0.4004		0.0253		28.659 (15.873)	0.4004		0.0237	
			0.3933		0.0249			0.3933		0.0239	
			0.3973		0.0251			0.3973		0.0237	
*	12-30	27.41 (15.18)	0.3626		0.0239		27.623 (15.290)	0.3623		0.0237	
			0.3626		0.0239			0.3623		0.0237	
			0.3678		0.0242			0.3674		0.0240	
*	1-5-73	26.92 (14.91)	0.3579		0.0240		27.189 (15.059)	0.3579		0.0238	
			0.3575		0.0240			0.3575		0.0237	
			0.3575		0.0240			0.3575		0.0237	
**	1-31	26.99 (14.94)	0.3574		0.0239		27.309 (15.116)	0.3574		0.0237	
			0.3550		0.0238			0.3550		0.0235	
**	2-7	25.68 (14.21)	0.3638		0.0256		25.975 (14.378)	0.3638		0.0253	
			0.3622		0.0255			0.3622		0.0252	
			0.3821		0.0269			0.3821		0.0266	
			0.3821		0.0269			0.3821		0.0266	
**	2-13	25.78 (14.28)	0.3503		0.0245		25.975 (14.378)	0.3503		0.0244	
			0.3535		0.0248			0.3535		0.0246	
			0.3476		0.0243			0.3476		0.0242	
			0.3508		0.0246			0.3508		0.0244	
**	2-26	25.89 (14.38)	0.3434		0.0240		25.062 (13.873)	0.3434		0.0248	
			0.3421		0.0239			0.3421		0.0247	
			0.3455		0.0241			0.3455		0.0249	

* Standard Methods
** Katz (1964)

TABLE 15B

SITE 3 - EDTA CALCIUM

	Date	Chlorinity S o/oo (Cl)	g/kg	mean	Ca/Cl	mean (S.D.)	Conductivity S o/oo (Cl)	g/kg	mean	Ca/Cl	mean (S.D.)
*	11-22-72	24.36 (13.49)	0.3437	0.3388	0.0255	0.0255 (0.0009)	24.506 (13.573)	0.3437	0.3388	0.0253	0.0254 (0.0005)
			0.3300		0.0245			0.3300		0.0243	
			0.3379		0.0251			0.3379		0.0249	
			0.3363		0.0249			0.3363		0.0248	
			0.3390		0.0251			0.3390		0.0250	
			0.3359		0.0250			0.3359		0.0248	
*	12-20	25.46 (14.09)	0.3694		0.0262		25.506 (14.127)	0.3694		0.0261	
			0.3722		0.0264			0.3722		0.0264	
			0.3622		0.0257			0.3622		0.0256	
*	12-30	24.46 (13.55)	0.3350		0.0247		24.776 (13.714)	0.3350		0.0244	
			0.3429		0.0253			0.3429		0.0250	
			0.3421		0.0253			0.3421		0.0250	
*	1-5-73	24.14 (13.37)	0.3252		0.0243		24.443 (13.538)	0.3252		0.0240	
			0.3323		0.0249			0.3323		0.0246	
			0.3292		0.0246			0.3292		0.0243	
**	1-31	24.23 (13.41)	0.3283		0.0245		24.522 (13.573)	0.3283		0.0242	
			0.3283		0.0245			0.3283		0.0242	
**	2-7	22.86 (12.65)	0.3470		0.0274		23.173 (12.827)	0.3473		0.0271	
			0.3510		0.0278			0.3513		0.0274	
			0.3350		0.0245			0.3353		0.0261	
			0.3374		0.0247			0.3377		0.0263	
**	2-13	22.98 (12.72)	0.3350		0.0263		23.173 (12.827)	0.3353		0.0261	
			0.3374		0.0265			0.3377		0.0263	
			0.3325		0.0261			0.3328		0.0260	
			0.3317		0.0260			0.3320		0.0259	
**	2-26	23.16 (12.82)	0.3287		0.0256		23.408 (12.957)	0.3287		0.0253	
			0.3298		0.0257			0.3298		0.0255	
			0.3300		0.0257			0.3300		0.0255	

* Standard Methods
** Katz (1961)

TABLE 16B

SITE 4 - EDTA CALCIUM

	Date	Chlorinity S o/oo (Cl)	Chlorinity g/kg	Chlorinity mean	Ca/Cl	Ca/Cl mean (S.D.)	Conductivity S o/oo (Cl)	Conductivity g/kg	Conductivity mean	Conductivity Ca/Cl	Conductivity Ca/Cl mean (S.D.)
*	11-22-72	21.74 (12.04)	0.2793	0.3200	0.0232	0.0254 (0.0025)	21.124 (11.700)	0.2795	0.3201	0.0239	0.0253 (0.0009)
			0.2773		0.0230			0.2776		0.0237	
			0.2773		0.0230			0.2776		0.0237	
			0.2812		0.0234			0.2815		0.0241	
			0.2832		0.0235			0.2835		0.0242	
			0.2832		0.0235			0.2835		0.0242	
*	12-20	23.53 (13.03)	0.3420		0.0262		23.820 (13.193)	0.3427		0.0260	
			0.3490		0.0268			0.3486		0.0264	
			0.3442		0.0264			0.3439		0.0261	
*	12-30	22.85 (12.65)	0.3239		0.0256		23.149 (12.813)	0.3236		0.0253	
			0.3235		0.0256			0.3232		0.0252	
			0.3274		0.0259			0.3271		0.0255	
*	1-5-73	22.50 (12.46)	0.3084		0.0248		22.744 (12.597)	0.3084		0.0245	
			0.3072		0.0247			0.3072		0.0237	
			0.3084		0.0248			0.3084		0.0245	
**	1-31	22.44 (12.42)	0.3142		0.0253		22.818 (12.631)	0.3142		0.0249	
			0.3093		0.0249			0.3093		0.0245	
**	2-7	22.92 (12.68)	0.3350		0.0264		23.167 (12.823)	0.3353		0.0262	
			0.3366		0.0266			0.3369		0.0263	
			0.3350		0.0264			0.3353		0.0262	
			0.3383		0.0267			0.3387		0.0264	
**	2-13	23.03 (12.75)	0.3350		0.0263		23.167 (12.823)	0.3353		0.0263	
			0.3390		0.0266			0.3393		0.0265	
			0.3372		0.0265			0.3376		0.0263	
			0.3317		0.0260			0.3320		0.0259	
**	2-26	23.60 (13.06)	0.3429		0.0263		23.813 (13.181)	0.3429		0.0260	
			0.3458		0.0265			0.3458		0.0262	
			0.3444		0.0264			0.3444		0.0261	

* Standard Methods
** Katz (1964)

TABLE 17B
SITE 5 - EDTA CALCIUM

	Date	Chlorinity S o/oo (Cl)	g/kg	mean	Ca/Cl	mean (S.D.)	Conductivity S o/oo (Cl)	g/kg	mean	Ca/Cl	mean (S.D.)
*	11-22-72	30.73 (17.02)	0.3576	0.3555	0.0210	0.0216 (0.0010)	30.657 (16.980)	0.3576	0.3555	0.0211	0.0215 (0.0010)
			0.3518		0.0207			0.3518		0.0207	
			0.3537		0.0208			0.3537		0.0208	
			0.3537		0.0208			0.3537		0.0208	
			0.3576		0.0210			0.3576		0.0211	
			0.3576		0.0210			0.3576		0.0211	
*	12-20	27.03 (14.97)	0.3408		0.0228		27.294 (15.117)	0.3408		0.0225	
			0.3452		0.0231			0.3452		0.0228	
			0.3380		0.0226			0.3380		0.0224	
*	12-30	29.79 (16.50)	0.3564		0.0216		29.988 (16.609)	0.3564		0.0215	
			0.3608		0.0219			0.3608		0.0217	
			0.3608		0.0219			0.3608		0.0217	
*	1-5-73	29.60 (16.39)	0.3473		0.0212		29.670 (16.433)	0.3473		0.0211	
			0.3445		0.0210			0.3445		0.0210	
			0.3493		0.0213			0.3493		0.0213	
**	1-31	29.58 (16.38)	0.3464		0.0211		29.786 (16.488)	0.3464		0.0210	
			0.3367		0.0206			0.3367		0.0204	
**	2-7	30.54 (16.91)	0.3426		0.0203		30.849 (17.076)	0.3426		0.0201	
			0.3331		0.0197			0.3331		0.0195	
			0.3608		0.0213			0.3608		0.0211	
			0.3489		0.0206			0.3489		0.0204	
**	2-13	30.79 (17.04)	0.3830		0.0225		30.849 (17.076)	0.3830		0.0224	
			0.3846		0.0226			0.3846		0.0225	
			0.3847		0.0226			0.3847		0.0225	
			0.3706		0.0218			0.3706		0.0217	
**	2-26	28.30 (15.66)	0.3594		0.0230		28.420 (15.731)	0.3594		0.0229	
			0.3644		0.0233			0.3644		0.0232	
			0.3649		0.0233			0.3649		0.0232	

* Standard Methods
** Katz (1961)

TABLE 18B

SITE 6 - EDTA CALCIUM

	Date (Site)	Chlorinity S o/oo (Cl)	g/kg	mean	Ca/Cl	mean	Conductivity S o/oo (Cl)	g/kg	mean	Ca/Cl	mean (S.D.)
**	1-31-73 (B)						36.224 (20.051)	0.4084 0.4076	0.4137	0.0204 0.0203	0.0208 (0.0003)
**	2-7 (B)						36.224 (20.051)	0.4131 0.4147 0.4186 0.4202		0.0206 0.0207 0.0209 0.0210	
**	2-13 (B)						36.224 (20.051)	0.4226 0.4265		0.0211 0.0213	
**	2-26 (A)	34.68 (19.19)	0.4072 0.4046 0.4072	0.4063	0.0212 0.0211 0.0212	0.0212 (0.0001)	34.666 (19.188)	0.4072 0.4046 0.4072		0.0212 0.0211 0.0212	

** Katz (1961)

TABLE 19B

SITE 1 - GRAVIMETRIC CALCIUM

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	Ca/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	Ca/Cl	mean (S.D.)
4-18-73	26.74 (14.80)	0.3450 0.3092	0.3673	0.0233 0.0209	0.0249 (0.0021)	26.747 (14.805)	0.3450 0.3092	0.3673	0.0233 0.0209	0.0249 (0.0016)
4-21		0.3772 0.3787		0.0255 0.0256			0.3772 0.3787		0.0255 0.0256	
4-23	27.34 (15.13)	0.3786 0.3809		0.0250 0.0252		27.264 (15.092)	0.3786 0.3809		0.0251 0.0252	
4-29	27.19 (15.05)	0.4101 0.3683		0.0273 0.0245		27.320 (15.123)	0.4101 0.3683		0.0271 0.0244	
5-3	27.00 (14.95)	0.3734 0.3680 0.3750 0.3690 0.3721 0.4113		0.0250 0.0246 0.0251 0.0247 0.0249 0.0275		27.074 (14.986)	0.3734 0.3680 0.3750 0.3690 0.3721 0.4113		0.0249 0.0246 0.0250 0.0246 0.0248 0.0275	

TABLE 20B

SITE 2 - GRAVIMETRIC CALCIUM

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	Ca/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	Ca/Cl	mean (S.D.)
4-18-73	23.82 (13.19)	0.3267 0.3316	0.3375	0.0248 0.0251	0.0257 (0.0011)	23.828 (13.190)	0.3267 0.3316	0.3371	0.0248 0.0251	0.0257 (0.0011)
4-21		0.3752		0.0285			0.3752		0.0285	
4-23	23.65 (13.09)	0.3470 0.3214		0.0265 0.0246		23.574 (13.049)	0.3470 0.3214		0.0266 0.0246	
4-29	23.97 (13.27)	0.3444 0.3511		0.0260 0.0265		24.211 (13.402)	0.3444 0.3511		0.0257 0.0262	
5-3	23.75 (13.15)	0.3270 0.3272 0.3304 0.3301 0.3349 0.3407		0.0249 0.0249 0.0251 0.0251 0.0255 0.0259		23.779 (13.162)	0.3273 0.3276 0.3308 0.3304 0.3349 0.3407		0.0249 0.0249 0.0251 0.0251 0.0254 0.0259	

TABLE 21B

SITE 3 - GRAVIMETRIC CALCIUM

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	Ca/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	Ca/Cl	mean (S.D.)
4-18-73	22.71 (12.57)	0.3122 0.3165	0.3472	0.0248 0.0252	0.0270 (0.0010)	22.763 (12.600)	0.3122 0.3165	0.3473	0.0248 0.0251	0.0269 (0.0010)
4-21		0.3430 0.3450		0.0273 0.0275			0.3430 0.3450		0.0272 0.0274	
4-23	23.06 (12.76)	0.3469 0.3526		0.0272 0.0276		23.114 (12.794)	0.3465 0.3522		0.0271 0.0275	
4-29	23.39 (12.95)	0.3643 0.3652		0.0281 0.0282		23.621 (13.075)	0.3647 0.3655		0.0279 0.0280	
5-3	23.62 (13.08)	0.3532 0.3588 0.3608		0.0270 0.0274 0.0276		23.685 (13.110)	0.3535 0.3592 0.3612		0.0270 0.0274 0.0276	
5-8		0.3464 0.3492		0.0265 0.0267			0.3464 0.3492		0.0264 0.0266	

TABLE 22B

SITE 4 - GRAVIMETRIC CALCIUM

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	Ca/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	Ca/Cl	mean (S.D.)
4-22-73	22.38	0.3228	0.3276	0.0261	0.0257	22.657	0.3228	0.3286	0.0257	0.0255
	(12.39)	0.3238		0.0261	(0.0005)	(12.542)	0.3238		0.0258	(0.0004)
4-26	22.60	0.3326		0.0266			0.3326		0.0260	
	(12.51)	0.3303		0.0264			0.3303		0.0258	
5-1	22.96	0.3286		0.0259		23.106	0.3286		0.0256	
	(12.71)	0.3281		0.0258		(12.790)	0.3281		0.0255	
5-3	23.49	0.3277		0.0252		23.221	0.3280		0.0252	
	(13.00)	0.3377		0.0260		(12.853)	0.3381		0.0260	
		0.3243		0.0250			0.3247		0.0250	
5-8		0.3228		0.0248		23.504	0.3228		0.0248	
		0.3246		0.0250		(13.010)	0.3246		0.0250	

TABLE 23B

SITE 5 - GRAVIMETRIC CALCIUM

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	Ca/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	Ca/Cl	mean (S.D.)
4-22-73	31.31	0.4031	0.4133	0.0233	0.0222	31.485	0.4031	0.4133	0.0231	0.0221
	(17.33)	0.4014		0.0232	(0.0016)	(17.427)	0.4014		0.0230	(0.0017)
4-26	32.75	0.4312		0.0238		33.330	0.4312		0.0234	
	(18.13)	0.4397		0.0243		(18.449)	0.4397		0.0238	
5-1	34.01	0.4604		0.0245		34.156	0.4604		0.0244	
	(18.83)	0.4424		0.0235		(18.906)	0.4424		0.0234	
5-3	34.68	0.3603		0.0191		34.684	0.3603		0.0191	
	(19.20)	0.3678		0.0195		(19.199)	0.3678		0.0195	
		0.4097		0.0213			0.4097		0.0213	
		0.3912		0.0204			0.3912		0.0204	
		0.4072		0.0212			0.4072		0.0212	
		0.4104		0.0214			0.4104		0.0214	
		0.4325		0.0225			0.4325		0.0225	
		0.4287		0.0223			0.4287		0.0223	

TABLE 24B

SITE 6 - GRAVIMETRIC CALCIUM

	Chlorinity					Conductivity				
Date (Site)	S o/oo (Cl)	g/kg	mean	Ca/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	Ca/Cl	mean (S.D.)
4-22-73(A)	36.00 (19.92)	0.4322 0.4398	0.4224	0.0217 0.0221	0.0209 (0.0007)	35.958 (19.903)	0.4322 0.4398	0.4230	0.0217 0.0221	0.0211 (0.0030)
4-26 (B)						36.230 (20.054)	0.4168 0.4317		0.0208 0.0215	
5-1 (B)						36.230 (20.054)	0.5724 0.4789		0.0285 0.0239	
5-3 (B)						36.228 (20.086)	0.3241 0.3191		0.0162 0.0159	
5-3	36.28 (20.08)	0.4280 0.4199 0.4026 0.4295 0.4132 0.4142		0.0213 0.0209 0.0201 0.0214 0.0206 0.0206			0.4280 0.4199 0.4026 0.4295 0.4132 0.4142		0.0213 0.0209 0.0200 0.0214 0.0206 0.0206	

TABLE 25B

SITE 1 - EDTA MAGNESIUM

Date	S o/oo (Cl)	Chlorinity g/kg	mean	Mg/Cl	mean (S.D.)	S o/oo (Cl)	Conductivity g/kg	mean	Mg/Cl	mean (S.D.)
1-31-73	29.05 (16.08)	1.093 1.072	1.031	0.0680 0.0667	0.0701 (0.0039)	29.258 (16.195)	1.093 1.072	1.031	0.0695 0.0662	0.0695 (0.0037)
2-7	25.91 (14.34)	1.063 1.062 1.098 1.105		0.0741 0.0741 0.0766 0.0771		26.203 (14.504)	1.063 1.062 1.098 1.105		0.0733 0.0732 0.0757 0.0762	
2-13	25.98 (14.38)	0.9741 0.9679 0.9521 0.9613		0.0677 0.0673 0.0662 0.0669		26.203 (14.504)	0.9741 0.9679 0.9521 0.9613		0.0672 0.0667 0.0656 0.0663	
2-26	26.69 (14.77)	1.011 1.023 1.023		0.0685 0.0693 0.0693		26.872 (14.874)	1.011 1.023 1.023		0.0680 0.0688 0.0688	

TABLE 26B

SITE 2 - EDTA MAGNESIUM

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	Mg/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	Mg/Cl	mean (S.D.)
1-31-73	26.99 (14.94)	0.9974 0.9740	0.9869	0.0668 0.0652	0.0687 (0.0023)	27.309 (15.116)	0.9869 0.9740	0.9869	0.0660 0.0644	0.0687 (0.0026)
2-7	25.68 (14.21)	1.001 1.001 1.027 1.028		0.0704 0.0704 0.0723 0.0723		25.975 (14.378)	1.001 1.001 1.027 1.028		0.0696 0.0696 0.0714 0.0715	
2-13	25.78 (14.28)	0.9627 0.9541 0.9517 0.9497		0.0674 0.0668 0.0667 0.0665		25.975 (14.378)	0.9627 0.9541 0.9517 0.9497		0.0670 0.0664 0.0662 0.0661	
2-26	25.89 (14.38)	0.9918 0.9955 0.9959		0.0692 0.0695 0.0695		25.062 (13.873)	0.9918 0.9955 0.9959		0.0715 0.0718 0.0718	

TABLE 27B

SITE 3 - EDTA MAGNESIUM

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	Mg/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	Mg/l	mean (S.D.)
1-31-73	24.23 (13.41)	0.8977 0.8864	0.8922	0.0669 0.0661	0.0695 (0.0038)	24.522 (13.573)	0.8977 0.8864	0.8927	0.0661 0.0653	0.0689 (0.0023)
2-7	22.86 (12.65)	0.9040 0.9098 0.9195 0.9215		0.0715 0.0712 0.0727 0.0729		23.173 (12.827)	0.9049 0.9107 0.9204 0.9224		0.0706 0.0710 0.0718 0.0719	
2-13	22.98 (12.72)	0.8680 0.8651 0.8577 0.8510		0.0682 0.0680 0.0674 0.0669		23.173 (12.827)	0.8688 0.8660 0.8581 0.8518		0.0677 0.0675 0.0669 0.0664	
2-26	23.16 (12.82)	0.8998 0.9092 0.9092		0.0702 0.0709 0.0709		23.408 (12.957)	0.8998 0.9092 0.9092		0.0694 0.0702 0.0702	

TABLE 28B

SITE 4 - EDTA MAGNESIUM

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	Mg/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	Mg/Cl	mean (S.D.)
1-31-73	22.44 (12.42)	0.8441 0.8305	0.8630	0.0677 0.0669	0.0677 (0.0019)	22.818 (12.631)	0.8441 0.8305	0.8637	0.0668 0.0658	0.0671 (0.0020)
2-7	22.92 (12.68)	0.8260 0.8298 0.8531 0.8250		0.0651 0.0654 0.0673 0.0651		23.167 (12.823)	0.8268 0.8306 0.8540 0.8258		0.0645 0.0648 0.0666 0.0644	
2-13	23.03 (12.75)	0.8713 0.8642 0.8548 0.8577		0.0683 0.0678 0.0670 0.0673		23.167 (12.823)	0.8722 0.8660 0.8556 0.8581		0.0680 0.0675 0.0667 0.0669	
2-26	23.60 (13.06)	0.9169 0.9218 0.9255		0.0702 0.0706 0.0709		23.813 (13.181)	0.9169 0.9218 0.9255		0.0696 0.0699 0.0702	

TABLE 29B

SITE 5 - EDTA MAGNESIUM

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	Mg/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	Mg/Cl	mean (S.D.)
1-31-73	29.58	1.078	1.101	0.0658	0.0665	29.786	1.078	1.101	0.0654	0.0661
	(16.38)	1.111		0.0678	(0.0022)	(16.488)	1.111		0.0674	(0.0024)
2-7	30.54	1.065		0.0630		30.849	1.065		0.0624	
	(16.91)	1.066		0.0630		(17.076)	1.066		0.0624	
		1.087		0.0643			1.087		0.0637	
		1.092		0.0646			1.092		0.0640	
2-13	30.79	1.130		0.0663		30.849	1.130		0.0662	
	(17.04)	1.144		0.0671		(17.076)	1.144		0.0670	
		1.161		0.0681			1.161		0.0680	
		1.130		0.0663			1.130		0.0662	
	28.30	1.083		0.0692		28.420	1.083		0.0689	
	(15.66)	1.082		0.0691		(15.731)	1.082		0.0688	
		1.084		0.0692			1.084		0.0689	

TABLE 30B

SITE 6 - EDTA MAGNESIUM

	Chlorinity					Conductivity				
Date (Site)	S o/oo (Cl)	g/kg	mean	Mg/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	Mg/Cl	mean (S.D.)
1-31-73 (B)						36.224 (20.051)	1.367 1.361	1.333	0.0682 0.0679	0.0673 (0.0010)
2-7 (B)							1.330 1.329 1.357 1.358		0.0663 0.0663 0.0677 0.0677	
2-13 (B)							1.333 1.340		0.0668 0.0665	
2-26 (A)	34.68 (19.19)	1.292 1.298 1.299	1.296	0.0673 0.0676 0.0677	0.0675 (0.0001)		1.292 1.298 1.299		0.0673 0.0677 0.0677	

TABLE 31B

SITE 1 - GRAVIMETRIC MAGNESIUM

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	Mg/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	Mg/Cl	mean (S.D.)
4-18-73	26.74 (14.80)	0.9922 0.9388	0.9811	0.0670 0.0634	0.0656 (0.0012)	26.747 (14.805)	0.9922 0.9388	0.9811	0.0670 0.0634	0.0655 (0.0012)
4-21		0.9763 0.9687		0.0660 0.0655			0.9763 0.9687		0.0659 0.0654	
4-23	27.34 (15.13)	0.9976 0.9714		0.0659 0.0642		27.264 (15.092)	0.9976 0.9714		0.0661 0.0644	
4-29	27.19 (15.05)	0.9778 1.023		0.0650 0.0680		27.320 (15.123)	0.9778 1.023		0.0647 0.0676	
5-3	27.00 (14.95)	0.9638 0.9850 0.9901 0.9943 0.9951 0.9619		0.0645 0.0655 0.0662 0.0665 0.0666 0.0643		27.074 (14.986)	0.9638 0.9850 0.9901 0.9943 0.9951 0.9619		0.0643 0.0651 0.0661 0.0664 0.0664 0.0642	

TABLE 32B

SITE 2 - GRAVIMETRIC MAGNESIUM

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	Mg/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	Mg/Cl	mean (S.D.)
4-18-73	23.82	0.8583	0.8609	0.0651	0.0644	23.828	0.8583	0.8609	0.0651	0.0661
	(13.19)	0.8749		0.0663	(0.0011)	(13.190)	0.8749		0.0663	(0.0011)
4-21	23.65	0.8704		0.0660		23.574	0.8704		0.0660	
	(13.09)	0.8878		0.0673		(13.049)	0.8878		0.0673	
4-23		0.8674		0.0664			0.8674		0.0665	
		0.8651		0.0660			0.8651		0.0663	
4-29	23.97	0.9181		0.0692		24.211	0.9181		0.0685	
	(13.27)	0.9102		0.0686		(13.402)	0.9102		0.0679	
5-3	23.75	0.8692		0.0661		23.779	0.8692		0.0660	
	(13.15)	0.8657		0.0658		(13.162)	0.8657		0.0658	
		0.8673		0.0660			0.8673		0.0659	
		0.8669		0.0659			0.8669		0.0659	
		0.8702		0.0662			0.8702		0.0661	
		0.8592		0.0653			0.8592		0.0653	

TABLE 33B

SITE 3 - GRAVIMETRIC MAGNESIUM

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	Mg/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	Mg/Cl	mean (S.D.)
4-18-73	22.71 (12.57)	0.8379 0.8362 0.8286 0.8192	0.8526	0.0667 0.0665 0.0657 0.0652	0.0663 (0.0011)	22.763 (12.600)	0.8379 0.8362 0.8286 0.8192	0.8535	0.0665 0.0664 0.0658 0.0650	0.0662 (0.0008)
4-23	23.06 (12.76)	0.8574 0.8613		0.0672 0.0675		23.114 (12.794)	0.8566 0.8605		0.0670 0.0673	
4-29	23.39 (12.95)	0.8827 0.8731		0.0682 0.0674		23.621 (13.075)	0.8836 0.8739		0.0676 0.0668	
5-3	23.62 (13.08)	0.8505 0.8419 0.8637 0.8632 0.8684		0.0650 0.0644 0.0660 0.0660 0.0664		23.685 (13.110)	0.8513 0.8419 0.8637 0.8632 0.8684		0.0649 0.0648 0.0659 0.0658 0.0662	

TABLE 34B

SITE 4 - GRAVIMETRIC MAGNESIUM

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	Mg/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	Mg/Cl	mean (S.D.)
4-21-73	22.38 (12.39)	0.8392 0.8361	0.8465	0.0677 0.0675	0.0666 (0.0026)	22.657 (12.542)	0.8392 0.8361	0.8467	0.0669 0.0667	0.0661 (0.0023)
4-26	22.60 (12.51)	0.8462 0.8566 0.8562 0.8620		0.0683 0.0691 0.0684 0.0689		23.106 (12.790)	0.8462 0.8566 0.8562 0.8620		0.0675 0.0683 0.0669 0.0674	
5-3	22.96 (12.71)	0.8623 0.8514 0.7700 0.8211		0.0678 0.0670 0.0592 0.0632		23.221 (12.853)	0.8632 0.8522 0.7708 0.8219		0.0672 0.0663 0.0593 0.0632	
5-8	23.49 (13.00)	0.8560 0.8595 0.8720 0.8620		0.0659 0.0661 0.0671 0.0663		23.504 (13.010)	0.8560 0.8595 0.8720 0.8620		0.0658 0.0661 0.0670 0.0663	

TABLE 35B

SITE 5 - GRAVIMETRIC MAGNESIUM

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	Mg/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	Mg/Cl	mean (S.D.)
4-22-73	31.31 (17.33)	1.166 1.141	1.232	0.0673 0.0658	0.0661 (0.0010)	31.483 (17.427)	1.166 1.141	1.232	0.0669 0.0655	0.0658 (0.0008)
4-26	32.75 (18.13)	1.224 1.212		0.0675 0.0669		33.330 (18.449)	1.224 1.212		0.0664 0.0657	
5-1	34.01 (18.83)	1.247		0.0662		34.156 (18.906)	1.247		0.0660	
5-3	34.68 (19.20)	1.227 1.270 1.280 1.256 1.264 1.229 1.266		0.0652 0.0661 0.0666 0.0654 0.0658 0.0640 0.0659		34.684 (19.199)	1.227 1.270 1.280 1.256 1.264 1.229 1.266		0.0649 0.0662 0.0667 0.0654 0.0658 0.0640 0.0659	

TABLE 36B

SITE 6 - GRAVIMETRIC MAGNESIUM

	Chlorinity					Conductivity				
Date (Site)	S o/oo (Cl)	g/kg	mean	Mg/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	Mg/Cl	mean (S.D.)
4-22-73 (A)	36.00 (19.92)	1.322 1.311	1.283	0.0664 0.0658	0.0654 (0.0008)	35.958 (19.903)	1.322 1.311	1.297	0.0664 0.0659	0.0657 (0.0008)
4-26 (B)						36.230 (20.054)	1.332 1.335		0.0664 0.0666	
5-1 (B)						36.230 (20.054)	1.331 1.298		0.0664 0.0647	
5-3 (B)	36.28 (20.08)	1.292 1.300 1.318		0.0643 0.0647 0.0656		36.288 (20.086)	1.292 1.300 1.318		0.0643 0.0647 0.0656	

TABLE 37B

SITE 1 - SULFATE

Date	Chlorinity					Conductivity				
	S o/oo (Cl)	g/kg	mean	SO_4/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	SO_4/Cl	mean (S.D.)
2-13-73	25.98 (14.38)	2.041	2.080	0.1420	0.1394 (0.0068)	26.203 (14.504)	2.041	2.080	0.1407	0.1389 (0.0067)
2-26	26.69 (14.77)	2.082		0.1409		26.872 (14.874)	2.082		0.1400	
4-23	27.34 (15.13)	1.951 1.930		0.1290 0.1276		27.264 (15.092)	1.951 1.930		0.1293 0.1279	
4-29	27.19 (15.05)	2.134 2.215		0.1418 0.1472		27.320 (15.123)	2.134 2.215		0.1411 0.1465	
5-3	27.00 (14.95)	2.161 2.123		0.1446 0.1420		27.074 (14.986)	2.161 2.123		0.1442 0.1417	

TABLE 38B

SITE 2 - SULFATE

Date	Chlorinity					Conductivity				
	S o/oo (Cl)	g/kg	mean	SO_4/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	SO_4/Cl	mean (S.D.)
2-13-73	25.78 (14.28)	1.985	1.871	0.1390	0.1396 (0.0065)	25.975 (14.378)	1.985	1.872	0.1381	0.1398 (0.0049)
2-26	25.89 (14.38)	2.015		0.1406		25.062 (13.873)	2.015		0.1453	
4-17	23.82 (13.19)	1.820 1.865		0.1380 0.1414		23.828 (13.190)	1.820 1.865		0.1380 0.1414	
4-23	23.65 (13.09)	1.657 1.722		0.1266 0.1316		23.574 (13.049)	1.657 1.722		0.1270 0.1320	
4-29	23.97 (13.27)	1.906 1.927		0.1436 0.1452		24.211 (13.402)	1.906 1.927		0.1422 0.1438	
5-3	23.75 (13.15)	1.851 1.965		0.1408 0.1494		23.779 (13.162)	1.853 1.967		0.1408 0.1495	

TABLE 39B

SITE 3 - SULFATE

Date	Chlorinity					Conductivity				
	S o/oo (Cl)	g/kg	mean	SO_4/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	SO_4/Cl	mean (S.D.)
2-26-73	23.16 (12.82)	1.812	1.825	0.1413	0.1416 (0.0031)	23.408 (12.957)	1.812	1.825	0.1399	0.1410 (0.0030)
4-17	22.71 (12.57)	1.782		0.1418		22.763 (12.600)	1.782		0.1414	
4-23	23.06 (12.76)	1.732 1.802		0.1357 0.1412		23.114 (12.794)	1.730 1.800		0.1352 0.1407	
4-29	23.39 (12.95)	1.900		0.1467		23.621 (13.075)	1.900		0.1453	
5-6	23.62 (13.08)	1.833 1.882 1.855		0.1401 0.1439 0.1418		23.685 (13.110)	1.835 1.884 1.857		0.1400 0.1437 0.1417	

TABLE 4OB

SITE 4 - SULFATE

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	SO_4/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	SO_4/Cl	mean (S.D.)
2-13-73	23.03 (12.75)	1.837	1.779	0.1440	0.1389 (0.0033)	23.167 (12.823)	1.837	1.779	0.1433	0.1376 (0.0044)
2-26	23.60 (13.06)	1.849		0.1415		23.813 (13.181)	1.849		0.1403	
4-26	22.60 (12.51)	1.694 1.675		0.1354 0.1339		23.106 (12.790)	1.694 1.675		0.1325 0.1308	
5-1	22.96 (12.71)	1.745 1.721		0.1373 0.1354		23.221 (12.853)	1.745 1.721		0.1358 0.1339	
5-8	23.49 (13.00)	1.833 1.833 1.823		0.1410 0.1410 0.1402		23.504 (13.010)	1.833 1.833 1.823		0.1409 0.1409 0.1401	

TABLE 41B

SITE 5 - SULFATE

	Chlorinity					Conductivity				
Date	S o/oo (Cl)	g/kg	mean	SO_4/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	SO_4/Cl	mean (S.D.)
2-26-73	28.30 (15.66)	2.217	2.595	0.1416	0.1407 (0.0027)	28.420 (15.731)	2.217	2.594	0.1409	0.1402 (0.0042)
4-26	32.75 (18.13)	2.488		0.1372		33.330 (18.449)	2.488		0.1349	
5-1	34.01 (18.83)	2.625 2.604		0.1394 0.1383		34.156 (18.906)	2.623 2.601		0.1389 0.1377	
5-8	34.68 (19.20)	2.706 2.741 2.784		0.1409 0.1427 0.1449		34.684 (19.199)	2.706 2.741 2.784		0.1410 0.1428 0.1450	

TABLE 42B

SITE 6 - SULFATE

	Chlorinity					Conductivity				
Date (Site)	S o/oo (Cl)	g/kg	mean	SO_4/Cl	mean (S.D.)	S o/oo (Cl)	g/kg	mean	SO_4/Cl	mean (S.D.)
2-7-73 (B)						36.224 (20.051)	2.810	2.781	0.1402	0.1403 (0.0046)
2-13 (B)							2.781		0.1387	
4-26 (B)						36.230 (20.054)	2.821 2.765		0.1407 0.1379	
5-1 (B)							2.797 2.813		0.1395 0.1403	
5-8 (B)	36.28 (20.08)	2.845 2.884 2.872	2.850	0.1417 0.1411 0.1430	0.1419 (0.0039)	36.288 (20.086)	2.845 2.834 2.872		0.1416 0.1411 0.1430	

TABLE 43B

Ion/Chlorinity Ratios

Site	Chlorinity Na/Cl (S.D.)* (#) **	K/Cl (S.D.) (#)	EDTA Ca-Sr/Cl (S.D.) (#)	Ca-Sr/Cl (S.D.) (#)	EDTA Mg/Cl (S.D.) (#)	Mg/Cl (S.D.) (#)	SO_4/Cl (S.D.) (#)
1	0.5544 (0.0067) (9)	0.0200 (0.0017) (12)	0.0235 (0.0013) (28)	0.0249 (0.0021) (14)	0.0701 (0.0039) (13)	0.0656 (0.0012) (14)	0.1394 (0.0068) (8)
2	0.5508 (0.0067) (9)	0.0190 (0.0020) (18)	0.0246 (0.0022) (27)	0.0257 (0.0011) (13)	0.0687 (0.0023) (13)	0.0664 (0.0011) (14)	0.1396 (0.0065) (10)
3	0.5555 (0.0115) (10)	0.0190 (0.0020) (13)	0.0255 (0.0009) (28)	0.0270 (0.0010) (13)	0.0695 (0.0038) (13)	0.0663 (0.0011) (13)	0.1416 (0.0031) (8)
4	0.5560 (0.0105) (8)	0.0199 (0.0010) (12)	0.0254 (0.0025) (28)	0.0257 (0.0005) (11)	0.0677 (0.0019) (13)	0.0666 (0.0026) (14)	0.1389 (0.0033) (9)
5	0.5549 (0.0076) (7)	0.0197 (0.0023) (11)	0.0216 (0.0010) (28)	0.0222 (0.0016) (14)	0.0665 (0.0022) (13)	0.0661 (0.0010) (12)	0.1407 (0.0027) (7)
6	0.5545 (0.0072) (5)	0.0195 (0.0010) (13)	0.0212 (0.0001) (3)	0.0209 (0.0007) (8)	0.0675 (0.0001) (3)	0.0654 (0.0008) (5)	0.1419 (0.0039) (3)

* Standard Deviation
** Number of Analyses

TABLE 44B

Ion/Chlorinity Ratios

Site	Conductivity Na/Cl (S.D.) * (#) **	K/Cl (S.D.) (#)	EDTA Ca-Sr/Cl (S.D.) (#)	Ca-Sr/Cl (S.D.) (#)	EDTA Mg/Cl (S.D.) (#)	Mg/Cl (S.D.) (#)	SO4/Cl (S.D.) (#)
1	0.5531 (0.0071) (9)	0.0199 (0.0017) (12)	0.0234 (0.0013) (28)	0.0249 (0.0016) (14)	0.0695 (0.0037) (13)	0.0655 (0.0012) (14)	0.1389 (0.0067) (8)
2	0.5500 (0.0071) (9)	0.0190 (0.0020) (18)	0.0245 (0.0022) (27)	0.0257 (0.0011) (13)	0.0687 (0.0026) (13)	0.0664 (0.0011) (14)	0.1398 (0.0067) (10)
3	0.5537 (0.0120) (10)	0.0189 (0.0020) (13)	0.0254 (0.0005) (28)	0.0269 (0.0010) (13)	0.0689 (0.0023) (13)	0.0662 (0.0008) (13)	0.1410 (0.0030) (8)
4	0.5508 (0.0095) (8)	0.0197 (0.0009) (12)	0.0253 (0.0009) (28)	0.0255 (0.0004) (11)	0.0671 (0.0020) (13)	0.0661 (0.0023) (14)	0.1367 (0.0044) (9)
5	0.5517 (0.0059) (7)	0.0196 (0.0023) (11)	0.0215 (0.0010) (28)	0.0221 (0.0017) (14)	0.0661 (0.0024) (13)	0.0658 (0.0008) (12)	0.1402 (0.0042) (7)
6	0.5536 (0.0068) (10)	0.0198 (0.0011) (17)	0.0208 (0.0003) (11)	0.0211 (0.0030) (14)	0.0673 (0.0010) (11)	0.0657 (0.0008) (9)	0.1403 (0.0046) (8)

* Standard Deviation
** Number of Analyses

TABLE 45B

Chlorinity Ionic Concentrations in 35 o/oo Sea Water

Site	Na g/kg (S.D.)	K g/kg (S.D.)	EDTA Ca-Sr g/kg (S.D.)	Ca-Sr g/kg (S.D.)	EDTA Mg g/kg (S.D.)	Mg g/kg (S.D.)	SO_4 g/kg (S.D.)
1	10.74 (0.13)	0.387 (0.033)	0.448 (0.025)	0.475 (0.040)	1.358 (0.076)	1.271 (0.023)	2.700 (0.132)
2	10.67 (0.13)	0.368 (0.039)	0.469 (0.042)	0.490 (0.021)	1.331 (0.045)	1.286 (0.021)	2.705 (0.126)
3	10.76 (0.22)	0.368 (0.039)	0.489 (0.017)	0.515 (0.019)	1.346 (0.074)	1.284 (0.021)	2.743 (0.060)
4	10.77 (0.20)	0.385 (0.019)	0.485 (0.048)	0.490 (0.010)	1.311 (0.037)	1.290 (0.050)	2.691 (0.064)
5	10.75 (0.14)	0.381 (0.045)	0.412 (0.019)	0.424 (0.031)	1.288 (0.045)	1.280 (0.019)	2.726 (0.052)
6	10.74 (0.14)	0.377 (0.019)	0.405 (0.002)	0.399 (0.013)	1.308 (0.002)	1.267 (0.016)	2.749 (0.076)

TABLE 46B

Conductivity Ionic Concentrations in 35 o/oo Sea Water

Site	Na g/kg (S.D.)	K g/kg (S.D.)	EDTA Ca-Sr g/kg (S.D.)	Ca-Sr g/kg (S.D.)	EDTA Mg g/kg (S.D.)	Mg g/kg (S.D.)	SO_4 g/kg (S.D.)
1	10.71 (0.14)	0.385 (0.033)	0.431 (0.025)	0.475 (0.031)	1.346 (0.072)	1.269 (0.023)	2.691 (0.130)
2	10.65 (0.14)	0.368 (0.039)	0.467 (0.042)	0.490 (0.021)	1.331 (0.050)	1.286 (0.023)	2.708 (0.095)
3	10.73 (0.23)	0.366 (0.039)	0.485 (0.010)	0.513 (0.019)	1.335 (0.045)	1.282 (0.016)	2.731 (0.058)
4	10.67 (0.18)	0.381 (0.017)	0.483 (0.017)	0.487 (0.008)	1.300 (0.039)	1.280 (0.045)	2.666 (0.085)
5	10.69 (0.11)	0.379 (0.045)	0.410 (0.019)	0.422 (0.032)	1.280 (0.047)	1.275 (0.016)	2.716 (0.081)
6	10.72 (0.13)	0.383 (0.020)	0.397 (0.006)	0.403 (0.057)	1.304 (0.019)	1.273 (0.016)	2.718 (0.089)

TABLE 47B

SPENCER REFRACTIVE INDEX
(Sodium D line)

Date	T °C	Site 1	2	3	4	5	6
4-17-73	30.0	1.3370	1.3367	1.3365			
4-22	32.0				1.3362	1.3379	1.3383
4-24	30.0	1.3371	1.3366	1.3365			
4-25	30.0				1.3367	1.3382	
4-30	30.0	1.3373	1.3368	1.3368			
5-1	30.0				1.3367	1.3383	1.3385
5-3	30.0	1.3371	1.3368	1.3367	1.3366	1.3379	1.3381

TABLE 48B

Refractive Index of Sea Water*
(Riley, 1965)

S o/oo	Temperature (°C)					
	0	5	10	15	20	25
0	1.3 3395	1.3 3385	1.3 3370	1.3 3340	1.3 3300	1.3 3250
5	3500	3485	3465	3435	3395	3345
10	3600	3585	3565	3530	3485	3435
15	3700	3685	3660	3625	3580	3525
20	3795	3780	3750	3715	3670	3620
25	3895	3875	3845	3805	3760	3710
30	3991	3966	3935	3898	3851	3798
31	4011	3985	3954	3916	3869	3816
32	4030	4004	3973	3934	3886	3834
33	4049	4023	3992	3953	3904	3851
34	4068	4042	4011	3971	3922	3868
35	4088	4061	4030	3990	3940	3886
36	4107	4080	4049	4008	3958	3904
37	4127	4099	4068	4026	3976	3922
38	4146	4118	4086	4044	3994	3940
39	4166	4139	4105	4062	4012	3958
40	(4185)	(4157)	(4124)	(4080)	(4031)	(3976)
41	(4204)	(4176)	(4143)	(4098)	(4049)	(3994)

* Sodium D line

TABLE 49B

Refractive Index at 30 °C and 32 °C *

S o/oo	30 °C	32 °C
20	1.3 3590	1.3 3580
25	3680	3665
30	3740	3730
35	3810	3800
37	3860	3845

* Sodium D line

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Section III, Article 10

The Quantitative Determination of Chlorophyll in the Indian River Lagoon

Max Raymond Carey

1973

The Quantitative Determination of Chlorophyll in the Indian River Lagoon

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B. Sc. in Chemistry, University of Nebraska, 1953

Submitted to the Graduate Faculty
in partial fulfillment of
the requirements for the degree of
Master of Science
in
Oceanography

Florida Institute of Technology
1973

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FOREWORD

The original objective of this study was to apply accepted methods for measuring the amounts of chlorophylls a, b, and c in sea water to the measurement of these substances in the lagoonal waters of the Indian River, in a manner that would permit these determinations to be made an integral part of the routine analyses being made by the Oceanography Department of the Florida Institute of Technology. Although this objective has not been attained, the study has shown that phaeophytins, which are the degradation products of chlorophylls, are present in unexpectedly large amounts, while the chlorophylls are present in rather small amounts.

The Indian River is a classical lagoon, divided into a series of large shallow pools by man-made causeways but all connected by the Intracoastal Waterway. Its waters are saline, having essentially the same chemical structure as the ocean, but diluted and modified by run-off from the narrow rim of land around it. Although it is frequently called estuarine, its connection with the sea is so remote and tenuous that tidal effects are negligible. It appears that evaporation nearly equals rainfall and run-off, so that there is little net transport out of the lagoon.

This study was supported by a grant from the Kennedy Space Center, National Aeronautics and Space Agency, grant number 10-015-008, 1972. The original impetus for this study came from classroom remarks by Drs. James A. Lasater and Kerry Clark, and I was much assisted by discussions

with them during the study. Grateful appreciation is given Dr. T. A. Nevin, who listened carefully to my frequent problems and gave much assistance and shrewd advice.

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I. INTRODUCTION

In 1936, Kurt Kalle reported the use of spectrophotometry as a means of measuring the concentration of plant pigments in sea water. Subsequent developments throughout the world resulted in a growing recognition that the concentration of chlorophylls in sea water was proportional to the total autotrophic metabolism occurring in the water, hence could be used as a direct measurement of sea water productivity. In 1952, F. A. Richards with T. G. Thompson (1) determined the spectrophotometric values of chlorophyll a, b, and c, from a series of purified extracts and then developed a set of simultaneous equations (trichromatic equations) by which the chlorophyll content of sea water could be computed. With a technique and a standard of measurement thus provided, many other groups used chlorophyll content as a measure of biological productivity. As refinements in the procedure were developed, it was determined that the original trichromatic equations required modification. A new set of equations, reported by T. R. Parsons and J. D. H. Strickland in 1963 (2) were based on newer and more exact values for specific absorption, and became an accepted basis for computing chlorophyll content. There still remained many variables in the preparative procedures in use, the effects of which were unknown. For instance, it was suspected that the various filter papers and filtration procedures in use might give considerable difference in results obtained, because of variations in retention of extremely small plant cells, or in the rupturing of delicate cells with

n.b. References are numbered serially, in the order of their first appearance. The serial number, in parentheses, follows the author's name.

subsequent loss of the cell contents. Similar variations in procedures for extraction of chlorophyll, centrifugation, light frequencies to be used, and times to be allowed for extraction were in need of investigation and standardization. In 1963, the International Council for the Exploration of the Sea (ICES) and the Committee on Oceanography of the United States National Academy of Sciences each established small groups of experts to consider possible standardization of methods for determination of photosynthetic pigments in sea water. Dr. T. R. Parsons, then with the Scientific Committee on Oceanographic Research (SCOR) of the United Nations Educational, Scientific & Cultural Organization (UNESCO) was appointed convenor of the ICES Working Group. This working group became known as SCOR-UNESCO Working Group #17. The report of this Group (3) was published in 1966 and proposed a "Tentative Standard Method" of procedures to be followed. Also in 1966, the U. S. National Academy of Sciences, through their Biological Methods Panel of the Committee on Oceanography (4) reviewed this field again, and confirmed the recommendations of the SCOR-UNESCO Working Group. Neither the International Council for the Exploration of the Sea (ICES), nor the National Oceanographic Data Center (NODC) has agreed to accept the recommendations of the SCOR-UNESCO Working Group as international standard procedures, although the "Tentative Standard Method" has become the guideline for much current work.

Chlorophylls d and e have been described and their structures partially elucidated. They are present in very small quantities and their

characteristics are poorly known. They are usually ignored completely. Many other colored plant pigments have been isolated and identified. Of these, only the carotenes and xanthines, yellow and brown colored substances respectively, are usually present in large enough quantities to make their measurement rewarding. Investigators recognize a need to include these substances in their calculations, and simultaneous equations were developed by Richards with Thompson (op. cit.) to compute their concentration in sea water. The SCOR-UNESCO Working Group #17 report does not contain any equations for these substances, but notes a need for better specific absorption values and preparative procedures. The amounts of these substances in sea water are quite small, while the uncertainties in their measurement are quite large, so that their computation is now seldom included in routine procedures, although their identification and quantification is an important phase of much current research.

More recent work has tended to de-emphasize the use of the trichromatic measurements for routine field work, noting that chlorophyll a is usually present in preponderant amounts, and that chlorophylls b and c have large uncertainties connected with their calculations. Several authors have proposed equations for chlorophyll a only.

Others, noting the large amounts of blue-green algae in shallow tropical waters, have proposed measurements for chlorophylls a and c. C. J. Lorenzen, (5) has noted that estuarine waters frequently contain large amounts of phaeophytins, the brown-colored break-down products of chlorophyll, and has proposed a pair of equations to measure the amounts of chlorophyll and phaeophytins. There appears to be no generally accepted

simple procedure available at the present time.

II. OBJECTIVE: A SIMPLIFIED FIELD PROCEDURE FOR CHLOROPHYLL DETERMINATION

The saline waters of the Indian River in Brevard County, Florida are frequently called "highly productive", and it was thought that a large portion of this productivity was in the form of the minute algal cells commonly referred to as phytoplankton. If this were so, then the chlorophyll levels in the river should be high, and the usual chlorophyll measurement methods used for sea water should have direct application to the Indian River. But these procedures, especially the use of the trichromatic procedure, are rather lengthy. Further, they require the use of very precise spectrophotometers, such as the Beckman DU or the Unicam 600, which are not suitable for rough field use.

The objective of this study was to apply one or more of these procedures to the determination of chlorophylls in the Indian River, and to attempt to develop a simplified procedure that could be used routinely in the various investigations of lagoonal waters being carried out at the Florida Institute of Technology.

III. THE TRICHROMATIC EQUATION APPROACH

A. General

The procedure initially attempted was the "Tentative Standard Method for Determination of Chlorophylls in Samples of Sea Water", proposed by the SCOR-UNESCO Working Group #17. The "Tentative Standard"

procedure is essentially that proposed by Richards with Thompson in 1952, modified by Parsons and Strickland in 1963 and published as Strickland and Parsons, "A Practical Handbook of Sea-Water Analysis" (1968) (6). The modifications consist of 1) substitution of filtration using Millipore filters for the continuous flow centrifugation described by Richards with Thompson, and 2) a complete revision of the equations used to compute chlorophyll weights.

B. Filtration

The first of these modifications, the use of Millipore filters for concentration of phytoplankton, was recognition of the availability of a new material that provided an easier, quicker and cheaper means of separating out phytoplankton from large volumes of sea water. Other workers proposed other kinds of filters (paper, glass fiber) and various filtering aids, for it was found that filters frequently clogged with small volumes, and extended filtration times were necessary to get adequate samples. As a part of the discussions leading up to the "Tentative Standard", G. F. Humphrey and M. Wooten (7) made an extensive test of many kinds of filters and filtration procedures. Their findings confirmed the usability of Millipore filters, and that a number of other filters and filter papers were comparable in results. Accordingly, the "Tentative Standard" recommends filtration as the method of concentration, but does not recommend any specific filter. The choice of Millipore filter, Type RA (1.2 μ) as currently used at F.I.T., is compatible with the findings of Humphrey and Wooten.

C. Trichromatic Equations

The second modification, the revision of the trichromatic equations, was based on later values of specific absorption coefficients. The first

chlorophyll a and b values were based on work by Zscheile (8) in 1934 and Zscheile, Comar and Mac Kinney (9) in 1941, wherein the chlorophylls had been separated and purified by chromatography, dried to crystalline form, and then redissolved in diethyl ether to determine their specific absorption coefficients. Subsequent work by these and many others demonstrated that chlorophylls that had been dried in preparation had absorption spectra that differed from those that had never been dried. Koski and Smith, 1948 (10) postulated isomeric changes in configuration during drying as a possible explanation for such a shift. Smith and Benitez, 1955 (11), in their extensive monograph on chlorophylls, discuss their findings and cite those of many others, then conclude:

> "Since the specific absorption coefficients of chlorophyll which has been isolated and dried may differ from samples which have not been so treated, it is preferable for analytical purposes to use a standard which has not been isolated in the pure state."

Parsons and Strickland (2) in 1963 reviewed the work to that time, made their own determinations based on never-dried chlorophyll in 90% acetone and compared their results with those recently obtained by others. They adopted values obtained by Vernon, 1960, (12) for chlorophylls a and b, and the values of Jeffrey, 1962,(13) who had succeeded in isolating, crystallizing and measuring chlorophyll c. The new values had the effect of reducing the computed value for chlorophyll a by about 25% and for chlorophyll c by about 50% from those computed by Richards with Thompson (1).

The SCOR-UNESCO Working Group in June, 1964, reviewed all of the published values for never-dried chlorophylls, and arrived at a consensus by averaging the highest values obtained by recognized analysts. From these averaged values, revised coefficients were computed for the

equations, and included in the "Tentative Standard Method". These values vary only slightly from those proposed by Parsons and Strickland (2) and do not materially alter the relationships among the three chlorophylls. Although not officially accepted as standard, they are in widespread use today, and have been accepted for use by the U.S. National Academy of Science.

D. Procedure

Briefly, the "Tentative Standard Method" calls for the filtering of a volume of sea water sufficient to contain about 1 μg of chlorophyll a (this implies a preliminary testing to determine sample size), using a filter covered by a thin layer of $MgCO_3$ (about 0.1 mg). The damp filter is placed in a glass pestle homogenizer, 3 milliliters (mls) of 90% acetone/water (v/v) added, and is then ground at 500 rpm for 1 minute. The ground material is poured into a centrifuge tube, and the mortar and pestle washed two times with 3 mls of acetone, the washings being added to the centrifuge tube. The total volume of the acetone should be about 10 mls. The tube is centrifuged for 5 minutes at 5000 x g. to clear the extract. The clear supernatant fluid is decanted into a graduate and diluted to a convenient volume, usually in this study, 15 mls.

Using a spectrophotometer with a band-width of 3 nm. or less, and cells with a light path length of 4 to 10 centimeters, the absorbance of the extract is read at 750, 663, 645 and 630 nm. against a 90% acetone blank. Subtract the absorbance at 750 nm. from the absorbances at 663, 645 and 630 nm. and divide these absorbance values by the length of the light path of the cell in centimeters. Denoting these values as e_{663}, e_{645}, and e_{630},

the concentration of the chlorophylls, in μg/ml, are given by the following trichromatic equations;

$$\text{Chl } \underline{a} = 11.64\ (e_{663}) - 2.16\ (e_{645}) + 0.10\ (e_{630})$$

$$\text{Chl } \underline{b} = -3.94\ (e_{663}) + 20.97\ (e_{645}) - 3.66\ (e_{630})$$

$$\text{Chl } \underline{c} = -5.53\ (e_{663}) - 14.81\ (e_{645}) + 54.22\ (e_{630}).$$

To convert μg/ml to μg/1 (=mg/m^3), multiply the computed values by the volume of the extract, in milliliters, and divide by the volume of the original sample in liters.

E. Testing a Field Spectrophotometer

Most of the work reported in literature has been done with either a Beckman DU, or a Unicam 600 Spectrophotometer, both of which are capable of being set to within 1/2 nm. of a desired wavelength with both accuracy and precision. The Bausch and Lomb Spectronic 20 spectrophotometer is a small, light weight, low cost instrument which had previously been selected for field use in other work. The Beckman DU has an adjustable slit, which was set at 0.3 to 0.6 mm for most of this study, (approximately 3 nm.) while the Spectronic 20 had a fixed slit width of 20 nm. There was an obvious need to compare the two instruments and to determine whether field measurements taken on the Spectronic 20 could be converted to values comparable to the Beckman DU values being reported by others.

(1) Selection of Wave-length Settings

The Bausch and Lomb Spectronic 20 instrument is graduated in 5 nm. increments, and the graduations are rather close together, so that it

is neither accurate nor precise at the 1 nm. level of setting. One may set it to a 5 nm. graduation mark with considerable precision. The peak of the spectral curve for chlorophyll a has been variously reported as 665, 664 or 663 nm., but both Vernon and Jeffrey did their work at 663 nm. The SCOR-UNESCO Working Group recommended 663 nm. without comment concerning its selection. The difference in spectral energy, hence peak height, between 663 and 665 nm. is very small. While the peak is quite steep, it never-the-less is rounded in the 663-665 nm. region, which accounts for the several wave lengths used. It also serves to make any error created by the use of 665 nm. instead of 663 nm. very small. The Spectronic 20 has a fixed slit width of 20 nm., which is wider than the entire peak of spectral energy for chlorophyll a. The difference in absorption readings between settings of 665 and 663 was less than the variations between successive absorption readings of the same sample at a fixed wave length setting. Since a difference in accuracy between the two settings could not be demonstrated, this study used a setting of 665 nm. in order to take advantage of the precision available in the use of a fixed index mark.

(2) Test Procedure

A series of three chlorophyll extractions from the leaves of hibiscus (Hibiscus chinensis) were made. For each of these extracts, 5 grams of fresh leaves were ground in a Waring Blender for 5 minutes in 100 mls of 90% acetone, then the homogenate was centrifuged to separate the plant residue. The supernatant liquid was decanted, and diluted with additional acetone to a final volume of 200 mls for further use. The initial extracts were too dense to be read directly, so a dilution curve was set up to determine those concentrations which would give absorption values lying between

0.05 and 0.8, as recommended by several authors. The exploratory curve demonstrated that a 1:1 (50%) dilution gave an absorption reading of 1.05 on the Beckman, thus setting the upper limit. The selected dilutions were 50%, 40%, 30%, 20%, 10%, and 5% of the extract in 90% acetone. The three dilution series thus derived were measured on both the Spectronic 20 and the Beckman DU-2 at 665, 645, and 630 nm. Samples were measured in matched 1 cm square flint glass cuvettes in the Beckman DU-2. Samples in the Spectronic 20 were measured in matched, 13 mm outside diameter, cylindrical flint glass cuvettes, having approximately a 1 cm light path in the beam from the instrument slit. The three sets of values were averaged for each of the 3 wave lengths. The average values are shown as Table 1, and plotted as Figs. 1, 2, and 3. The complete data and the computed results, using the trichromatic equations, are included in Table 1, Appendix A.

	Spectronic 20 Data			Beckman DU Data		
% Dilution	665 nm.	645 nm.	630 nm.	665 nm.	645 nm.	630 nm.
50%	.638	.483	.281	1.04	.358	.226
40%	.539	.402	.231	.837	.289	.183
30%	.424	.308	.174	.637	.219	.142
20%	.295	.209	.114	.415	.145	.090
10%	.150	.106	.059	.206	.072	.046
5%	.072	.053	.030	.102	.037	.023

Table 1. Mean absorption values for chlorophyll extracts from Hibiscus leaves.

(3) Results

The data from the Beckman for each frequency could be fitted to a straight line with a maximum error of 3% of the observed value. Data from

the Spectronic 20 revealed a curve at 665 nm. and a lesser curve at 645 nm., while at 630 nm., a straight line fitted as well for the Spectronic 20 as it did for the Beckman. It was observed that at 665 nm., for absorption values from 0.05 to 0.3, the data fitted a straight line with no measurable error. At 0.4 absorption, the error was slightly over 3% of observed value.

The sensitivity of the two instruments is not the same, so their response curves lie at different angles. Again using the Beckman as the reference, the Spectronic 20 gives lower absorption values than the Beckman at 665 nm., but higher values at 645 and 630 nm. This results in Spectronic 20 computed values for chlorophyll a that are lower than the Beckman DU, and higher values for chlorophylls b and c. For chlorophyll a the Spectronic 20 values are from 55% to 67% of the Beckman values. For chlorophyll b the Spectronic 20 data is from 240% to 270% higher and for chlorophyll c from 255% to 377% higher. The inversion of sensitivity and the extreme variations found in the Spectronic 20 computed results appear to rule out its use for measuring and reporting the three chlorophylls as separate entities.

In computing the total chlorophylls in a sample, the situation appears to be slightly different. Total chlorophyll is given by the equation:

$$\text{Total chl} = \text{chl } a + \text{chl } b + \text{chl } c$$

The lowered chlorophyll a results will be offset by the higher chlorophyll b and c values. In addition, chlorophyll a is normally present in quantities 4 to 5 times greater than chlorophyll b, and up to 10 times greater than chlorophyll c. Analyses of the total chlorophyll values computed from the

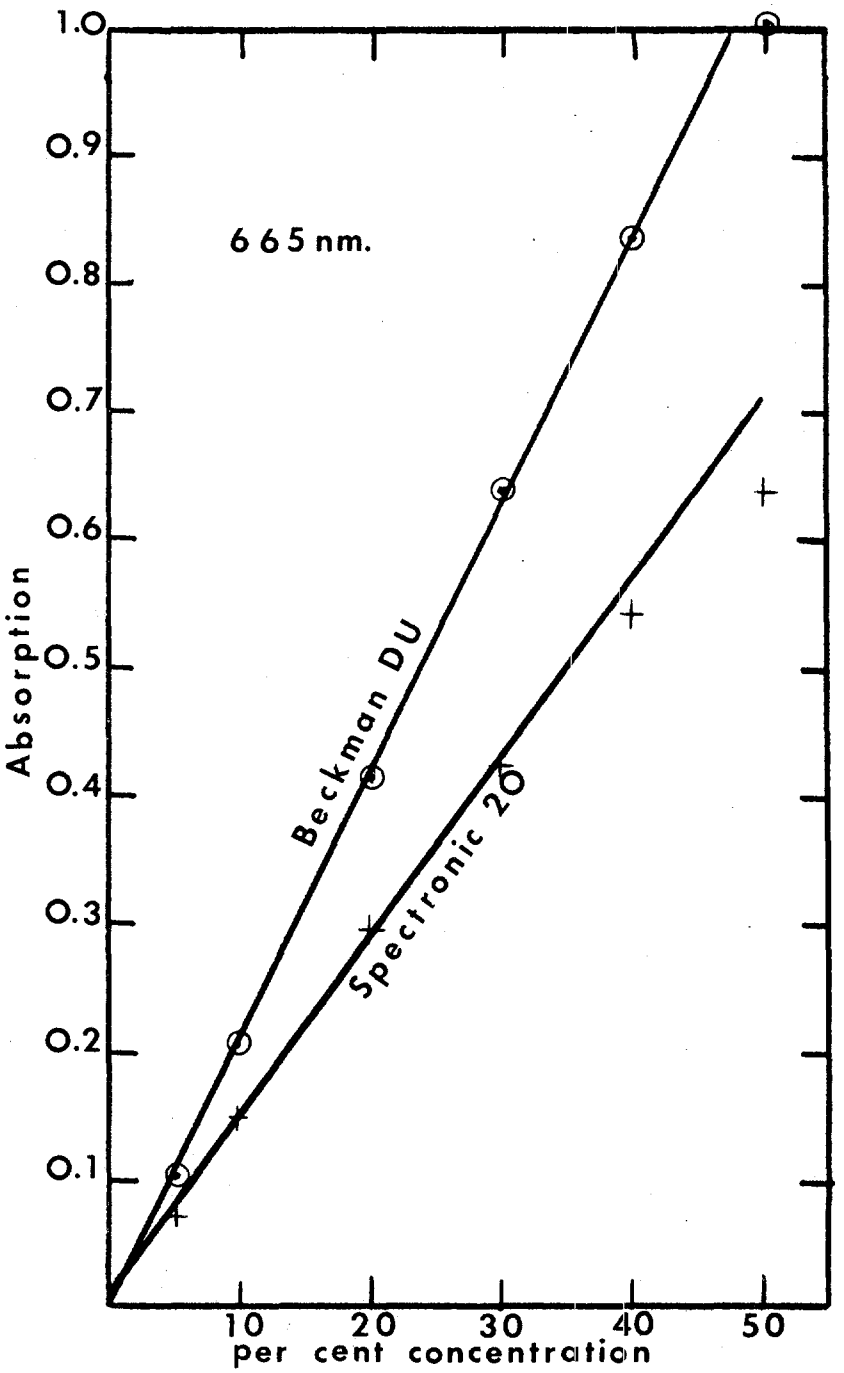

Fig. 1 Mean absorption values for chlorophyll extracts from Hibiscus leaves, at 665 nm.

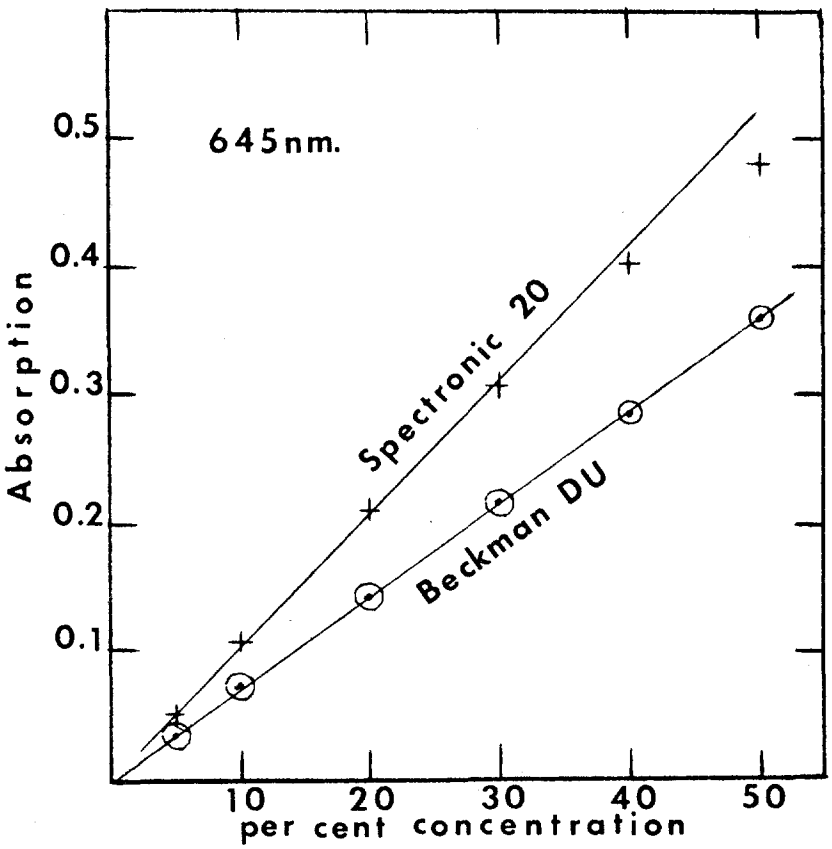

Fig. 2 Mean absorption values for chlorophyll extracts from Hibiscus leaves, at 645 nm.

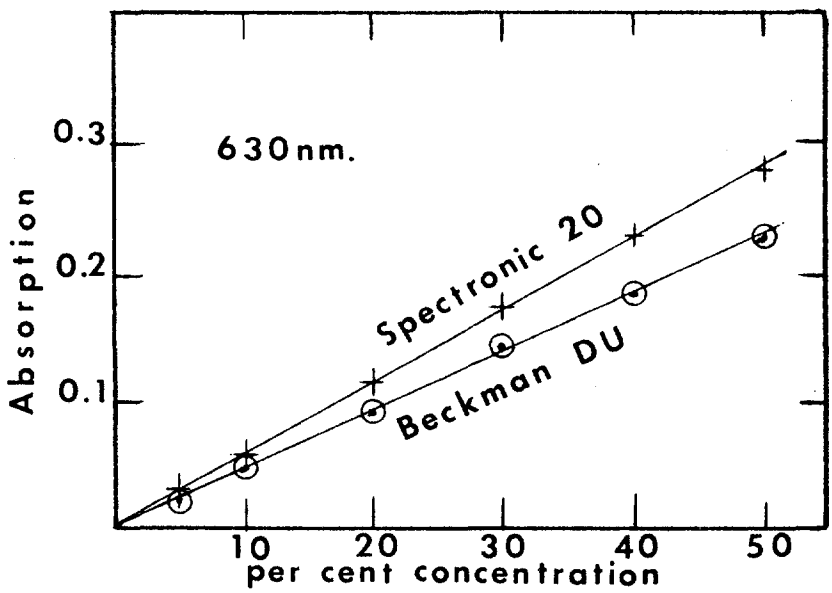

Fig. 3 Mean absorption values for chlorophyll extracts from Hibiscus leaves, at 630 nm.

two instruments shows that they are indeed more nearly alike than are the individual chlorophyll values, but the mean values still differ by more than 18% and the range of variation is 27%. Determining a correction factor under these conditions does not appear feasible. Accordingly, attempts to use the trichromatic equations to determine the three major chlorophylls separately were abandoned, on the grounds that the field equipment available would not support the effort.

IV. DETERMINATION OF CHLOROPHYLL AGAINST A STANDARD

A. Selection of a Standard

Determination of a single chlorophyll (eg. chlorophyll a) in a sample at a single wavelength is within the capability of the Spectronic 20, provided that some form of absolute value or standard measurement is available for comparison. This is the usual method of operation for the Spectronic 20. A number of procedures have been proposed, from colorimetric standards made up from highly colored inorganic salts to gravimetric determinations of the amount of magnesium in the sample. The method described by Smith and Benitez (11) is based upon colorimetric determination of the amount of magnesium in solution using Titan yellow (Clayton's yellow) dye. They ascribe the development of the Titan yellow procedure to Koski and Smith (ref. 10), and state that it is more rapid and sensitive than the gravimetric methods. It is also one of 3 major methods described in "Standard Methods for the Examination of Water and Waste Water" (14). Because it is colorimetric in character, and its interpretation is based upon a set of dilutions derived from a known "standard" solution, measured at the same time as the unknown samples, it is particularly well adapted for the Spectronic 20.

Smith and Benitez used this method with solutions of the various chlorophylls after separation and purification, so that they had no need for the simultaneous equations, although they did state the mathematical foundation for such equations. The separation of chlorophylls a, b, and c from natural water samples is a long and laborious chromatographic procedure, not suited to the routine field procedure that is the object of this study. However, it appeared that the magnesium determination of a few mixed chlorophyll samples in a laboratory might permit the estimation of many samples of similarly mixed chlorophyll samples in the field. More specifically, if it could be shown that the amount of chlorophyll in the river was reasonably constant for any given day of sampling, then samples from a wide area could be measured for absorption, but only a few, representing the extremes and middle values of absorption would need to be analyzed for magnesium in order to establish an absolute value for the absorption curve for that day.

B. Procedure

It is necessary first to release all of the magnesium ions from the chlorophyll molecules and convert them to sulfates. This is done by evaporating a known sample volume of chlorophyll extract to dryness, and digesting the organic material with sulfuric acid. The resulting carbonaceous residue is ignited, converting the mineral salts to oxides in the process. These are converted to sulfates by treating again with sulfuric acid and evaporating to dryness. The resultant salts are taken up with dilute sulfuric acid and distilled water and transferred to a 25 ml graduate, washing the crucible carefully with additional small aliquots of distilled water and adding the washings

to the graduate. Two milliliters of a 1% solution of soluble starch are added to give stability to the magnesium lake formed by the Titan yellow dye. Next, 5 mls of a saturated solution of calcium sulfate are added, to assure that the dye solution is completely saturated with calcium. The calcium ion also reacts with the Titan yellow dye and thus is an interfering ion, but its reaction saturates at low levels of color change. The addition of excess calcium to a blank and to all other samples assures that its effect will be the same on all solutions measured, and the effect can be subtracted from the magnesium reaction by subtracting the reading of the blank from all other readings. In the case of the Spectronic 20, this subtraction is most easily done by resetting the machine to zero absorption using a calcium-saturated blank. As a matter of procedural caution, the absorption of the blank should always be read against a distilled water blank and the reading recorded. In this study, the blank had an energy absorption value of 0.220 to 0.280 when the test was working properly. Higher values were a clear indication of contamination in some part of the procedure, and caused an immediate halt to further measurements until the source could be found and corrected. A much lower value was an indication that the test dye solution had lost its effectiveness and needed to be replaced.

One milliliter of an 0.125% solution of Titan yellow in distilled water is added to each graduate, and the graduates brought to a volume of 23 mls with distilled water. Two milliliters of 2.5 normal sodium hydroxide are added, and the graduate shaken to assure complete mixing. As the solution goes from acid to basic, it changes color from straw or light brown color to magenta red, the amount of change being a function of the calcium and

magnesium present. If a test solution contains more than 1 mg of magnesium, a floc of magnesium hydroxide may form. Vigorous shaking for up to 5 minutes may cause the floc to break up and the solution to clear. If it does not clear completely, this test solution must be abandoned and a more dilute sample tried. A sample containing 2 mg of magnesium could not be cleared by shaking.

A standard dilution curve based upon known amounts of magnesium is made up and measured at the same time that chlorophyll samples are being measured. The absorption values versus the weights of magnesium from the standard dilution curve are plotted on a graph and the results of the chlorophyll samples are then read as weights of magnesium. To derive the total weight of chlorophyll, the weight of magnesium is divided by its gram-molecular weight and multiplied by the gram-molecular weight of the chlorophyll molecule.

$$\text{Wt of Chl} = \frac{(\text{Wt of } Mg^{++}) \times (\text{gram-mol wt of chl})}{(\text{gram-mol wt of } Mg^{++})}$$

In this study, a gram-molecular weight of 902 was used for all chlorophylls. Although each chlorophyll has a different gram-molecular weight, the difference between them is approximately 1%, and chlorophyll a at 901.92 is in the middle. The gram-molecular weight of magnesium was taken as 24 grams.

A detailed procedure for the magnesium determination of chlorophyll is contained in Appendix B.

C. Results

A test of the magnesium colorimetry procedure was made to

determine the appropriate limits of concentration for the standard dilution curve. It was found that quantities of magnesium greater than 2 mg produced a magnesium hydroxide floc that could not be dispersed, rendering any colorimetric reading invalid. At the other end of the scale, quantities less than 0.02 mg were barely detectable on the Spectronic 20. Accordingly, amounts of 0.02, 0.05, 0.1, 0.2, 0.4, 0.8 and 1.0 mg were chosen for the standard calibration curve.

On 5 successive laboratory days, standard calibration curve sets were made up and measured on the Spectronic 20. On each day, at least three series of readings were taken. The series of readings were averaged and the averaged values plotted. The plots showed excellent repeatability from day to day. All data for the 5 tests were then averaged to give a single set of values for a representative standard calibration curve. These data, and the percent variation from the averaged values are shown in Table 2, Appendix A. The data are plotted as Figure 4.

It is readily apparent from the graph that the lowest value (0.02 mg) does not fit with the rest of the data. The variation of the measurements for this value (55%) would indicate that the Spectronic 20 is not usable for readings below absorbancies of 0.2. Other test data, not included in Table 2, showed that the magnesium test begins to saturate when the magnesium content of the sample approaches 2 mg. At larger values, the magnesium hydroxide floc renders the test invalid. It is recommended that the Spectronic 20 be used for magnesium determinations only in the range 0.05 to 0.8 mg of magnesium.

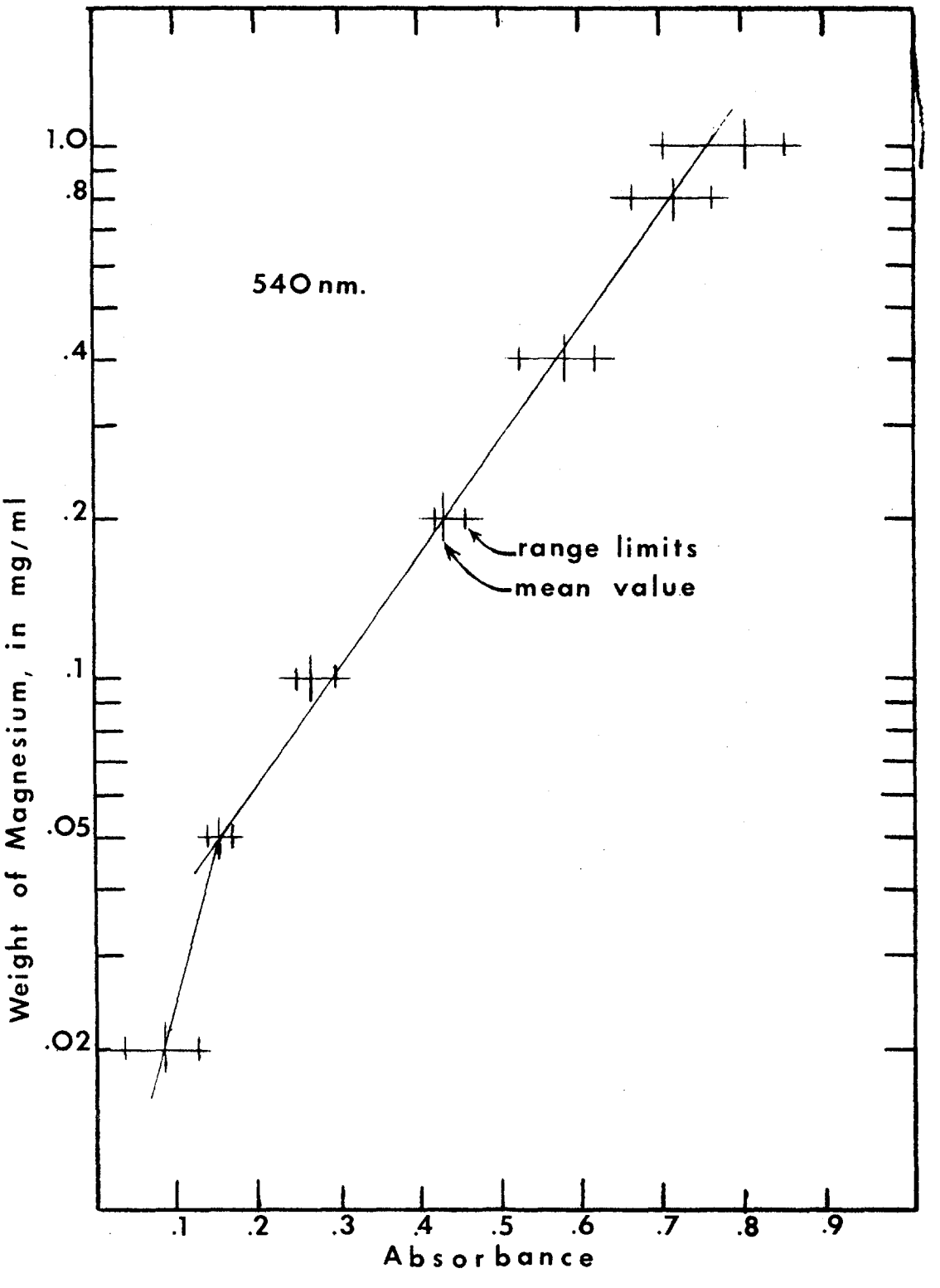

Fig. 4 Standard Curve for colorimetric determination of Magnesium, using the B & L Spectronic 20.

Using a weight of 902 grams per mole for chlorophyll a, between 3 mg and 30 mgs of chlorophyll would be required to provide the weight of magnesium recommended above. On the basis of the chlorophyll absorption readings on the Beckman DU-2 spectrophotometer, it would take all of the chlorophyll from 10 liters of river water to get a magnesium sample large enough to fit the criteria above. Processing a sample of such size is not compatible with routine field operations, at least as now conducted.

D. Some Additional Considerations

Several problems connected with the magnesium procedure are worthy of noting:

(1) The first concerns the method of digesting and ashing the chlorophyll to release the magnesium as an inorganic salt. Smith and Benitez evaporated an ether extract of chlorophyll to dryness, then digested the organic material with 5.0 mls of dilute (0.03N) sulfuric acid which was also evaporated to dryness. As the solution passes from sulfuric acid to sulfur trioxide fumes, the organic material is reduced to a carbonaceous residue which must then be ashed at red heat to remove the carbon. The thick viscous liquids that result late in both stages of drying frequently spatter, losing part of the sample, unless they are evaporated very slowly over low heat. Such evaporations have required up to 3 hours per stage, making this a slow and tedious process. Further, during the ashing process, a small bead of molten salts frequently forms and fuzes to the porcelain crucibles if the temperature becomes too high. To prevent this kind of loss, ashing was carried out at 1200°F (808°C), dull red heat, but complete oxidation of the carbonaceous residues frequently took 6 hours. Platinum crucibles ignited at 1000°C (1800°F) developed hard glassy

coatings that proved insoluble in either concentrated nitric or hydrochloric acids, even when heated.

(2) Dissolved Magnesium in Lagoonal Waters. The second problem arises from the high concentrations of magnesium dissolved in the river waters. The Millipore filters, even when sucked to near dryness on the vacuum filter holder, retain significant amounts of the river salts and hence of magnesium. Procedure blank filters, made with already-filtered river water, gave magnesium readings nearly as great as the chlorophyll samples, and occasionally gave higher readings. Brief rinsing under vacuum with a little distilled water was attempted but did not appreciably lower the blank value, while chlorophyll values that were already at the lower threshold of detection were still further reduced by the rinsing. In view of the other inadequacies of the magnesium determination, this problem was not pursued further. A possible avoidance of this problem lies in the use of a diethyl ether extraction step following the initial acetone extraction and centrifugation. The ether is then removed by evaporating nearly to dryness, flushing the dish with chloroform and evaporating nearly to dryness 3 times to remove all of the ether, then taking up the chlorophyll in chloroform. Inorganic magnesium salts are insoluble in chloroform, and so will not be transferred in the final chloroform extract. The procedure is tedious and must be performed in an exhaust hood. It is not suitable for routine analyses.

It is also worth noting that magnesium is the 5th most abundant element in the ocean (Riley & Skirrow, 16). Tests by other workers have shown that it is present in the Indian River in the same proportion to salinity as it is in the ocean. Thus, if the oceans have 1350 mg/l of magnesium at $35^{o}/oo$

salinity (Riley & Skirrow, op. cit.) then the Indian River can be expected to have 1002 mg/l at a salinity of 26 °/oo, a value often found in the river. It would seem to follow that the amount of magnesium that might be contributed by decaying chlorophyll would be negligible compared to the amount already present.

(3) A Possible Effect of Turbidity. An Indian River water sample was taken on a day of high winds and waves. The sample, taken from near the middle of the river, was very turbid. The filter began to block at about 300 mls, and at 400 mls was nearly completely blocked. The filtering was interrupted at 500 mls, a new filter installed and a second 500 mls run through it. The two filters were dissolved, ground and centrifuged as one in order to get a one liter test sample. A parallel sample from the Banana River was clear enough to be filtered in a single pass. The two samples gave nearly identical readings for chlorophyll on the Spectronic 20 but differed by a factor of 10 in magnesium content.

Sample	A. Chlorophyll by Spectrophotometry	B. Chlorophyll by Magnesium	Ratio B:A
Banana River (clear)	265 µg/l	371 µg/l	1.4:1
Indian River (turbid)	267 µg/l	4083 µg/l	15.3:1

Table 2. Comparison of Clear vs Turbid Water Samples

Some part of the difference in the magnesium determination can be ascribed to the second filter used on the Indian River sample, but the effect should not be greater than twice the total weight of magnesium reported for the Banana River sample, even if all the magnesium from the river water were adsorbed onto the filter instead of coming from the chlorophyll. On the other hand, the turbid particles are clay-sized, and clays are known to have very high adsorption abilities. Magnesium is known to be selectively exchanged for calcium on sedimentary clays and to adsorb onto clays (Horne, 17; Martin, 18). It is possible that the turbid particles in the Indian River are adsorbing magnesium from the water, and that either the mechanical grinding operation or the suspension in 90% acetone, or both, desorbs the magnesium, so that turbid samples will always give results that are unreasonably high. If so, then turbid samples will have to be treated by the chloroform extraction procedure outlined above.

(4) Filtration and Centrifugation. Long filtering times and filter blocking are well-known problems in oceanographic work. Richards with Thompson (1) originally recommended a continuous-flow centrifuge for sample separation, but improved filters and filtration procedures caused a swing away from centrifugation. Recently, a simple inexpensive continuous flow centrifuge has been built around a Waring Blender by J. F. Kimball and E. J. Furgeson-Wood (15). With it, oceanographic samples are routinely processed at the rate of 1 liter per 8 minutes. Experience in this study indicated that centrifugation followed by filtering should take about 15 minutes per liter sample, where direct filtering frequently took an hour. One very

turbid sample required 3 changes of filter, and took an hour and a half to complete. Whether centrifugation is used or not, the sample should always be filtered to assure that all the algal cells are collected. It is recommended that a small continuous-flow centrifuge be used whenever samples show turbidity.

(5) Storage of Solutions. Another problem arose when a steadily increasing absorption value of the blank was detected. It was traced to a solution that had been stored in an ordinary glass (lime-soda glass) bottle. At this point, all solutions were made up fresh and stored in borosilicate glass (Pyrex or Kimax) that had been leached for 24 hours with concentrated hydrochloric acid. Storage in Pyrex for up to one month did not contribute to increasing magnesium background absorption. Storage of any solution beyond one month is not recommended. Solutions of Titan yellow indicator dye are not stable beyond one week, regardless of the kind of bottle used for storage. The indicator dye solution should be prepared daily.

(6) Selection of a Stabilizer Compound. Smith and Benitez had used soluble starch as a stabilizer, while the APHA Standard Methods called for the use of Methocell, a commercial form of methyl cellulose. Methocell was tried, but found to be contaminated with high levels of magnesium, so soluble starch was selected for this study.

V. EFFECTS OF DEGRADATION PRODUCTS ON CHLOROPHYLL DETERMINATIONS

A. General Discussion

The first degradation products of chlorophylls are phaeophytins,

yellow-green to brown pigments that arise from the removal of the magnesium ion from the center of the porphyrin ring that is common to the three chlorophylls. Phaeophytin a has an energy absorption peak very near to the energy absorption peak of chlorophyll a from which it arises (chlorophyll a at 665 nm., phaeophytin a at 666 nm.) hence it has the effect of masking chlorophyll a if it is present in significant quantity. Further, phaeophytin a absorbs light energy at 55.2 liters per gram per centimeter ($1g^{-1}cm^{-1}$), while chlorophyll a absorbs at 90.8 $1g^{-1}cm^{-1}$(Vernon, 1960;19), so that a solution having a large amount of phaeophytin a in comparison to the amount of chlorophyll a would have a reduced total absorbancy. If the chlorophyll a of such a solution is computed by the usual equations, the result will be significantly understated. The energy absorption peaks for phaeophytins b and c are far removed from their respective chlorophylls (480 and 430 nm. vs 645 and 630 nm.) so the masking effect does not occur. On the other hand, measurement and computation of phaeophytins b and c would require the development and use of hexachromatic equations as opposed to the trichromatic equations for the chlorophylls alone. Such equations have not been reported in literature, in part because the specific absorptions for phaeophytins b and c have not been determined with an accuracy comparable to that of chlorophyll a.

> "The changes in the absorption spectra that occur on the conversion of chlorophylls to phaeophytins are particularly large at 645 nm. and 630 nm., the wavelengths used to compute chlorophylls b and c, so the estimation of these chlorophylls in the presence of their phaeophytins, by the trichromatic method is particularly unreliable." Moss, 1967 (20)

Strickland and Parsons (6) state that phaeophytins are generally absent from the open ocean, but this is not so in fresh and estuarine waters. Moss (21) has conducted an extensive series of tests on fresh water algae and found large amounts of degradation products present, especially when muds

are present. Similar findings by others have led to simplified equations using only chlorophyll a determinations (Odum, McConnell and Abbot, 1958 (22); Talling and Driver, 1961 (23)). C. J. Lorenzen, 1967 (5) recommended that early in any series of samples, the investigator should, after taking the usual trichromatic readings, take a series of additional spectrophotometric readings at 750 nm. and 665 nm. after acidifying the sample with 2 drops of 1 N HCl. The acidification converts all of the chlorophylls present to their respective phaeo-forms by extraction of the magnesium ion. The readings before and after acidification are compared to develop a ratio of chlorophyll to phaeo-pigments. If this ratio is of the order of 1.7 or greater, it may be assumed that phaeo-pigments are present in so small an amount that they will not interfere with the chlorophyll readings. If the ratio turns out to be less than 1.6, then Lorenzen recommends that his alternate equations be used as corrections, subtracting the chlorophyll readings after acidification from that obtained from a basic solution. He notes further that estuarine and bay waters frequently contain rather large amounts of phaeo-pigments from dead plant materials, and quotes T. E. Bailey (personal communication)

> "In the Sacramento River delta, chlorophyll samples usually show a rather low acid ratio at 665 mμ, which would indicate that phaeo-pigments frequently form a large fraction of the green pigments absorbing light at 665 mμ."

Since these are typical of the conditions observed in the Indian River, it may be supposed that the phaeophytin levels in the Indian River are high, and that consequently the amount of chlorophyll found is being greatly understated. Computations run on Indian River water samples do indeed show

very high levels of phaeophytins; from 5 to 7 times as much phaeophytin a as chlorophyll a, when computed by Lorenzen's formulae (Table 3).

On the other hand, the amount of chlorophyll a reported by Lorenzen's equation is usually much less than that computed by the trichromatic equations. On one set of dilutions made from hibiscus leaves, the Lorenzen values for chlorophyll a were 73% (Spectronic 20) and 79% (Beckman DU) of the trichromatic values (Table 4).

B. The Lorenzen Procedure

The Lorenzen procedure is as follows:

a) The filtered sample is prepared for absorption reading in the same manner as described for the trichromatic determination.

b) Absorption is read at two settings, 750 nm. and 665 nm. The 750 nm. reading is to determine a blank value, which is later subtracted from the 665 nm. absorption reading. After the readings have been taken on the basic solution, two drops of 1.0 normal hydrochloric acid are added to the cuvette and the contents mixed by shaking. The absorption is again read at 665 nm. and recorded as 665 a.

c) An "acid ratio" is determined by dividing the absorbancy value of the basic sample by the absorbancy of the acidified sample.

$$\text{Acid Ratio} = 665_o \div 665_a .$$

If the acid ratio is 1.7 or greater, the amount of phaeo-pigments present is probably so small that they will not affect the basic sample absorbancies and the normal trichromatic equations can be used. If the acid ratio is less than 1.6, phaeophytins are present in amounts that will interfere with the

chlorophyll a computations by the trichromatic equations.

d) Lorenzen's equations are:

$$\text{chl } a. \ (\text{mg/m}^3) = \frac{A \times K \times (665_o - 665_a) \times v}{V_f \times 1}$$

$$\text{phae } a \ (\text{mg/m}^3) = \frac{A \times K (R[665_a] - 665_o) \times v}{V_f \times 1}$$

A = specific absorption coefficient of chlorophyll a. 11.64 (SCOR-UNESCO)

K = factor to equate the reduction in adsorbancy to initial chlorophyll concentration (1.7 : 0.7 or 2.43)

665_o = absorbancy before acidification

665_a = absorbancy after acidification

v = volume in milliliters of acetone used for extraction (normally 10 mls)

V_f = volume in liters of sample filtered

l = light path length, in centimeters, of the cuvette

R = maximum ratio of $665_o : 665_a$ in the absence of phaeo-pigments, 1.7.

In the case of this study, V_f was always one liter, l was always one centimeter, and v was always 15 mls, so the equations were reduced to

$$\text{chl } a \ (\text{mg/m}^3) = 424.28 \ (665_o - 665_a)$$

$$\text{phae } a \ (\text{mg/m}^3) = 424.28 \ (1.7 \ [665_a] - 665_o)$$

A detailed procedure, suitable for field use, is contained in Appendix C.

Spectronic 20 Data in mg/m^3							
Sample Number	Trichromatic Equations			Tot. chl	Lorenzen Equations		
	Chl a	Chl b	Chl c		Acid ratio	Chl a	Phaeo a
1 - 3	33.75	42.60	175.05	251.4	Turned cloudy - no data		
1 - 6	29.25	46.65	172.50	248.4	1.11	8.49	33.52
1 - 10	27.75	45.15	171.00	243.90	1.10	4.24	46.12
1 - 14	26.40	44.85	171.10	242.35	1.00	---	57.02
1 - 19	27.90	44.70	165.45	238.05	1.06	5.09	50.74
Beckman DU-2 Data in mg/m^3							
1 - 3	62.85	92.93	326.55	482.33	.98	---	140.14
1 - 6	56.10	92.40	321.30	469.80	1.04	5.94	109.89
1 - 10	37.35	85.80	321.45	444.60	1.06	9.33	101.45
1 - 14	52.20	91.80	315.00	459.00	1.04	6.79	102.21
1 - 19	55.20	82.65	318.75	456.60	1.04	5.94	107.81

Table 3. Chlorophyll content of Indian River lagoon waters computed according to Trichromatic and Lorenzen equations.

Spectronic 20 Data in mg/m^3							
Sample Number	Trichromatic Equations			Tot. chl	Lorenzen Equations		
	Chl a	Chl b	Chl c		Acid ratio	Chl a	Phaeo a
H-6-50	130.7	132.9	235.4	499.0	1.32	96.7	93.9
H-6-40	116.4	116.6	216.0	449.0	1.38	91.2	75.1
H-6-30	90.8	99.0	208.1	397.9	1.32	63.6	73.0
H-6-20	72.5	81.0	203.6	357.1	1.32	50.9	59.0
Beckman DU-2 Data in mg/m^3							
H-6-50	206.4	124.7	339.9	671.0	1.46	176.1	92.7
H-6-40	173.1	121.4	332.4	626.9	1.56	170.6	42.7
H-6-30	138.9	113.7	327.6	580.2	1.36	101.8	97.2
H-6-20	109.7	107.3	324.6	541.6	1.28	64.5	100.6

Table 4. Chlorophyll content of Hibiscus leaf extracts, computed according to the Trichromatic and Lorenzen equations.

C. Applicability in the Indian River

River water samples frequently gave results that could not be computed by the Lorenzen formulae. Whenever the absorption value of the acidized sample is greater than the absorption of the original basic sample, the acid ratio ($665_o \div 665_a$) becomes less than one and the chlorophyll a computation yields a negative amount of chlorophyll a present. This is a logical absurdity, and represents a failing case for the equations. The effect appears to arise as a concomitant of river turbidity, for in every case where the sampling notes record high turbidity, the acid ratio is less than one, ranging in values from 0.96 for moderately turbid samples to 0.66 for one recorded as "very turbid".

The values computed for chlorophyll a by the Lorenzen equations have no relationship to results reported by other workers using the trichromatic method, hence any data accumulated using the Lorenzen procedure cannot be compared to data reported by others. Further, the Spectronic 20 was shown earlier to be less sensitive than the Beckman DU, so that data taken on the Spectronic 20 must always be treated as relative data. Never-the-less, data taken on the Spectronic 20 at a single wavelength can be considered to be internally consistent, and can be used to monitor changes in the relative amount of chlorophyll a to phaeophytin a from day to day or season to season. The determination of what these relative data mean in terms of actual weights of chlorophyll a and phaeophytin a will require chromatographic investigations beyond the scope of this study, but data recorded now perhaps can be interpreted at a later date.

Data from other studies have shown that the Indian River lagoonal complex is normally a well-mixed body of water, largely as the result of the prevailing winds. While some variation with depth in the deeper parts of the River are known to exist, the distribution of salinity, temperature and dissolved oxygen have shown remarkable uniformity in the upper waters. It follows that a relatively few surface samples, selected to give the widest possible geographic distribution, can be expected to give a reasonably good representation of the entire body of water in any one of the major basins of the lagoon. On this basis, it is recommended that a small continuing sampling program be undertaken for one year, to cover each of the major basins involved in the KSC Baseline Study, to determine whether there are significant seasonal changes in the relative amounts of chlorophyll a and phaeophytin a.

VI. SUMMARY

It is shown that the Bausch and Lomb Spectronic 20 spectrophotometer is not suitable for use as a field instrument for determining chlorophylls a, b, and c by the trichromatic equations developed for use on the Beckman DU or comparable instruments. An attempt was made to develop a standard, using a magnesium colorimetric procedure, against which one could make chlorophyll measurements at a single wavelength and graphically interpret the absorption readings as weights of chlorophyll. The attempt was unsuccessful because the very large amounts of dissolved magnesium in the river waters, acting as background contaminant, rendered the amount of magnesium released from the chlorophyll insignificant by comparison.

The amount of phaeophytins and other degradation products of chlorophyll in the natural river waters is shown to be very large in comparison to the amount of chlorophyll present. Such large amounts of phaeophytins probably render the computation of chlorophylls by the trichromatic equations invalid, regardless of the equipment by which the absorption values are determined. The relative amounts of chlorophyll a and phaeophytin a can be determined by a simplified procedure using the Spectronic 20 instrument and the Lorenzen equations, but even this procedure fails when the river waters are turbid.

Sample Number	% Dilution	Absorption Values				Computed Weight mg/gm				Corrected for Dilution mg/gm			
		750 nm.	665 nm.	645 nm.	630 nm.	Chl a	Chl b	Chl c	Tot. Chl.	Chl a	Chl b	Chl c	Tot. Chl.
H-1	50	0.01	.680	.510	.310	278.0	268.4	204.4	750.8	556	537	409	1502
	40	0.009	.570	.427	.248	226.0	227.6	146.8	600.4	565	569	367	1501
	30	0.005	.450	.327	.186	178.0	173.6	103.2	454.8	587	579	344	1510
	20	0.001	.320	.222	.125	129.6	116.8	67.6	314.0	648	584	338	1570
	10	0.002	.156	.110	.062	62.8	57.2	40.8	160.8	628	572	408	1608
	~~05~~	~~0.001~~	~~.147~~	~~.102~~	~~.060~~					error in dilution - invalid			
	01	0.001	.018	.010	.007	7.20	4.0	4.4	15.6	720	400	440	1560
H-2	50	0.005	.630	.489	.279	250.4	267.6	169.2	687.2	501	535	338	1374
	40	0.003	.535	.408	.236	213.6	221.2	147.6	582.4	534	553	369	1456
	30	0.002	.420	.310	.178	168.8	166.4	106.8	442.0	563	556	356	1475
	20	none	.283	.207	.117	114.0	111.6	68.4	294.0	570	558	342	1470
	10	0.001	.148	.108	.062	59.6	57.6	38.4	155.6	596	576	384	1556
	05	0.001	.080	.060	.038	31.6	32.4	30.0	94.0	632	648	600	1880
	01	none	.015	.010	.009	6.0	4.0	10.4	20.4	600	400	1040	2040
H-3	50	0.005	.625	.470	.275	250.0	252.8	172.8	675.6	500	506	346	1352
	40	none	.523	.383	.220	211.2	206.4	134.8	552.4	528	516	337	1381
	30	none	.410	.295	.165	166.0	158.8	92.4	417.2	533	529	308	1370
	20	none	.283	.201	.112	114.8	107.2	61.2	283.2	574	536	306	1416
	10	none	.150	.102	.058	61.6	53.6	32.0	147.2	616	536	320	1472
	05	none	.066	.048	.023	26.8	26.8	7.2	60.8	536	536	144	1216
	01	none	.015	.010	.006	6.0	4.4	4.0	14.4	600	440	400	1440

Table 1. Spectrophotometer Test. Trial Run #12. Bausch & Lomb Spectronic 20 data.

Sample Number	% Dilution	Absorption Values 750 nm.	665 nm.	645 nm.	630 nm.	Computed Weight mg/gm Chl a	Chl b	Chl c	Tot. Chl.	Corrected for Dilution mg/gm Chl a	Chl b	Chl c	Tot. Chl.
H-1	50	0.011	1.09	.379	.252	471.6	103.6	65.8	641.0	943.2	207.7	131.7	1282.6
	40	0.008	.898	.306	.200	389.6	81.6	43.2	514.4	974.0	204.0	108.0	1286.0
	30	0.008	.741	.244	.161	321.7	60.0	29.8	411.5	1072.3	200.0	99.4	1371.7
	20	0.005	.456	.161	.104	196.8	45.2	22.7	264.7	983.3	226.0	113.6	1322.9
	10	0.002	.217	.078	.050	94.1	22.4	11.2	127.7	941.0	224.0	112.0	1277.0
	05	0.001	.200	.072	.046	error in dilution, readings invalid							
	01	none	.019	.008	.003	7.6	3.6	--	11.2	760.0	360.0	--	1120.0
H-2	50	0.005	1.05	.364	.227	456.0	104.0	37.5	597.5	912.0	208.0	74.9	1194.9
	40	0.007	.840	.308	.194	362.8	94.0	42.8	499.6	907.0	235.0	107.0	1249.0
	30	0.005	.628	.219	.150	272.4	60.4	49.7	382.5	908.0	201.3	165.6	1274.9
	20	0.003	.405	.145	.090	175.2	43.2	19.6	238.0	875.9	216.0	98.0	1189.9
	10	0.001	.205	.073	.047	88.8	21.6	11.6	122.0	887.6	216.0	116.0	1219.6
	05	0.001	.111	.040	.025	48.0	12.0	4.45	64.4	960.3	240.0	89.0	1289.3
	01	none	.018	.007	.004	4.8	2.8	.800	8.4	476.0	280.0	80.0	836.0
H-3	50	0.007	.995	.354	.221	430.8	104.4	40.1	575.3	861.6	208.8	80.2	1150.6
	40	0.005	.795	.282	.175	344.6	83.2	29.9	457.7	861.6	208.0	74.7	1144.3
	30	0.004	.559	.210	.133	241.2	66.4	33.6	341.2	804.0	221.3	112.0	1137.3
	20	0.002	.393	.138	.087	170.8	40.0	17.5	228.3	854.0	200.0	87.7	1141.7
	10	0.001	.200	.069	.046	86.8	19.6	13.2	119.6	868.0	196.0	131.9	1195.9
	05	none	.094	.034	.023	40.8	10.4	9.1	60.3	816.0	208.0	181.6	1205.6
	01	-0.001	.017	.006	.004	7.6	2.4	2.8	12.8	760.0	240.0	284.4	1284.4

Table 2. Spectrophotometer Test. Trial Run #13. Beckman DU-2 data.

Wt. of Mg^{++} in mg/ml	Average Spectronic 20 Values							
	Run 1	Run 2	Run 3	Run 4	Run 5	$\bar{x}$	Variation	% Variation
0.02	.035	.050	.123	.105	.113	.085	.050	59.0
0.05	.141	.152	.157	.148	.170	.154	.016	10.4
0.1	.253	.250	.250	.285	.300	.268	.032	11.9
0.2	--	.440	.415	.420	.463	.434	.029	6.7
0.4	--	.625	.610	.530	.575	.585	.055	9.4
0.8	--	.77	.74	.67	.72	.72	.05	6.9
1.0	.83	.86	.83	.71	.83	.81	.10	12.3

Table 3. Spectronic 20 Absorption Values for a Standard Curve for Magnesium Determination

Sample Number	% Dilution	Absorption Values 750 nm.	665 nm.	645 nm.	630 nm.	665 acid	mg/m^3 SCOR-UNESCO equations Chl a	Chl b	Chl c	Tot. chl.	Lorenzen equations Acid ratio	Chl a	Pheo a
Spectronic 20 Data													
H-6	50%	-0-	.87	.685	.565	.642	130.7	132.9	235.4	499.0	1.32	96.7	93.9
	40%	.003	.775	.605	.510	.560	116.4	116.6	216.0	449.0	1.38	91.2	75.1
	30%	.001	.610	.509	.457	.460	90.8	99.0	208.1	397.9	1.32	63.6	73.0
	20%	.005	.490	.420	.405	.370	72.5	81.0	203.6	357.1	1.32	50.9	59.0
Beckman DU-2 Data													
H-6	50%	-0-	1.32	.778	.765	.905	206.4	124.7	339.9	671.0	1.46	176.1	92.7
	40%	-0-	1.12	.772	.720	.718	173.1	121.4	332.4	626.9	1.56	170.6	42.7
	30%	-0-	.91	.650	.673	.670	138.9	113.7	327.6	580.2	1.36	101.8	97.2
	20%	-0-	.732	.590	.635	.570	109.7	107.3	324.6	541.6	1.28	64.5	100.6

Table 4. Chlorophyll Content of a Hibiscus leaf extract, computed according to the SCOR-UNESCO and Lorenzen Equations.

Site	Depth	Absorption Values					mg/m^3 SCOR-UNESCO equations				Lorenzen equations		
		750 nm	665 nm	645 nm	630 nm	665 acid	Chl a	Chl b	Chl c	Tot. Chl.	Acid ratio	Chl a	Pheo a
Spectronic 20 Data													
1-3	Surface	-0-	.222	.245	.300	.200	31.2	47.6	171.2	250.0	1.11	9.33	50.1
1-12	"	-0-	.161	.213	.270	.172	21.6	42.8	159.0	223.4	.93	--	55.8
1-17	"	.005	.183	.230	.286	.187	24.9	45.8	166.4	237.1	.97	--	57.2
1-18	"	.005	.173	.223	.288	.179	22.4	44.3	170.4	237.1	.96	--	55.7
1-19	"	.003	.172	.221	.283	.170	22.2	41.9	166.8	230.9	1.01	.085	49.6
1-26	"	-0-	.217	.245	.300	.200	30.5	47.9	171.6	250.0	1.08	7.21	52.2
Beckman DU-2 Data													
1-3	Surface	.003	.428	.484	.580	.394	59.9	95.1	328.7	483.7	1.09	14.4	102.6
1-12	"	.004	.354	.457	.550	.365	47.9	92.7	316.4	457.0	.97	--	113.1
1-17	"	.005	.372	.465	.553	--	50.9	93.9	315.5	460.3	--	--	--
1-18	"	.002	.348	.453	.548	--	46.8	91.8	316.2	454.8	--	--	--
1-19	"	-0-	.352	.457	.549	--	47.6	107.7	315.8	471.1	--	--	--
1-26	"	-0-	.410	.473	.570	--	57.2	93.2	324.5	474.9	--	--	--

Table 5. Chlorophyll Content of Indian River waters, KSC Area 1, sampled 5-30-73.

Site	Absorption Values					SCOR-UNESCO equations mg/m^3				Lorenzen equations		
	750 nm	665_o	645	630	665_a	Chl a	Chl b	Chl c	Tot. Chl.	Acid ratio	Chl a	Pheo a
Spectronic 20 Data												
1-3	0.006	.244	.260	.315	--	33.75	42.60	175.05	251.40	--	--	--
1-6	0.0	.210	.240	.299	.190	29.25	46.65	172.50	248.40	1.11	8.49	33.52
1-10	0.0	.199	.232	.294	.181	27.75	45.15	171.00	243.90	1.10	4.24	46.12
1-14	neg.	.192	.230	.293	.192	26.40	44.85	171.10	242.35	1.00	--	57.02
1-19	0.0	.200	.230	.287	.188	27.90	44.70	165.45	238.05	1.06	5.09	50.74
								$\bar{x}$ =	244.82			
Beckman DU-2 Data												
1-3	.006	.450	.486	.584	.459	62.85	92.93	326.55	482.33	.98	--	140.14
1-6	.001	.404	.469	.565	.390	56.10	92.40	321.30	469.80	1.04	5.94	109.89
1-10	.004	.395	.447	.560	.373	37.35	85.80	321.45	444.60	1.06	9.33	101.45
1-14	.004	.383	.462	.555	.367	52.20	91.80	315.00	459.00	1.04	6.79	102.21
1-19	neg.	.397	.463	.559	.383	55.20	82.65	318.75	456.60	1.04	5.94	107.81
								$\bar{x}$ =	462.67			

Table 6. Chlorophyll Content of Indian River waters, KSC Area 1, sampled 7-11-73.

Site	Spectronic 20 Data mg/m^3 Absorption Values 750 nm	665_o	645	630	665_a	SCOR-UNESCO equations Chl a	Chl b	Chl c	Tot. Chl.	Lorenzen equations Acid ratio	Chl a	Pheo a
2-6	-0-	.195	.230	.289	.181	26.85	44.85	167.70	239.40	1.08	5.94	32.97
2-9	0	.201	.237	.299	.190	27.75	46.35	173.85	247.95	1.06	4.67	51.76
2-11	0	.197	.230	.290	.184	27.15	44.70	168.30	240.15	1.07	5.52	49.13
2-16	0.007	.190	.230	.290	.179	25.05	43.80	165.45	234.30	1.06	4.67	48.50
2-22	0	.183	.228	.290	.175	24.90	45.00	169.95	239.85	1.05	3.39	48.58
2-27	0	.169	.218	.280	.166	22.80	43.20	165.30	231.30	1.02	1.27	48.03
								=	238.83			

Table 7. Chlorophyll Content of Indian River waters, KSC Area 2, sampled 7-13-73.

APPENDIX B

Procedure for Magnesium Determination in Chlorophyll

The procedure is taken from Smith and Benitez (ref. 10) p. 161, who credit Koski and Smith (see ref. 11) 1948 for developing the titan yellow colorimetric method. The procedure is essentially the same as quoted for magnesium determination in "Standard Methods for Water and Waste Water Analysis" 13 th Ed., 1972, except for a minor difference in dyes used, and in the concentration of the dye solution. The Smith and Benitez procedure calls for a dye concentration approximately 10 times greater than Standard Methods, and is consequently an order of magnitude more sensitive in its level of detection. Smith and Benitez state that quantities of magnesium as small as 5 micrograms can be determined with an accuracy of $\pm$ 4 percent (Granick, 1950, ref. 14).

This procedure is given in two parts: Part 1. Preparation of a Chlorophyll Sample for Magnesium Determination, and Part 2. Magnesium Determination by Colorimetry. The two parts are entirely separate, and can be carried out at different times if care is used to protect the sample from contamination between times.

Part 1. Preparation of a Chlorophyll Sample for Magnesium Determination

To determine the amount of magnesium in a sample of chlorophyll, it is necessary to digest the chlorophyll in such a way that the magnesium is completely converted to a soluble inorganic salt. This is accomplished by wet digestion with sulphuric acid.

A known aliquot of the chlorophyll extract in 90% acetone/water is carefully evaporated to dryness in a crucible on an electric heater. The size of the aliquot is chosen to give a final reading of 0.1 to 0.8 mg of magnesium in the colorimetric analysis, which usually means that an initial series of samples must be prepared to determine the appropriate aliquot amount. Because the digestion procedure is time-consuming, it was convenient to prepare a three-sample series, in the proportion 1 : 2 : 4 to make this initial determination on each new series of extractions.

Evaporation of the sample must be accomplished over low heat to prevent spattering and consequent loss of sample. This is especially likely to occur after the bulk of the acetone has evaporated, leaving a thick scum in the bottom of the crucible.

To the dried residue add 5 ml of 0.3 N H_2SO_4, and again evaporate. The final evaporation is carried out over a bunsen burner or in a high temperature oven, to drive off the last of the H_2SO_4 and to completely ash the carbon residue. The ashed residue is taken up in 5 ml of 0.3 N H_2SO_4 and again evaporated to dryness over an open flame. The drying should be stopped when sulfur trioxide fumes cease to be given off. If drying is carried further, the $MgSO_4$ in combination with the other inorganic salts present may fuse to an insoluble glaze on the crucible, losing the sample.

The acid treated ash is dissolved in 0.25 ml of 1.0 N H_2SO_4 and 3 ml of distilled water by heating gently on an electric heater. Use a rubber policeman to wash down the walls of the crucible, continuing the heating until the water is steaming but has not boiled. Pour off into the 25 ml graduate previously acid washed with HCl for magnesium determination. Rinse the crucible 3 times, using approximately 3 mls of distilled water each time, and using the rubber policeman to rub down the walls of the crucible. Add the rinsings to the graduate. This is the prepared sample.

If the magnesium determination is not to be run immediately after sample preparation, the sample may be stored dry in the covered crucible, and dissolved when it is convenient.

Part 2. Magnesium Determination by Colorimetry

Because magnesium is a common constituent in most glass, and is leached out of the glass by acid solutions, it is necessary in this determination that only boro-silicate glassware (Pyrex, Kimax) be used, and that it be freshly washed in concentrated hydrochloric acid prior to each use. All the solutions used in the procedure should be recently prepared and should be stored in polyethylene bottles or boro-silicate glass. When glass is used for storage, the vessel should be cleaned with chromic acid, then filled with concentrated hydrochloric acid and leached for 24 hours before use.

This procedure depends upon a color change of titan yellow dye, (also known as Clayton's yellow) when it changes from acid to alkaline conditions in the presence of magnesium ions. Straw yellow in acid solution, the dye changes to magenta red when sodium hydroxide is added, the intensity of the color change being proportional to the amount of magnesium present in the solution. After mixing and standing to "ripen" for 10 minutes, the intensity of the color is read on a Spectronic 20 set at 540 n. m. Because the amount of color change is affected by many variables, it is necessary to prepare a standard dilution curve for each series of sample determinations.

Prepare acid-washed 25 ml graduates, colorimeter cuvettes and other glassware on the basis of the number of samples to be measured, plus 7 for the standard dilution curve and 1 for the blank. (After some experience with the densities of the chlorophyll samples, the standard curve can probably be reduced to 4 values without sacrificing accuracy.)

Prepare a standard magnesium sulfate solution by dissolving 1.000 gm of pure magnesium metal in 200 mls of distilled water and 2.5 mls of concentrated H_2SO_4. Because the acid is nearly consumed by the metal, and therefore the final bits of metal are slow to dissolve, it is helpful to heat and agitate the solution. Make the solution up to 1 liter in a volumetric flask, resulting in final strength of magnesium of 1 mg/ml. For working solutions, make up dilute solutions of 0.1 mg/ml and 0.01 mg/ml.

Other working solutions required are:

1) 1% solution of reagent soluble starch
2) Saturated $CaSO_4$ solution
3) 0.125% solution, by weight, of titan yellow in distilled water
4) 2.5 N NaOH

At this point, a single blank sample should be prepared and run through the procedure at the start of each day, to determine whether any of the solutions have become contaminated or the dye solution has lost its strength.

The dissolved samples and their wash waters are poured into 25 ml graduates. Reference solutions are prepared for 0.02; 0.05; 0.1; 0.2; 0.4; 0.8; and 1.0 mg of magnesium by pipetting into successive graduates. The graduate for the blank gets no magnesium, of course. To these reference standards, and the blank, add 0.25 ml of 1 N H_2SO_4.

To all graduates, add in order, 2 ml of 1% soluble starch, 5 mls saturated $CaSO_4$, and 1 ml of the 0.125% titan yellow solution. Make all graduates up to 23 mls with distilled water, then add 2 mls of 2.5 N NaOH. Shake each graduate vigorously to assure complete mixing. Allow the graduates to stand 10 minutes from the time of adding the sodium hydroxide for complete color development,

then pour into the colorimeter cuvette and measure color intensity. Using a distilled water blank, zero the Spectronic 20, then read the blank from the standard reference set. Record this blank value. The blank should measure between 0.2 and 0.3 absorption. If it is in excess of 0.3 absorption, it indicates contamination, and the procedure should be stopped until the contaminant has been found. Using the blank, set the colorimeter to zero absorption, measure each of the standard reference solutions in order, then the samples, recording all absorption values. Recheck the zero setting frequently with the blank, resetting as necessary. All measurements should be completed within 20 minutes of initial mixing, as the color fades slightly on standing.

Reference solutions containing large amounts of magnesium (circa 1 mg/ml and greater) may develop a floc when the NaOH is added. Vigorous shaking for an extended period, up to five minutes, may be necessary to redissolve this floc. It is not possible to get accurate, repeatable readings with floc present. If the floc persists in spite of vigorous shaking, this end of the scale should be abandoned. If the floc occurs in a sample, dilute 1:1 with distilled water, shake vigorously until the floc is dissolved, then measure. Record the amount of dilution on the log sheet.

APPENDIX C

Detailed Procedure for the Determination of Chlorophyll by the Lorenzen Method

1. Sampling Technique

One liter of sample water is required for a chlorophyll determination. The chlorophyll sample may be combined with the surface water quality sample provided that a) the sample is taken from below the surface of the river and b) the sample bottle is of 2 liters (1/2 gallon) size or larger.

Shake the sample bottle well to remix the water, then decant 1 liter into a graduate or into an Erlenmeyer flask previously calibrated to hold 1 liter.

If the water sample is clear or only slightly turbid, procede with direct filtration on the Millipore filter. If the water sample is turbid or muddy, it may be necessary to centrifuge the sample to throw down the bulk of the turbidites before trying to filter, but all samples must be filtered.

Set up a Millipore filtration apparatus with an RA (1.2 μ) filter in place. With the vacuum pump turned OFF, pour approximately 100 ml of sample water into the top of the filter. Add 1 dropperful (approximately 0.1 gm) of $MgCO_3$ mixture to the sample and allow it to mix. Turn on the pump and suck the filter dry. Add the rest of the sample as rapidly as possible.

Rinse the sample container with a wash bottle filled with previously filtered river water, using as little as possible, and pour the rinsings into the Millepore filter. Suck the filter dry, and transfer the filter paper to a capped and labeled pill bottle. Roll the filter with the sample material on the inside of the roll, and use tweezers to slip it into the pill bottle, so that none of the sample

is lost.

Store the pill bottle in the dark (put it back into the box it came in) and at the end of the day, return all samples to the laboratory and store in a refrigerator.

If the water sample is turbid or muddy, it may not be possible to filter a 1 liter sample in a reasonable length of time. If a trial run of 1 liter results in a filtration time greater than 15 minutes, then centrifugation will be necessary. If no centrifuge is available in the field laboratory, retain a 1 liter sample in its original sample bottle, adding one dropperful (approx. 0.1 gm) of $MgCO_3$, and return the sample to the laboratory.

If a continuous flow centrifuge is available, process the liter sample through it at a flow rate of 1 liter per 2 minutes. Catch and retain the centrifuged liquid for filtration. Filter the centrifuged water through the Millipore RA (1.2 μ) filter as for a clear water sample, but before removing the filter, add the thrown-down material from the centrifuge cup. Remove the centrifuge cup, and working carefully with a spatula so that the inside of the cup is not scratched, remove as much of the thrown-down material as possible and add it to the Millipore filter. Rinse the cup with a wash bottle filled with previously filtered river water, using as little as possible, and pour the rinsings into the Millipore filter. Suck the filter as dry as possible then roll and store the filter as before.

2. Chlorophyll extraction

Remove the filter paper from the pill bottle with tweezers and put it into the bottom of a 10 ml tissue grinder tube. If necessary, rinse the pill bottle with a small amount (1 ml) of 90% acetone and add to the tissue grinder. Bring the total amount of acetone in the tissue grinder to approximately 3 mls and allow

the filter to dissolve for several minutes. Insert the pestle and grind at 500 rpm for 1 minute. The Millipore filter should be nearly completely dissolved before the pestle is inserted, or a semi-liquid mass will form at the bottom of the tissue grinder that is very difficult to dissolve completely. After grinding, decant into a centrifuge tube, then rinse the tissue grinder 2 times using no more than 3 mls of acetone each time, and add the rinsings to the centrifuge tube. Allow the sample to extract in the centrifuge tube for at least 10 minutes, then centrifuge at 5000 rpm for 5 minutes.

Decant the supernatant acetone solution, which should be green and clear, into a 25 ml graduate and make up to 15 mls with additional acetone as necessary.

3. Spectrophotometer Determination

Prepare a blank by placing a new Millipore filter in the filter holder, then pouring approximately 100 mls of previously filtered river water into the cup. Add 1 dropperful of $MgCO_3$ mixture, turn ON the vacuum pump and suck the filter dry. Roll and fold this filter blank as for a sample, insert in a tissue grinder and dissolve it in 3 mls of 90% acetone. Grind it for 1 minute at 500 rpm, as for a chlorophyll sample, decant into a 25 ml graduate, rinse the tissue grinder with 90% acetone, adding the rinsing to the graduate. Bring the blank to 15 mls with additional acetone.

Set up and balance a Spectromatic 20 spectrophotometer on the red scale at 750 nm. in accordance with manufacturers instructions, using a Bausch & Lomb 13 mm cuvette (a nominal 1 cm light path) filled with distilled water. Half fill a second cuvette with the blank, read and record the absorption at 750 n.m. then reset the absorption scale to zero with the blank. Retain the blank.

Pour sample cuvettes, read and record samples at 665 n. m. Add 2 drops of 1. 0 N HCl to the cuvette, shake well, then read and record the absorption value. Check and adjust the zero set after each sample has been read.

If the initial reading at 665 n. m. is greater than 0. 35 absorption, the sample must be diluted to bring it into the range 0. 05 to 0. 35. Record the dilution factor so that it can be accounted for in later computations. Data should be reported on the standard "Oceanographic Data Sheet".

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Section IV, Article 11

Heavy Metal Distribution in the Sediments of the Waters near Kennedy Space Center

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I. INTRODUCTION

The objective of this study was to investigate the heavy metal concentration and distribution in the lagoonal sediments surrounding the John F. Kennedy Space Center (KSC), Florida. This work is part of a general baseline investigation being conducted in the lagoonal waters and sediments around KSC by Florida Institute of Technology. It was hoped that the relatively unpolluted nature of the area would yield a natural baseline level for heavy metals in these sediments. This information along with other baseline knowledge being accumulated can be used to monitor the effects of future growth and development on the environment. Any heavy metal pollution in the system should be evident by the metal levels found in the sediments. An effort was made to correlate heavy metal concentration and distribution with other parameters such as grain size, organic carbon and sulfide levels, and any known sources of pollution. Since KSC is the only industrial complex affecting the study area, its impact on the environment with respect to heavy metals was examined.

Heavy metals occurring in coastal waters including estuaries and waters over the continental shelf have become a significant topic of concern for scientists and engineers as well as the general public. Anthropogenic increases of these metals (in some cases equal to natural fluxes) are being transported to the marine environment by land runoff, rivers and streams, direct discharge and aerosols (Bruland 1974). Although many heavy metals such as cobalt, copper, iron and zinc are necessary for the healthy growth of organisms, the same elements are not necessarily essential to all species and may even be toxic if present in high enough concentrations (Burrell 1974).

Other metals such as lead, mercury and cadmium are highly toxic in very small concentrations. The ability of many organisms to concentrate trace elements above the levels in their surrounding environment also poses a potential problem. The possibility of food chain magnification is of particular concern to man who occupies a high trophic level in the food chain.

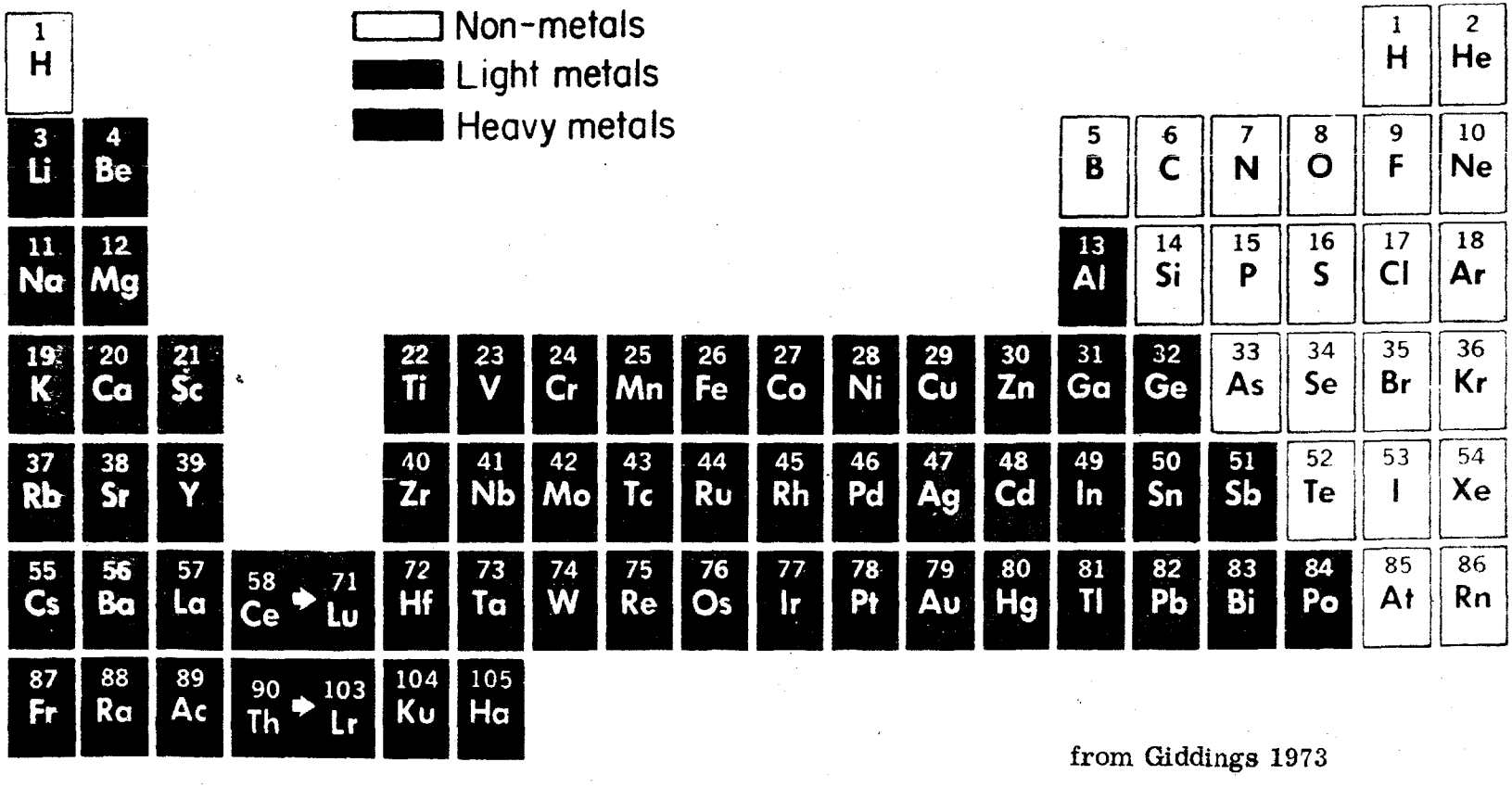
Geologically speaking, on the short term scale of man, metals can almost be considered permenent once they are introduced into the environment (Giddings 1973). Most pollutants such as insecticides and air pollutants are a threat because of unique bonding arrangements among atoms in the molecules. When these molecules are altered or degraded, the pollutant can be destroyed. But, when molecules containing heavy metals are altered, the problem-causing metal atoms are still present in the new chemical form.

In the past it has taken disasters such as the mercury and cadmium poisonings in Japanese waters (Irukayama 1966; Friberg, et al. 1971), to draw attention to these heavy metals and others as environmental pollutants. While specific disasters of heavy metal poisoning are localized and relatively easily remedied or forestalled, there does seem to be a steady buildup of some heavy metals in the environment. Riley and Chester (1971) estimate that lead is being introduced into the sea at a rate 27 times greater than it was during the Pleistocene epoch. A need for comprehensive baseline data from which to observe the changes as well as predict the significance of future activities on the system seems obvious. Unfortunately in too many cases the study is begun only after the area has become dangerously polluted with heavy metals making natural baseline values for the area more difficult to determine.

II. BACKGROUND

Heavy metals are considered to be those metals in the middle of the periodic table as seen in Figure 1, whose specific gravity is greater than five. These metals are far less common in the earth's crust than the lighter metals (Giddings and Monroe 1972), and are also referred to as trace metals or trace elements because they occur usually in concentrations less than one part per million (ppm) in the environment. As rocks are worn down to form soil and particulate aerosols, heavy metals are released naturally into the environment from the earth's crust. These metals are eventually transported to the ocean by rivers, atmospheric fallout and precipitation. They are then incorporated into the sediments becoming part of the earth's crust once again through diagenesis. This entire cycle takes anywhere from decades to millions of years. At any point in the cycle, metals may be taken up by organisms and later released back into the cycle (Giddings 1973). Since Cambrian time the relative composition of sea water has been kept fairly constant because there is a balance between the rate at which dissolved matter is added to the ocean from the land and atmosphere, and the rate at which it is removed from the sea by incorporation into the sediment or by being returned to the atmosphere. This balance prevents the build-up of toxic concentrations of trace elements (Riley and Chester 1971). Table 1 contains values of metal concentrations in different phases of the geochemical cycle.

Heavy metals are highly reactive and generally widely dispersed in nature in association with or as part of a variety of solid phases. Heavy metals in solution strive for stability through bonding with inorganic ligands



from Giddings 1973

Figure 1. **Periodic Table of Elements divided** into non-metals, light metals **and heavy metals.**

and organic chelating agents, and through oxidation state change reactions. According to Burrell (1974) it is theoretically possible to predict from available thermodynamic data the equilibrium distribution of any specific metal within a variable pH/Eh field so long as the components and physical parameters of the system are limited and closely defined. Much of the information available on the chemical speciation of heavy metals in the environment is the result of such predictions based on modeling of the system. Since it is impossible to take all factors into account, predicted values should be used with some caution. Table 1 lists the probable main dissolved species of heavy metals in sea water. The natural pathways of heavy metals are controlled largely by the incorporation on or in various solid phases acting to restrict solubilization and by chemical complexation in solution acting to promote solubilization. Immobilization to various solid sinks predominates and trace metal concentrations in all natural waters tend to be less than might be calculated from a general geochemical knowledge of the environment (Burrell 1974).

All solid particles in natural waters have electrically charged surfaces and given the large surface areas of normal particulate matter (up to 10 - 100 m^2/g for clay minerals), the resultant surface charge density will clearly exhibit a profound effect on the distribution of heavy-metal complexes (Burrell 1974). Trace elements entering natural waters through runoff, erosion, direct discharge and atmospheric inputs apparently are sorbed on suspended particles which are transported by water and eventually deposited in greater abundance in fine grained sediments. Leland, et al. (1973) observed that efficient uptake of trace elements directly from water cannot occur at the

TABLE 1

Element	Fe	Zn	Cu	Cr	Pb	Cd
[1]Earth's crust, $^{ug}/g$	$5.6x10^4$	70	55	100	12.5	0.2
[1]Average river water, $^{ug}/l$	670	10	5	1	3	
[1]Oceanic water, $^{ug}/l$	3	5	3	0.6	$3x10^{-2}$	$5x10^{-2}$
[2]Oceanic residence times, yrs.	140	$1.8x10^5$	$5x10^4$	350	$2x10^3$	$5x10^5$
[2]Probable main dissolved species	$Fe(OH)_2$ $Fe(OH)_4^-$	Zn^{2+}, $ZnSO_4$ $ZnCl^+$, $ZnCO_3$ $Zn(OH)^+$, $Zn(OH)_2$	Cu^{2+}, $CuSO_4$ $CuCO_3$	CrO_4^{2-} (OH species)	Pb^{2+}, $PbCl^+$, $PbOH^+$	Cd^{2+}, $CdCl_2$, $CdCl^+$

[1]Data from Riley and Chester (1971)

[2]Data from Burrell (1974)

TABLE 1

Average abundance of heavy metals in the earth's crust, river waters, and ocean waters; oceanic residence times and probable dissolved species.

sediment-water interface, and therefore the enrichment of certain trace elements in surficial sediments results from deposition of particles with associated trace elements.

Other solid phases are important in these waters either as primary constituents or as surface impurities on clay minerals. Probably the most important are the redox sensitive hydrous oxides whose surface charge is a function of pH (Burrell 1974). Under oxidizing conditions, hydrous oxides of iron and manganese are excellent scavengers of trace elements. But, under reducing conditions they are solubilized and may result in increases in concentrations of cations and anions in overlying waters. Several elements including lead have been found to be highly mobile from hydrous oxides upon the addition of fermenting plant material. The released metals were present as organic complexes (Leland, et al. 1973).

Organic matter is important in the complexation of heavy metals in natural waters and sediments. Leland, et al. (1973), state that the exchange capacity of soil organic matter is satisfied before significant sorption of heavy metals by clay minerals occurs. The high molecular weight humic acid content of many natural waters may play a major role in mobilizing and transporting heavy metals. Organic pollutants may play a role as well. They can concentrate at the air-water interface where they have been shown to enrich the concentrations of some trace metals (Duce, et al. 1972). Lerman and Childs (1973) believe that the behavior of metals in natural waters may be controlled to a greater extent by any of the more abundant inorganic ligands such as SO_4^{2-}, HCO_3^-, CO_3^{2-} and OH^-.

Despite an emphasis on clay minerals as vehicles for transport of

heavy metals to the oceans, more recent literature stresses the importance of organic matter and hydrous oxides in transport of heavy metals. Although there are conflicting reports as to whether heavy metals are desorbed or precipitated upon entering the marine environment, Burrell (1974) states that the majority of evidence points to the estuarine and coastal deposition of river-borne sediment as being the major sink within the heavy metal cycle. The mixing of fresh with saline waters can result in an increase in pH and dissolved oxygen content which favors the formation of ferric hydroxide. Other heavy metals may coprecipitate with this compound as already mentioned. Reduction of ferric hydroxide in the sediments may lead to the release of sorbed metals. Recombination of these metals with sulfides common in reducing conditions is likely a result of the strong affinity of heavy metals for sulfur compounds. The resonance structure formed between sulfur compounds and heavy metals is unusually stable (Giddings and Monroe 1972). Most metal sulfides are highly insoluble and would therefore precipitate out of the water column into the sediments. According to Horne (1969), ion exchange is considered to be the most important mechanism for chemical control at the sediment-water interface in the ocean.

Marine organisms play an important role in the distribution of heavy metals in the marine environment. As has already been mentioned, some marine organisms have the ability to concentrate heavy metals to levels much greater than in their surrounding environment. Andelman (1973) suggests five mechanisms of concentration: 1) particulate ingestion of aqueous suspended matter, 2) ingestion of food materials, 3) complexation by biological chelating agents, 4) incorporation into physiological systems, 5) and ion exchange and

sorption on tissue or membrane surfaces. Riley and Chester (1971) suggest that specific enzymes are present in the organism which can break down the chelates of the essential metals and allow them to be assimilated. Such metals as cobalt, copper, iron, manganese, zinc, chromium, molybdinum and nickel all function in various physiological roles including enzyme activation, redox and transport processes etc. (Bowen 1966). The non-essential elements are retained in chelated and thus detoxified form (in some cases) until gradually discarded to the water during renewal of the mucous surfaces. Excretory products of many organisms are a concentrated source of some elements and may facilitate their transport to the sediments. When organisms die or moult, bacterial attack returns trace elements to the water, perhaps initially as organic complexes. Further decomposition liberates ionic or colloidal species. The efficiency of trace metal transport from water to sediments depends in part on the rate of decay. Hallberg (1974) points out that organic matter provides the nutrients for heterotrophic bacteria, which together with autotrophic bacteria affect the chemical environment and hence the metal accumulation in the sediment.

It seems from the above discussion that the distribution of heavy metals in the environment can be quite complicated. Particularly in coastal and estuarine environments, sediments reflect the nature of the overlying waters at the time of deposition because of their capacity to incorporate organic and inorganic constituents during transport and deposition. Sediments provide both a record of past climatic and geologic events as well as an indication of man's activities which may be polluting the system. This is particularly applicable to heavy metals because of their normally low concentration

and short residence time in sea water. Anthropogenic and natural fluxes of heavy metals are therefore recorded in coastal sediments (Bruland, et al. 1974). Chen and Lu (1974) state that in general, sediments are regarded as permanent sinks of pollutants and nutrients from overlying waters, but dynamic exchanges between the sediment-water interface can occur, especially when redox conditions are changed. Heavy metals can also be removed from the sediments through uptake by organisms. Detritus feeders have been observed to remobilize metals from the sediments (Renfro 1973).

Caution should be used when reviewing the literature on heavy metals. Comparing data often presents problems due to the variation in sampling and laboratory procedures. With the advent of more sophisticated instrumentation, monitoring trace elements in the environment is becoming a common practice for many environmental and industrial laboratories. Burrell (1974) points out that citing mean values for heavy metal concentrations in the environment is risky since reliable analytical techniques have only recently become widely available. According to Burrell the frequently cited numbers given by Goldberg (1965) may serve as an order of magnitude guide for most of the common heavy metals, but advances in analytical techniques in the last decade make many of these values doubtful. Recent investigations have indicated that the reliability of even recently published analyses of heavy metal concentrations in the environment, particularly lead, are questionable. These findings resulted from an Interlaboratory Lead Analysis (1974). Lead determinations in this study ranged from 4 to 100 times higher than the actual concentration of lead in the sample. These high values resulted mainly from contamination of the samples during analysis. Chow, et al. (1974) point out

that in the case of sea water, these new findings suggest that recent studies of the hazards of lead pollution may be misleading if clean laboratory techniques and necessary sensitivity and accuracy were not maintained.

The metals chosen for this study (lead, cadmium, copper, chromium, zinc and iron) are among the heavy metals most often appearing in the literature. See Table 1 containing data on these metals in the environment.

Lead: With the exception of mercury, more studies have dealt with lead in the environment and lead poisoning than any other heavy metal, see e.g. Hall (1972), Shukla and Leland (1973), and Ewing and Pearson (1974). Lead has been mined for years, and of the non-ferrous metals, it is one of the most widely used in industry and everyday life. The annual consumption in the U.S. alone is well over a million tons. The largest consumer is the storage battery industry using 40% with the petroleum industry next using 20% (Hall 1972). According to Burrell (1974) the major sources of environmental pollution by lead are from gasoline, pesticides, fertilizers and the smelting industry, but atmospheric lead pollution derives overwhelmingly from the combustion of tetraethyl lead antiknock gasoline additives. The finer aerosol particles may travel great distances before being deposited as evidenced by a 500 fold increase over prehistoric background levels in the lead content of Greenland ice (Burrell 1974). Lead enters the human body through the alimentary and respiratory tracts. About 7% of the lead ingested is actually absorbed while up to 50% of the lead particles (1 μ or smaller) inhaled are retained in the body. About 75% of particulate lead in vehicle exhaust fits this category (Hall 1972). As far as is known, lead contributes nothing to the development or maintenance of life (Craig 1972). Lead is a highly cumulative

poison in mammals and can lead to a number of symptoms from mental retardation to death. It is also highly toxic to plants. Whether or not the lead concentrations measured are hazardous to life, any further increase of lead in the environment will undoubtedly result in further concentrations in some food chains which could lead to toxic doses for top predators and ultimately man.

Cadmium: The current focus in heavy metal concern is shifting to cadmium (Burrell 1974; Friberg, et al. 1971). Cadmium is a relatively rare metal in the earth's crust but as greater quantities are refined, more and more of it becomes available in the environment. In 1971 the U.S. consumption of cadmium was greater than 15 million pounds, with the electroplating industry being the primary consumer. The natural aqueous base levels and distributions are poorly understood. The major transportation pathway appears to be atmospheric. Cadmium is emitted to the atmosphere from the incineration of ferrous scrap and from metallurgical processing. According to Eisler (1971), there is no evidence that cadmium is biologically essential or beneficial although Bowen (1966) cites cadmium proteins found in the mollusc Pecten and in the horse kidney. Cadmium is moderately toxic and has a long biological half life in man. It can replace zinc which is an important component of metalloproteins. Approximately 40% of inhaled cadmium is absorbed by the body compared to only about 5% of ingested cadmium. According to Burrell (1974), there is some evidence that cadmium is less susceptible to abiotic removal than most of the other heavy metals in aqueous systems. The cadmium marine biota concentration factor is commonly 100 - 1000. The concentration of cadmium in sea otter kidneys suggests a possible food chain link from shellfish and could be evidence for the amplification of at

least one heavy metal through an aqueous food web.

Copper: Copper is derived from many industrial processes and is an important product of boiler corrosion (Burrell 1974). It is common in industrial smoke as well as being a freshwater pollutant particularly when associated with acid mine drainage. Copper is used an an anti-fouling agent in marine paints. The amounts of copper mined are large compared with its annual cycle (Bowen 1966). Copper is a constituent of many metalloenzymes concerned with oxidation, and other proteins including respiratory pigments of blood in many invertebrates. It can be toxic to algae, fungi, seed plants, bacteria, fish and invertebrates if present in elevated concentrations.

Chromium: Chromium is a relatively common element. According to Szekielda (1973), the world mining production of chromium is about 2 million tons per year of which 0.04 million tons are discharged into natural waters annually. Chromium is also frequently used as a rust inhibitor. Chromium (III) and chromium (IV) are the main species present in near shore waters. Bowen (1966), suggests that the function of chromium in living systems may be as an enzyme activator and as the active ingredient of the glucose tolerance factor. Trivalent chromium can be moderately toxic while hexavalent chromium is very toxic but noncumulative.

Zinc: Zinc is a widely used metal. It may be dissolved from galvanized metal, and is also present in industrial waste. It is used in several types of insecticides (Pettyjohn 1972). Zinc blocks are used on steel boat hulls as sacrificial anodes to protect the hull from electrolysis in sea water. Zinc is a common local pollutant of rivers. It is essential to all organisms and is a constituent of many metalloenzymes and of several proteins of unknown

function. Zinc in industrial smoke may cause lung disease. It is moderately toxic to plants and slightly toxic to mammals in elevated concentrations (Bowen 1966). The impact of zinc on the environment closely parallels that of copper (Burrell 1974).

Iron: Iron is an abundant and widespread constituent of rocks and soil. Iron is objectionable mainly because of the taste and color it imparts on water and its staining and depositional characteristics. According to Hem (1971), a concentration of only a few tenths of a part per million of iron in a body of water can make it unsuitable for some use. Iron is an essential element in both plant and animal metabolism. It activates a number of oxidases and is a constituent of many oxidizing metalloenzymes, respiratory pigments and proteins of unknown function (Bowen 1966). Iron can be slightly toxic to organisms if present in very high concentrations. A summary of industrial sources of these heavy metals is given in Table 2. Table 3 compares heavy metal levels introduced into the environment by some anthropogenic sources to levels introduced naturally. Federal and State drinking water standards are also presented.

TABLE 2

Element	Fe	Zn	Cr	Cu	Pb	Cd
General Industrial and Mining	X	X	X	X	X	
Plating		X	X	X	X	X
Paint Products			X		X	
Fertilizers	X	X	X	X	X	X
Insecticides/Pesticides				X		
Tanning			X			
Paper Products		X	X	X	X	
Photographic			X			
Fibers		X		X		
Printing/Dyeing			X		X	
Cooling Waters			X			
Pipe Corrosion				X	X	

Data from Burrell (1974)

TABLE 2

General Distribution of Heavy Metals in Particulate Industrial Effluents

TABLE 3

	Fe	Zn	Cu	Cr	Pb	Cd
[3]kg/yr. mined	2.1×10^{11}	3×10^{9}	4×10^{9}	2×10^{9}	2.2×10^{9}	10^{7}
[4]Fossil fuel concentration, ppm						
Coal	10,000	50	15	10	25	
Oil	2.5	0.25	0.14	0.3	0.3	0.01
[4]Fossil fuel mobilization, ($\times 10^{9}$g/yr)						
Coal	1,400	7	2.1	1.4	3.5	
Oil	0.41	0.04	0.023	0.05	0.05	0.002
Total	1,400	7	2.1	1.5	3.6	
[4]Weathering mobilization($\times 10^{9}$g/yr)						
River flow	24,000	720	250	36	110	
Sediments	100,000	80	80	200	21	0.5
[5]Drinking water standards, ppm				Cr VI		
Not to be exceeded	0.3	5	1	0.05	0.05	0.01
Desirable	virtually absent	virtually absent	virtually absent	absent	absent	absent
[6]State of Florida waters, mg/l						
Not to be exceeded	0.3	1.0	0.5	0.05	0.05	

[3]Data from Bowen (1966)

[4]Data from Bertine and Goldberg (1971)

[5]Federal Water Pollution Control Administration (1968)

[6]Department of Pollution Control, Florida Chapter 17-3

TABLE 3

Anthropogenic levels of heavy metals introduced into the environment compared to natural levels. Federal and State drinking water standards.

III. DESCRIPTION OF STUDY AREA

The area under investigation is part of the Indian River system which appears in figure 2. This system is actually lagoonal in nature with a barrier island separating it from the ocean. The barrier island along with the Florida mainland and Indian River Lagoon (Mosquito Lagoon) form the eastern, western and northern boundaries respectively of the river. The Indian River is one of the major water resources of East Central Florida providing recreation and commercial fishing (Lasater 1970). It is 123 miles long extending from latitude $28^{o}48'$ about 10 miles north of Titusville southward to latitude $27^{o}07'$ near Port Salerno. St. Lucie Inlet, Fort Pierce Inlet and Sebastian Inlet allow direct contact with the ocean resulting in saline water throughout the system. North of Sebastian Inlet, which is man-made, there is only indirect contact with the ocean. Between Melbourne and Cocoa, the Indian River connects with the Banana River which in turn connects to the ocean through the locks at Port Canaveral. North of Titusville, Haulover Canal links the Indian River with the Indian River Lagoon (Mosquito Lagoon) which connects to the ocean at Ponce de Leon Inlet.

The Indian River is estuarine in character due to a significant amount of fresh water entering the system from a number of rivers, streams and small man-made canals as well as from precipitation and runoff from adjacent land masses. Little ecological work has been done in the Indian River system. The area is relatively undeveloped and considered to be one of the least polluted estuaries available for study (Simmons 1975).

Man's presence in the area is evidenced by a number of causeways across the river at various locations along its length. Many of the causeways are the result of massive fill operations which result in the division of the river into discrete sections slowing down the flow of water. Another anthropogenic influence on the river is the Intracoastal Waterway which runs nearly its total length. Numerous spoil islands were created all along the waterway as a result of the dredging and initial maintenance of the 100-foot wide, 12-ft. deep channel. The only major industrialized area is the Kennedy Space Center located on Merritt Island between the Indian and Banana Rivers. The citrus and tourist industries are the only other large industries that could affect the study area. For detailed information on the biological, chemical and physical water quality of the system see the Semi-Annual Reports to the Kennedy Space Center (1972, 1973, 1974).

Banana Creek (Figures 3 and 4) was chosen as the location for the majority of sample sites in this study. Much of the runoff from the KSC complex drains into Banana Creek. More insight might be gained into the impact of KSC on the environment through the trace metal levels introduced into the Creek. In spite of the Space Center the nature of the area would suggest a relatively unpolluted system. There is no other industrial development in the area and very little traffic, both automobile and boat. Banana Creek could yield baseline information for trace metals in the sediments if no major pollution sources are encountered. Another reason for concentrating the sampling effort in Banana Creek is the relatively high incidence of sulfide mud encountered there in previous investigations (Beazley, et al. 1974). The strong affinity of heavy metals for sulfur suggest that the Creek might

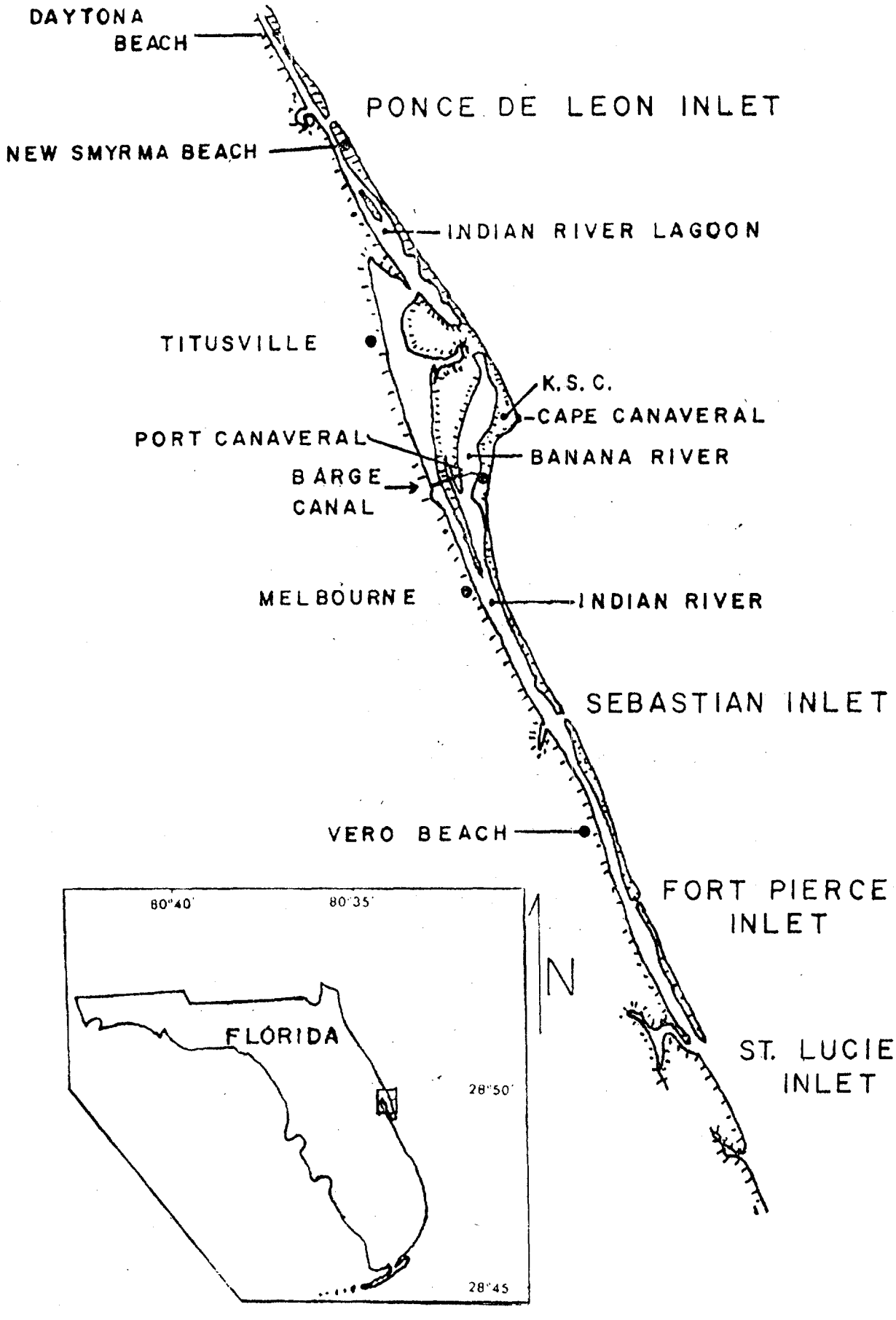


Figure 2. Indian River System

be a good sink for metals in the system. A number of other studies are being conducted in Banana Creek which include the weekly monitoring of the water chemistry, a pesticide degradation study and an investigation of the trace metals in the mangroves along the shore. A survey of heavy metals in the sediments combined with the information gained by these and previous studies will help in formulating an understanding of the total system in the Creek.

Banana Creek is a shallow drainage channel for much of the northern half of Merritt Island. The Creek is about 7 miles long extending from the headwaters of the Banana River west to the Indian River. It is divided by State Road No. 3 into a basin on the east side and the main creek on the west side connected by a culvert under the road. The Creek can be considered as a permanently flooded part of the Indian River Lagoonal System. Its normal flow is from east to west with the prevailing easterly winds. The direction of flow will reverse when the wind shifts and causes the Indian River to pile up along its eastern shore. Under these conditions, the flow in the Creek is from west to east and river water is driven into the basin on the east side of the culvert. As a result, the basin and Creek remain saline at all times, even during periods of high rainfall and runoff.

In 1963 Banana Creek was cut off from the Banana River for the construction of the crawlerway from the Verticle Assembly Building (VAB) to the launch pads. Starting in 1964 a series of dikes were constructed along nearly the entire north and south banks of the Creek from State Road No. 3 to the Indian River as well as along some parts of the banks in the eastern basin of the Creek as indicated in Figure 4. These dikes serve to impound the normal runoff waters for mosquito control. As a result surface

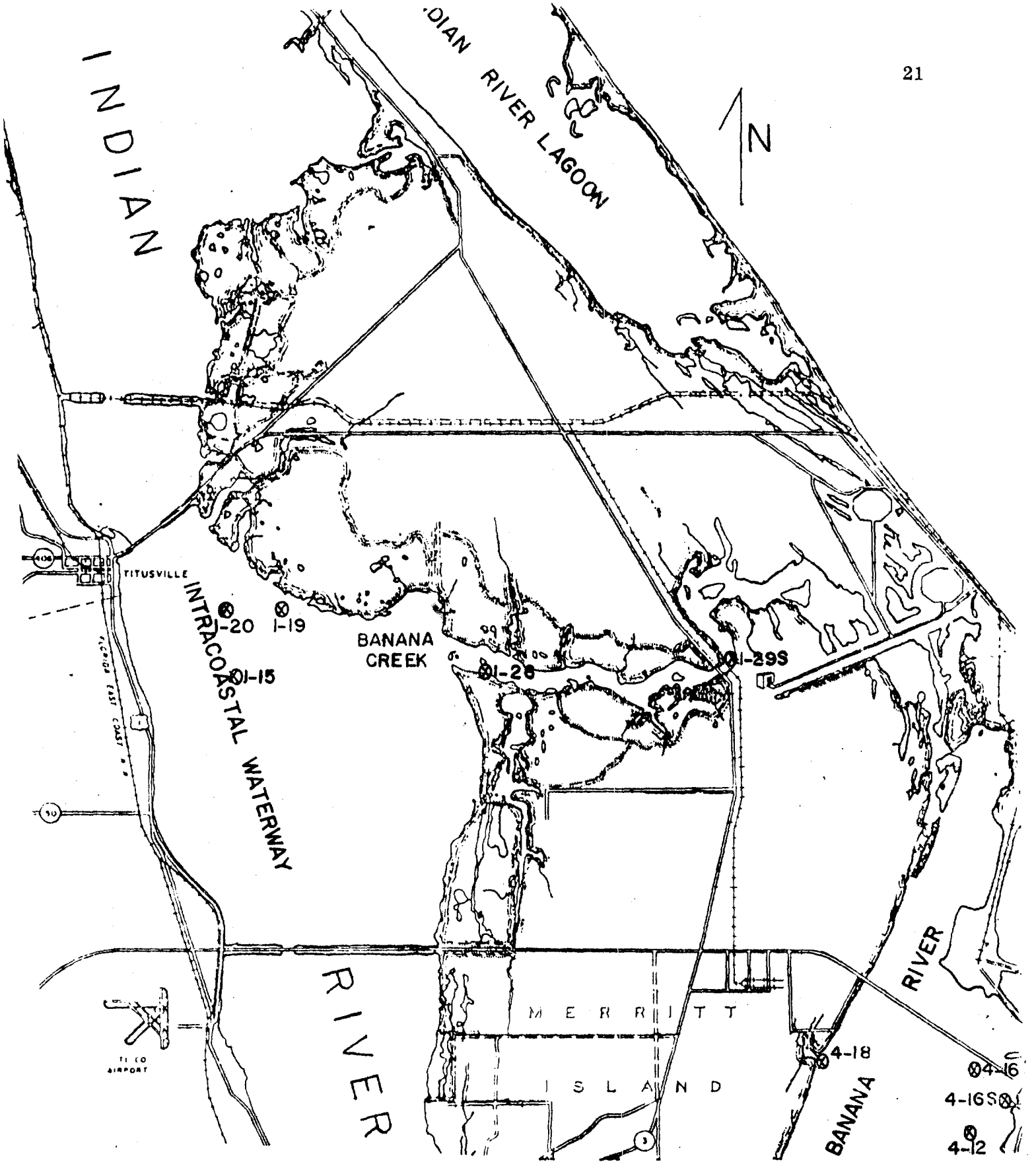


Figure 3. Study Area and location of sites sampled in the Indian River and Banana River, and two sites in Banana Creek.

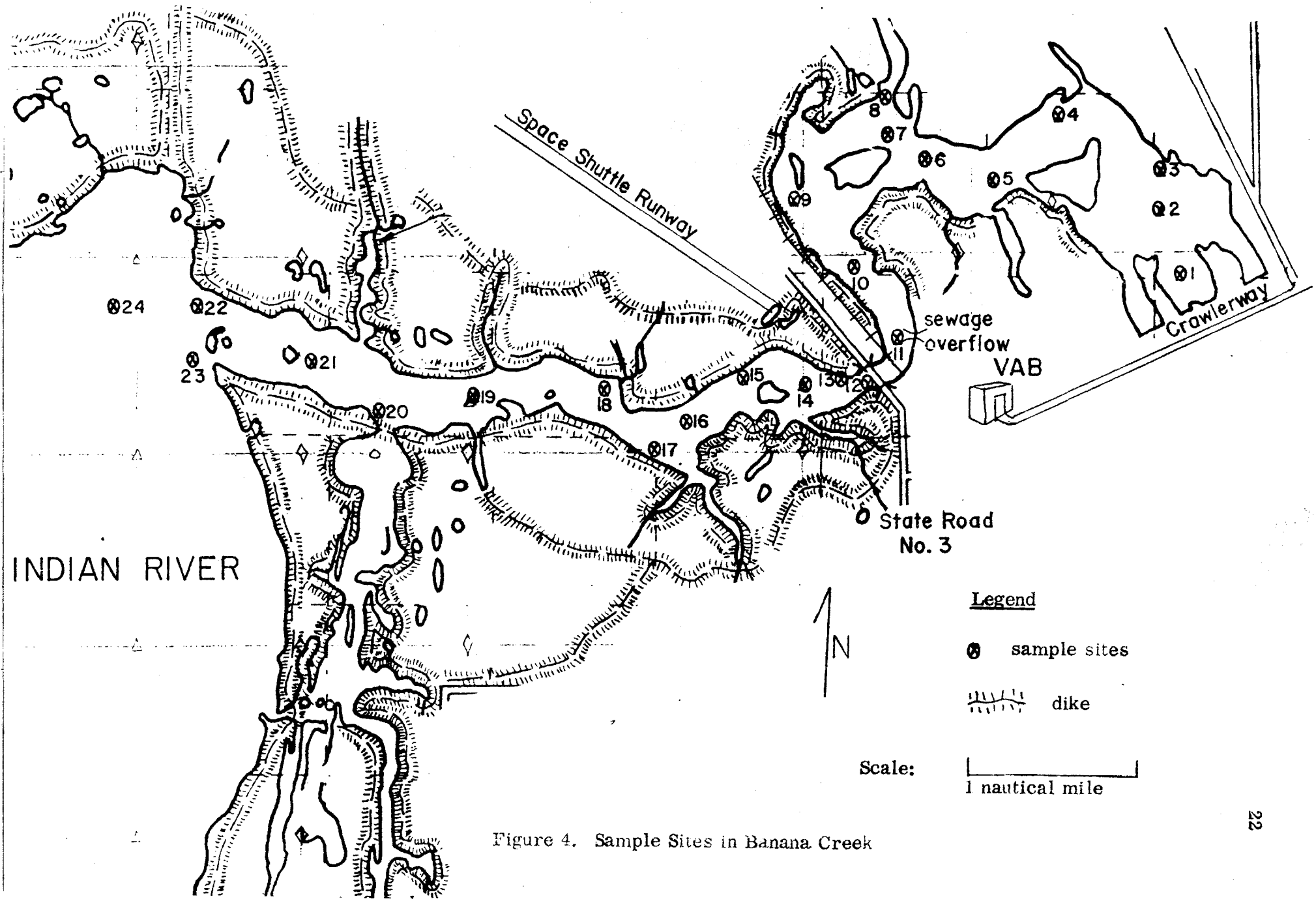


Figure 4. Sample Sites in Banana Creek

runoff reaches the Creek only during the heaviest rains.

Banana Creek has an average depth of 0.5 meter except for a borrow pit located just east of State Road No. 3. Throughout the eastern basin and along the north side and middle of the Creek, the sediment consists of a soft "oozy" black mud with a faint odor of hydrogen sulfide. Shell layers are found at different depths in the sediments. Closer to the mouth of Banana Creek the bottom consists of fine uniform sand which is common throughout the Indian River System. Towards the mouth of the Creek and out into the Indian River the water depth increases, the water becomes clearer and a number of grass beds occur. Throughout most of the creek, the water is very turbid due to the shallowness and fine particulate sediments. The water temperature is equal to that of the air and is constant throughout ranging from 22°C in the winter to 28°C in the summer. Dissolved oxygen is normally at the saturation level and the average pH is 8. The nutrient levels are low probably because they are tied up in the biomass. For a detailed report on the water quality in the Creek see Sramek, et al. (1974, 1975).

Banana Creek is lines intermittantly with red and black mangroves, Rhizophora mangle and Avicennia germinans respectively, and Spartina marshes. Although much of the bottom is barren of vegetation, nearshore Diplanthera (shoal grass) is common and is displaced by manatee grass, Syringodium (=Cymodocium) at depths greater than 0.5 meters. The macro-algal forms of Gracilaria and Eucheuma appear in patches throughout. Eucheuma is abundant in the southern shallows.

To the north (east of State Road No. 3) and quite far south (west of State Road No. 3) of the Creek there are citrus groves. Just west of State

Road No. 3 and north of the Creek is the construction site for the Space Shuttle landing strip. There is a former sewage outfall at site 11. The treatment plant now employs an infiltration pond; thus, the flow in the outfall is at a rate of flow from 10 to 100 gallons per minute. The overflow from the pond empties into the Creek at site 11.

Samples were also taken at specific sites in the Banana River and the Indian River, as indicated in Figure 3. Also two other sites in Banana Creek were sampled. This sampling was in conjunction with another investigation of sediment chemistry in the hope of correlating heavy metal distribution with other chemical and physical parameters of the sediment and overlying water column. These areas also are influenced by the KSC Complex, particularly the sites in Banana River. Site 4-16S is at an outfall from the southern half of the Air Force Base industrial area and the Creek at site 4-18 carries the storm drainage from much of the Space Center industrial area as well as flow down water from testing cells (Carey 1975). Site 1-15 is at the edge of the Intracoastal Waterway.

IV. MATERIALS AND METHODS

Contamination of samples is one of the biggest problems to be faced in trace metal analysis. Losses due to adsorption on surfaces which come in contact with the samples also pose a problem. An effort was made to minimize contamination as much as possible, attempting to make sure that samples never came in direct contact with metal surfaces. Robertson's (1968) paper on contamination during trace metal analysis of sea water was used as a guide in choosing equipment and reagents for the analyses. Losses due to adsorption were minimized by acidifying all solutions that were stored for any length of time as recommended by the United States Environmental Protection Agency (1974).

A. Sampling Procedure

A total of 33 sites indicated on figures 3 and 4 were sampled during the spring and early summer of 1975. Whenever possible, sampling was done from a fiberglass boat although no difference was found when an aluminum boat was used. Care was taken to collect samples away from any influence by the outboard motor. In shallow water an inverted ziplock plastic bag was used to take samples by hand. In deeper water, a 30 cm T-type PVC corer was used (Daggett 1973). The PVC pipe was split lengthwise so that the core could be easily opened on site. A band clamp was used to hold the pipe together while the core was taken (Peffer 1975). Samples were removed from the center of the surface sediment in the cores. Using either method, samples were taken only from the top few centimeters of the sediment. All samples were transported back to the laboratory in an ice chest and frozen immediately if analysis

could not be carried out within 12 hours. At the Banana River and Indian River sites plus sites 1-26 and 1-29S in Banana Creek, other chemical parameters of the sediment and bottom water were measured. These included temperature, salinity, pH, Eh and dissolved oxygen. Cores were taken for laboratory analysis of grain size, water content, volatile solids, chemical oxygen demand, Kjeldahl nitrogen, nitrates, total phosphorus, phosphates, carbonates, total and organic carbon, and sulfides. For detailed reports on these analyses see Mendelsohn (1975) and Peffer (1975).

B. Laboratory Analysis

Everything that came in contact with the samples was washed thoroughly in detergent and rinsed in tap water followed by rinses with 1:1 nitric acid (HNO_3), tap water, 1:1 hydrochloric acid (HCl), and glass distilled water in accordance with the procedure recommended by the United States Environmental Protection Agency (1974). All solutions and digested samples were kept in high density Nalgene polyethylene bottles.

Trace metal determinations were done using Atomic Absorption Spectrophotometry which is the most common and widely accepted method (Burrell 1974). Iron and zinc were analyzed for in the Chemical Oceanography Laboratory at Florida Institute of Technology using a Jarrell-Ash Model 82-270 Atomic Absorption Spectrophotometer. Cadmium, copper, chromium and lead were present in concentrations below the detection limits of the Jarrell-Ash. To avoid having to concentrate the samples which adds to the possible sources of error, tests for these metals were run in the Support Operations Laboratory (SO-LAB-32) at the Kennedy Space Center using a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer equipped

with a strip chart recorder and a Model HGA-2000 Heated Graphite Atomizer.

An oxidizing acid digestion of the sediments is necessary to solubilize the metals for instrumental analysis. After much preliminary experimentation, a 4:1 nitric acid (HNO_3) : perchloric acid ($HClO_4$) mixture along with heating was found to be most effective. According to Burrell (1974) a nitric acid perchloric acid mixture for the digestion of sediments is widely used. The extraction technique was designed to yield trace metal concentrations within the direct reading limits of the spectrophotometers so that no concentration or dilution of the samples was involved after the digestion procedure was complete. In this study, only the "environmentally active" metals were of interest because of their potential availability to the biota (Bopp and Biggs 1973), therefore a total digestion of the sediments was not sought. Difficulty was encountered during the digestion due to extreme bumping of the sediments upon heating in the acid mixture. Another problem was the lack of a hood equipped to handle perchloric acid fumes. Doing the digestion under reduced pressure solved these problems. The dried sediment along with the acid mixture was placed in a 250 ml long-neck sidearm boiling flask. The flask was connected to a sink aspirator with Tygon polyethylene vacuum tubing. To ensure even heating the flask was set in a hot sand bath. The aspirator reduced the pressure in the flask which facilitated even boiling, eliminating bumping and cutting down the digestion time considerably. The acid fumes were drawn off and washed down the drain with the running water. Unfortunately with the equipment available, only two digestions could be run at the same time.

Sediment samples were dried in an oven at 105°C for 12 hours.

Frozen samples were first allowed to thaw at room temperature before being placed in the oven. The dried sediment was ground as finely as possible in a mortar and pestle and large shell fragments were eliminated. One gram of ground dried sediment was placed in a boiling flask along with 25 ml of the mixed acid solution. The flask was stoppered tightly with a teflon stopper, hooked up to the aspirator and placed in the hot sand bath. A digestion was considered complete when the solution turned clear, white fumes appeared and only white sand was left undigested. Most digestions took a little over an hour. Upon completion of the digestion, the flask containing the solubilized metals was allowed to cool and then the solution was filtered through a 47 mm Gelman fiber type A glass filter using a 125 ml Millipore filtering apparatus. A 1:1 nitric acid (HNO_3) solution was run through the filtering system as a rinse followed by glass distilled water to remove any metals in the filter prior to filtering the sample. After rinsing the flask thoroughly with glass distilled deionized water, the sample was filter. The filtrate from the sample was quantitatively transferred to a 100 ml volumetric flask which was then filled to volume with glass distilled water. The solution was placed in a 125 ml Nalgene bottle ready for analysis. Blanks were run through the entire procedure periodically to check for contamination. Spectrophotometric analyses of the samples and blanks were run as soon as possible although the U. S. Environmental Protection Agency (1974) cites holding times as 6 months for metals in solution at $pH < 2$ in plastic or glass containers. Standards were made daily from 1000 ppm stock solutions of the metals.

The operating conditions of the Atomic Absorption Spectrophotometers were in accordance with the instrument manuals and are listed in

Appendix 1. Samples were introduced into the graphite furnace using a Centaur microliter pipet with disposable plastic tips. To insure high precision a standard procedure was adopted. The pipet was rinsed with the sample. It was again filled with sample which was injected into the furnace by applying a constant pressure. A blank of glass distilled water was injected between each set of samples to check for memory effects and also as a check on background absorption. Standards were run often to check on conditions. The plastic tip on the pipet was changed for each new set of samples. Graphite tubes were replaced when loss of sensitivity and repeatability occurred, usually after about 200 injections.

A number of checks were placed on the procedure to obtain results of the highest precision and accuracy possible. In testing the sampling procedure, some of the sites were sampled a number of different times. Also, two separate sediment samples were collected at many of the sites using both sampling techniques and were analyzed separately. Frozen and non-frozen samples from the same sites were also analyzed. None of these tests yielded any significant differences using the Student's t-distribution at the 5% significance level (Sokal and Rohlf 1969). The average readings of the blanks from each set of determinations on the Atomic Absorption Spectrophotometers were subtracted from the sample readings to compensate for any contamination in the procedure as has already been mentioned. Losses of heavy metals due to adsorption during processing were checked by adding a known amount of the metals being tested for to some of the samples and running through the entire digestion and filtering procedure. The percent recoveries obtained were: iron - 91.5%, zinc - 98.5%, chromium - 85.1%, copper - 91.2%, lead - 80% and cadmium - 88.7%. Since

all metal concentrations were obtained by the method of direct determination (by comparison of the absorbances or peak heights of unknown samples with those of aqueous standards), the samples used for percent recovery data were a good check for matrix interferences. When the sample matrix interferes giving erroneous readings, samples with known amounts of metals added must be used as standards, thus duplicating the matrix of the sample. This is called the method of standard additions and is usually applied when analyzing samples of complex matrices such as sea water. While direct determination values in this study were slightly higher than those obtained by the method of standard additions, the difference was not great enough to warrant the more complex and time consuming standard additions method.

C. Treatment of Data

Standard curves were prepared by plotting absorbance versus concentration in the case of iron and zinc, and relative peak height versus concentration for the other metals. These standard curves appear in Appendix 2. A computer program was used to find the best line for each calibration curve by the method of least squares linear regression (Sokal and Rohlf 1969). Using these equations for the best line, the concentration of each sample was determined and reported in mg/kg of dry weight of the sample. In most cases concentration values were averages of triplicate atomizations with individual absorption or peak height values varying not more than $\pm$ 2 absorption or peak height units full scale.

V. RESULTS

In order to establish good baseline data, as many sites should be sampled as possible, thus time die not permit a detailed physical and chemical analysis of every site sampled. Some of these parameters determined in earlier investigations are summarized below and will be used in an effort to understand the heavy metal distributions found in this study. Appendix 3 contains the physical and chemical data for the sediments sampled during this investigation.

A. Physical Characteristics

The sediments sampled ranged in color from gray to black. Most of the sites in Banana Creek yielded black sediment as did those in Banana River. The sediments in the Indian River tended to have a dark gray to an olive green color. The sediments sampled were found to be predominantly fine sand (425 μ - 75 μ) with shell or shell fragments. Grain size analyses were not done on the Banana Creek sediments during this study, but data from an earlier study are available and appear in Figure 5. Sites 4-16, 4-16S, and 4-18 in Banana River exhibited some sandy silt fractions but still were about 90% fine sand (Mendelsohn 1975). The grain size was very uniform in all the areas sampled.

A strong to weak odor of hydrogen sulfide in the sediments was reported in previous studies, particularly in Banana Creek (Beazley, et al. 1974, and Daggett 1973). This odor did not seem to be as evident during the present investigation although it was faint at many of the sites in Banana Creek and sites 4-18 and 4-16S in Banana River.

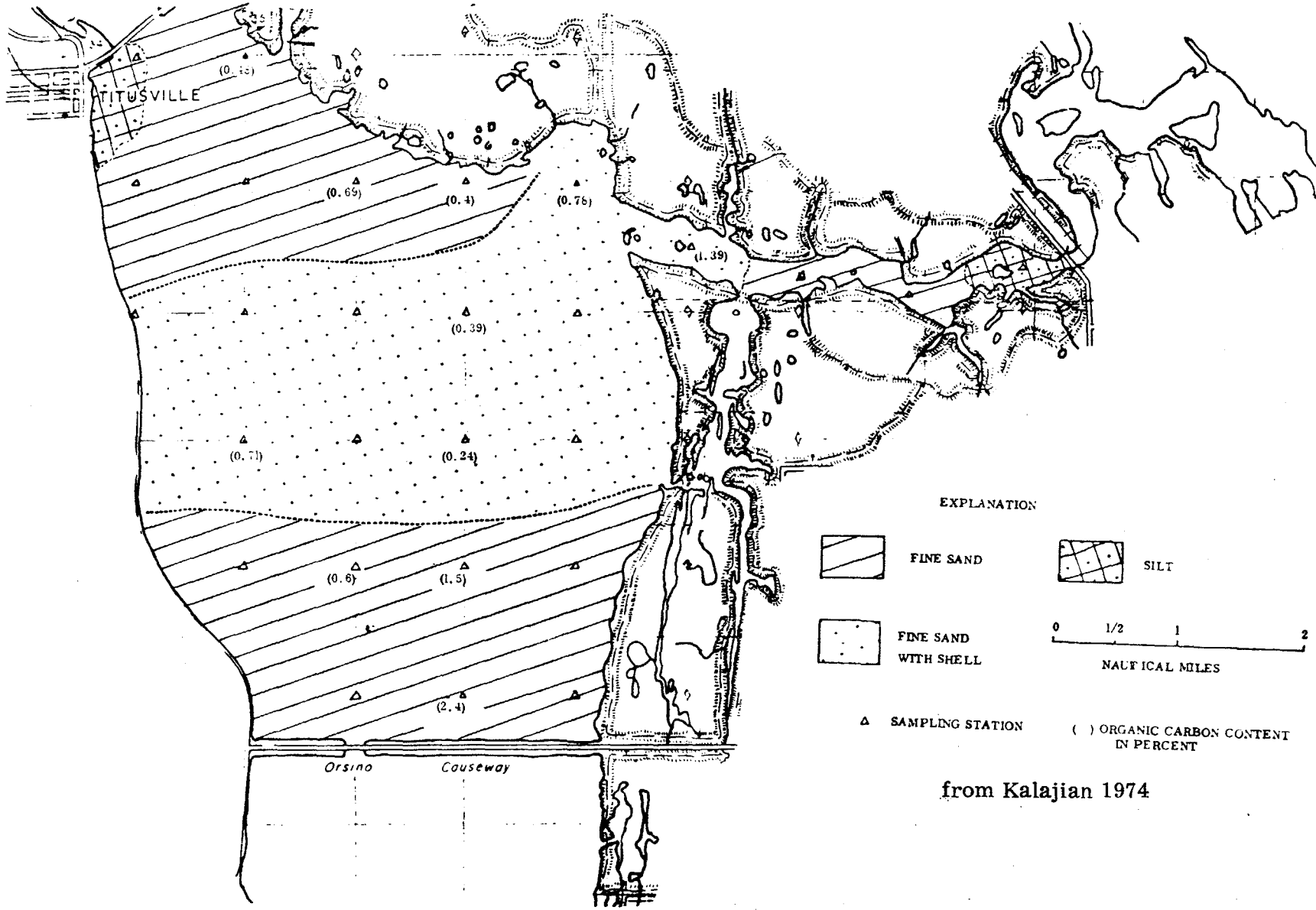


Figure 5. The distribution of sediments and their organic carbon content in Banana Creek and the associated Indian River.

B. Chemical Characteristics

Data is available for pH, Eh and sulfide levels in Banana Creek sediments for only two sites. Appendix 3 contains this data for these sites and the sites sampled in the Indian River and Banana River. All sediment pH values were very close with an average of 6.6. These values were just slightly less than those for the bottom water. The lower sediment pH values are probably due to respirational activity of microorganisms involved in the decomposition of organic detritus in the sediments resulting in an evolution of CO_2 and thus a lowering of pH. The redox potential or Eh values for all samples measured were very similar and were all negative indicating a reducing environment in these sediments. Sulfide values were significantly different for the sediments tested. The values do not seem unusual although the sites in Banana River did exhibit higher values compared to Indian River sites. Beazley, et al. (1974) found high sulfide values in the Banana Creek sediments relative to the sulfide values in the Indian River sediments.

Organic carbon values for Banana Creek sediments are available from Daggett (1973) and values for the Indian River between the Orsino and Titusville causeways appear in Figure 5. The organic carbon data collected during the present investigation appear in Appendix 3. According to Kalajian (1974), the majority of the sediments in the area have an organic carbon content of less than 1% which compares well with other coastal locations for similarly textured sediments. The organic carbon levels determined in this study were fairly uniform with the highest levels being found in Banana Creek and Banana River corresponding to the areas of smaller grain size. Daggett (1973) found an inverse relationship between organic carbon and sediment grain size.

C. Heavy Metal Concentrations

The heavy metal concentrations in the sediments analyzed are fairly uniform and appear to be low compared with other studies of a similar nature. The water depth for each sample site and the concentration of heavy metals found in the sediments at those sites appear in Tables 4 and 5. The highest metal levels were found at the sites in Banana Creek and the Banana River where the sediment grain size was the smallest, and the organic carbon and sulfide levels the highest. The lowest metal values were found in the Indian River where the sediment is a larger grain size and the organic carbon and sulfide levels are lower.

Regression analysis was run and the metal levels were found to correlate well with the sulfide levels at the 1% significance level. The correlation coefficients obtained are 0.972 for iron, 0.958 for zinc, 0.960 for chromium, 0.953 for copper, 0.939 for lead and 0.915 for cadmium. The heavy metal concentrations also correlated well with the organic carbon content yielding correlation coefficients of 0.928 for iron, 0.992 for zinc, 0.912 for chromium, 0.969 for copper, 0.965 for lead and 0.818 for cadmium.

TABLE 4

Heavy Metal Concentrations found in the Sediments of Banana Creek

Site	Depth in m	Fe mg/kg	Zn mg/kg	Cr mg/kg	Cu mg/kg	Pb mg/kg	Cd mg/kg
1	0.99	2588.3	7.3	12.3	1.1	5.4	0.1
2	1.00	2259.0	13.7	8.8	2.2	6.7	0.1
3	0.30	2103.0	0.8	5.7	1.0	3.0	0.2
4	1.00	404.5	4.1	4.7	0.5	0.8	0.1
5	1.00	1509.6	7.3	7.2	0.5	2.5	0.4
6	0.91	1774.5	7.3	10.5	1.1	5.1	0.6
7	0.20	2358.2	4.6	5.9	0.3	3.5	0.7
8	0.30	1991.6	3.1	4.0	1.9	4.1	0.2
9	0.30	925.1	1.6	1.2	2.5	2.8	0.5
10	1.00	1650.4	13.7	9.1	1.4	8.2	0.1
11	0.75	1106.9	7.7	4.5	1.8	2.4	0.3
12	0.25	316.2	0.9	4.0	0.6	2.7	0.2
13	0.20	681.4	7.3	4.1	0.4	1.8	0.1
14	1.00	2860.4	20.2	7.9	6.4	9.8	0.1
15	0.25	2927.2	17.0	10.3	4.2	8.8	0.1
16	1.00	1631.3	13.7	3.2	0.6	3.5	0.1
17	0.25	533.4	7.0	2.5	0.1	1.8	0.1
18	0.20	552.5	10.5	2.6	0.1	2.4	0.2
19	0.61	905.7	10.5	3.5	0.2	2.6	0.1
20	0.15	333.7	10.5	5.1	10.7	18.0	0.1
21	1.00	459.4	0.9	2.6	0.7	1.6	0.1
22	0.75	459.4	7.3	0.8	0.2	1.5	0.1
23	0.75	514.3	10.5	2.9	0.1	1.4	0.1
24	1.5	423.6	4.1	2.4	0.2	2.5	0.1

TABLE 5

Heavy Metal Concentrations found in the Sediments of Banana Creek, the Indian River and the Banana River

Site	Depth	Fe mg/kg	Zn mg/kg	Cr mg/kg	Cu mg/kg	Pb mg/kg	Cd mg/kg
1-26	0.75	1029.3	3.3	2.6	1.1	2.2	0.4
1-29S	0.50	889.4	7.0	3.6	2.3	1.2	0.6
1-15	2.00	437.4	1.8	2.1	3.0	3.1	0.3
1-19	1.00	983.2	4.1	1.9	1.0	1.4	0.1
1-20	1.75	781.8	1.7	1.9	2.6	2.6	0.2
4-12	0.25	1730.7	2.6	5.8	3.1	2.1	0.6
4-16	1.25	1533.5	7.1	4.9	3.1	2.9	0.8
4-16S	0.25	3998.7	54.7	13.0	16.6	10.6	1.4
4-18	0.50	1256.1	7.8	4.5	1.5	3.8	0.3

VI. DISCUSSION

It appears from a comparison of the heavy metal levels found in this study with those found in other studies of a similar nature (Bruland, et al. 1974; Bopp, et al. 1973 and Segar and Pellenbarg 1973) that the metal concentrations in the study area are relatively low and with a few exceptions may be close to natural background levels. Most trace metals entering the sediments are associated in some way with particulates. They may be sorbed on the surface of particulate matter; bound to humic materials; precipitated as sulfides; attached to an oxide coating; sorbed on the exchange sites of clay minerals; or incorporated in detrital, organic or mineral phase. The major fraction within the crystalline lattice of the mineral is not likely to be released upon deposition, and is therefore not of interest in this study. Changes in redox potential, pH, composition of the solution, biological activity etc. can bring about changes in the availability of trace substances. The parameters observed to be important for the heavy metal distribution in this study are grain size, sulfide concentration and organic carbon content. High concentrations of metals corresponded to smaller grain size, high sulfide and organic carbon contents, with the converse being true for low metal concentrations.

Some caution should be exercised in comparing heavy metal concentrations between sites in this study and also in comparison with other studies. Some of the problems associated with the latter have already been discussed. Since the metal concentration of the sediments is definitely related to surface area (Oliver, 1973), only data on sediments with the same surface area should be compared. Many investigators seive the sediment samples and analyze only

that portion that passes through a U. S. Standard No. 230, 63-micron mesh sieve (Bopp and Biggs, 1973). This is not a useful procedure in this investigation because 90% of the sediments had a mean diameter of greater than 75 microns. Since the particle sizes found were very uniform and an effort was made to use as homogeneous samples as possible, a problem was not anticipated in the comparison of different sample sites.

Low heavy metal concentrations would be expected in this study area due to the lack of fine grained sediments. Fine sands do not have as much surface area for binding metal ions as clays do. In this study it was found that the highest concentrations of trace metals occurred in areas where the sediment was the finest and also levels tended to be greater in deeper water. Fine particles tend to stay in suspension longer, especially close to shore. They can be transported away from their source and precipitate into sediment sinks in deeper water. Leland, et al. (1973) found that the sediment heavy metal concentration in southern Lake Michigan was greatest in the middle of the lake where active sedimentation occurred in deep water, although most pollution sources were close to shore. Thomas (1974) cites high organic carbon content of dredged borrow pits in the Banana River as indicating that these holes have become sedimentary traps.

The sulfide levels found in the sediments exhibited a very good positive correlation with the heavy metal concentration. Due to the stability of the resonance structure formed, heavy metals have quite an affinity for sulfur, and combine with it whenever possible which explains the good correlation. Sulfur acts like carbon in the energy exchange, acting as an electron acceptor. Sulfides and elemental sulfur occur in the earth's crust. Organic

materials can also serve as a source of sulfur by anaerobic degradative processes. This seems to be the case in Banana Creek as well as the sites sampled in the Banana River. Sulfur containing pesticides are regularly used in the area. Ethion is used on the citrus trees, and malathion and fenthion are sprayed by plane for mosquito control. These are organic pesticides as are most pesticides today, and are eventually decomposed in the environment by biochemical and physiochemical processes. Since these pesticides contain sulfur, their interaction with sulfur metabolizing microorganisms may be of significance to the equilibrium of the sulfur cycle (Sherman, et al. 1974). Sulfur water rich in hydrogen sulfide is common to artesian wells in the area, and could possibly be an additional source of sulfur to the study area.

Organic matter is important in the complex action of heavy metals in waters and sediments. Chen and Lu (1974) state that there is a linear relationship of total organic carbon to other pollution parameters such as heavy metals. Total organic carbon can be used as a major parameter in determining the pollution status. The organic carbon distribution in the sediments of the study area exhibits a good negative correlation with grain size (Daggett 1973), and also correlates well with trace metal levels. The food chain in this area is detrital. Very few herbivorous species have been found suggesting that bacterial and fungal action is necessary to convert marine flora to an assimilable form. The microorganisms acting on the flora can cause the release of heavy metals from the plants into the water and ultimately the sediments.

There is a marked uptake of heavy metals from the sediments by plants (Banus et al. 1974). This can cause a problem when the plant dies or is broken off by wave action because it can be transported to a detritus or

sediment sink in deeper water. Banus, et al. (1974) found that marsh vegetation removes lead from the sediments and incorporates it into plant tops which may be exported to deeper waters. Increasing the plant standing crop, as occurs with an increase in nutrients, can increase the amount of lead exported from the marshes. This can cause a trace metal accumulation far from the source. Segar and Pellenbarg (1973) point out that this is also a beneficial phenomenon in that the plants can remove heavy metals from contaminated sediments, thus getting the metals back into the water column and detritus food chain before toxic levels have had a chance to build up. Another interesting phenomenon has been reported by Lindberg and Harriss (1974). They found a 3.2 fold enrichment of mercury concentrations in mangrove litter as compared to undecomposed leaves and a 10.4 fold enrichment in suspended detritus. Two hypotheses to explain this concentration of mercury in the decomposing leaves were presented. A strong chemical association between mercury and the organic constituents most resistant to degradation could result. The total mercury in the original plant tissue would be selectively concentrated into the decreasing volume of solid material during decomposition. An increase in the mercury per unit weight of plant detritus would result. Alternatively, the mercury could be concentrated by the microorganisms that associate with the detritus particles. This detrital concentration of mercury could have far reaching implications as organisms in the detritus-based food web are subjected to a higher natural flux of mercury than organisms which feed primarily on plankton.

The role of hydrous oxides in the study area is difficult to determine with the data available. Since the negative charge characteristics of iron and manganese oxides increases with pH, it might be expected that an increased

uptake of cations would accompany passage from fresh into saline waters. This has not been found to be the case in most studies (Burrell 1974). Under reducing conditions, as were present in the surface sediments of the study area, hydrous oxides of iron and manganese are solubilized and may result in increases in concentrations of cations and anions in overlying waters. The metal cations thus released are probably bound to sulfides and precipitated to the sediments again. To really understand the role of trace metals in the environment, a knowledge of the forms and mechanisms of transformation of these trace metals in the system is necessary. The scope of this investigation did not include a detailed physical, chemical and biological analysis of the sediment and water at each site. Any conclusions have been carefully drawn on the basis of the data available.

Looking at the data, generally speaking, sites 1 and 2 have relatively high metal levels. These sites are in a large open basin where the water depth approaches the maximum in the creek. It is possible that this basin could act as a sediment sink especially since it has been cut off from the headwaters of Banana River resulting in decreased flow. This area was previously found to contain high concentrations of hydrogen sulfide mud and would therefore be effective in the uptake of heavy metals. There are no dikes in this area so runoff is probably greater and may contribute trace metals to the area, especially with the proximity to the crawlerway and launch pads. No data could be obtained on the heavy metal content of rocket exhaust. Site 10 also showed generally higher levels of the metals tested and is also in deeper water. Although runoff is restricted by dikes this site could possibly be receiving particulate matter with sorbed metals from the periodic overflow of the

infiltration pond occurring at site 11. Chen and Lu (1974) report that sewage effluent particulate matter may settle out at quite a distance from the outfall. Metals sorbed to particles that do settle out near the outfall can become re-mobilized and be redistributed. The borrow pit is just west of the outfall and could be acting as a sink for the overflow particulates and sorbed heavy metals and thus could account for the low metal concentrations encountered. In 1972 Nevin and Beazley encountered the highest bacterial population in the sediments of the entire area at this outfall. No information is available as to when the treatment plant began employing an infiltration pond.

The first two sites on the west side of the culvert generally showed low metal concentrations. From the sediment analysis (see Figure 5), higher concentrations would be expected due to the finer grained sediment. Also the proximity to State Road No. 3 would seem to warrant higher levels. In the beginning of December 1975, Banana Creek was dammed while a crawlerway from the Space Shuttle Runway to the Verticle Assembly Building (VAB) was built. This isolated the east end of the Creek from any flow or flushing and cut down on the flow in the west end near the dam. Buried sediments were washed up during the jetting of piling for the bridge across State Road No. 3. Heavy metals buried with the sediment could also have been released. The stress on the environment was evidenced by a fish kill, in January preceded by an algal bloom. The returning to solution of buried nutrients is one explanation (Sramek et al. 1975). A similar fish kill occurred in May. The jetting of piling was completed in the beginning of February. Diapers were placed on either side of State Road No. 3 to contain the sedimentation but turbidity still increased. The effects of these activities on the trace metal

distribution is extremely difficult to assess without any concrete data.

The next two sites (14 and 15) had relatively high metal concentrations for all metals. These sites also occur within the silt bottom area but are in deeper water than the two previous sites (12 and 13). This fact combined with the fine grain size could account for the elevated metal levels. This area may act as a sink for particulates entering from runoff and particularly from the construction site. The rest of the sites out to the Indian River had relatively average to low values which would be expected due to the fine sand sediment. Both banks of the creek are completely diked. The vegetation along the shore has been described in Section III. There is some accumulation of detrital material near shore but the metal levels indicate a fairly even distribution. From site 21 westward, the sediment has more shell fragments in it and the metal levels are generally lower. The water is a little deeper and clearer and grass beds appear near the mouth of Banana Creek. These grass beds could be taking up trace metals from the sediments as mentioned before, and therefore contributing to the lower levels in the sediments.

Three sites are worth mentioning because of unusual values obtained. Site 1 had a very high concentration of chromium possibly due to the proximity of the site to the crawlerway and launch pads where chromium was used in construction of the towers. In the east side of the Creek, the chromium and lead levels were high at site 6 while none of the other metals seemed affected. At this site there is a large metal cylinder about 3 meters in diameter stuck in the sediment and extending well out of the water. It is badly corroded which could account for the elevated chromium and lead levels. The origin of the cylinder is unknown. On the west side of the Creek, site 20 exhibited high levels of

copper and lead. This site was adjacent to a dike protected from wave action by a large number of old tires which could be releasing these metals to the water. Many empty mollusc shells were also found at this site and it is possible that these organisms were concentrating the metals which are now being returned to the sediments by decomposition.

Cadmium values appeared to be uniformly low. They did not vary as the other metal values did from site to site. According to Burrell (1974), there is some evidence that cadmium may be considerably less susceptible to abiotic removal than most of the other heavy metals. This would explain the uniform values. Also the low concentrations may be more subject to analytical error than the other metals. Zinc too poses somewhat of a problem because it does not seem to follow all the same trends as the other metals. On the whole the values seem lowest close to shore and highest at the sites in deeper water. The levels are much higher for the sites in the west side of Banana Creek than the east side. None of the other metals follow this trend. A probable source of zinc is the culvert under State Road No. 3. It is made of galvanized metal which has a high zinc content. While the culvert is coated with a layer of asphalt, many places have cracked and worn away. Since the flow of water in the Creek is generally from east to west, a higher concentration of zinc would be expected on the west side of the culvert. Also the pipes running through the dikes to control the level of the impounded waters are galvanized. Much more the the west side of the Creek is contained by dikes.

Sites 1-29S and 1-26 were also in Banana Creek. Site 1-29S is located at the site of the infiltration pond overflow (Site 11). 1-29S was a little closer to the overflow location than site 11. The heavy metal concentrations

at site 1-29S were somewhat lower than those at site 11 which may support the theory that effluent particles settle out at distances from the outfall or overflow in this case. Site 1-26 showed higher metal levels than site 21 which was the closest of the other sites. Site 1-26 could be located in a sink created by the water flow around the adjacent island.

The sites in the Indian River (1-15, 1-19, 1-20) all exhibited low concentrations of heavy metals as did the other sites in the river (10, 11, 12). The fine sand sediments at these sites would indicate lower metal levels than sites with smaller grain size. At site 1-15 slightly higher levels of copper and lead could be a result of the boat traffic in the Intracoastal Waterway. Periodic maintenance dredging of the Waterway would tend to eliminate the evidence of a sediment sink there and thus finer grained material is not evident in Figure 5.

The Banana River sites (4-12, 4-16, 4-16S, 4-18) all had relatively high concentrations of metals particularly site 4-16S. The sediments in the River were the finest encountered with the possible exception of some sites in Banana Creek. The sulfide levels were very high compared with other areas sampled. Site 4-18 is at the mouth of a creek that acts as a storm drain for much of the KSC Industrial Complex. This creek also receives wash down water from rocket testing cells (Carey 1975). A large mat of manatee grass (Syringodium) was present at this site. The decomposing grass could add considerable amounts of metals to the sediment as discussed previously. The runoff and wash down waters are also potential sources of heavy metals that would tend to precipitate out with increasing salinity in the River. Site 4-16S is located at the outfall for an industrial sewage plant serving much of the Air Force Base Industrial Complex. The nature of the effluent could not be

determined. The treatment is secondary so most of the heavy metals should be removed by activated sludge uptake. According to Cheng, et al. (1975), secondary treatment significantly reduces the trace metal level in the effluent. The canal running from the treatment plant to the river is long and narrow. Its entrance into the river is nearly blocked by a large red mangrove tree (Rhizophora mangle) which contributes a lot of decaying leaf litter and detrital matter to the water. There is very little circulation in the area and the mangrove roots trap much of the fine sediment creating a sink at the mouth of the channel from the treatment plant. It seems possible that some of the metals are taken up by the mangrove tree but are eventually returned to the same area in decaying leaf litter with little transport due to reduced circulation. Site 4-16 could also be influenced by the sewage outfall and decomposing plant material. It was located in deeper water so it could act as a sink for any fine particulate matter transported from site 4-16S. Runoff from the NASA Parkway East is also a potential metal source. Site 4-12 was located near the shore of a small spoil island accommodating a large number of birds. The metal levels were somewhat elevated but do not appear to indicate any unusual problem. It is possible that the large bird population is contributing heavy metals to the area on and around the island in their waste products. Many of these birds are top predators and could be victims of food chain magnification of heavy metals. Although the metal levels were elevated at these sites in Banana River relative to the other sites sampled, they are still low in comparison to other studies.

VII. SUMMARY AND CONCLUSIONS

The heavy metal levels found in the sediments of the waters near the Kennedy Space Center were low compared with other similar studies. The highest levels encountered appeared to be a consequence of high sulfide and organic carbon levels and smaller grain size in the sediments. Any heavy metals entering the system were probably sorbed to fine particulate matter and thus ended up in sediment sinks where these fine particles tend to settle out. The sulfide muds of the area are very effective in scavenging heavy metals which have a strong affinity for sulfur compounds. Areas with a lot of plant detritus had higher metal levels possibly due to the concentration of metals by decaying plant matter and the attraction heavy metals have for organic compounds. The vegetation of the area seems to be efficient at recycling the heavy metals. Plants take up heavy metals from the sediments as evidenced by low levels in the grass beds. When the plants are decomposed the metals are returned to the water column and sediments by bacterial action. A similar cycling can take place by detritus feeders.

The sources of metals to this system are limited. The area is relatively undeveloped with no industrialization except for KSC. The sewage treatment plants are a probable source although the plant in Banana Creek only discharges directly into the Creek during periods of overflow. Runoff is a possible source although it has been cut down in Banana Creek due to the impoundments for mosquito control. The areas the runoff comes from are mostly undeveloped land and citrus groves. Insecticides and pesticides are a potential source of copper and lead in the runoff but the amounts are probably negligible. Boat

traffic particularly in the Waterway where it is heaviest would be expected to contribute some metals such as copper, zinc, iron and lead. The atmosphere is probably the biggest source contributing metals through aerial fallout and precipitation. The metals in the atmosphere probably originate mostly from the burning of fossil fuels, especially gasoline used by cars. There is little traffic in the area compared to large urban centers and thus the low lead levels encountered in the sediments.

Although sediments are considered to be sinks for heavy metals, they are not necessarily permanent. The metals can be remobilized by changes in the chemical conditions such as the redox potential. Plants and animals are also important in remobilizing metals. Plants can take up metals from the sediments and introduce them back into the water column upon decay. Metals may be exported great distances from the original sediment sink by plant detritus. Many marine organisms have the ability to concentrate heavy metals well above the levels in their surroundings. Food chain magnification can occur with possible serious consequences to man and other top predators at high trophic levels. Some detritus feeders are capable of remobilizing significant amounts of heavy metals from the sediments.

A lot more work needs to be done on heavy metal levels in the environment of the Indian River system. In order to understand the complete cycle of the metals entering and leaving the system, a number of parameters should be tested. The more complete the knowledge of the chemical speciation of the metals in the sediments the easier it is to determine their source and more importantly their potential effect on the system. Unfortunately this information is lacking. Analytical methods that are sensitive enough are seldom sufficient

to differentiate as to species. Those methods that combine specificity and sensitivity such as mass spectrometry are hardly in the class of routine methods available for most laboratories. Much of the data available on chemical speciation of metals is obtained from modeling of the system. Predictions made from modeled systems should be used cautiously since it is impossible to duplicate the complexity of the natural environment. To determine the sources of heavy metals entering a system, all sources should be checked for metal levels e.g. atmospheric fallout, precipitation, runoff, ground water, stream and river inputs, etc. For the area under investigation in this study; heavy metal levels of the atmosphere, runoff, ground water and any fresh water inputs as well as interstitial water and the water overlying the sediments would provide a good insight into the sources of the metals found in the sediments. Metal concentrations in the biota particularly the plants along the shore and the marine plants would be very helpful in the overall metal level picture of the system.

Because of the good record of heavy metal concentration provided by the sediments, they should be carefully monitored in this area, not only as an indicator of pollution but as a potential source of these metals to the food chain. Even low metal levels could be potentially dangerous through concentration and food chain magnification in this detritus based food web. At present the levels of heavy metals encountered seem to be largely natural with the exception of a few isolated sites. This conclusion stems from a lack of anthropogenic sources and good comparison with other baseline natural levels reported in the literature.

In conclusion it appears from this study that the only industrialized

complex affecting the study area, the Kennedy Space Center, has not had a great impact on the heavy metal levels in the surrounding environment. A baseline of heavy metal concentrations in the sediments has been determined and can be used in the future to monitor the inevitable development of the area. Hopefully through careful planning and monitoring a relatively unpolluted system can be maintained.

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APPENDIX 1

Operating Conditions for Atomic Absorption

Jarrell-Ash Model 82-270 Atomic Absorption Spectrophotometer

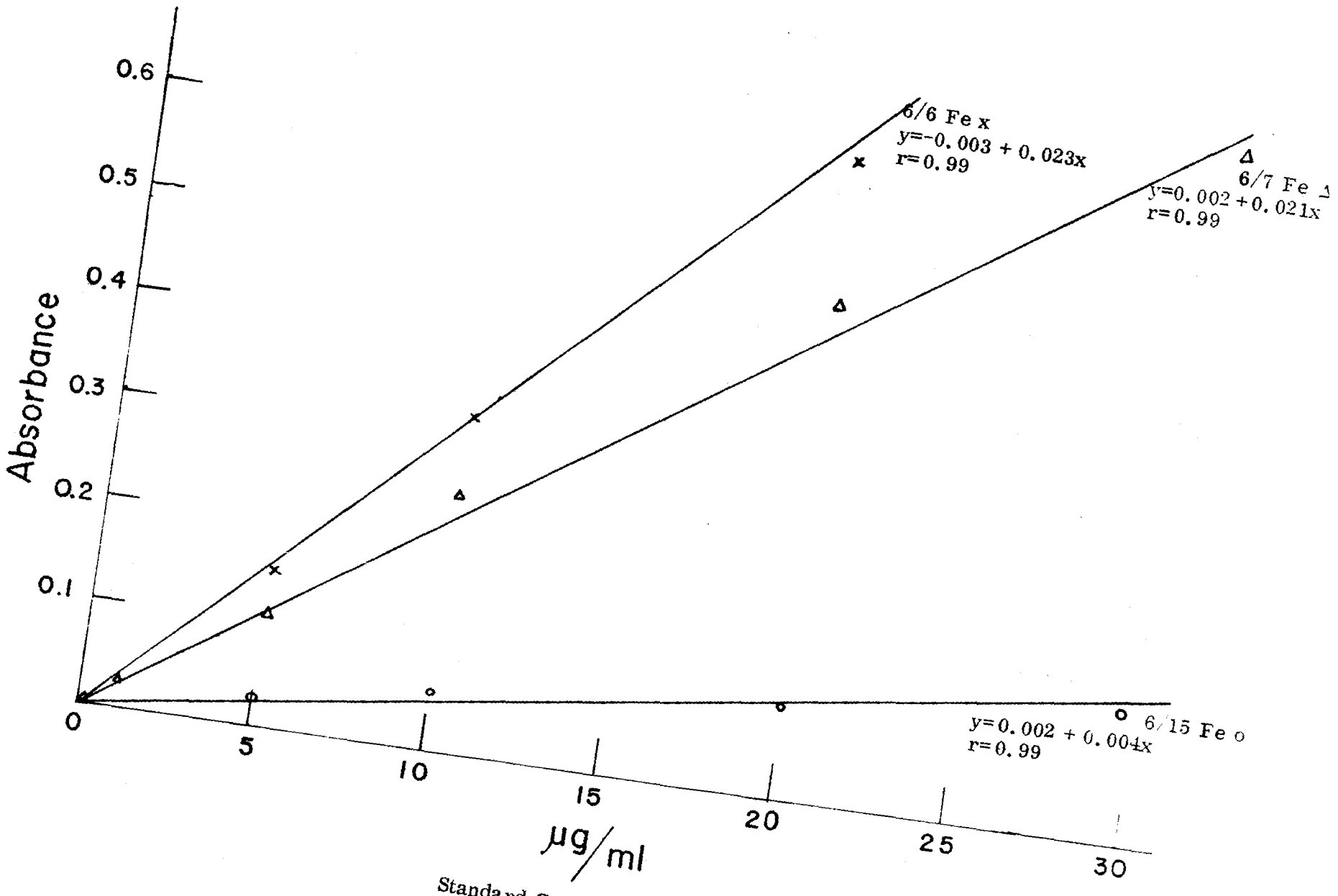
	Iron		Zinc	
Date	6/6&6/7	6/18	6/7	6/18
Wavelength, nm	248.5	248.0	214.3	213.9
Slits, μ	25,50	25,50	25,50	25,50
Lamp Current,mA	8	17	13	17.5
Mode	% absorption	% absorption	% absorption	% absorption
Damping	2	2	2	2
Gain	9	10	8	9
Fuel-Acetylene	4	4	4	3
Oxidant - Compressed Air	20	20.5	20	20
*Sensitivity, μg/ml (from Perkin-Elmer manual)	0.1	0.1	0.015	0.015

*Sensitivity refers to concentration in aqueous solution which will generate a signal of 1% absorption

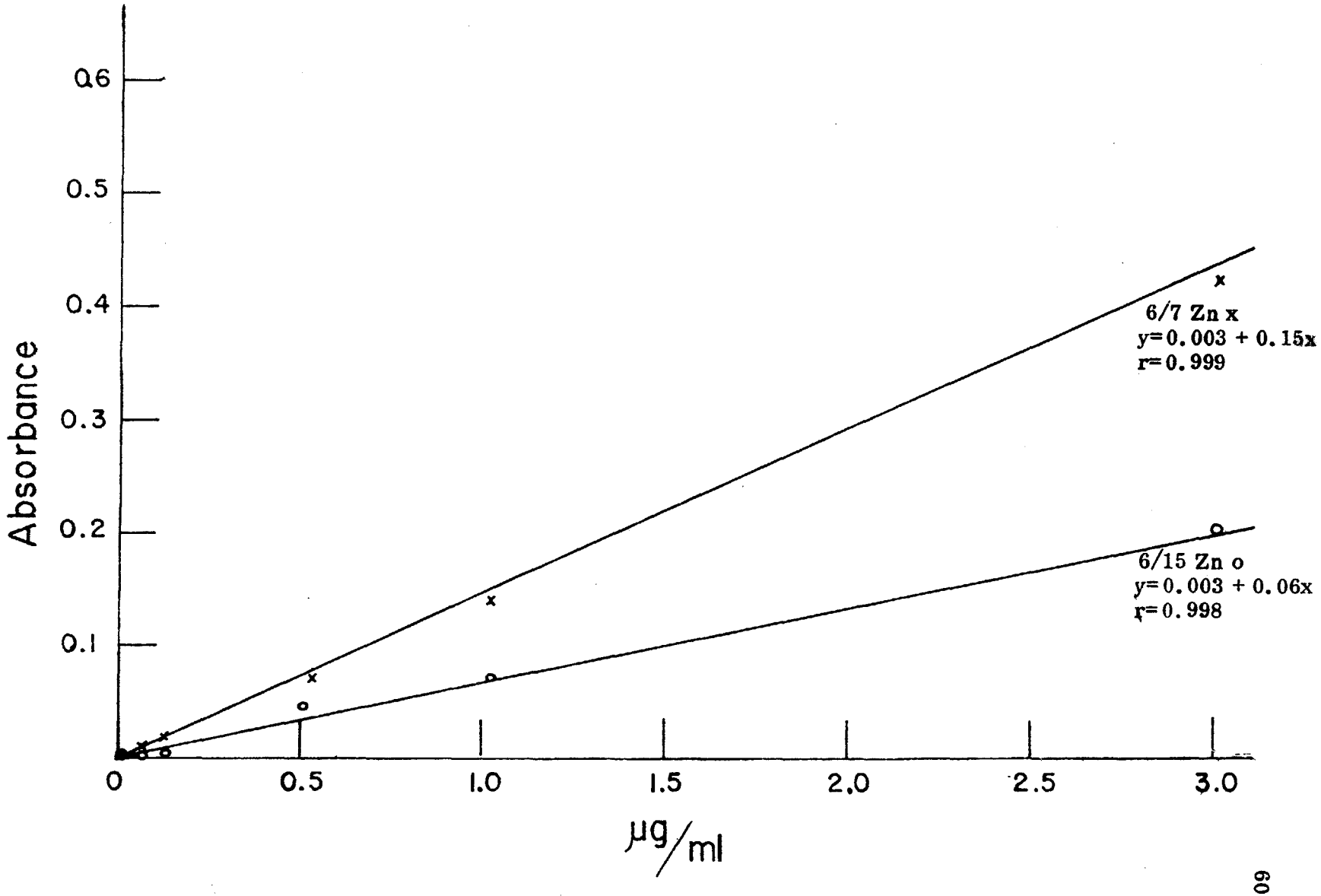
Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer with HGA-2000

	Chromium		Copper	Lead		Cadmium
Date	6/2&6/13	6/19	5/30, 6/11&6/18	5/30&6/11,	6/17	6/2, 6/10, 6/17&6/18
Wavelength, nm	357.9	357.6	324.7	283.3	283.5	228.8
Spectral Band Width, nm	0.7		0.7	0.7		0.7
Lamp Current, mA	40		40	30		12
Scale Expansion	1X		1X	1X		1X
Noise Suppression	1		1	1	2	1
Purge Gas - Helium reading	4		4	4		4
Drying Temperature, ^{o}C	100		100	100		100
Drying Time, sec.	30		30	30		30
Charring Temperature, ^{o}C	900		1000	340		300
Charring Time, sec.	60		60	60		60
Atomizing Temperature, ^{o}C	2650		2500	2000		1500
Atomizing Time, sec.	15		15	15		15
Injection size, μl	20		20	20		20
Chart Speed, inch/min.	1/4		1/4	1/4		1/4
*Sensitivity, pg/0.004 Abs. (from Perkin-Elmer manual)	25		50	50		2

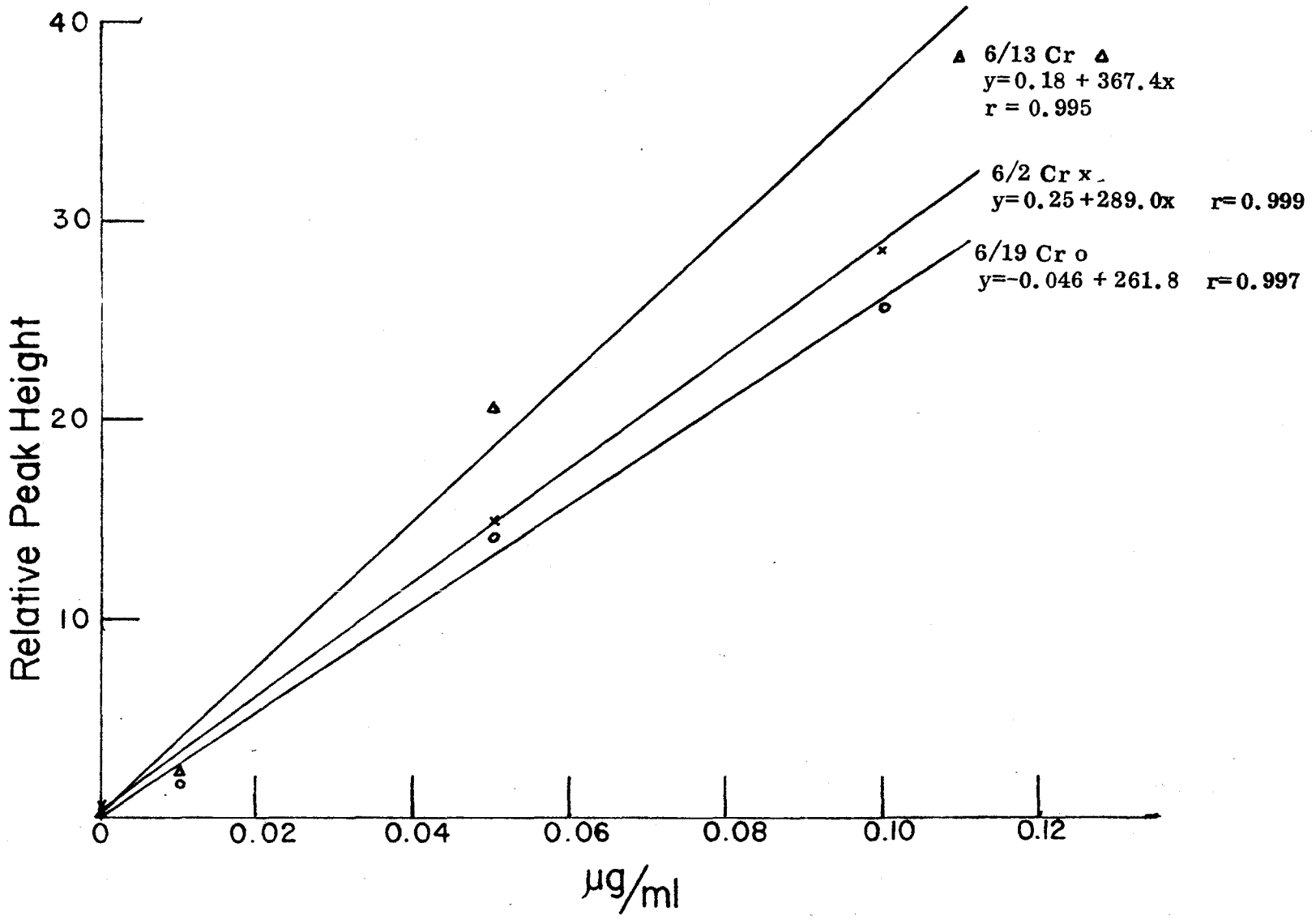
*Sensitivity refers to the concentration in aqueous solution which will generate a signal of 1% absorption (0.004 A.U.)



Standard Curves for Fe



Standard Curves for Zn



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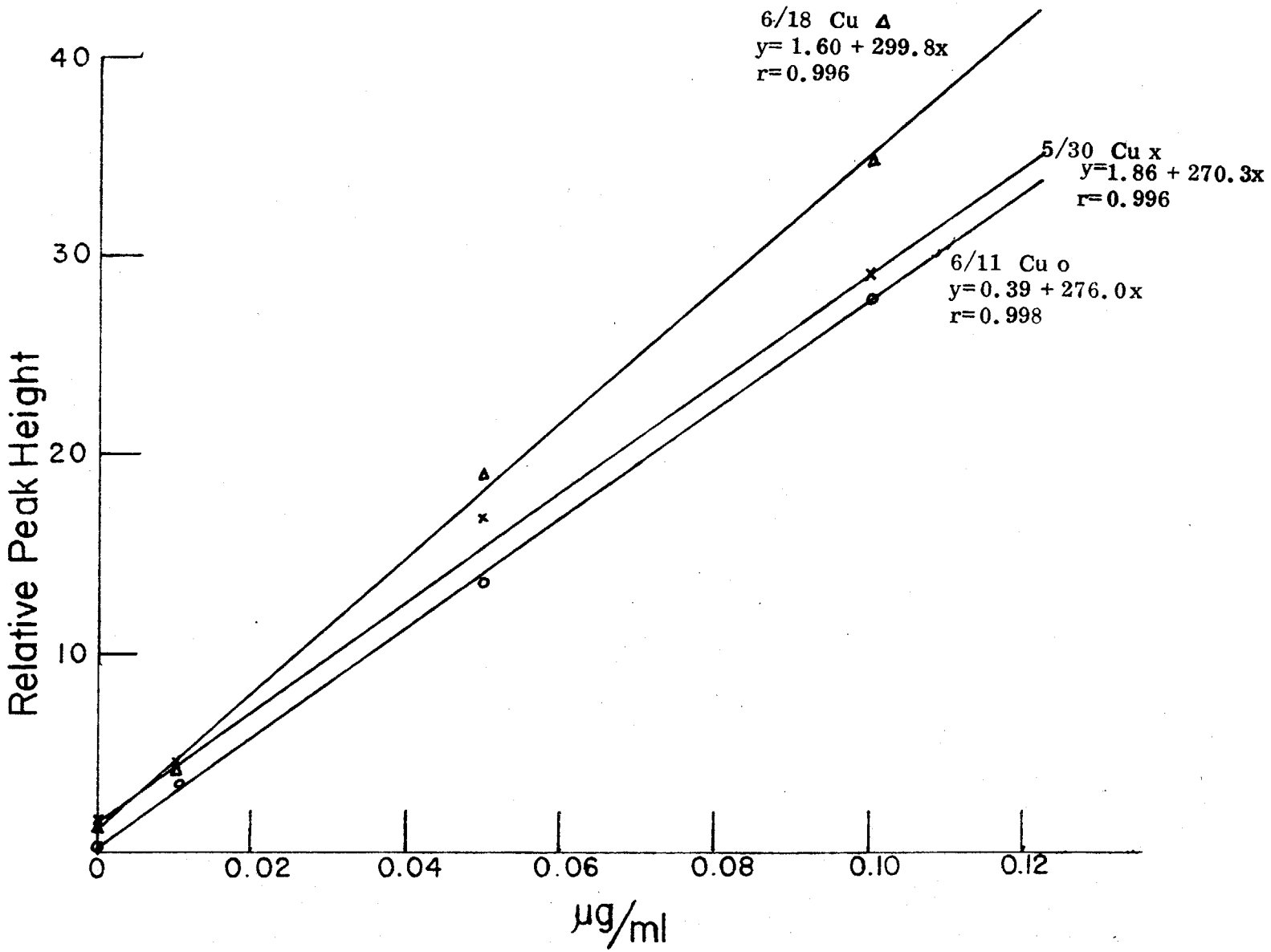

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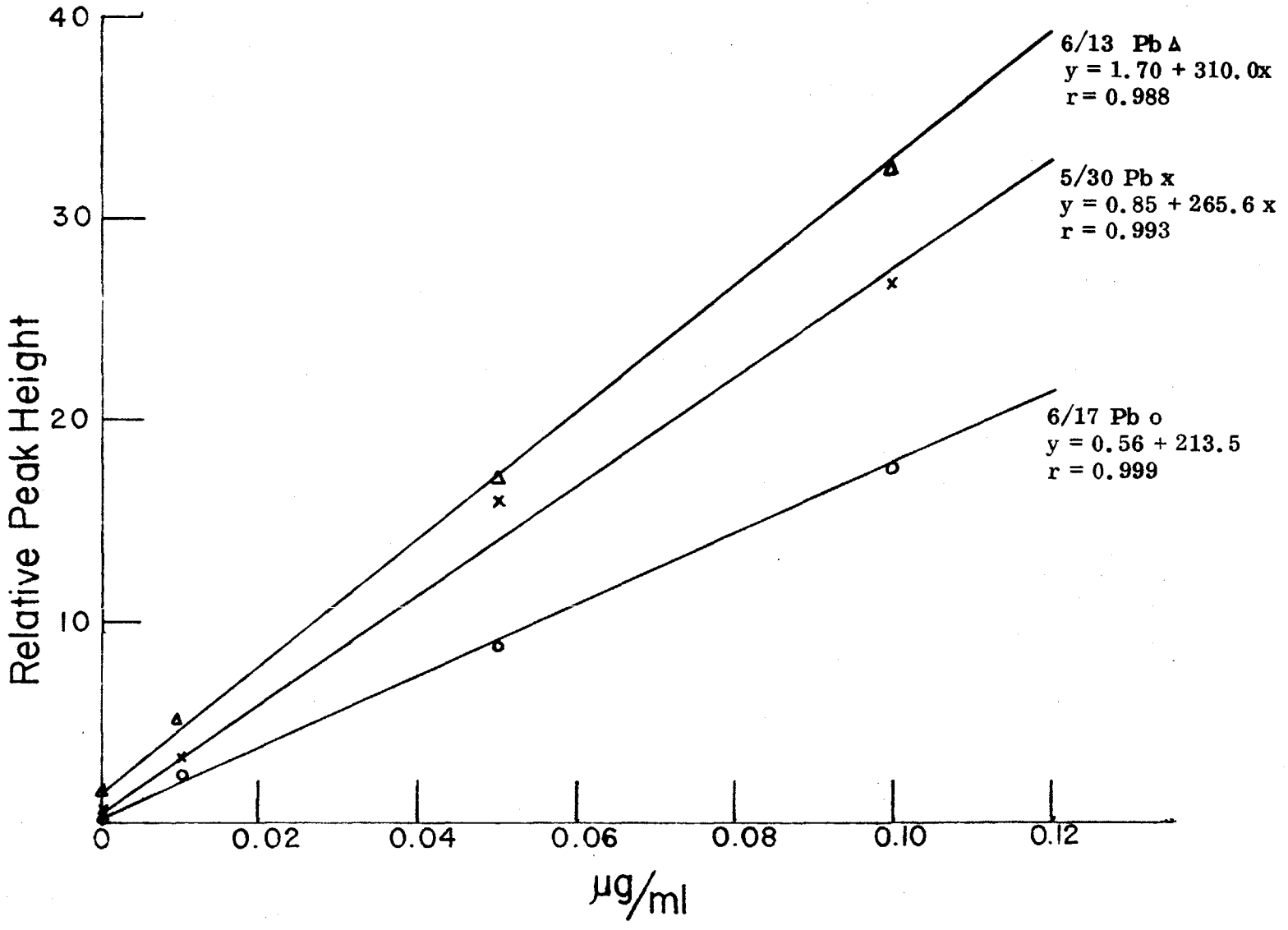

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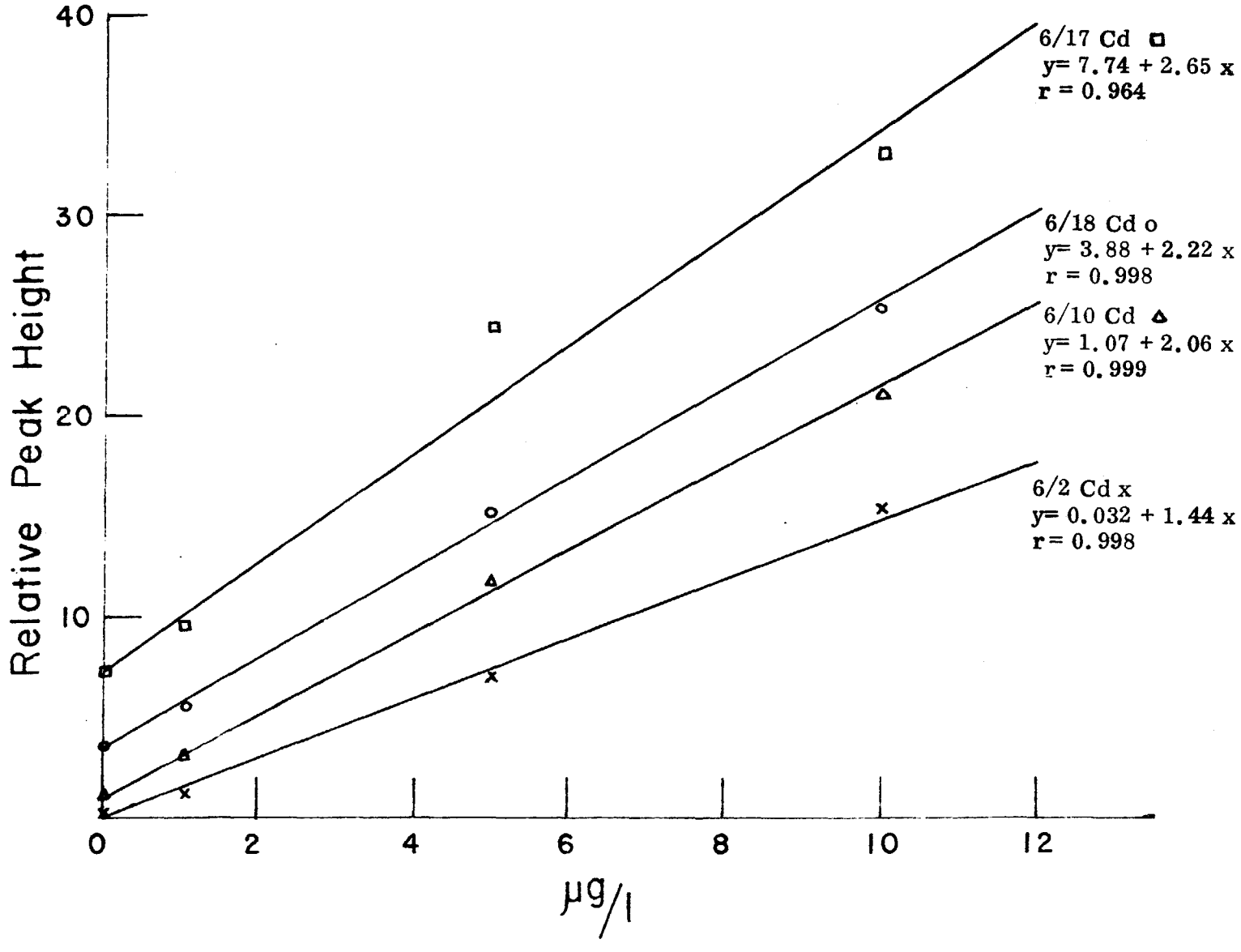

Standard Curves for Cd

APPENDIX 3

Chemical and Physical Parameters of Sediments Sampled

		Bottom Water Parameters						Sediment Parameters						
	Site	Depth in m	Dissolved Oxygen ppm	Salinity °/oo	pH	Eh mV	Temp. °C		pH	Eh mV	C.O.D. %dry wt.	Volatile Solids % dry wt.	Water Content %	*Sulfides µg/g dry wt.	Organic Carbon mg/g dry wt.
Banana Creek	1-26	0.75	6.87	30	6.6	+90	30.0		6.5	-410	1.08	2.60	46.2	69.0	4.81
	1-29S	0.50	5.60	26	6.6	+60	28.0		6.567	-200	1.11	2.30	42.8	59.6	2.98
Indian River	1-15	2.00	7.07	28	6.6	+85	27.0		6.554	-300	1.29	2.63	39.0	47.0	3.00
	1-19	1.00	8.07	32	6.6	+110	22.0		6.572	-310	0.77	1.43	25.9	53.7	3.52
	1-20	1.75	7.87	29	6.6	+60	28.0		6.539	-370	1.18	3.53	47.4	68.8	2.86
Banana River	4-12	0.25	8.80	25	6.8	+80	29.0		6.724	-300	1.39	4.69	26.5	89.3	2.52
	4-16	1.25	6.80	26	6.8	+85	26.0		6.692	-380	1.60	6.59	49.0	134	3.08
	4-16S	0.25	7.00	23	6.8	+82	28.0		6.767	-330	12.8	19.44	188.7	303	53.5
	4-18	0.50	3.60	25	6.8	+95	26.0		6.718	-490	3.37	2.99	50.4	84.7	6.06

From Mendelsohn 1975

*From Peffer 1975

Section IV, Article 12

Nutrient Characteristics of the Lagoonal Sediments Surrounding the Kennedy Space Center

Stephen O. Peffer

1975

NUTRIENT CHARACTERISTICS OF THE LAGOONAL SEDIMENTS SURROUNDING THE KENNEDY SPACE CENTER, FLORIDA

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Master of Science
in

Bio-environmental Oceanography

Florida Institute of Technology
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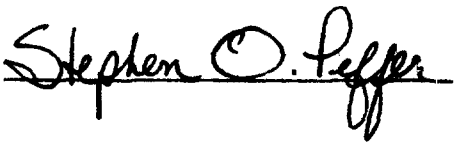

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I. INTRODUCTION

The Department of Oceanography and Ocean Engineering and the Department of Biology at the Florida Institute of Technology, Melbourne, Florida, have been involved in an ecological baseline study of the lagoons surrounding the John F. Kennedy Space Center (KSC) since April 1972. Much of the information gathered by the many investigators involved has been compiled in a series of reports entitled "A Study of Lagoonal and Estuarine Ecological Processes in the Area of Merritt Island Encompassing the Space Center". These studies have focused on the assessment of the chemical, biological, physical, and geological parameters most likely to be affected by man's activities. The research described herein was designed for the purpose of measuring the concentrations of the major nutrients (Nitrogen, Phosphorus, Carbon, Sulfur) in the surface sediments at selected sites throughout the lagoons in order to compare natural areas with those under the influence of man. The results of this study will supplement the large amount of data already collected concerning the ecological conditions of this study area.

While the focus of any ecological baseline survey must ultimately be the interaction of the biological community with the physical environment, it is not the resident organisms but their physiochemical environment which is the subject of this investigation. Chemical analysis alone, however, does not reveal as much about an ecosystem as does a study that encompasses the resident biota, because chemical measurements are instantaneous, while organisms represent longer lasting conditions (Thomas 1974). Thomas (1974) has given a description of the benthic biological communities found in this region. It is widely recognized that the nature of the substrate is the most important environmental parameter affecting distribution of the benthic fauna. The parameters that have been chosen for study are those that are thought to have the most significant bearing on the quality of life of the resident biota and thus on the ecosystem as a whole. These parameters closely follow guidelines for investigation established by the Environmental Protection Agency as expressed in a number of their published reports. (See Chemistry Laboratory Manual, Bottom Sediments, 1969 ed.

This research effort was divided into two main parts. This investigator was responsible for measuring the concentrations in the sediment of ammonia and organic nitrogen, total and dissolved phosphorus, sulfur (as sulfides), carbonates,

and organic carbon. The other investigator, Stuart Mendelsohn, of the Department of Environmental Engineering at F.I.T. was responsible for measuring the dissolved oxygen content, pH, salinity, and temperature of the water column just above the sediment surface, the chemical oxygen demand (COD) of the sediment, their water and volatile solids content, color and grain size. Both investigators sampled and analyzed their sediments simultaneously, with the intention of combining their results for the report to NASA. The results of Mendelsohn are included in the appendix of this thesis and are referred to in the text. For a complete description of the techniques he employed and a discussion of his results, see Mendelsohn (1975).

II. THE SEDIMENTARY ENVIRONMENT

An ecological system consists of populations of organisms, flows of water, invisible pathways of cycling chemical elements and various organizational mechanisms which produce an integrated interrelationship of the parts (Odum and Copeland 1974). Because these parameters never combine in exactly the same manner, each ecosystem is unique in its own way, yet there are often similarities in the major components that allow certain comparisons to be made.

The sediments in a lagoonal ecosystem form one part of a highly complex biological and physio-chemical system that includes the land, sea, air, and resident biota. The texture and composition of the bottom sediments in estuaries and lagoons are a function of the geology, bathymetry, hydrology, and biology of the area (Folger 1972). The physical and chemical characteristics of the surface sediments (herein defined as the top 4 cm.) in some cases control, and in others are controlled by the resident biological community. The sediments that accumulate in lagoons of the type under study here consists primarily of terregenous detritus, biogenic debris, and various pollutants. A characteristic redox profile and a well defined redox discontinuity layer are nearly always present in sediments reflecting the zonation of chemical factors and microbial processes (Fenchel 1969). Surface sediments also provide a geochemical record of human activity in the recent past. Natural inputs to the sediments are provided by rivers, surface runoff, aerial fallout, and other minor sources. Baseline studies such as this one are used to help differentiate natural from man-made conditions, and can help assess the impact of human activity on natural environments.

The physio-chemical characteristics of the sediments and the biota found therein occur in a complex interrelationship with one another. The sorbtion and release of chemicals in the sediments is in a dynamic equilibrium, and their composition and geochemistry vary through such processes as the diffusion of ions within the sediment, reactions in the pore water, humic binding forces, the ratio of organic to inorganic complexes, nutrient mobilization, reactions at the sediment water interface, mobility of sedimentary cations, water-sediment reactions, and others (Soule and Oguri 1974). Many of these processes are interrelated and exist

in positive or negative feedback relationships with one another. For example, the diffusion of ions at the sediment-water interface is influenced by the redox potential (Eh), various ionic interactions, and the physical structure of the sediment. Metallic cations migrate within the sediment to oxidized or reduced layers according to the solubility, mobility, and electric charge of the respected ions (Soule and Oguri 1974).

Even if the sedimentary environment was completely lifeless, there would be a dynamic chemical interaction between the sediments, the water, the land, and the atmosphere. Solar energy and its many manifestations such as radiation, wind, and precipitation would produce a steady turnover and relocation of ions from sea to sediment to land to sea (or other similar pathways) throughout geologic time. With the superimposition of a living biotic community, however, ionic interactions are greatly accelerated, new equilibria are established, and the entire physio-chemical system takes on a new character.

Bacteria are the chief micro-organisms that assist in chemical changes of a permanent order (Wood 1965). Microbes make use of chemical reactions which release energy in order to perform their metabolic functions (Wood 1967). They catalyze reactions that normally would take place only at higher temperatures and/or pressures, and thereby accelerate the chemical interactions of the ecosystem. In many cases, they merely catalyze a reaction that would occur even in their absence. In others, they use the energy derived from such reactions to help drive other reactions which are vital to their well being, and that would not occur without their presence (Wood 1972). Photosynthetic bacteria combine efforts with plants to produce compounds whose absence would make life as we know it impossible.

According to Wood (1965), bacteria play the most important biological role of any organism, large or small, in the aqueous environments. They build and destroy organic material, convert and translocate minerals, and alter such physiochemical properties as Eh and pH. In the shallow lagoons that surround the Kennedy Space Center, the water mass and the sediments are quite close spatially. Some authors believe that the microbes of the sediment, particularly those concerned with the sulfur cycle and photosynthesis, actually control the marine environment (Wood 1965).

A comprehensive understanding of the chemistry of the sedimentary substrate not only contributes to knowledge of sediment geochemistry and diagenesis, but also helps to define the conditions that are imposed on those organisms living on or near the bottom (Nelson 1972). A major determinant of sedimentary chemistry is the nature and condition of the overlying water. An understanding of the chemical composition of the sediments therefore becomes very useful in assessing present as well as past ecological conditions. The biogeochemical character of bottom sediments is a good integrator of such influences as sedimentation rates of allochthonous and autochthonous organic particles, sediment redistribution by currents, and the introduction of man-made contaminants (Nelson 1972). Thus, sediment profiles and their chemical properties are indicators of the dynamic equilibrium existing between the water, the sediment, and the organisms of the area.

Although this investigator measured nutrient concentrations only, it is nonetheless useful to briefly review the significance of some of the physio-chemical parameters which were measured by Mendelsohn. The two of greatest significance to this study are those of Eh and pH.

The reduction-oxidation potential, or Eh, is a measure of the electrochemical environment, and is used to measure the oxidizing or reducing capability of the immediate environment, a factor of such critical importance that it is often necessary to specify the Eh when discussing many of the reactions occuring in the sediment (Blatt, et. al. 1972). The redox potential depends on the ratio of oxidized to reduced forms in the system and not on their absolute concentration (Whitfield 1969). It is the contention of Blatt that the control of the Eh in the sediments is based on the supply of gaseous oxygen in relation to the amount of organic matter to be decomposed (oxidized). Brock (1966) notes that gaseous oxygen will generally be absent from any sediment, as it is quickly depleted by organismic respiration and auto-oxidation of various chemical species. Fenchel (1969) is also of the opinion that anaerobic decomposition of organic matter is always the primary cause of reducing conditions, while others, notably Wood (1967), stress the importance of the bacteria involved in the cycling of sulfur as the major controllers of the Eh level, and thus of the chemistry and biology of the sediments. Thomas (1974) reported a significant correlation between species richness and redox potential in the sediments of the northern Indian River.

Most sediments exhibit a redox profile with an oxidized (positive) layer at the surface, a discontinuity (change from positive to negative) slightly below the surface, and negative conditions prevailing from there on down. Even in highly aerated waters, the aerobic (positive) zone may extend only a few millimeters into the sediment because of the greatly reduced convection currents in the sediments (Brock 1966, Fenchel 1969). The oxidized layer at the surface has been shown to act as an effective barrier to the migration of ions from the reduced conditions below. If stagnation and oxygen depletion of the overlying water are sufficient to change the Eh of this layer from positive to negative, extensive amounts of nutrients may be liberated into the water (Brock 1966).

The Eh of a sediment is a difficult parameter to measure accurately. Whitfield (1969) notes seven different difficulties associated with Eh equipment and sampling techniques, with the result that accuracy is rarely within $\pm$ 10 mv and is more commonly within $\pm$ 50 mv. Even this large variation, however, is small enough for the basic redox characteristics of a sediment to be understood, and Whitfield further remarks that Eh appears to be well suited to act as a chemical parameter used to describe the environment, especially when used to describe the relative degrees of stagnation which are found to occur. When Eh measurements are used in this way, they provide a simple, rapid means of characterizing and mapping estuarine sediments (Whitfield 1969).

The pH of bottom sediments reflects such environmental variables as salinity, carbon dioxide concentration of the pore waters, dissociated organic acids and bases, dissociated organic decomposition products (such as ammonia) and dissociated clay minerals (Nelson 1972). Variations in any of these parameters can cause variations in the sedimentary pH, and gradients are often found in estuaries which reflect salinity gradients (Nelson 1972). The pH may control, or be controlled by the micro-organisms in the environment, and pH is widely known to reflect the level of photosynthetic activity. In the sediments, the reduction of sulfates to sulfides tends to hold the pH around 7 (Wood 1967).

A. Sediment-faunal Relationships

A common concept in benthic animal-sediment relationships is that the feeding type of the infauna is in some way correlated to the sediment (Bloom, et. al. 1972). Sanders (1958) has shown a direct relationship between sediment characteristics and trophic distribution. The influence of water circulation on sedimentation and trophic distribution was shown by McNulty, et. al. (1962) and it is probable that the redistribution of the sediments in the shallow lagoons surrounding the Kennedy Space Center are greatly dependent on local currents, which are primarily wind driven (Thomas 1974, Dill 1974). Benthic species are known to prefer a particular type of substrate, and those that show low preferences are usually found to be low in the order of succession (Johnson 1971).

There are basically four ways in which benthic animals gather food; they filter suspended particles from the water, they collect food particles which settle on the surface of the sediment, they obtain nutriment from the organic material which has become incorporated in the deposit, or they prey upon other animals. Many, of course, take nourishment from several sources (Tait and DeSanto 1972). The food of the benthos is concentrated at or near the sediment-water interface, and any disturbance that affects this interface will, therefore, affect the food resources of the whole community (Johnson 1974). Dissolved organic complexes are adsorbed and concentrated on the surfaces of particles in the sediment. Here they exist in concentrations sufficient to nourish colonies of bacteria, which nourish the protozoa (especially ciliates), which then nourish the metazoa.

To a considerable extent, the chemical elements of an ecosystem tend to remain within it, so that the substances from the environment which are converted to protoplasm by the primary producers are eventually returned to the environment after passing through the various trophic levels (Brock 1966). While energy travels through an ecosystem, elements cycle within the system. Any energy that is temporarily stored ties up a certain proportion of the chemical substances from which protoplasm is constructed, principally carbon, nitrogen, phosphorus, and sulfur. If an ecosystem has an efficient food chain, with organic substances passing quickly from one link to another, and if there is no appreciable export of nutrients, then this system may have a rapid turnover of material and a high rate of production,

even though the surrounding environment may be poor in nutrients (Brock 1966). This is often the type of condition that exists in shallow, tropical lagoons.

Much of the organic matter that exists in aqueous environments exists in soluble form and in non-living particles, the latter probably being formed spontaneously from organic matter which has been excreted by phytoplankton or derived from dead organisms by fermentation. This organic matter forms a matrix which alters the physical, chemical, and geological properties of the sediments (Johnson 1974). It also constitutes part of the detritus; that combination of animal, vegetable, and mineral that provides food for many benthic organisms. Thomas (1974) and others have shown that the primary food chain in the lagoons studied here is a detritus type pathway, with suspension feeders and filter feeders comprising a large portion of the benthic fauna. The detritus originates primarily from the broken and dead blades of the area's abundant grasses, but terrigenous runoff also supplies a large portion. Unfortunately, "detritus" is a vague term, and in fact a large portion of the energy obtained from detrital food sources may actually come from the numerous bacteria adhering to the particles (Brock 1966). The most active microbial populations are those associated with sea grasses (Wood 1967).

In the anaerobic areas of an aqueous ecosystem, such as in the sediments, bacteria are practically the exclusive forms found. In reducing environments, bacterial production of reduced compounds of low molecular weight (H_2S, NH_3, CH_4, H_2) can and does occur. These compounds diffuse upwards where they may be oxidized in the presence of oxygen by chemoautotrophic bacteria or abiologically, or under anaerobic conditions, by the activity of photoreducing organisms (Fenchel 1969). This helps to produce a vertical zonation in the sediments, and the distribution of organisms on the vertical gradient will depend on their oxygen requirements, their tolerance to reduced compounds such as H_2S and NH_3 (both toxic) and their specialized ability to feed on the organisms there (Fenchel 1969).

Biogeochemical cycles such as those that involve carbon, nitrogen, phosphorus, and sulfur are concerned with the circulation of an element from the inorganic form into protoplasmic combinations and then back into the abiotic portion of the habitat. Microbes are the principle biological agents producing this cycling (Alexander 1971). Elements that participate in biogeochemical cycles exist in organic and inorganic pools, the sizes of which range from vast to minute. Figure 1

summarizes the pathways involved in the cycling of organic matter in the benthos (after Johnson 1974). The biogeochemical cycles of carbon, nitrogen, phosphorus, and sulfur are presented in Figures 2 and 3. For a good description of these cycles, see Odum (1971) or Alexander (1971).

While it is beyond the scope of this paper to give the details of the biogeochemical cycles, it is useful to review the processes involved in nutrient cycling. These cycles are run by microbial activities that can be divided into several broad categories. These groupings are not mutually exclusive, and a single type of chemical conversion may be accurately described by more than one of the following categories (Alexander 1971).

Mineralization - the conversion of an organic form of an element to the inorganic state, resulting in a decrease in biochemical complixity of the ecosystem; also known as nutrient regeneration.

Immobilization - the conversion of an inorganic nutrient element into an organic complex, resulting from assimilation and incorporation into protoplasm. Mineralization and immobilization are the two main opposing forces in the biogeochemical cycles.

Oxidation - linked to the organism's metabolism; the oxidation of organic compounds by heterotrophs provides the energy needed for growth.

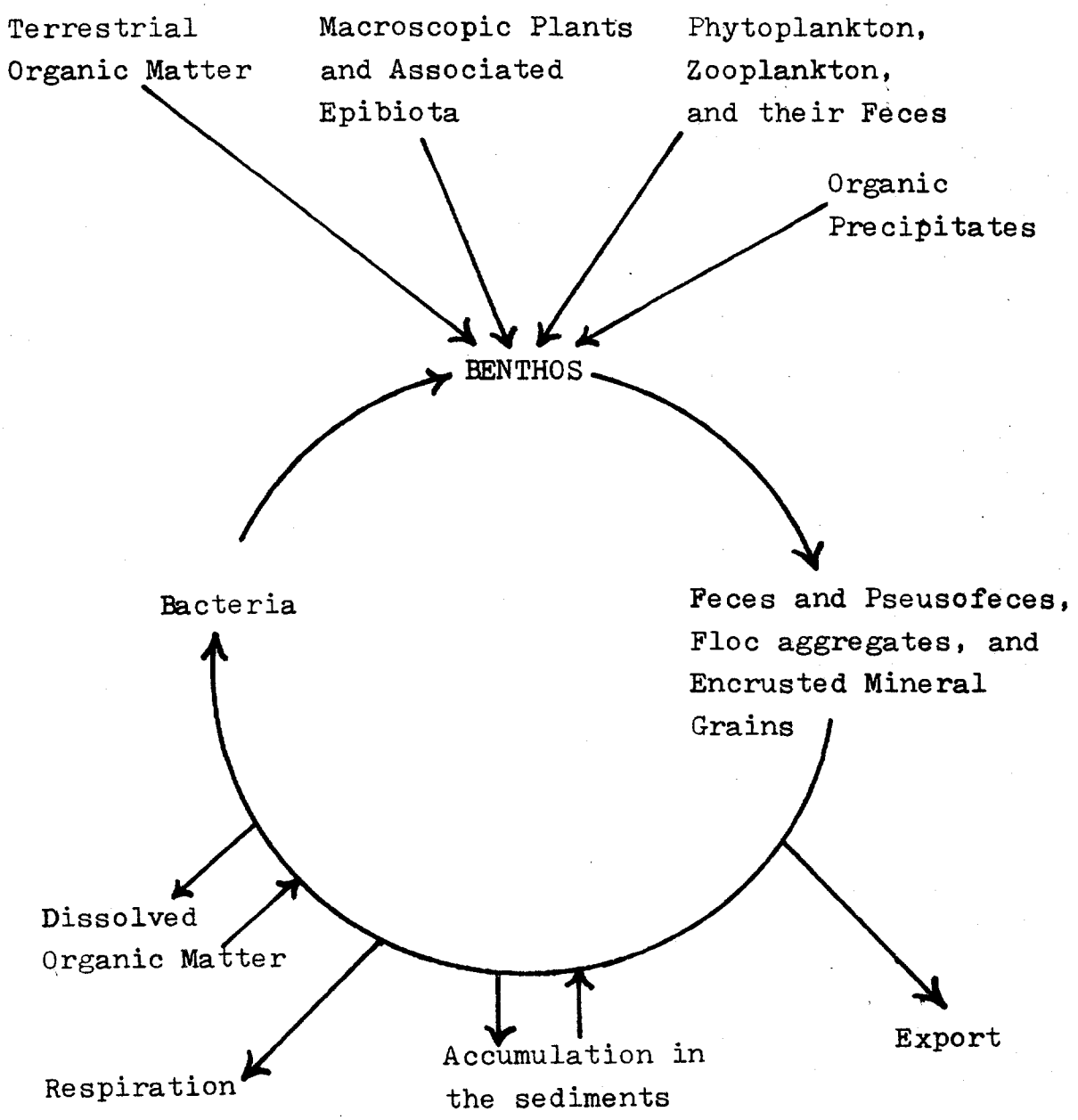
Reduction - reductions may occur through normal metabolic pathways, with reduced elements acting as electron receptors, or they may occur due to modifications in the environment produced by microbial activities such as the consumption of oxygen and the lowering of the Eh associated with the accumulation of reduced products, or the formation of acids.

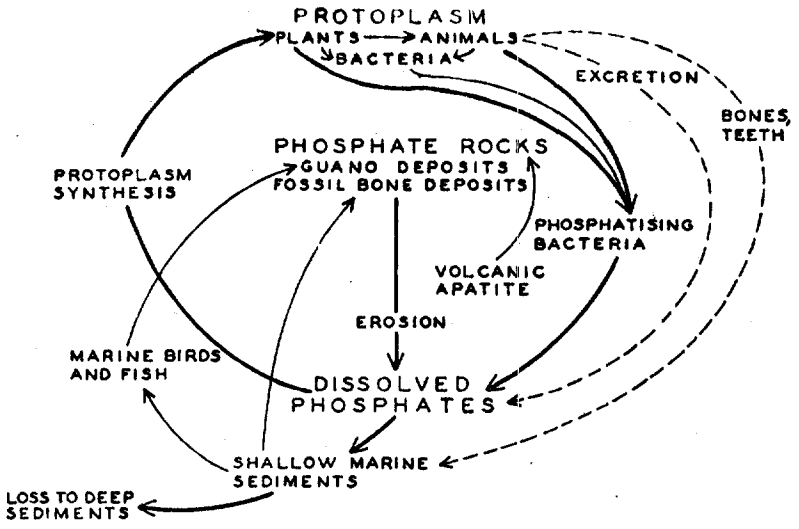
Fixation - the conversion of a gaseous form of an element into a non-gaseous compound.

Volitilization - the opposite of fixation, in which gaseous compounds are formed from non gaseous substances.

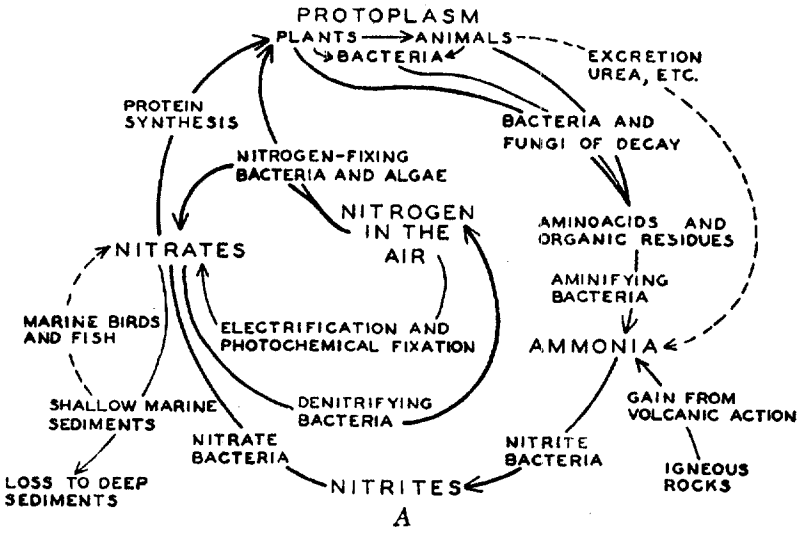
Solubilization - microbes produce organic chelating or complexing

Figure 1. The cycling of organic matter in the benthos. (After Johnson 1974.)





THE PHOSPHORUS CYCLE

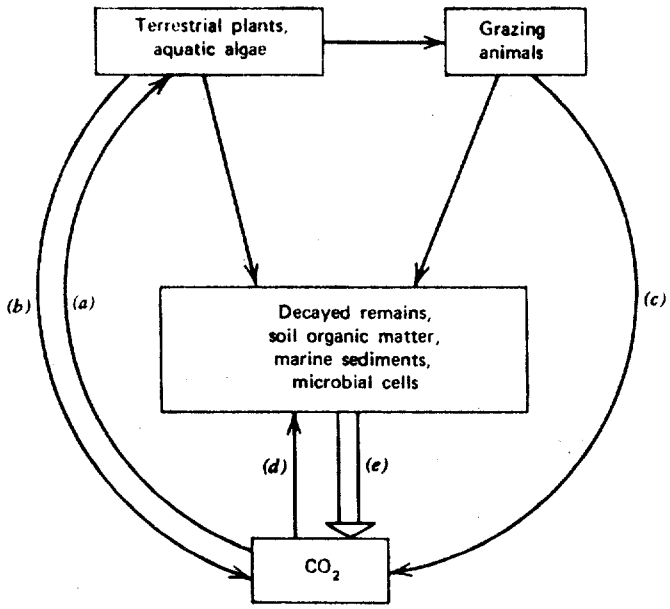


A

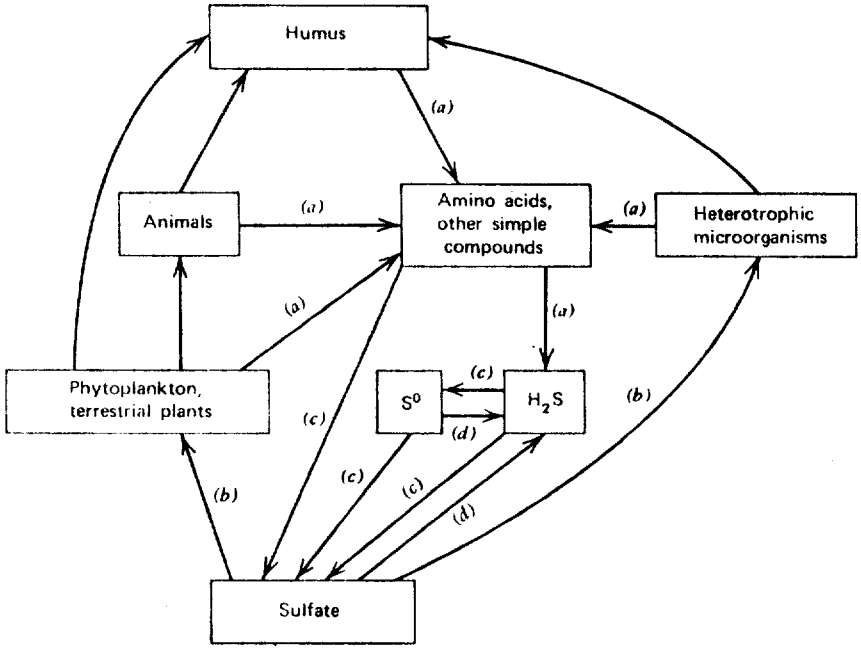
THE NITROGEN CYCLE

(After Odum 1971)

Figure 2.



THE CARBON CYCLE: a) Photosynthesis; b) respiration by plants; c) animal respiration; d) CO_2 fixation; e) mineralization.



THE SULFUR CYCLE: a) Mineralization; b) immobilization; c) oxidation; d) reduction. (After Alexander 1971)

Figure 3.

agents that solubilize relatively insoluble inorganic substances or maintain various compounds in soluble form.

Precipitation - microbes may serve as foci for adsorbtion of inorganic substances. The accumulation may be either active or passive on the part of the organism.

Another process of biogeochemical interest is that of isotope fractionization, in which certain isotopes of an element are selected in preference to other available isotopes by certain discriminating organisms. This means that the microbial product containing the element will have a different isotope ratio than the surrounding environment, and makes it possible to trace the origin of certain deposits. These processes and the major elements affected by them are summarized in Table 1, taken from Alexander (1971). Through these various activities, microorganisms often break bottlenecks which exist in food chains and biogeochemical cycles of macroecosystems (Brock 1966). Carbonaceous compounds are probably acted on first, followed by those of nitrogen and then those of phosphorus (Nelson 1972). This means that of these three elements, compounds of phosphorus can be expected to be mobilized last.

The importance of the major nutrients (carbon, nitrogen, phosphorus, and sulfur) in the ecosystem can be seen by the fact that the complete absence of any one of them would make life impossible. The most important factors limiting production are the inorganic nutrients, particularly nitrogen and phosphorus (Brock 1966). If the cycling of any nutrient is disturbed at any point, drastic changes in the biological and physio-chemical structure of the environment will result. Sediments are known to contain the major fractions of contaminants as well as nutrients in the aquatic environments. While sediments do serve as nutrient sinks, it is the fact that there is a dynamic interchange between the sediments and the aqueous environment that makes the assessment of nutrient concentrations valuable (Soule and Oguri 1974).

TABLE 1

Transformation Processes and the Elements Metabolized by Microorganisms (Alexander 1971)

Mineralization	C, N, P, S, K, Si, Fe, etc.
Immobilization	C, N, P, S, K, Si, Fe, etc.
Oxidation	C, N, P, S, H, Fe, Mn, As, Se
Reduction	C, N, P, S, Fe, Mn, Cl
Solubilization	P, S, Fe, K, Ca, Si, Mn, Mg, Al, Cu, Zn, Co
Precipitation	Se, Fe, Ca, Mg, Mn
Fixation	C, N, H, O
Volatilization	C, N, S, H, O, Se

B. Carbon

Carbon is the building block of all organic molecules, and the carbon compounds found in the sediments are extremely varied. The relationship of the oxidation and anaerobic decomposition of carbon to the Eh has already been mentioned. Organic detritus and light are the two sources of energy important to the sedimentary ecosystem. On the average, the organic content of the sediments is but a small part of the total composition, and yet it may be one of its most important physical, chemical, and biological properties (Johnson 1974). Organic molecules may be the crucial factors controlling the fate of trace contaminants in the sediments (Soule and Oguri 1974). The organic carbon content of the sediment may be used as a measure of the amount of food available to deposit feeders. Using a linear regression analysis, Thomas (1974) found a significant correlation between the number of deposit feeders and the organic carbon content at sites in the northern Indian River.

Carbon can enter the benthic ecosystem from several sources. Rainfall brings carbon as bicarbonate, compounds can leach from rocks and surrounding soils, and CO_2 diffuses into the water from the air. Terrestrial runoff and leaf litter from shoreline emergent vegetation (e.g., Rhizophora mangle - red mangrove) are the major contributors of organic carbon to the lagoons under study, while a smaller amount is supplied by domestic sewage plants. Organic substances in the sediments include aminoacids, carbohydrates, polysaccharides, lipids, browning reaction products, hydrocarbons, pesticides, and many others (Soule and Oguri 1974). Synthetic pollutants and spilled oil are also present.

Total organic carbon was measured and reported in this study. Unfortunately, the conventional methods of reporting carbon as a per cent of dry weight is misleading. As compared to the weight of the inorganic particles, the organic material seems to be an insignificant component. Johnson (1974) suggests that most of the organic particles encountered by benthic organisms are potential food particles of a diverse nature. These particles taken together provide an enormous surface area for micro-organisms. It seems probable, also, that these particles have different sedimentological properties (Johnson 1974). The mineral particles in the sediment are embedded in a loosely woven but continuous organic matrix.

Conventional methods ofgrain size analysis destroy this matrix and thereby create artifactual conditions (Johnson 1974). Thus, while bulk analysis may reveal only a small percentage of organic matter, that may be one of its most important geological as well as biological properties.

C. Phosphorus

The mobilization of phosphorus and nitrogen is of great interest in aquatic systems due to its relationship to eutrophication. While phosphorus is often reported to be the major limiting nutrient in aqueous environments, it does not appear to be limiting in the Kennedy Space Center area, possibly due to the input of phosphates from the sewage outfalls (Brock 1966). It is more likely, however, that the major input of phosphates to this lagoonal ecosystem is provided from terrestrial runoff. Sramek (1974) has shown a significant increase in the level of phosphates in Banana Creek following periods of rainfall. Of all the elements present in living organisms, phosphorus is likely to be the most important ecologically, because the ratio of phosphorus to the other elements in organisms tends to be considerably greater than the ratio of these elements in the natural environment. Phosphorus deficiency is therefore more likely to be limiting to productivity than is the deficiency of any other material except water (Hutchinson 1957).

Phosphorus occurs naturally in only two forms, either as the fully oxidized phosphate (PO_4) or as part of organic phosphate esters (Brock 1966). Pyrophosphate hydrolyzes readily to orthophosphate, and other reduced forms probably auto-oxidize, if they exist at all in nature. Phosphate exists as soluble inorganic phosphate, insoluble ferric and calcium phosphates, soluble and colloidal organic phosphate, and particulate organic phosphate (Brock 1966, Standard Methods, 13th ed.).

Ferric phosphate is very insoluble, and some phosphate may be kept out of solution this way. If H_2S is present, phosphate may be released anareobically by the formation of ferrous sulfide (FeS). Organic molecules often have reactive functional group sites that can capture PO_4 anions. In the sediments, a change in

redox conditions can free these bound phosphates from their organic and metallic cations, and in some instances, the release can be quantitative to the point where the pH drops to 5.8, buffered by acid phosphate (Wood 1967).

Plants contain organic phosphorus associated with phytins, phospholipids, nucleoproteins, and nucleic acids. Phosphate also acts as an inorganic buffer in cells and is found in food vacuoles. Phosphorus in certain organic compounds mobilizes more rapidly under alkaline conditions than acid. A lowering of the ratio of carbon to phosphorus in the environment favors the release of phosphate (Nelson 1972). Silicates, iron, and aluminum are all known to immobilize phosphate, especially under acid conditions, so it can be seen that the phosphorus budget is not determined exclusively by the organic decompositional processes. Near the sediment surface, where organic detritus is abundant, microbial demand for phosphate assimilates most of that made available by decomposition. At greater depths, after the evolution of CO_2 lowers the C:P ratio, excess phosphorus over demand appears in the pore water. Nelson (1972) reported highest phosphate concentrations at 25 cm. below the sedimentary surface in cores taken from the Rappahannock River Estuary. Microbes probably selectively decompose first carbonaceous and then nitrogenous components of the sediments in preference to phosphatic compounds with the result that the critical C:P ratio that mobilizes PO_4 is achieved more slowly than the critical C:N ratio that mobilizes ammonia (Nelson 1966).

D. Nitrogen

Nitrogen complements phosphorus as the major nutrient most likely to be limiting in aqueous environments, and past research has shown that the area around the Kennedy Space Center is limited by nitrogen (J.A. Lasater, personal communication). An established method of measuring the fertility of water has been the measurement of nitrate therein, on the assumption that this was the main source of nitrogen used by the phytoplankton. It is now known that many organisms (microbes) use ammonia or organic nitrogen sources directly, and that a number of them can fix nitrogen (Wood 1967). Nitrate content of the water may therefore indicate the presence or absence of organisms that use oxidized nitrogen sources, rather than fertility.

Nitrogen is found in the environment as a free gas (N_2), as nitrate (NO_3), nitrite (NO_2), ammonia (NH_3) and as organically bound nitrogen. Nitrate and ammonia enter the aqueous ecosystem through rainfall, and terrestrial runoff also provides nitrogenous compounds. The nitrogen transformations of most interest in aquatic environments are those of nitrogen fixation and denitrification, processes which oppose one another. Protein decomposition releases ammonia by deamination, and the remaining protein residue is attacked further which produces CO_2. Under anaerobic conditions, the end products of this process include NH_3, CO_2, and organic compounds such as amines and organic acids. The nitrogen budget must be interpreted in terms of the ammonia mobilized (Nelson 1972). Ammonia accumulation represents excess substrate nitrogen over the amount required by microbial demand. Since the microbes are known to prefer to mineralize the carbohydrate fraction before the protein fraction, CO_2 is evolved and volatilized while microbial demand utilizes the available nitrogen until the C:N ratio drops to a favorable level. Once the critical ratio is attained, excess nitrogen becomes available as ammonia (Nelson 1972).

E. Sulfur

While sulfur only rarely acts as an element limiting productivity or biological development under natural conditions, the toxicity of some sulfur compounds (especially H_2S and H_2SO_4) are of ecological significance. Sulfur has a large number of oxidation states, and is important geochemically as well as biologically. But the most important relationship concerning sulfur and the environment is that established by the cycling of sulfur through the sediments, a process of such great significance that some believe that the sulfur cycle is the singly most important phenomenon taking place in the sedimentary environment (Wood 1965, Fenchel 1969).

The concentration of sulfate (SO_4) is fairly high in sea water, and sulfate is second only to bicarbonate as the most common ion in rain water. Primary producers can use sulfate as a sulfur source, reducing it to the -II oxidation level (Brock 1966). Many decomposing bacteria are able to liberate H_2S from sulfur

containing amino acids, and this is a major source of H_2S in aerobic environments.

Four types of reaction sequences are prominent in the sulfur cycle: mineralization of organic sulfur containing compounds, assimilation of inorganic sulfur compounds and their incorporation into protoplasm, oxidation of the sulfur in amino acids and inorganic compounds, and of most significance here, the reduction of elemental sulfur and sulfate to sulfide (Alexander 1971).

The sulfur oxidizing bacteria such as Thiobacillus and the purple and green sulfur bacteria are found at or near the sediment surface. Below these lie the sulfur reducing bacteria, most notably the Desulfovibrio, a genus of anaerobic bacteria using sulfate as their terminal electron acceptor and thereby producing large quantities of H_2S. There is sufficient sulfate in sea water to allow for a substantial reduction, provided that there is sufficient saprotrophic digestion of organic matter to reduce the redox potential of the sea water system (pH of about 8.3) about +100 mv (Wood 1967). At this point the reduction of sulfate and/or extensive anaerobic digestion can further reduce the environment to about -300 mv. This low potential is limiting to some organisms and favorable to others. Where the reduction of sulfates is high, the phosphate content of the sediment will be low due to the release of phosphoric acid through the action of H_2S and the consequent precipitation of the iron cations (as sulfides) that formerly bound the phosphate. The redox potential, primarily under the control of the sulfur cycle, also affects the carbon cycle since the adsorbtion of organic material on inorganic particles is affected by redox conditions (Wood 1967). Thus the biogeochemistry of the sulfur cycle is unique because, in addition to the transformations expected of any element that enters into cell structure, the conversions undergone in the cycling of sulfur affect the behavior and reactions of the other elements.

It should be apparent from the foregoing discussion that the chemistry of the sediments cannot be totally understood without examining the microbiological communities as well. For details on the specific microbiology of the Kennedy Space Center lagoons, refer to the work of Beazley (1973), Noble (in press), Blevins (1974) and Beazley, Nevin, and Lasater (1974).

III. DESCRIPTION OF THE STUDY AREA

The Kennedy Space Center, located in Florida's central East Coast (Figure 4) is surrounded by three separate lagoons (Figure 5). Brown (1962) classifies this area of Brevard County as humid subtropical with normal monthly temperatures of about 17°C in January and 28°C in August, with the average at about 22.5°C. Annual rainfall in this area averages to about 50 inches (127 cm), with most of the precipitation resulting from thundershower activity commonly occuring from May through October. The water in these lagoons is polyhaline, having an average salinity of 27.8 % (standard deviation = 3.78). The sediments are primarily fine sands with varying amounts of shell debris and little or no silts or clays. "Cultural" inputs to the water and the sediments are supplied from sewage treatment plants, industrial wastes, boating, and other recreational activity. The most prominent man-made perturbation of the sedimentary environment has been the dredging of a 100 foot (30 m) wide, 12 foot (3.6 m) deep navigational channel which is part of the Intracoastal Waterway.

To the west of KSC complex lies the northern portion of the Indian River, which is bounded on the east by Merritt Island and on the west by the Florida mainland. The southernmost boundary of the Indian River study area is the NASA causeway, which runs east to west at approximately 28°32' N. latitude, and the northern end of the Indian River ends at approximately 28°49' N. latitude, at the lower end of the Turnbull Creek. The second lagoon, now known as the Indian River Lagoon (formerly and aptly known as Mosquito Lagoon) is bounded on the east by the beach barrier islands and on the west by Merritt Island. It extends approximately from southeast to northwest from 28° 40' to 29° 05' N. latitude, where there is a connection to the sea at Ponce de Leon Inlet. The Indian River and the Indian River (Mosquito) Lagoon are connected via Haulover Canal at 28° 05' (part of the Intracoastal Waterway) and the area of the Indian River Lagoon investigated here roughly brackets this canal, extending from 28°45' to 28°41'. The third lagoon under study is that of the northern portion of the Banana River, which connects with the ocean through the Canaveral locks. This lagoon is bounded on the east by the Cape Canaveral peninsula, and on the west by Merritt Island. The portion of the Banana River sampled in this study lies just south of the Nasa Parkway East Causeway, at approximately 28°29' N. latitude. Currents in the lagoons are determined primarily by wind direction and velocity (Dill 1974).

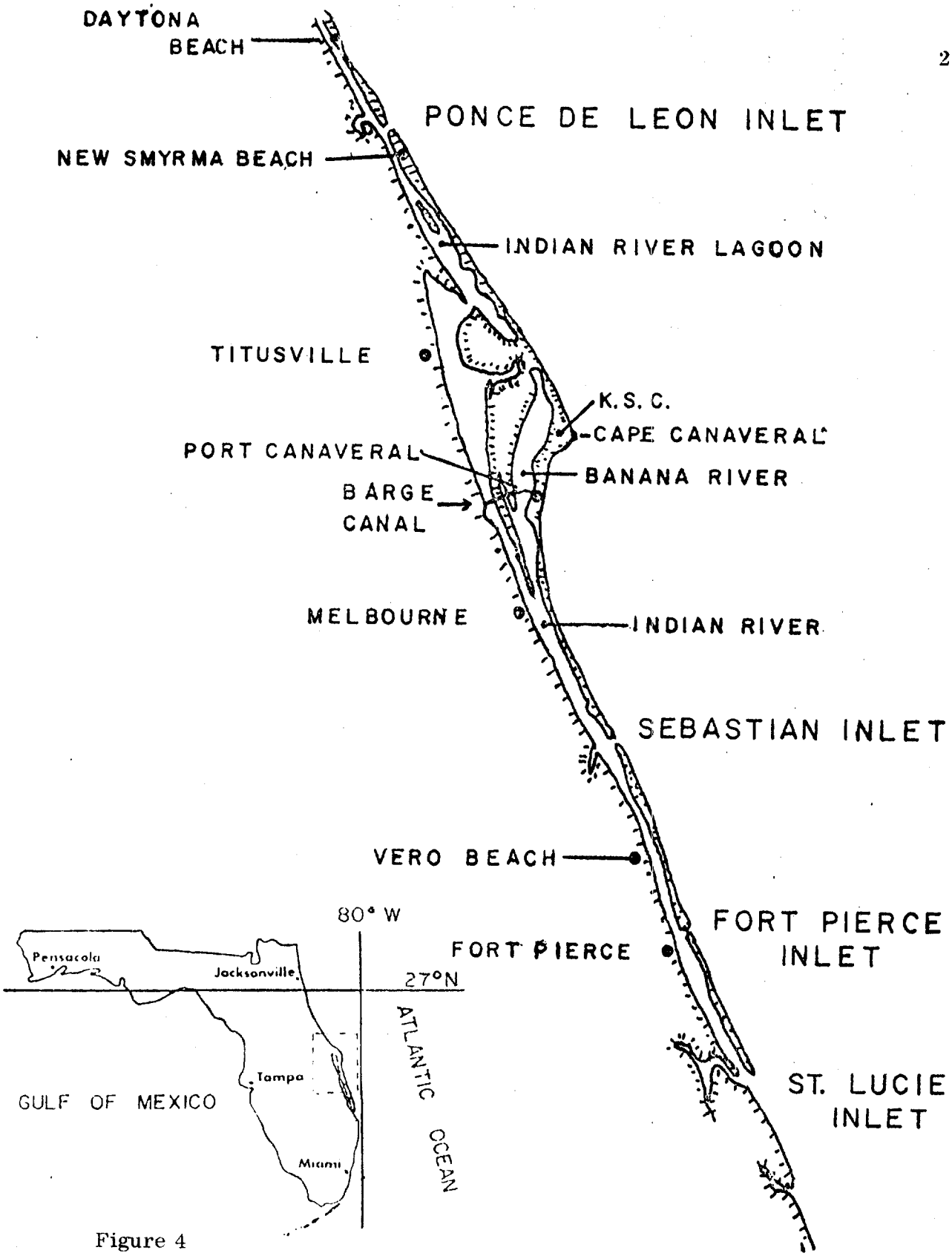
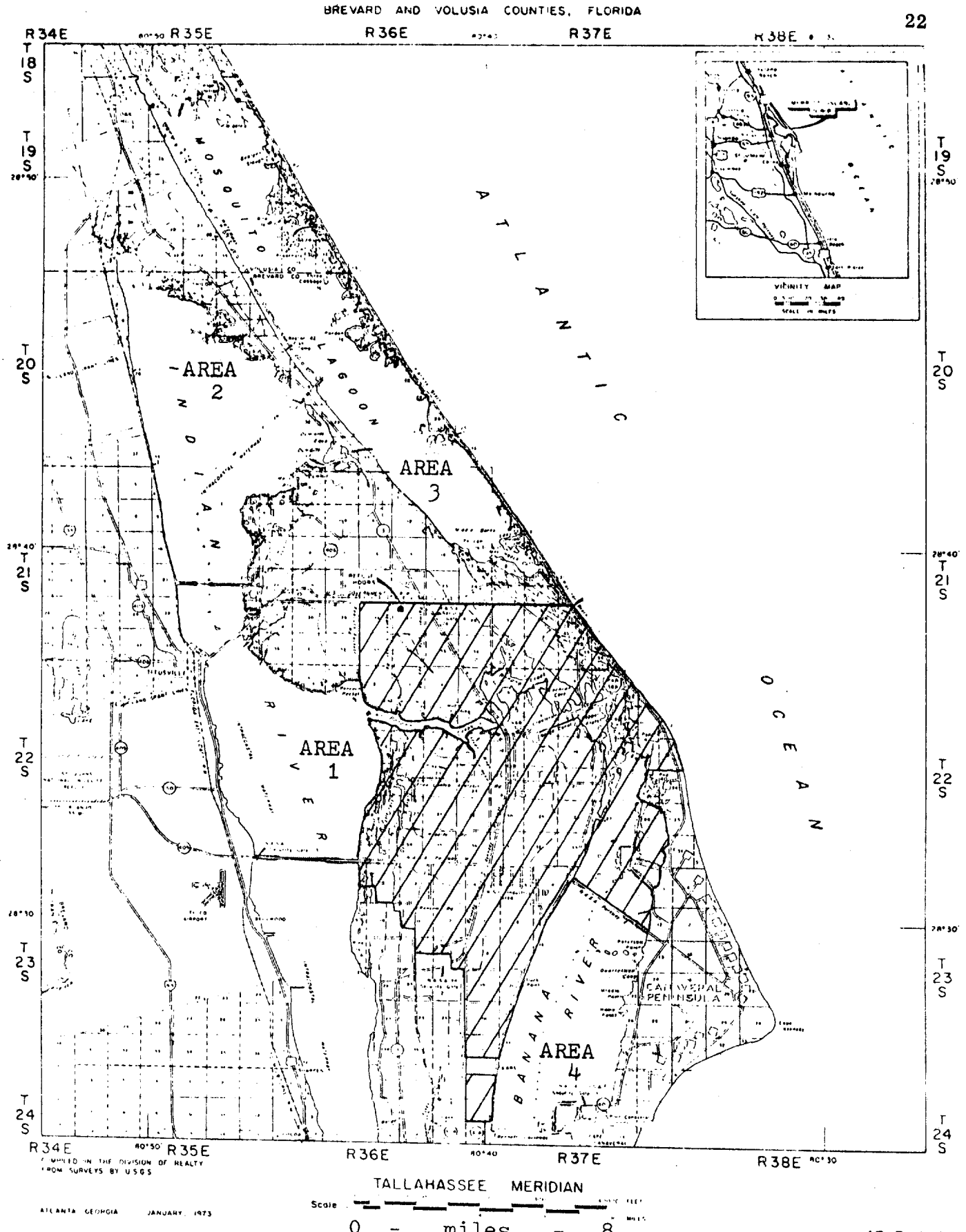


Figure 4

LAGOONS OF EAST CENTRAL FLORIDA

Figure 4.



4R-FLA-632-413

Figure 5. Area around the Kennedy Space Center.

In the initial stages of the research effort conducted for NASA by F.I.T., a sampling site network was established using the National Fish and Wildlife service chart no. 4R-FLA-632-406. The network was established by drawing a grid of lines at intervals of one minute of latitude and longitude, which provided each sample site with a unique geographical address that could be simply stated and easily re-created (M.R. Carey 1973). For convenience, the three lagoons were divided into four sampling areas; the Indian River was divided into two areas by the Titusville causeway, with the water to the south designated as Area 1, and the water to the north as Area 2. The Indian River Lagoon is known as Area 3, and the Banana River as Area 4. All sites carry a prefix numeral designating the area in which the site is located, and a suffix numeral designating the specific site, with the smaller numbers in the southern end of the area. For example, site 1-2 is located in the southern end of Area 1.

Twenty-six sites representing a variety of conditions were employed in this study of the sedimentary chemistry, and twenty-two of these corresponded with previously established sampling locations. This made it possible to correlate the new data with many months of observations of the water chemistry, and in some instances, the biology and geology of the area. In addition to these, four special sites were established, each located within ten meters of past or presently operating sewage treatment plant outfalls. These special sites are designated by a letter S following the numbers of the nearest previously established site, e.g. site 2-1 S. is at the point of effluent emission of the Titusville North sewage treatment plant which lies adjacent to site 2-1.

The sites selected for study fall into four major catagories. Sites 1-11, 1-15, 1-23, 1-26, 2-1, 2-2, 4-12, and 4-16 were chosen because of their proximity to the discharge pipes of the four treatment plants in the area. Sites 2-17, 2-9, 2-24, 3-12, and 1-6 (in addition to some of the sites previously mentioned) were selected for their close proximity to the Intracoastal Waterway. Sites 1-2, 1-8, 1-19, 2-30, 3-3, 3-7, 3-9, and 4-18 were selected because they are in rather remote areas and might give a picture of what "natural" conditions are like. Finally, certain sites, (including some mentioned) were selected for individually specific reasons. Sites 1-20 and 1-19 were chosen because this area had been previously shown to be one of high biological activity. Site 1-26, downstream in Banana Creek from the discharge site of a now inactive treatment plant, was selected because of a high bacteria count that had been observed there during the

summer of 1972. Sites 1-23, 2-2, 2-24, and 4-16 are all in an area of reduced water circulation due to the construction of causeways. Although this non-random method of choosing sample sites will not give the "average picture" of the area the way a random sampling procedure would, it will provide specific information about certain aspects of man's impact on the lagoonal sediments, and this is the primary research objective.

Samples were taken during the first five months of 1975, and each site was sampled only once. This implies that the results obtained may not be representative of the year-round physiochemical structure of the sediments; however, since the characteristics of sediments are longer lived than those of the water column, it is felt that the results are useful in assessing "baseline" conditions.

IV. SAMPLING TECHNIQUE

With the exception of three shallow water sites, all cores were taken from the side of a sixteen foot aluminum boat. Sample site location was determined by the use of a hand held compass using fixed points on the shoreline to help determine reference bearings. On arriving at a station, three anchors were deployed in a triangular pattern so as to minimize wind driftage. This was important, as a total of four cores were taken at most sites and it was desirable to have them in as close proximity as possible. The nature of the bottom in these lagoons, especially at depths of less than one meter, is often very patchy (visual observation) with areas of clean sand lying between areas of marine grasses (chiefly Diplanthera and Cymodoceum). Hence a small amount of drifting could place the boat over a somewhat different sedimentary substrate.

After securing the anchors, a water sample was taken close to the sediment surface for later testing of pH and salinity. The temperature and dissolved oxygen content of the water just above the surface were measured with a YSI Model 45 Dissolved Oxygen meter and recorded. Three cores were then taken for Mendelsohn's analysis using 2" PVC pipes approximately 30 cm. long and a T-type coring handle which has been employed by F.I.T. in previous sediment surveys. These were capped and taped for transport back to the laboratory. Finally, sediments for nutrient analysis were collected in a 30 cm., 2" diameter PVC pipe that had been cut in half lengthwise. The two halves were held together for coring by the core handle above and a hose clamp below. This arrangement was designed for the purpose of taking samples in the field directly from the corer and placing them in jars containing the appropriate preservative. Once the core was on board the boat, the hose clamp was removed and the corer extracted from the handle. Whatever water was collected in the corer above the sediment was allowed to slowly drain out the two slits along the side of the core tube, allowing suspended matter to settle onto the sediment's surface. The alternative method, that of pouring off the top portion of the water, was felt by this investigator to be unsuitable for surface sediment analysis, as it was impossible to avoid pouring off some of the sediment with the water. After the water was drained, a knife was inserted through the slits in the PVC pipe and pulled down through the

sediment, dividing it neatly into two halves. These were separated, and the Eh of the sediment was measured immediately using an Orion Model 404 Research Ionanalyzer. Finally, the top four cm. of sediment was removed and evenly divided into four separate containers, one each for carbon, phosphorus, nitrogen, and sulfide analysis. These were then placed in an ice chest until they could be frozen in the laboratory's freezer.

Four sites were sampled during each of six sampling trips. On one occasion (sites 2-2 and 2-1S), rough water and a balky motor made it necessary to limit sampling to only two sites.

V. LABORATORY PROCEDURES

The optimal method for analyzing nutrient concentrations in the sediments is to run all analyses immediately after sampling. Time and manpower considerations made this procedure impossible, so it was necessary to add preservatives to the samples to be analyzed for nitrogen, phosphorus, and sulfides (see Table 2). All preservatives were added to the sample containers in the laboratory prior to collection, and in the case of nitrogen and phosphorus, the sample containers were weighed before and after sample collection. This was made necessary by the fact that wet samples were used in the phosphorus and nitrogen tests, and certain corrections had to be made which required accurate knowledge of exactly how much sediment had been collected. (For a detailed description of the corrections and calculations used in this procedure, see Appendix A.) The samples were placed in an ice chest immediately after collection in order to slow biological activity as much as possible, and then placed in a freezer in the laboratory. They remained in the freezer at -1 to -5^{o}C until immediately prior to testing. Phosphate and nitrate tests were run immediately after thawing, while carbon and sulfide tests were conducted on sediments oven dried at 105^{o} C.

Table 2 gives a summary of the nutrient species analyzed, the preservatives used, and the laboratory technique employed for analysis.

A. Nitrogen Analysis

The nitrogen compounds studied in this report are those of ammonia and organic nitrogen. Nitrate nitrogen, originally proposed for study, was not found in the sediments tested in measurable quantities. This finding has been corroborated elsewhere (K.B. Clark, personal communication).

Nitrate begins to become unstable at a redox potential of about +220 mv (Willrich and Smith 1970), so it is not surprising to find no measurable quantities of nitrate in the sediments collected in this study, as field measurements showed all Eh values to be negative.

TABLE 2

Summary of Nutrient Species Analyzed,

Preservatives Used, and Laboratory Analysis Employed

Nutrient Species	Preservative Used	Lab Procedure Used
NH_3	Dilute H_2SO_4 (.8 ml conc. H_2SO_4 / liter)	Semi-micro Kjeldahl Hengar Co. Procedure adapted from Standard Methods
N-org	Dilute H_2SO_4 (.8 ml conc. H_2SO_4 / liter)	Semi-micro Kjeldahl Hengar Co. Procedure adapted from Standard Methods
P dissolved	HgCl Solution (40 mg HgCl/ liter)	Stannous Chloride determination (Standard Methods)
P total		Sulfuric acid - Nitric acid digestion followed by Stannous Chloride determination
Sulfides	2 N Zn Acetate solution	Titrimetric (Iodine) Method (Standard Methods) as modified by Soule and Oguri (1974)
CO_3	None	Acid attack, modified from Gross (1967) as outlined by Dagget (1973)
Organic Carbon	None	Chromic acid oxidation technique, Holme and McIntyre (1971)

The method employed for nitrogen analysis was a micro-Kjeldahl technique developed by the Hengar Company as a modification of standard Kjeldahl procedures. This method was chosen because it offered the convenience of requiring less time and fewer materials than the standard Kjeldahl procedure (Henwood and Garey, no date).

The procedure as outlined in the Hengar Co. instructions required a few modifications for sediment work. As it was desired to determine ammonia nitrogen as well as total organic nitrogen (the Hengar procedure is designed only for the latter) a preliminary ammonia distillation was designed following guidelines established in Standard Methods. Briefly stated, approximately two grams of accurately weighed wet sediment were added to a 100 ml. Hengar flask, followed by approximately 25 ml. water, two ml. of phosphate buffer solution, and two or three boiling chips. In preliminary laboratory tests, frothing of the sediment-water mixture became a serious problem, to the point where bubbles were traveling all the way from the reaction flask to the ammonia collecting flask, nullifying the results. This problem was solved by adding a small amount (approximately one g.) of pure parafin to the reaction flask.

After ammonia distillation was completed (distillation was allowed to run for one half hour, or until the upper part of the condenser leading into the collecting flask became hot - which even took longer), the digestion and final distillation procedure were performed, following established Hengar procedures with the following modifications.

The Hengar method calls for digestion with 2.5 mls. of concentrated sulphuric acid, a process that converts organic nitrogen to ammonia for collection in a final distillation. Due to the low quantities of organic nitrogen present in the sediments under study, this was reduced to two mls. A small amount of parafin was added again prior to the final distillation.

After the sediment has been digested and the organic nitrogen converted to ammonia, the solution is neutralized with sodium hydroxide (NaOH) and then distilled. In the Hengar method, this neutralization is to be brought about with the addition of three g. of NaOH. Preliminary laboratory investigations revealed, however, that this procedure was unsatisfactory. Not only did the addition of solid NaOH cause a violent reaction in the flask, but also it was found that three g.

were not sufficient to raise the pH to above seven, which was a necessary prerequisite if any ammonia was to be distilled. To overcome this difficulty, a solution of 9 N NaOH was made for purposes of neutralization. Since two mls. of concentrated sulphuric acid (36 N) were used in the digestion, approximately eight mls. of 9 N NaOH were used in neutralization. To assure that a pH change to basic conditions had occured, an indicator (phenolphthaline) was added to the solution. After successful pH adjustment was achieved, the procedure was run normally.

In both ammonia and organic nitrogen determinations, ammonia is distilled through along inverted U-shaped glass condenser (total length approximately 61 cm.) and collected in a 125 ml. flask containing 10.0 mls. of .02 N sulphuric acid. The amount of ammonia collected is determined by titrating the dilute acid to neutrality (methyl red as indicator) with .02 N NaOH. The one problem that persisted throughout the nitrogen determinations was that of bumping - the spontaneous "burst of boiling" that occurs when sediments and water are heated from below. The difficulty associated with this phenomenon lies in the fact that a bump of sufficient force could cause some of the collecting acid to be splashed out of the collecting flask, voiding the results. A number of early determinations had to be restarted because of this difficulty. The use of a 125 ml. erlenmeyer flask instead of the recommended beaker as the collecting vessel made this problem less extreme as the condenser was only slightly smaller than the opening at the top of the flask and acted as a stopper - so most of the splashing that occured as a result of bumping was contained in the flask. The heavy handed use of boiling chips was only slightly successful in reducing bumping.

All of the modifications to standard procedures listed above were shown to have no biasing effect on final results by the extensive use of "blank" determinations during testing. It is the retrospective opinion of this investigator, however, that the micro Kjeldahl technique employed here is of only marginal use in sediment analysis. The problem of bumping was never satisfactorily overcome, and many of the final results were erratic when bumping was severe. Lowering the boiling temperature had the effect of reducing the severity of bumping, but also lengthened the time required to run the experiments at least threefold. It is suggested that future sediment investigators run a comparison of time and collection

efficiency of this technique and the macro Kjeldahl as described in Standard Methods, 13th ed., prior to final technique selection.

To calculate the amount of ammonia or organic nitrogen present in the quantity of sediment analyzed, the following procedure was employed. The amount of ammonia collected in the receiving flask was determined by the mls. of .02 N NaOH required to neutralize the solution (x). Thus:

$$\frac{x \text{ mls.} \times .02 \text{ N}}{1000} = \text{equivalents of } NH_3$$

$$\text{equivalents of } NH_3 \times \text{molecular wt of } NH_3 = \text{g. of } NH_3$$

And for organic nitrogen:

$$\text{equivalents of } NH_3 \times \text{molecular wt of N} = \text{g. of N}$$

These lab results were then converted to ug/g dry sediment via the procedure outlined in Appendix A.

B. Sulfide Analysis

Sulfide concentrations were determined by an iodine titration technique as outlined in Standard Methods, 13th ed., and modified by Soule and Oguri (1974). In this procedure, sulfides are converted to hydrogen sulfide (H_2S) in a reaction flask by the addition of a strong acid (concentrated H_2SO_4). The H_2S that is given off is transported via a carrier gas (N_2) into two serially connected collection flasks containing zinc acetate. There the H_2S combines with the zinc acetate to form a precipitate. After acidification and the addition of an exact amount of iodine solution, the unreacted iodine is titrated with sodium thiosulfate ($Na_2S_2O_3$) using starch as an indicator. This procedure is straight-forward and efficient; standardization with a sulfide solution produced recoveries of >90% immediately. Sulfide content of the sediment was determined by the following formula:

$$\text{mg / kg } S^{=} = \text{ug / g } S^{=} = \frac{\text{ml Iodine - ml } Na_2S_2O_3 \times 400}{\text{g dry weight}}$$

C. Carbonate Carbon Analysis

The determination of carbonate carbon was achieved by a method described by Gross (1967). In this procedure, the sediment reacts with phosphoric acid dripped onto the sediment contained in a U-tube, and carbon dioxide (CO_2) is liberated from the carbonates by action with the acid. The CO_2 generated is carried via dry CO_2 free air through tubes containing magnesium perchlorate ($MgClO_4$) (water trap) and manganese dioxide (MnO_2) (to remove oxides of sulfur and nitrogen) and absorbed on NaOH contained in a collecting tube. The collecting tube is weighed before and after the test, to gravimetrically determine the amount of CO_2 absorbed. The weight of CO_2 collected is converted to per cent carbonate and per cent inorganic carbon by the following formulas:

$$\% \text{ Carbonate} = \frac{\text{weight } CO_2}{\text{weight sample}} \times \frac{60 \text{ gms } CO_3}{44 \text{ gms } CO_2} \times 100$$

$$\% \text{ Inorganic Carbon} = \frac{\text{weight } CO_2}{\text{weight sample}} \times \frac{12 \text{ gms C}}{44 \text{ gms } CO_2} \times 100$$

$$1 \% C_{inorg} = 10 \text{ mg/g } C_{inorg}$$

This procedure was standardized with calcium carbonate ($CaCO_3$) and recovery was found to exceed 95%.

D. Organic Carbon Analysis

The determination of organic carbon in the sediments followed the procedure outlined by Walkley and Black as presented in Holme and McIntyre (1971). This is a chromic acid oxidation technique in which the sediment sample is digested with a chromic acid-sulfuric acid mixture, and the excess of chromic acid not reduced by the organic matter is titrated with ferrous sulfate, a standard ferrous salt. A detailed description of the procedure and instructions for preparations of reagents can be found on pages 49 and 50 of Methods for the Study of

Marine Benthos, Holme and McIntyre, eds., (1971). Approximately 1.5 g. of dried, seived (425 micron mesh) sediments were used for this analysis, and organic carbon content was determined by the following formula:

$$\frac{(V_1 - V_2) \times 3}{W} = \text{mg C-org / g. dry sed. wt.}$$

where

V_1 = amount of N potassium di-chromate used;

V_2 = amount of N ferrous sulfate used;

W = weight of sample.

The number three reflects the fact that each ml. of oxidized dichromate represents three mg. of organic carbon. All values of organic carbon reported in this thesis are uncorrected values (see Discussion section).

E. Phosphorus Analysis

The analysis of phosphorus in this research followed the stannous chloride technique for measuring orthophosphate, as described in the 13th edition of Standard Methods. Soluble (dissolved and suspended) orthophosphate and total phosphorus were measured separately, the latter determination requiring a preliminary digestion with a nitric-sulfuric acid mixed reagent in order to convert the organic phosphate compounds to orthophosphate for measurement. In this determination, orthophosphate combines with ammonium molybdate to form molybdo-phosphoric acid. This complex is then organically extracted from an aqueous solution by a benzene-isobutanol solvent. After separation, the addition of methyl alcohol and sulfuric acid allows the reduction of the molybdophosphoric acid to molybdenum blue when stannous chloride is added. The molybdenum blue forms an intensely blue colored complex which can be measured colorimetrically with a Spectronic 20 colorimeter. A blank was run with each test to check for possible phosphate contamination and for use as a colorimetric standard. Standards were frequently run

to check for deviations of the calibration curve which can occur at higher concentrations. Concentrations of phosphorus were determined from a standard curve which plotted phosphate concentrations as a function of color intensity. Molybdenum blue methods for phosphate analysis are quite sensitive and are widely used in soil and sediment testing (Olsen and Dean 1965).

VI. PRESENTATION AND DISCUSSION OF DATA

Prior to discussing the results of this study in detail, it would be useful to examine and review some of the limitations of the results presented. As with any scientific research, it is desireable to gather as much data about a specific parameter as possible. A significant limitation to the results presented here may originate from the fact that each sample site was visited only once, and it was thus impossible to measure changes that might occur in a seasonal pattern. The sediments used in the nutrient analyses were taken from the same core sample, and therefore represent conditions prevailing at that one specific location. Unfortunately, however, the bottom of the lagoons studied here are quite patchy, and visual examination of some of the shallower sites revealed that even the sediment surface exhibited a "marbelized" color pattern; that is, areas of dark sediment were intermixed in areas of very clean sediment. This was especially apparent at the shallow sites when a fairly large current was in evidence. Since the results of the two investigators were to be eventually pooled, and since each would be drawing from the results of the other, the effort was made to take all cores at a site from sediments that looked representative of each particular site, and the extreme conditions were ignored. It was impossible to guage the success of this effort at the deep water sites, as the turbidity of the water generally made it difficult to see more than about a meter into the water.

One shortcoming of the sampling technique that may have had a significant effect on certain results arose from the method employed in the collection of samples for water content analysis. Water contents were determined on samples taken from cores opened in the laboratory. These cores were exposed to vibrations in transport from collecting site to the laboratory that varied from mild to extreme, creating the possibility of disturbing the water content values. The importance of accurate water content values can be appreciated by reading Appendix A concerning the calculations involved when analyses are made on wet samples. It is recommended that future researchers remove samples for water content analysis in the field.

The laboratory methods employed were generally satisfactory, with the possible exception of the micro-Kjeldahl technique. Difficulties associated with

this procedure have already been discussed. While most determinations were run in duplicate or triplicate for each site, some of the phosphate analyses, which were performed by an assistant, were run only once. This, of course, makes it impossible to judge the repeatibility of the measurement at that site. All laboratory determinations have been included in the appendix section.

The sites selected for this study were chosen to represent a wide variety of conditions in the lagoonal system. For this reason, pooling all of the results is of limited use in determining the relationships of one nutrient to the other, as different sites should be expected to have somewhat different characteristics. Therefore, sites have been pooled according to their dominant characteristics as outlined in the section on site selection (see Tables 3-7).

One final limitation must be discussed with regard to the sampling procedure. When the split core tube was opened for extraction of the sediments, a portion of the sediment was exposed to the air. Bray, et.al., (1973) report that this procedure can have the effect of decreasing the inorganic phosphate content of the sample, especially when iron is present, and the authors suggest that the sampling extraction be done in an inert atmosphere. For this reason, the figures reported for total phosphorus are probably more reliable than those given for total soluble phosphate and only total phosphate values are discussed here. Exposure to the air may also oxidize sulfides to sulfates, causing the reported sulfide results to be on the low side.

The sediments in the lagoons surrounding the Kennedy Space Center are without doubt acting as nutrient sinks with respect to the overlying body of water. The concentration of nitrogen in the organic form alone is on the order of five orders of magnitude greater than that reported in the water column as nitrate (Lasater 1974). Total phosphorus averages to six thousand times that level reported for the water column. In general, the sediments studied ranged from very clean sands with little organic material at all (such as at the south end of Area 1) to a highly enriched organic sediment as in that found at the sewage outfall in Area 4.

One finding which had been previously undiscovered in the research on these lagoons was the lower pH of the water at the sediment surface. In the past work on the water quality of these lagoons, water samples were either taken from

a pump and hose apparatus or by holding the water sample bottle under the surface in order to let it fill. In neither case was the water directly over the sediment sampled, and in some cases the deepest water collected may have been taken from as much as two feet (.6 m) above the bottom. Samples collected for this study were taken either by a messenger activated collection device lowered to just above the bottom, or by diving to the bottom and opening a collecting jar. The pH values obtained in this study are in the range of 6.5 to 6.9 for both the bottom water and the sediments, with the two correlating well. These figures contrast with the average value of eight for the pH of the overlying water mass as a whole (Lasater 1974). This discrepancy is easily explained, however, since the production of acids in the sediments, chiefly the phosphoric and sulfuric acids, will naturally lower the local pH. The pH of the water immediately above the sediments is known to be controlled by processes occuring in the sediments, so low pH values here are to be expected. These results could be easily tested in the future by deploying an immersible pH probe over the side of a boat and recording pH vs depth.

The concentration of organic carbon in the sediments is widely used as a major parameter for the evaluation of the nutrient levels present there. In a recent study by Folger (1972) in which 45 estuaries and lagoons around the United States were studied and compared for the Department of the Interior, organic carbon was in many cases the only nutrient species examined. While nitrogen levels were examined in some instances, the high degree of correlation between organic carbon and organic (Kjeldahl) nitrogen found in the present study (.97) supports the contention that organic carbon presents the best method of assessing nutrient characteristics in the sediment. (Organic carbon also had a high correlation (.97) with COD (Figure 6) and with Total Volatile Solids (.91) (Figure 7). The concentration of organic carbon in the sediments represents about half the total organic matter present there and consists of both natural plant and animal remains and of various pollutants (Folger 1972). Since the procedure for the determination of organic carbon was straightforward and the results were the most consistent of those obtained in this nutrient study, organic carbon values will provide the basic framework of this discussion section, with the other nutrients providing supplemental information where applicable. Each nutrient species will then

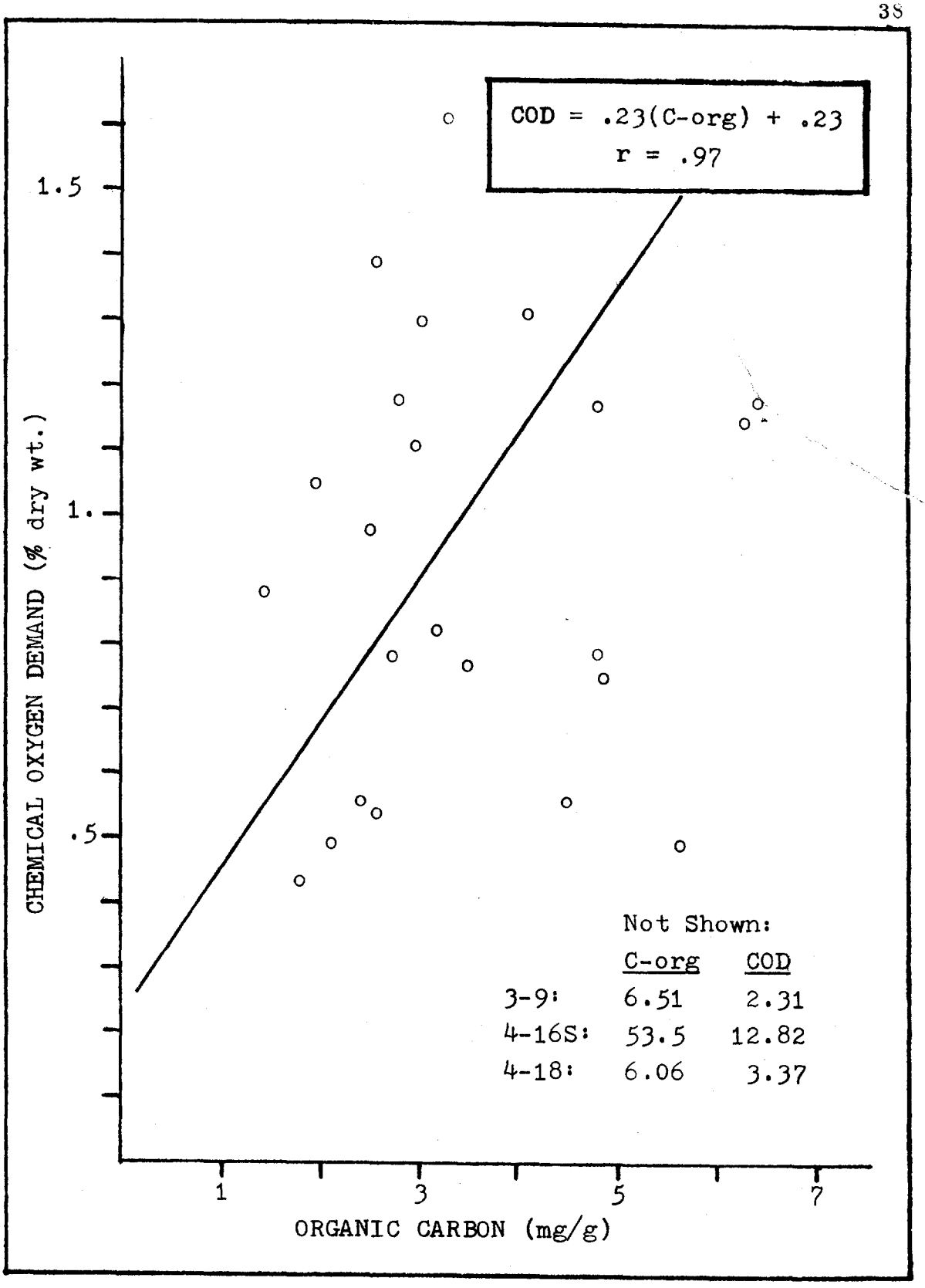


Figure 6. Organic Carbon vs Chemical Oxygen Demand.

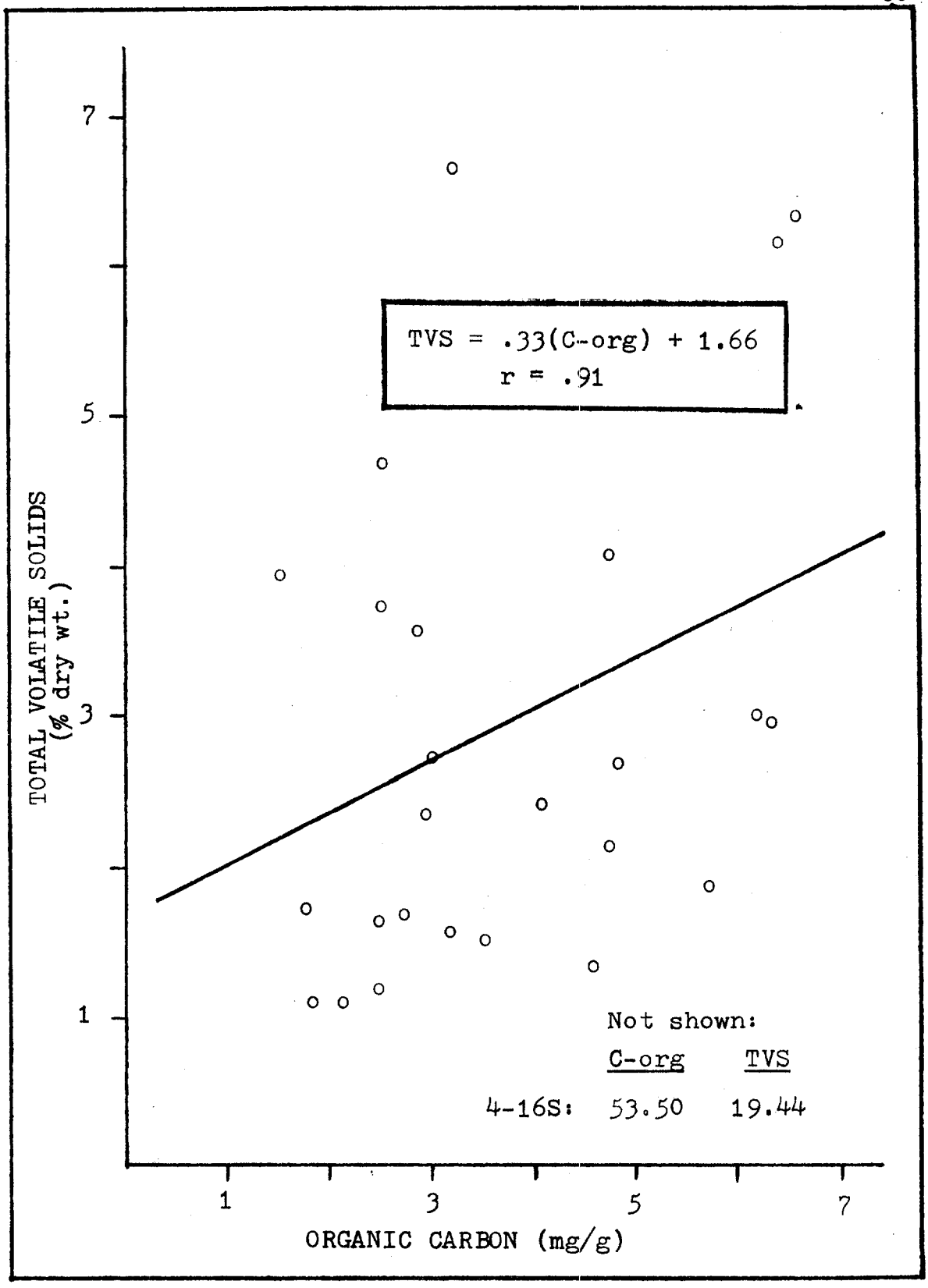


Figure 7. Organic Carbon vs Total Volatile solids.

be discussed individually with respect to high and low values and other miscellaneous findings.

One significant point should be mentioned prior to discussing the organic carbon values in detail. The figures indicated throughout this report represent uncorrected values as determined by the formula given in the section on laboratory procedures. The method used in this research was taken from Holme and McIntyre (1971) who report the technique as giving a recovery of from 75 to 90 per cent, and who do not feel that a correction factor should be used when reporting the results. Using the same technique however, Allison, in Black (1965) suggests that a correction factor of 1.3 or 1.33 be used when reporting the results. Since this discussion focuses primarily on relative rather than absolute values, the use of uncorrected results is quite sufficient, but this matter does become important when carbon-nitrogen ratios are discussed (see below).

In order to help differentiate between natural and man-made conditions in the lagoonal sediments, the sampled sites have been divided into four categories in Tables 3 - 8 according to guidelines established in the section on site selection. Since some sites represent more than one influence, some results are included in more than one category. These categories were further divided by sampling area and averages were calculated where applicable (no averages were made in the category referred to as "Other", since there was no unifying characteristic in the sites mentioned there). No table was made for soluble phosphorus (it is included in total phosphorus) or for carbonate carbon. The two outfalls in Area 1 were grouped separately, and in Area 4, averages for the outfall area were calculated with and without the value for Site 4-16S.

Mean organic carbon values are summarized in Figures 8 - 11 and Table 3. Six sites were considered representative of natural conditions in Area 1, although three of these are located in close proximity to the Intracoastal Waterway and are included in that grouping also (note that a number of sites fall into more than one category). The average value of organic carbon in these sites is 3.17 mg/g with highs of 4.81 mg/g and 4.55 mg/g found at the shallow Sites 1-26 (.75 m) and 1-8 (.5 m) respectively. The lowest values were found at the deeper Sites 1-2 (1.84 mg/g C, 1.6 m) and 1-6 (1.42 mg/g C, 2.0 m). This inverse correlation with depth is explained by the fact that high carbon values were obtained from those

TABLE 3 ORGANIC CARBON (mg/g)

SITE	DEPTH	NATURAL	WATERWAY	OUTFALL	OTHER
1-2	1.6m	1.84			1.84
1-6	2.0	1.42	1.42		
1-8	.5	4.55			
1-11	2.0		3.10	3.10	
1-11S	.5			1.97	
1-15	2.0		3.0	3.0	
1-19	1.0	3.52			3.52
1-20	1.75	2.86	2.86		
1-23	1.0				2.44
1-26	.75	4.81			
1-29S	.5			2.98*	
(MEAN)		3.17	2.60	2.69	
2-1	.5	2.11		2.11	
2-1S	.75			5.67	
2-2	1.25	6.30		6.30	
2-9	1.3	2.51	2.51		
2-17	1.75	4.04	4.04		
2-24	1.0	2.80			2.80
2-30	.5	4.78			
(MEAN)		3.77	3.27	4.69	
3-3	1.0	6.52			
3-7	1.75	2.50			
3-9	2.0	6.51			
3-12	.75	4.82	4.82		
(MEAN)		5.09			
4-12	.25	2.52		2.52	
4-16	1.25	3.08		3.08	3.08
4-16S	.25			53.5*	
4-18	.5	6.06			
(MEAN)		3.89		2.80	

* THIS SITE NOT COMPUTED IN THE MEAN FOR THIS AREA.
AVERAGE FOR BANANA CREEK (1-26 and 1-29S): 3.90mg/g
AVERAGE FOR AREA AROUND BANANA RIVER
OUTFALL INCLUDING THE VALUE AT SITE 4-16S: 19.7mg/g

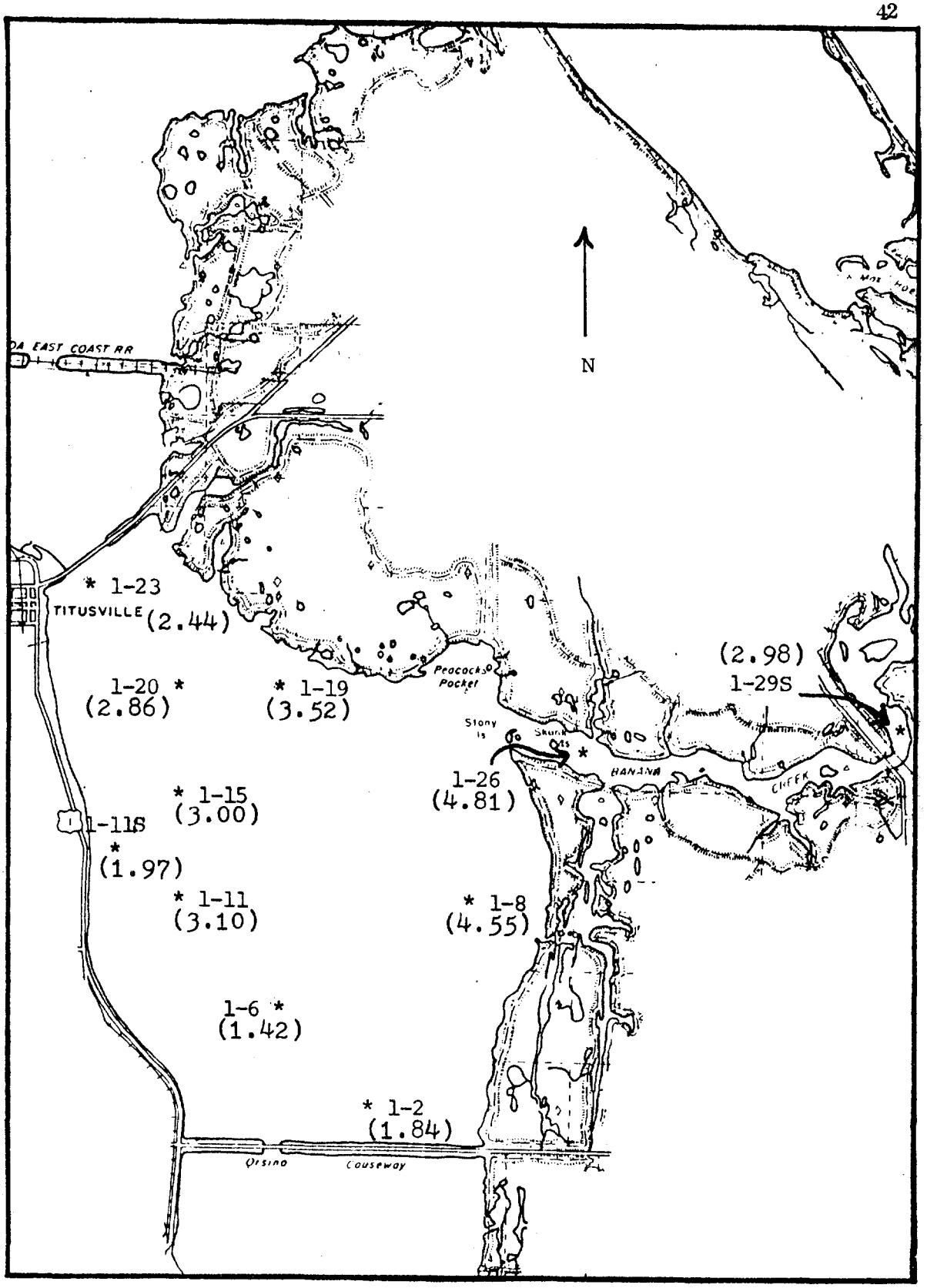


Figure 8. Organic Carbon values (mg/g) in Area 1.

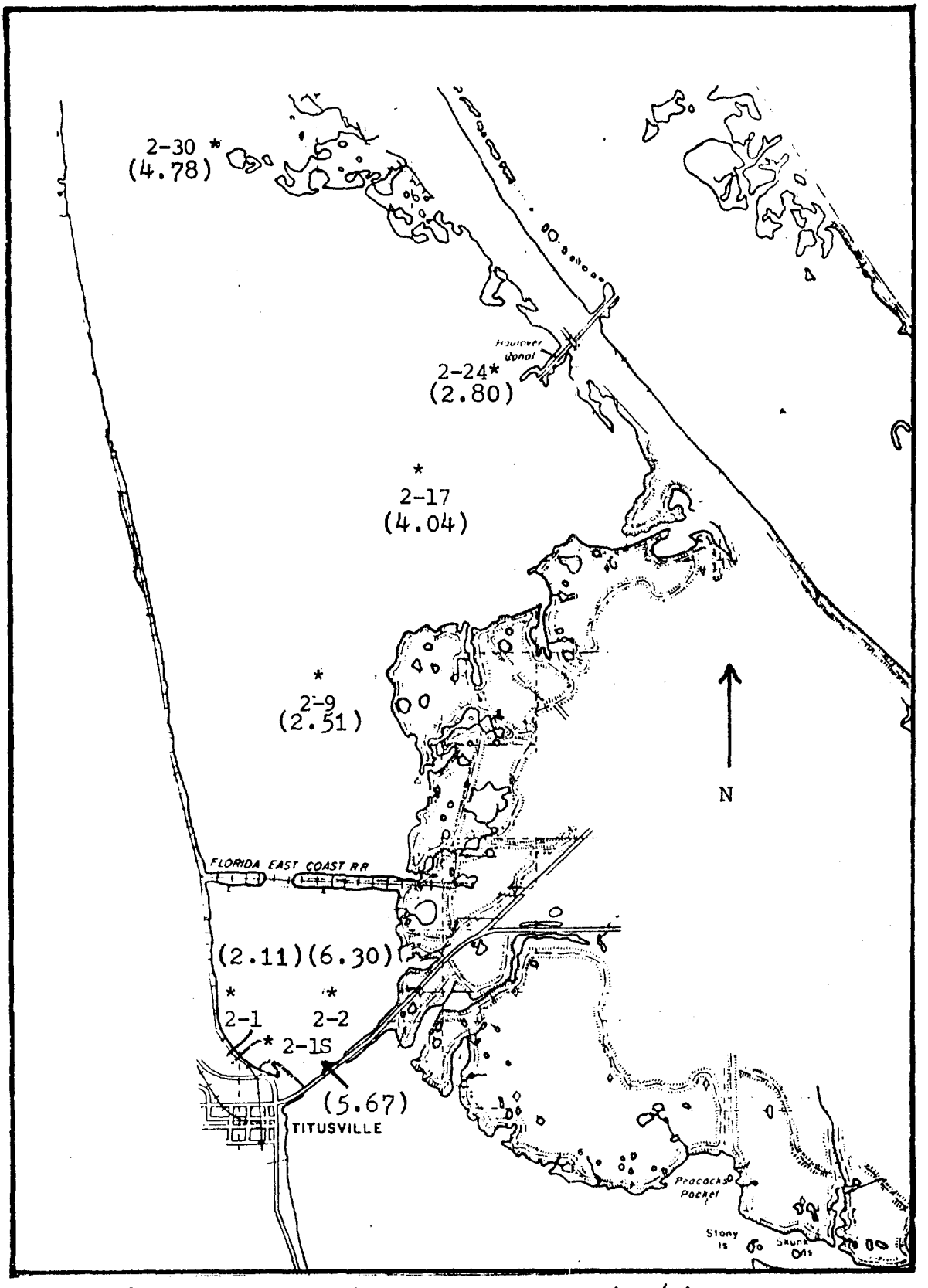


Figure 9. Organic Carbon values (mg/g) in Area 2.

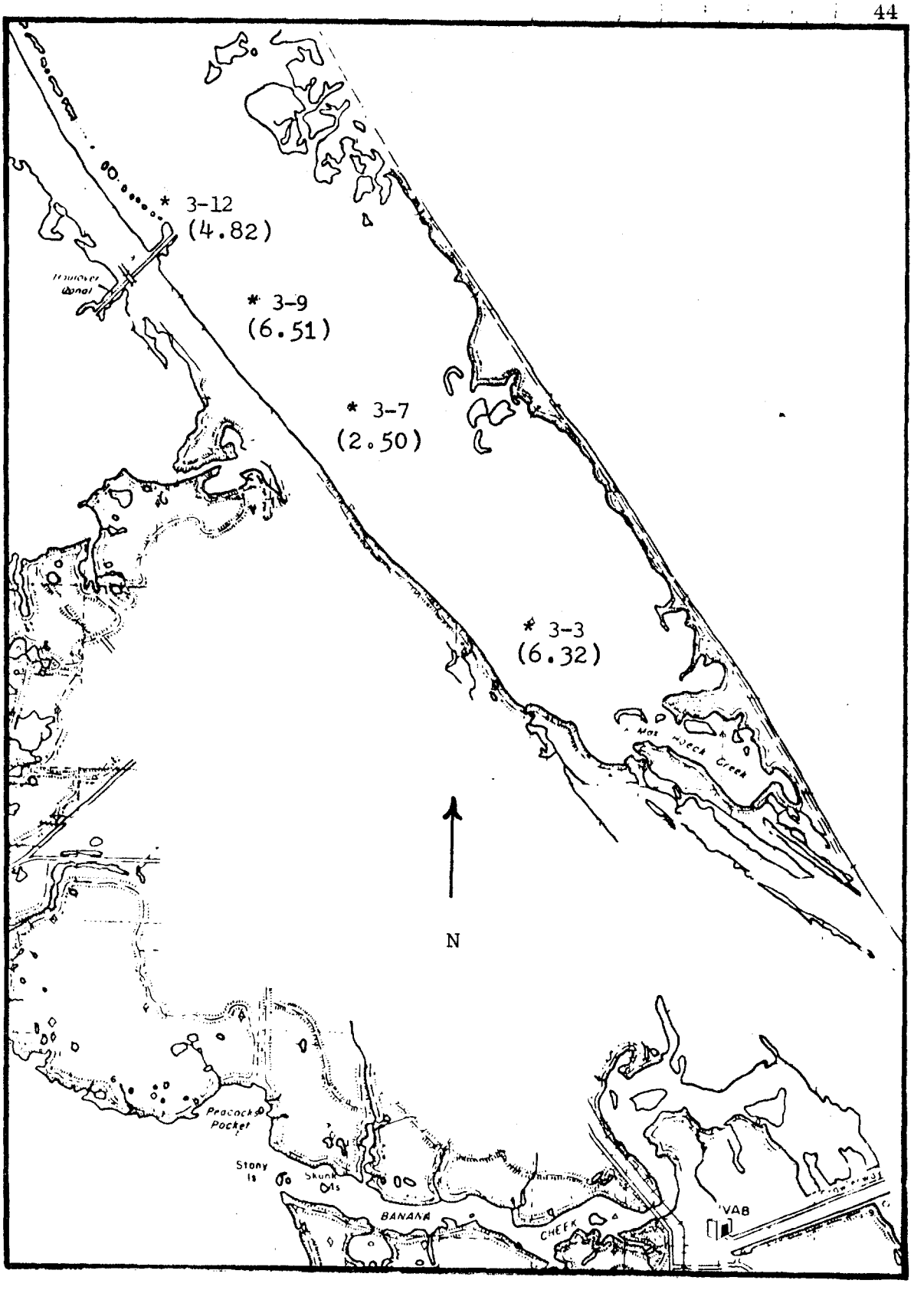


Figure 10. Organic Carbon values (mg/g) in Area 3.

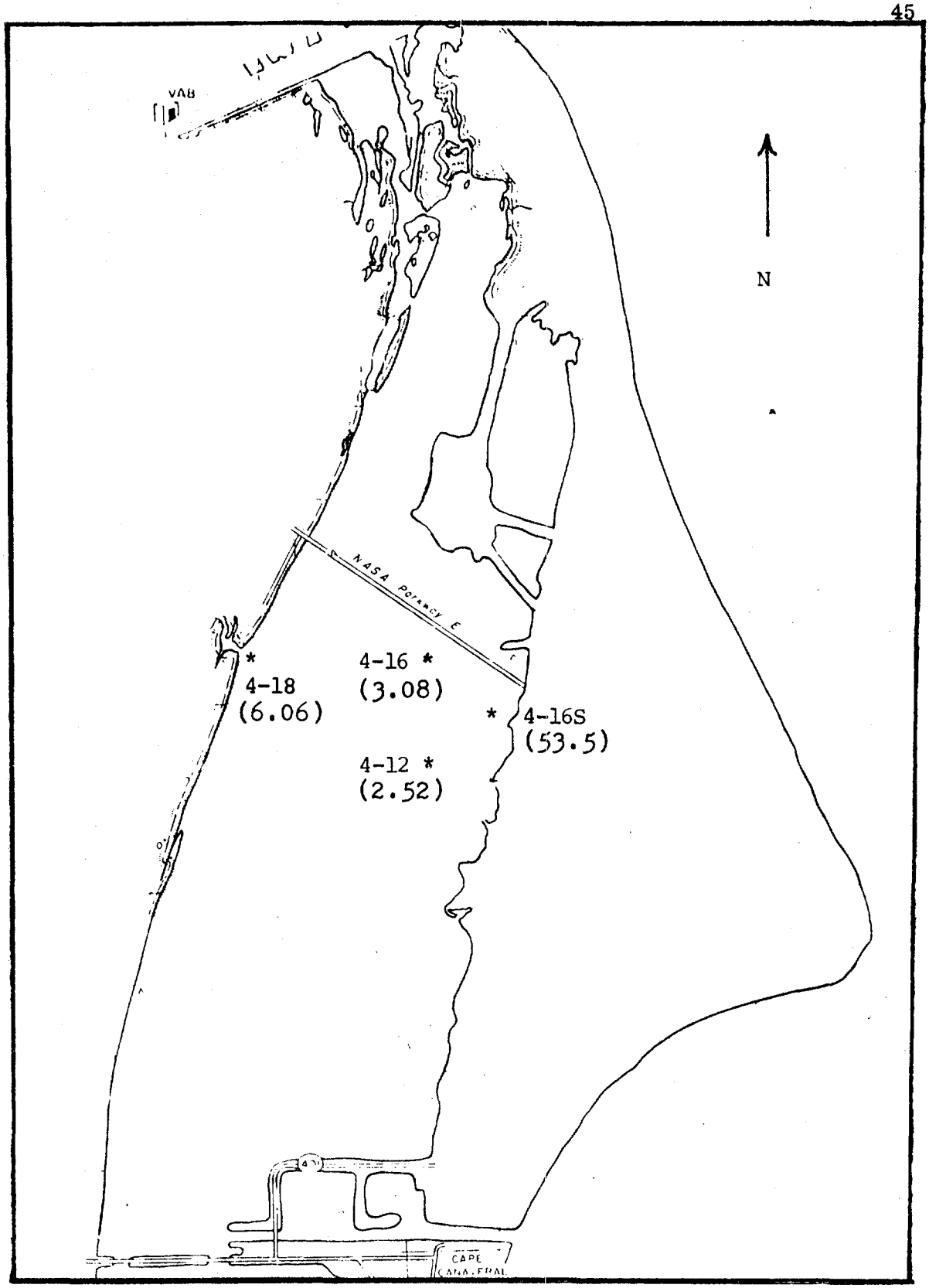


Figure 11. Organic Carbon values (mg/g) in Area 4.

shallow areas where there was extensive growth of rooted-vegatation, and thus a high level of organic detritus. Grasses are known to slow the circulation of water and allow suspended materials to settle out, while at the same time the broken and dead fragments of the grasses accumulate and are recycled through the food chain.

The sites near the Intracoastal Waterway in Area 1 have average organic carbon values of 2.60 mg/g, with a low at the south end (1-6, 1.42 mg/g) and a high near the Knox McCrae (Titusville South) treatment plant outfall (3.10 mg/g). The lower carbon values in these sites reflect their greater average depth compared to the natural areas.

The three sites used to measure the impact of the treatment plant have an average value between those of the waterway and the natural areas (2.69 mg/g), but here it is interesting to note that the depth relationship is reversed, with the shallower site (1-11S) showing lower values than the deeper values. Two factors probably account for this. Firstly, there was no evidence of rooted vegetation at 1-11S, and secondly, the turbulent boiling action resulting from the sewage plant's discharge evident in this vicinity could well have scoured the bottom clean (values for organic nitrogen and total phosphorus were also lower at 1-11S than at the two nearest sites). Another factor which may be of consequence here lies in the fact that the effluent from the treatment plant is fresh water, and therefore probably does not mix immediately with the saline waters of the lagoon. There may be a tendency for the lighter fresh water to disperse on the surface before intermixing with the river water, and suspended material may be carried some distance away from the discharge site prior to settling out.

Sites 1-26 and 1-29S, located on opposite sides of SR 3 in the Banana Creek, show the high average C-org value of 3.90 mg/g. Since the treatment plant adjacent to the VAB is now basically inactive, and since Banana Creek has been dammed midway between these sites during the construction of the Space Shuttle runway and crawlerway, this high value can be regarded as representative of the large amount of detritus present in the creek. Banana Creek has the highest shoreline to water volume ratio of all the areas studied here, and probably is the most affected by surface runoff. The averages for organic nitrogen, sulfides, and total phosphorus were higher in Banana Creek than in any other grouped category in Area 1.

In Area 2, averages for organic carbon are higher than in Area 1 in all three major categories (natural, waterway, and outfall). This may be due in part to the influence of the Titusville North treatment plant, which produces 3.5 times the effluent of its southern counterpart (the figures are 1.2 and 4.2 million gallons per day, respectively) (Mendelsohn 1975). The average for the sites in natural areas is 3.77 mg/g, while the average for the area of restricted circulation between the Titusville causeway and the railroad bridge which lies further north is 4.69 mg/g. While it is possible that the sewage effluent is having an enriching effect on the water mass and producing the concomitant proliferation of phytoplankton (which eventually find their way to the sediments), the fact that Area 3, which has no sewage input, shows an even higher average value (5.09 mg/g) leads one to suspect that the higher values in Area 2 compared with Area 1 are the result of a larger area of shallow water and a higher standing crop of biomass. The sites adjacent to the waterway in Area 2 have a C-org average of 3.27 mg/g, again reflecting lower average values with greater depth.

In Area 3, all sites can be considered natural, and the only site that is likely to be influenced by man is 3-12, which lies adjacent to the Intracoastal Waterway. The average C-org value found here was 5.09 mg/g, the highest of all four areas in the natural site category. The Indian River Lagoon (as Mosquito Lagoon is now known) is the least disturbed of all the areas studied. It is also the shallowest of the lagoons surrounding the space center, and has vast expanses of both rooted vegetation and unattached algae. A highly organic sludge has been reported near the southwestern shore here, but this was not encountered during sampling for this study. This sludge is thought to have originated from untreated sewage discharged from the houses along this shore before the Kennedy Space Center took control of the area, but this is still unconfirmed. It is not known whether this sludge deposit is influencing the C-org content of the sediments in Area 3, but the high values there are easily explained in context with the large area of grass flats. Sites 3-3 and 3-9 had the high values of 6.52 mg/g and 6.51 mg/g respectively, Site 3-12 had an intermediate 4.82 mg/g, and the low value was obtained at Site 3-7 (2.50 mg/g). The inverse correlation of organic carbon content and depth was not apparent in Area 3, and a closer examination of the proximity of the grass beds to the sampled sites would be necessary in order to explain this fact.

The sites selected in Area 4 represent a wide variety of natural conditions. The highest values for all nutrients (except ammonia) of all the sites sampled were found at the mouth of the small drainage canal that serves as the drain conduit for a sewage treatment plant. This plant serves the industrial area of the Air Force Station adjacent to the Kennedy Space Center. The carbon value measured here (53.5 mg/g) is nearly ten times the highest previously reported value. The flow from the canal is not fast, and there is no evidence of the turbulent boiling that characterizes the discharge of effluents in the Indian River plants. Furthermore, at the mouth of the canal stands a medium sized mangrove tree (Rhizophora mangle), which slows the current even more, allowing suspended materials to settle out. The net result is the deposition of a highly organic sediment, the only one that manifested a strong H_2S odor when opened in the field. Sites 4-12 and 4-16, which were the established sites closest to this outfall, did not show extraordinarily high values for C-org (2.52 mg/g and 3.08 mg/g respectively) indicating that the effect of the treatment plant was localized in the vicinity of the effluent canal. Values obtained for all other nutrients did show higher than average values for these sites, however, and when all factors are considered together, this area represented the most enriched area of all those studied in this project. On the opposite side of the Banana River is a small creek, in the mouth of which lies Site 4-18. On the day that this site was sampled, a large quantity of grass (principally Cymodoceum manatorum) was observed floating on the surface of the water there, and it appeared as if this accumulation was caused by an easterly wind, which was blowing at the time. The organic carbon value measured here was 6.06 mg/g, a relatively high value but not an unexpected one in light of the detritus that is flushed from the creek and the large amount of decomposing vegetation in the overlying water.

Organic (Kjeldahl) nitrogen had the highest correlation with organic carbon ($r = .97$) of all the nutrients measured (see Figure 12). The empirical relationship between these two nutrients was determined through a linear regression and produced the following equation:

$$\text{Organic nitrogen (ug/g)} = 256\,[\text{Organic carbon (mg/g)}] + 106$$

Since the relationship of ug/g to mg/g is 1:1000, the average carbon to nitrogen ratio for the entire lagoonal system is quite close to four (1000/256 = 3.9),

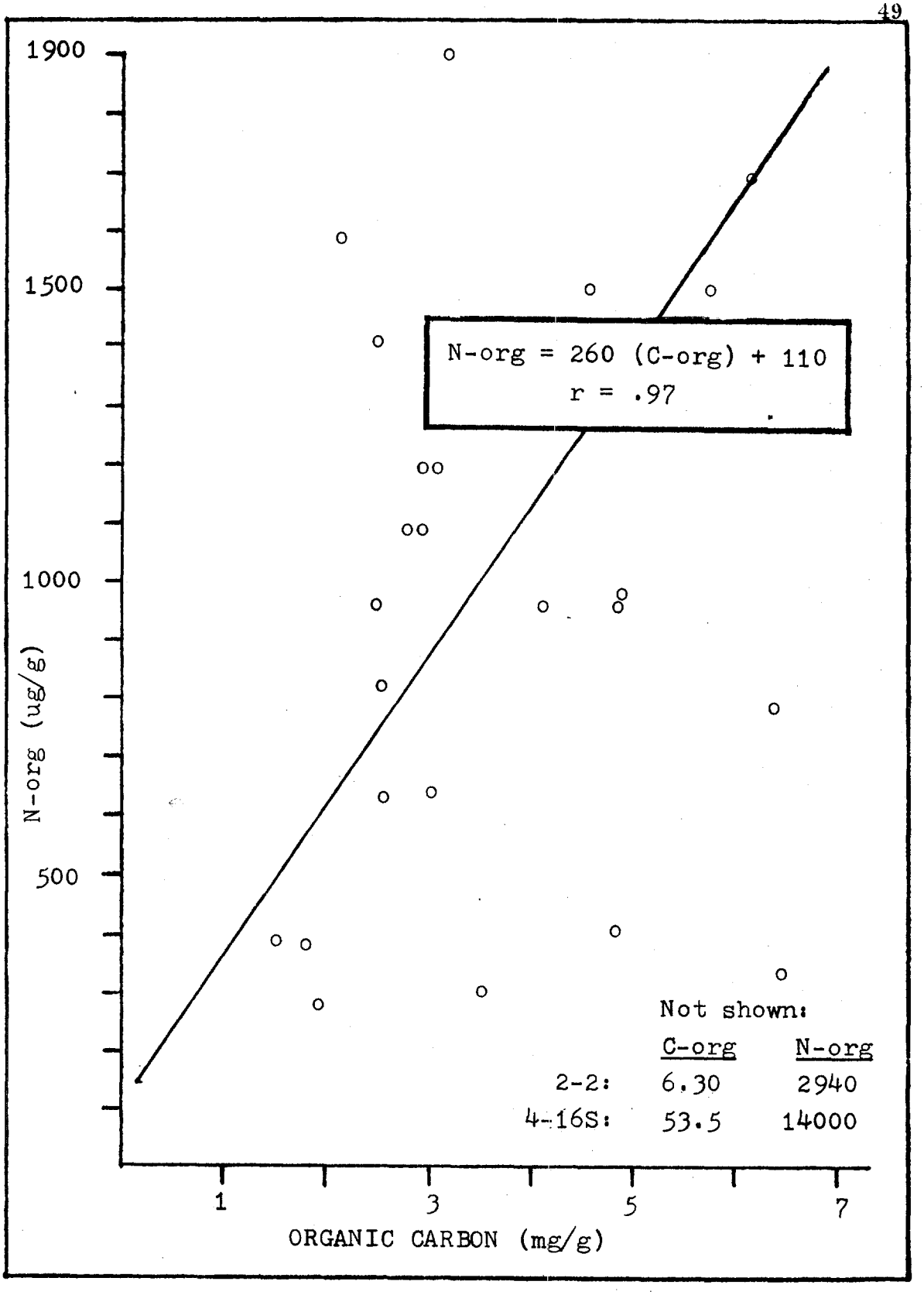


Figure 12. Organic Carbon vs Organic Nitrogen.

which compares to the C:N ratio of five that is often reported for detrital food sources with high bacterial populations (recall that carbon values are probably low). The relationship between carbon and nitrogen is graphed in Figure 12. The results of the N-org determinations are categorized in Table 4; Table 5 shows the results of the ammonia determinations. Area summaries for Org-N and ammonia are shown in Figures 13 - 16.

The natural sites in Area 1 had an average N-org value 780 ug/g, and ranged from a high of 1500 ug/g at 1-8 to a low 310 ug/g at 1-19. This low value coupled with the relatively high amount of carbon found at 1-19 produced the highest carbon to nitrogen ratio of any site in Area 1. Higher C:N ratios often indicate that the detritus has not been completely reworked, and that a large amount of the organic material is still only partially decomposed. On the other hand, this high value may indicate that the plants in the area have extracted most of the available nitrogen from the sediments, leaving the excess carbon. The above average value for ammonia found at this location may point to the fact that the available nitrogen it tied up as ammonia.

The deeper waterway sites contained a higher average N-org value than did the natural sites (860 ug/g), which contrasts with the relationship observed for organic carbon, and ammonia paralleled this result (820 ug/g) for the natural areas, and 340 ug/g for the waterway. While one may speculate that this is caused by a lack of uptake of nitrogen by rooted plants at the deeper sites, the fact that the natural areas in Area 2 have almost twice the N-org values as the waterway sites there (1400 ug/g vs 780 ug/g) would seem to indicate that another explanation is necessary.

The sites on and around the Titusville South treatment plant discharge pipe did not show an accumulation of N-org, but did show high levels of ammonia (730 ug/g N-org, 830 ug/g NH_3). Again, the sites sampled in Banana Creek showed the highest averages in both categories (1100 ug/g for N-org, 1000 ug/g for NH_3). Site 1-23, located just south of the western portion of the Titusville causeway and adjacent to a dredged navigational channel running from the Intracoastal Waterway to a nearby marina, showed very high values for both N-org (1400 ug/g) and ammonia (3000 ug/g). No explanation is apparent for this anomaly, since values for the other nutrients at this site are all somewhat below the area averages.

TABLE 4 ORGANIC (KJELDAHL) NITROGEN (ug/g)

SITE	DEPTH	NATURAL	WATERWAY	OUTFALL	OTHER
1-2	1.6m	380			380
1-6	2.0	390	390		
1-8	.5	1500			
1-11	2.0		1300	1300	
1-11S	.5			270	
1-15	2.0		630	630	
1-19	1.0	310			310
1-20	1.75	1100	1100		
1-23	1.0				1400
1-26	.75	1000			
1-29S	.5			1200*	
(MEAN)		780	860	730	
2-1	.5	1600		1600	
2-1S	.75			1500	
2-2	1.25	2900		2900	
2-9	1.3	620	620		
2-17	1.75	950	950		
2-24	1.0	1100			1100
2-30	.5	940			
(MEAN)		1400	780	2000	
3-3	1.0	800			
3-7	1.75	950			
3-9	2.0	320			
3-12	.75	390	390		
(MEAN)		620			
4-12	.25	820		820	
4-16	1.25	1900		1900	1900
4-16S	.25			14000*	
4-18	.5	1700			
(MEAN)		1500		1360	

* THIS SITE NOT COMPUTED IN THE MEAN FOR THIS AREA.
AVERAGE FOR BANANA CREEK (1-26 and 1-29S): 1100 ug/g
AVERAGE FOR AREA AROUND BANANA RIVER
OUTFALL INCLUDING THE VALUE AT SITE 4-16S: 5600 ug/g

TABLE 5 AMMONIA (ug/g)

SITE	DEPTH	NATURAL	WATERWAY	OUTFALL	OTHER
1-2	1.6m	1600			1600
1-6	2.0	49	49		
1-8	.5	1000			
1-11	2.0		920	920	
1-11S	.5			1200	
1-15	2.0		380	380	
1-19	1.0	1100			1100
1-20	1.75	0	0		
1-23	1.0				3000
1-26	.75	1200			
1-29S	.5			890*	
(MEAN)		820	340	830	
2-1	.5	2700		2700	
2-1S	.75			1000	
2-2	1.25	1500		1500	
2-9	1.3	1500	1500		
2-17	1.75	2200	2200		
2-24	1.0	940			940
2-30	.5	1100			
(MEAN)		1600	1800	1700	
3-3	1.0	250			
3-7	1.75	400			
3-9	2.0	780			
3-12	.75	990	990		
(MEAN)		600			
4-12	.25	470		470	
4-16	1.25	1400		1400	1400
4-16S	.25			2800*	
4-18	.5	480			
(MEAN)		780		940	

* THIS SITE NOT COMPUTED IN THE MEAN FOR THIS AREA.
AVERAGE FOR BANANA CREEK (1-26 and 1-29S): 1000 ug/g
AVERAGE FOR AREA AROUND BANANA RIVER OUTFALL INCLUDING THE VALUE AT SITE 4-16S: 1600 ug/g

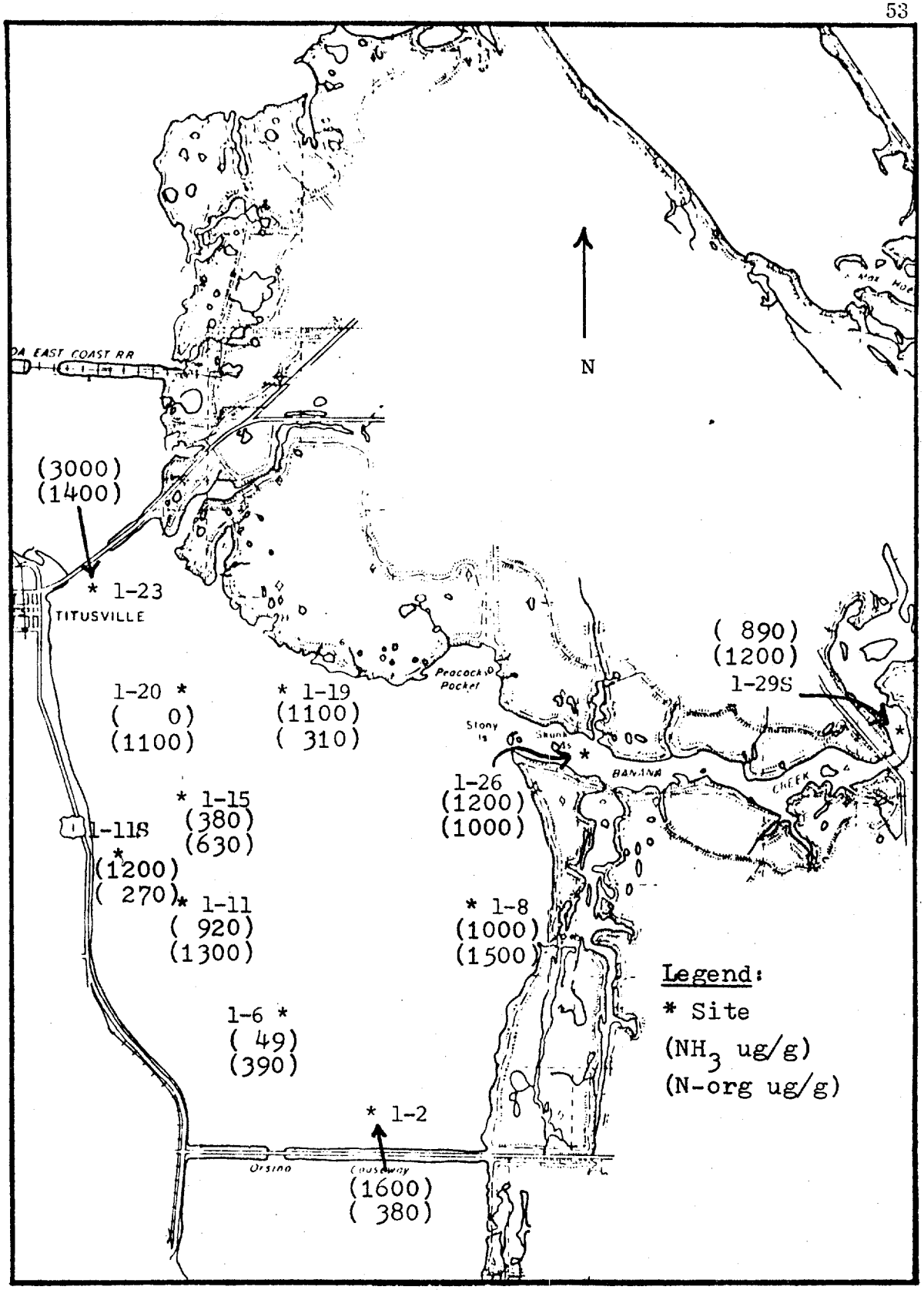


Figure 13. Ammonia (top) and Organic Nitrogen (bottom) values (ug/g) for Area 1.

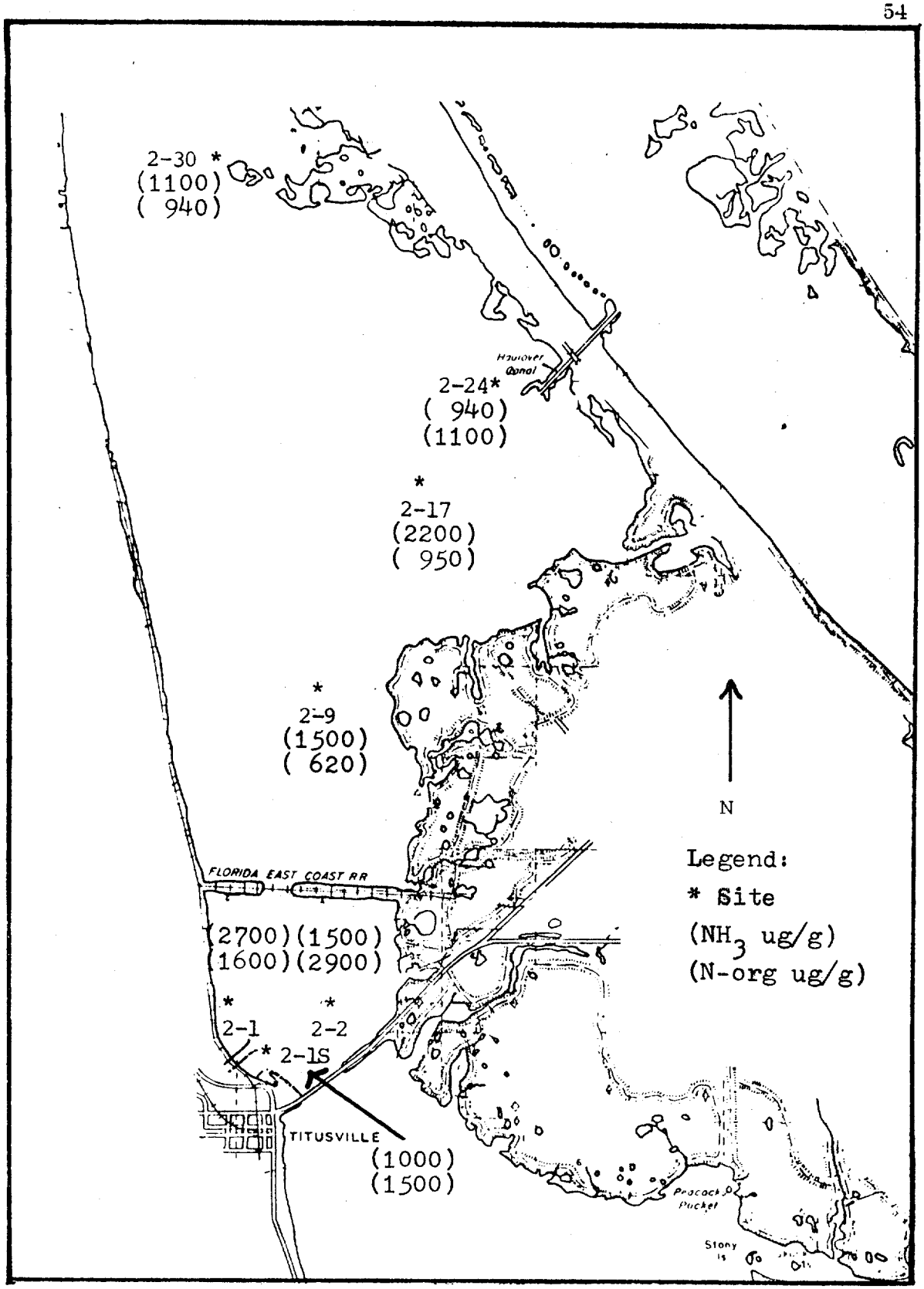


Figure 14. Ammonia (top) and Organic Nitrogen (bottom) values (ug/g) for Area 2.

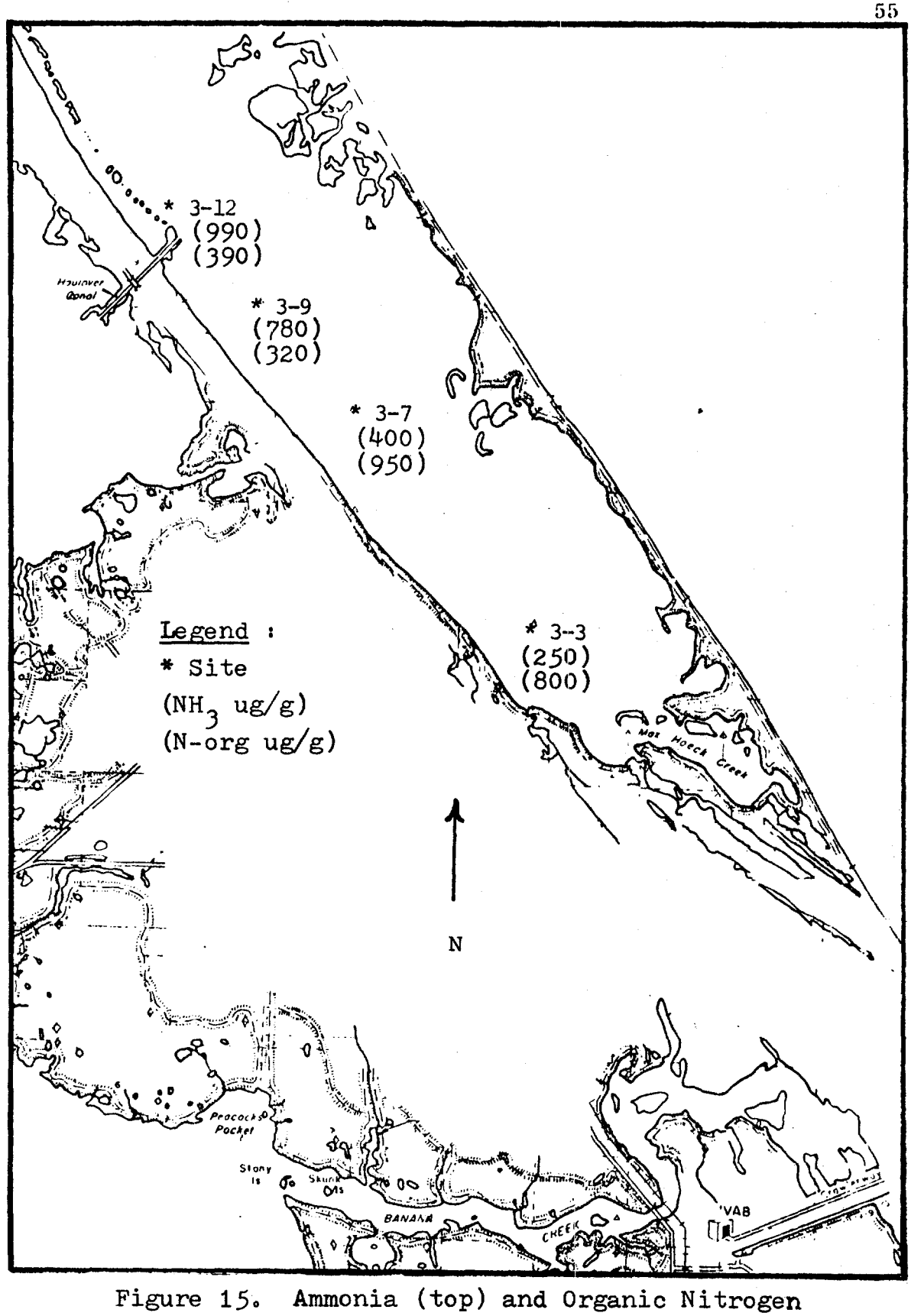


Figure 15. Ammonia (top) and Organic Nitrogen (bottom) values (ug/g) for Area 3.

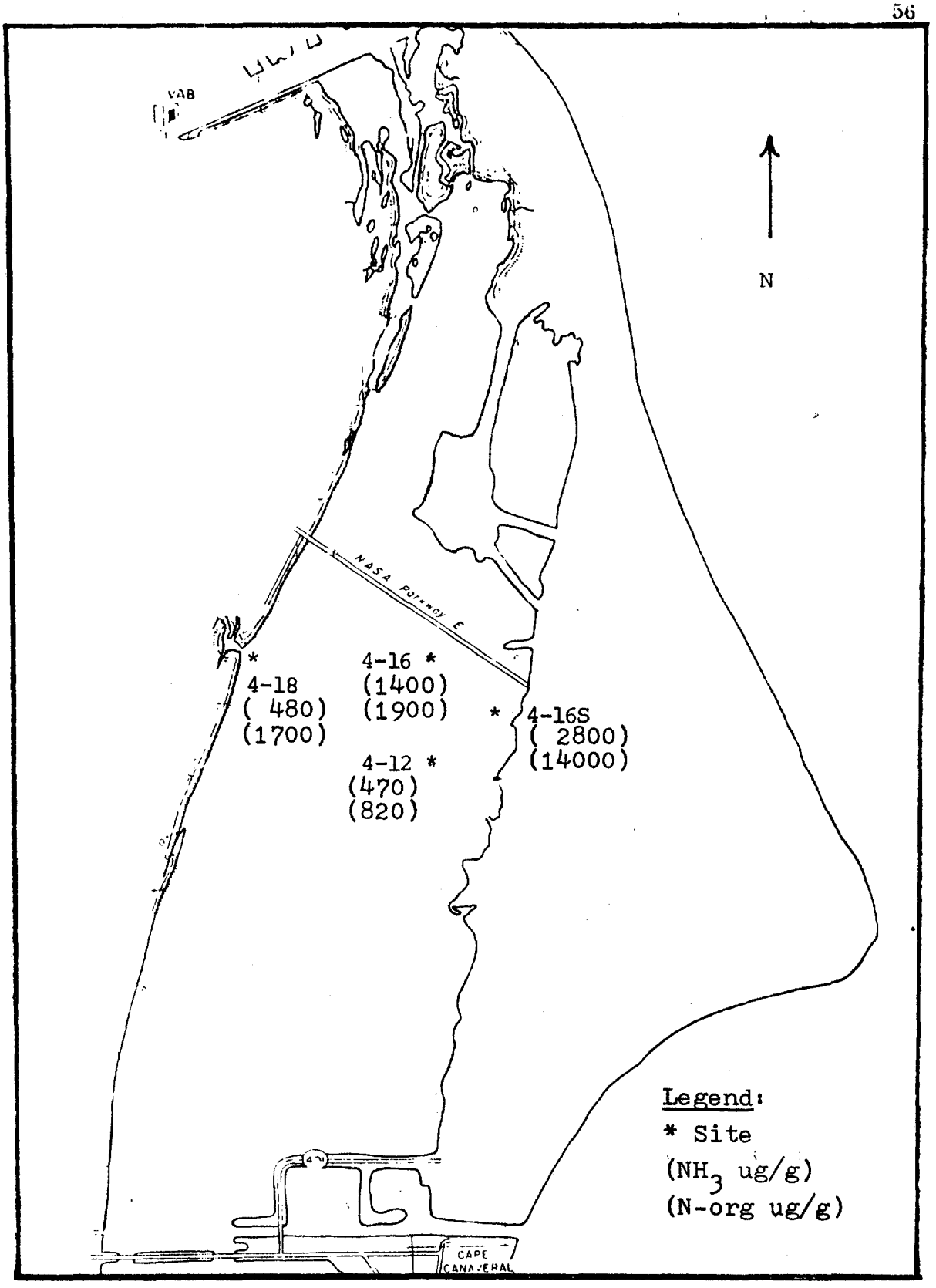


Figure 16. Ammonia (top) and Organic Nitrogen (bottom) values (ug/g) for Area 4.

The averages for the natural sites in Area 2 are almost double those for Area 1 for both organic nitrogen (1400 ug/g) and ammonia (1600 ug/g), which may again indicate the possible enrichment effect of the north treatment plant. The enclosed area around the outfall had the very high values of 2000 ug/g and 1700 ug/g for N-org and ammonia respectively. The highest N-org value reported in Area 2 was opposite the outfall at Site 2-2 (2900 ug/g) while the lowest values were obtained at the sites near the waterway (av. 780 ug/g). Ammonia averages were fairly consistent throughout the area (1600 ug/g natural, 1800 ug/g waterway, and 1700 ug/g outfall) and these differences are probably not significant given the difficulties associated with the laboratory determinations.

The average values for the sites sampled in the Indian River Lagoon are 620 ug/g for N-org and 600 ug/g for NH_3. The carbon to nitrogen ratios there were the highest found anywhere in the lagoonal complex (average 10.7 with a high of 20.2 at 3-9 and low of 2.64 at 3-7). This again points to the conclusions that the nitrogen here is either mostly bound in the vegetation or that the detritus is at a lower level of degradation.

In the Banana River the N-org value of 1500 ug/g, representing the averages of the natural sites, was the highest of all the four areas. The mouth of the discharge drainage canal had a value of 14,000 ug/g, about an order of magnitude greater than the averages in all other areas. The two sites adjacent to the outfall averages 1400 ug/g, with the closer 4-16 showing 1900 ug/g and 4-12 showing 820 ug/g. (It was observed that concentrations were higher for all nutrients at 4-16 than at 4-12, which can be assumed to indicate a gradient of high to low concentrations leading from the discharge site.) The sample taken from the mouth of the creek on the opposite bank of the river showed the relatively high value of 1700 ug/g for N-org, ranking it fourth among all the sites sampled. Contrary to expectations, the concentration of ammonia found at 4-16S was not the highest of all sites, but took second place behind the aforementioned anomolous 1-23. Grouping the other three sites in Area 4 produced the moderate average of 780 ug/g NH_3.

Total phosphorous and dissolved phosphate values are summarized by area in Figures 17 - 20. Total phosphorus concentrations (see Table 6) in the natural sites of Area 1 averaged 220 ug/g, with a high at 1-20 (419 ug/g) and a low at 1-6 (81 ug/g). The waterway average was slightly lower at 180 ug/g, while the sites

TABLE 6 TOTAL PHOSPHORUS (ug/g)

SITE	DEPTH	NATURAL	WATERWAY	OUTFALL	OTHER
1-2	1.6m	186			186
1-6	2.0	81	81		
1-8	.5	281			
1-11	2.0		142	142	
1-11S	.5			18	
1-15	2.0		100	100	
1-19	1.0	114			114
1-20	1.75	419	419		
1-23	1.0				34
1-26	.75	258			
1-29S	.5			556*	
(MEAN)		220	180	86	
2-1	.5	65		65	
2-1S	.75			193	
2-2	1.25	553		553	
2-9	1.3	118	118		
2-17	1.75	91	91		
2-24	1.0	192			192
2-30	.5	182			
(MEAN)		200	100	270	
3-3	1.0	231			
3-7	1.75	151			
3-9	2.0	707			
3-12	.75	441	441		
(MEAN)		382			
4-12	.25	1020		1020	1020
4-16	1.25	1130		1130	
4-16S	.25			1540*	
4-18	.5	215			
(MEAN)		788		1080	

* THIS SITE NOT COMPUTED IN THE MEAN FOR THIS AREA.
AVERAGE FOR BANANA CREEK (1-26 and 1-29S): 407 ug/g
AVERAGE FOR AREA AROUND BANANA RIVER OUTFALL INCLUDING THE VALUE AT SITE 4-16S: 1230 ug/g

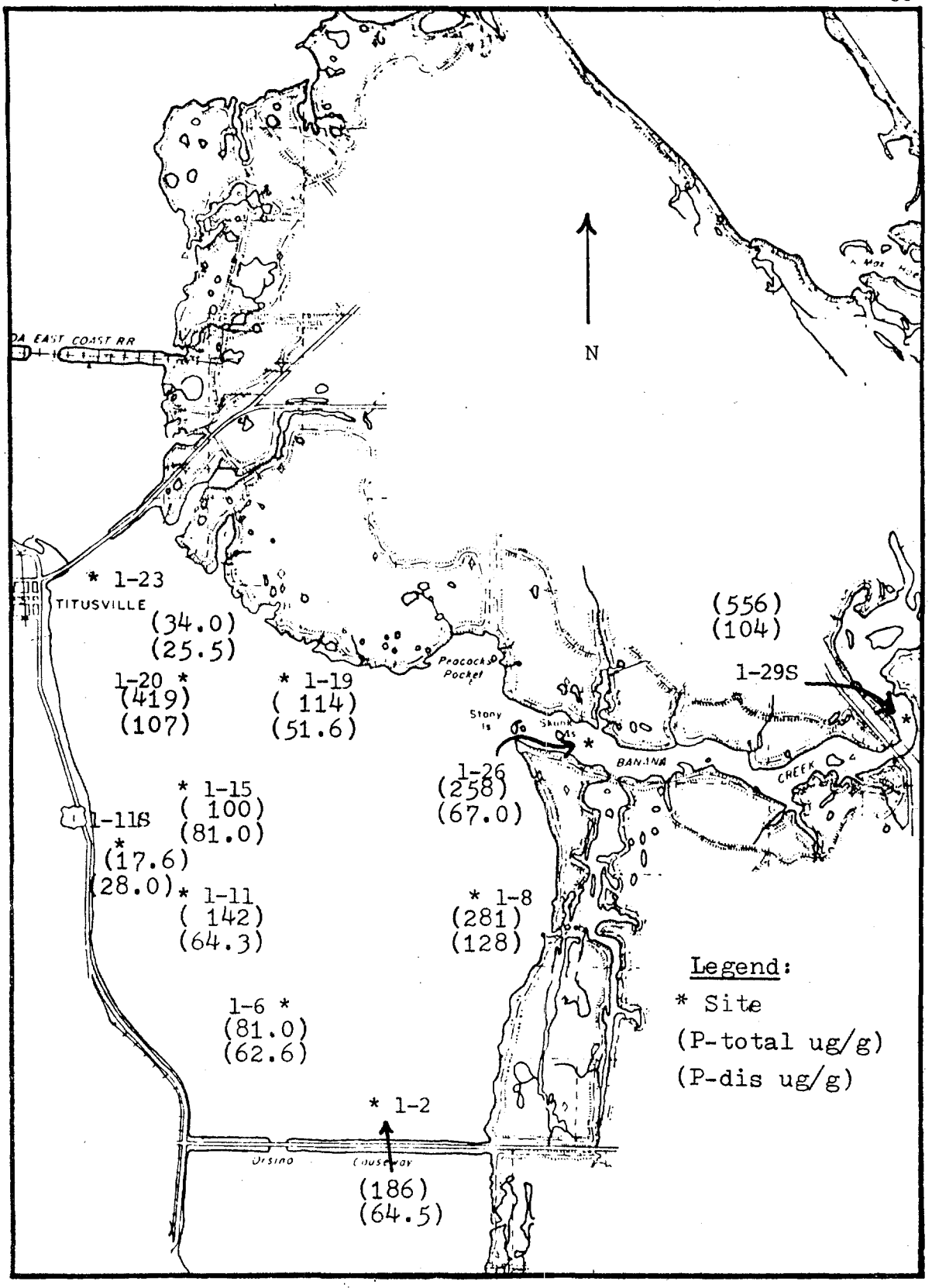


Figure 17. Total (top) and Dissolved (bottom) Phosphorus values (ug/g) for Area 1.

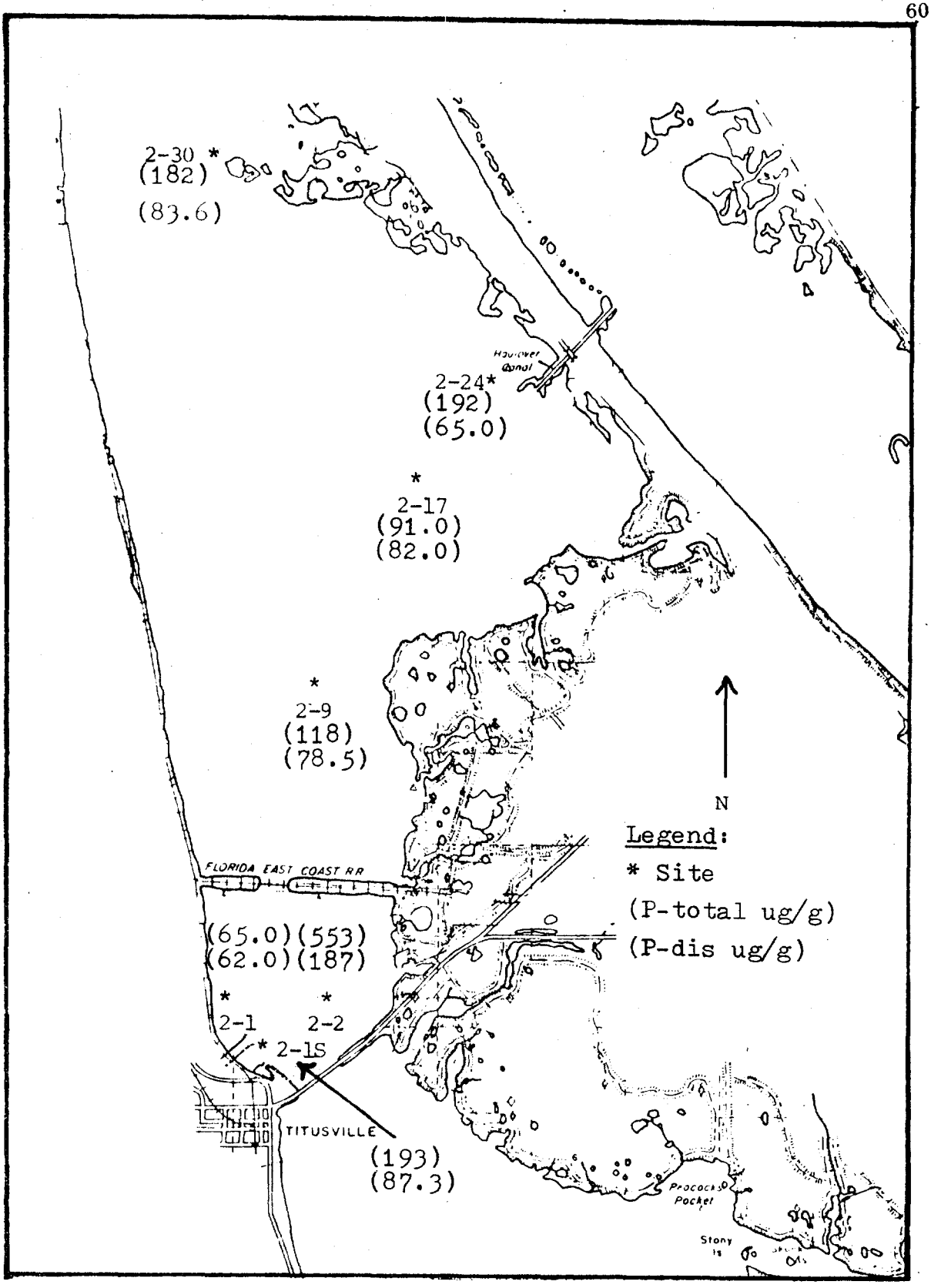


Figure 18. Total (top) and Dissolved (bottom) Phosphorus values (ug/g) for Area 2.

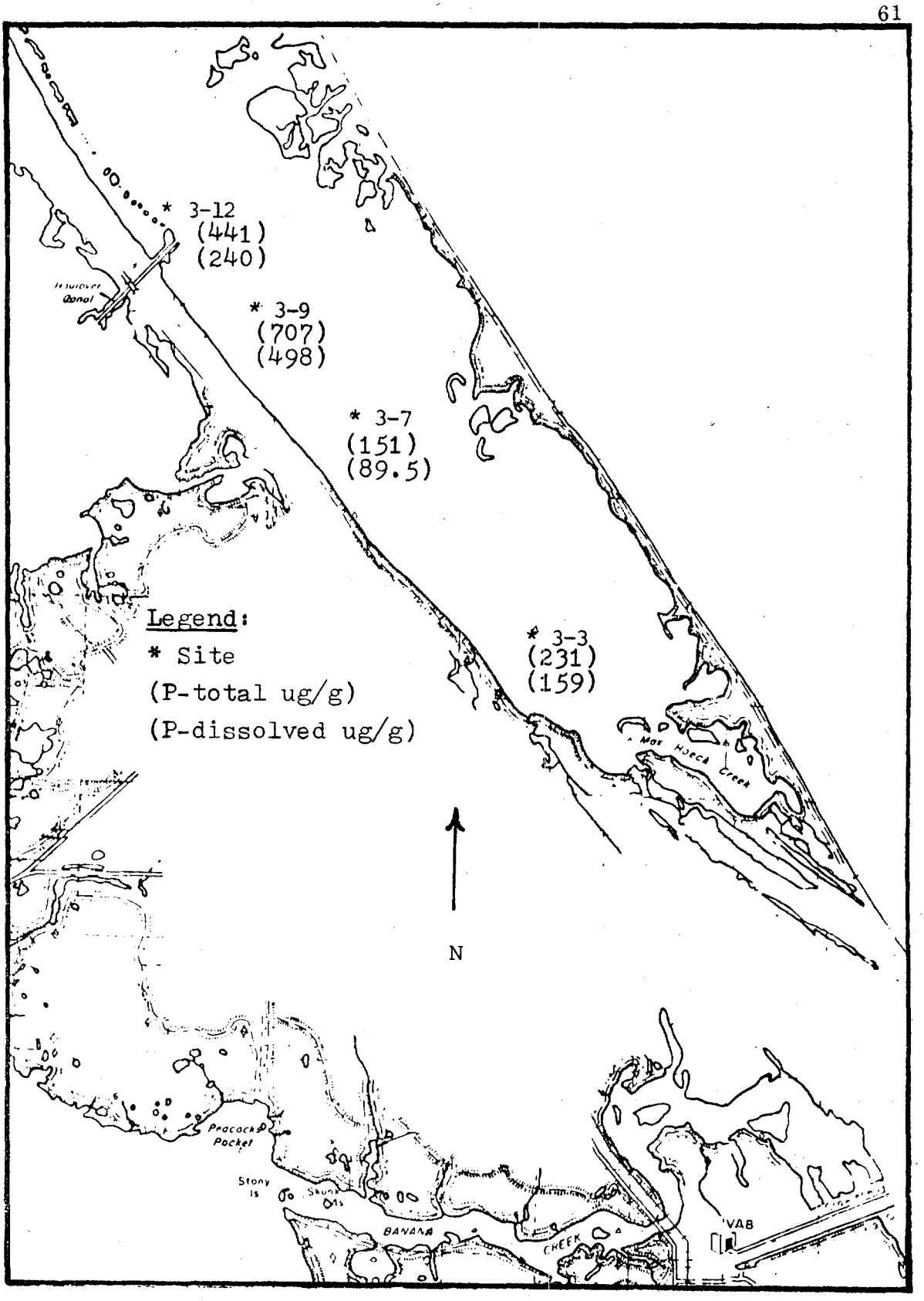


Figure 19. Total (top) and Dissolved (bottom) Phosphorus values (ug/g) for Area 3.

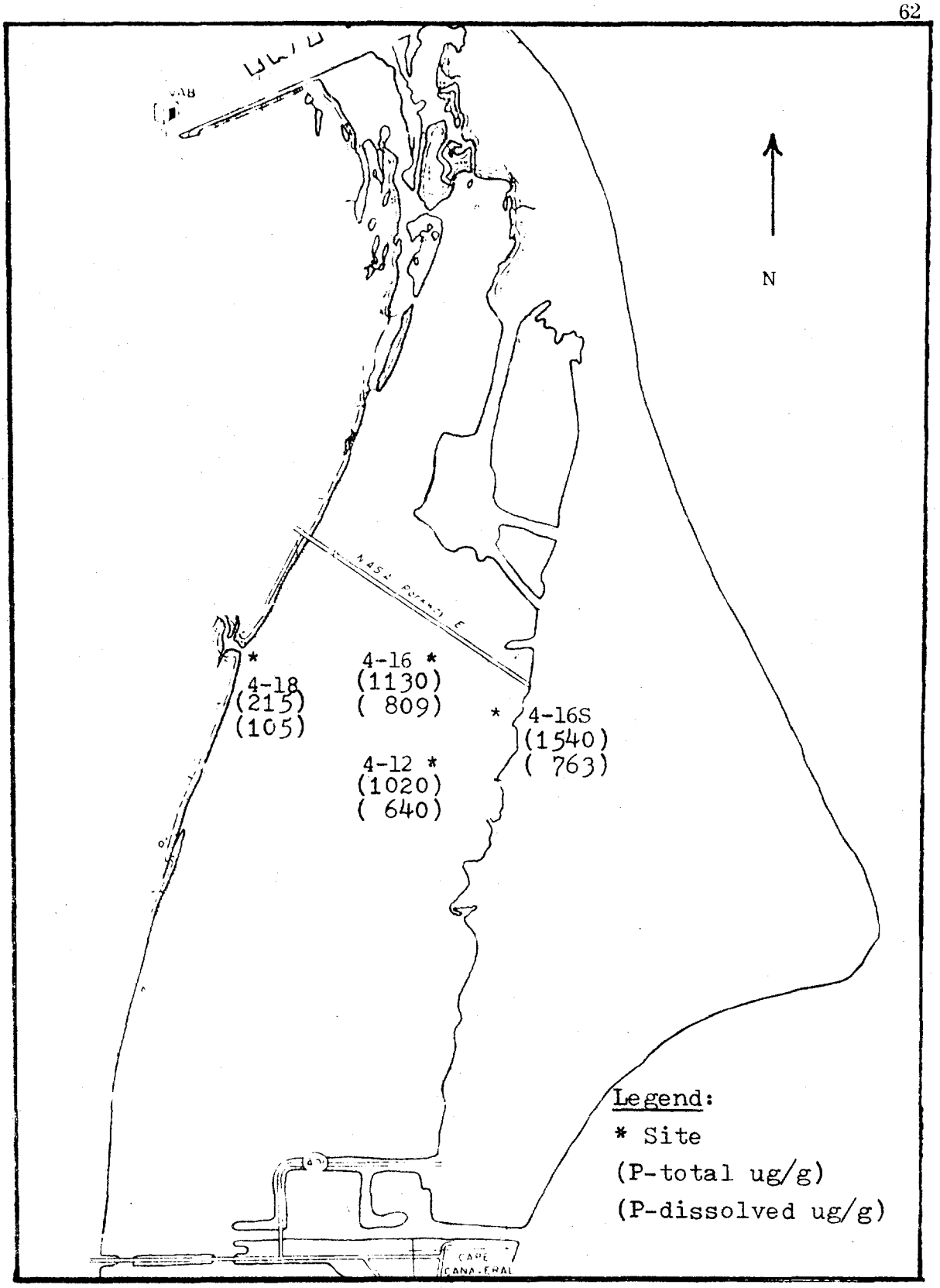


Figure 20. Total (top) and Dissolved (bottom) Phosphorus values (ug/g) for Area 4.

around the outfall had a very low concentration average of only 86 ug/g. Indeed, the lowest total phosphorus value found anywhere in the lagoonal system was immediately next to the discharge pipe at Site 1-11S. Since sewage effluent is known to contain large quantities of phosphates, this is a clear indication that the nutrients from the treatment plant are not settling in the immediate area of the outfall but are being transported via currents and mixing to more distant locations. The averages of the Banana Creek sites again yielded the highest P-tot concentration of all the averages in Area 1, and on a system wide basis were surpassed only by the values obtained in Area 4.

The natural sites in Area 2 averaged 200 ug/g, which is lower than that reported for Area 1. This is the first indicator which strongly suggests that the higher nutrient characteristics generally observed in Area 2 are due to natural causes, rather than due to the influence of the north treatment plant. If the treatment plant was the primary source of enrichment, high phosphate levels should be observed here. The sites near the outfall did show a higher concentration average of 270 ug/g, but this is not substantially greater than the averages for the natural areas in the Indian River.

The average level of total phosphorus in the Indian River Lagoon was 382 ug/g, with a high of 707 ug/g at 3-9 and a low of 151 ug/g at 3-7. Site 3-9 also had a high concentration of organic carbon, yet it showed the lowest organic nitrogen level in Area 3. It would be necessary to know more about the circulation and biology of this area in order to explain this odd result.

In Area 4, where the natural sites had the highest average value for all four areas (788 ug/g), the highest concentration of all was of course found at the discharge canal at 4-16S (1540 ug/g). This concentration is only about 150% the average for the adjacent sites (1080 ug/g), which is in sharp contrast to the differences reported for the other nutrients (where the factor was about 1000%). The high level reported for Site 4-12 probably reflects the fact that this site was immediately adjacent to an island used as a rookery by a number of species of shore birds. (These birds did not appreciate the intrusion of a noisy outboard motor and three graduate students!)

Nitrogen is concentrated in protoplasm by a factor of 15 times that of phosphorus (Hill 1966). Since the concentrations of organic nitrogen in these lagoons

averages to only three times that of the total phosphorus in the natural areas, evidence is again presented to support the contention that nitrogen is the limiting nutrient in these ecosystems.

Sulfides and organic carbon correlated with a coefficient of +.86 (see Figure 21), and the equation produced by regression analysis was:

$$\text{Sulfides (ug/g)} = 4.72\left[\text{Organic carbon (mg/g)}\right] + 48.9$$

Sulfide concentrations are summarized by area in Figures 22 - 25.

The natural sites of Area 1 had an average sulfide concentration of 57.4 ug/g, while the waterway sites showed an only slightly higher concentration of 61.5 ug/g (see Table 7). There was no strong correlation of sulfides with depth, and the magnitude of difference between the lowest and highest measured values was the least for sulfides compared to the other nutrients (approximately 15:1). The second highest concentration measured in the sediments of Area 1 was found at Site 1-26 near the mouth of Banana Creek (69.0 ug/g) while the other site in the creek, 1-29S, had a more normal value of 59.6 ug/g. The highest concentration measured in Area 1 was 76.3 ug/g at Site 1-8, where high organic values are often observed. The sites around the Knox McCrae treatment plant showed an average of 58.7 ug/g.

In Area 2, the natural areas showed higher averages (68.6 ug/g $S^{=}$) than those in Area 1, while the sites near the waterway were somewhat lower (48.6 ug/g). This time, however, the area of reduced circulation around the north treatment plant outfall showed the lowest average for Area 2 (32.7 ug/g). The highest concentration of sulfides here was observed at Site 2-24 near the mouth of Haulover Canal. The lowest concentration occured at 2-1S, adjacent to the effluent discharge pipe.

The sites in Area 3 ranked second highest in sulfide concentration with an average of 78.8 ug/g. The high value (112.10 ug/g) was observed at the deepest site (3-9), while the lowest concentration was measured at the southernmost location (3-3, 46.0 ug/g).

The Banana River showed the highest average sulfide concentrations with

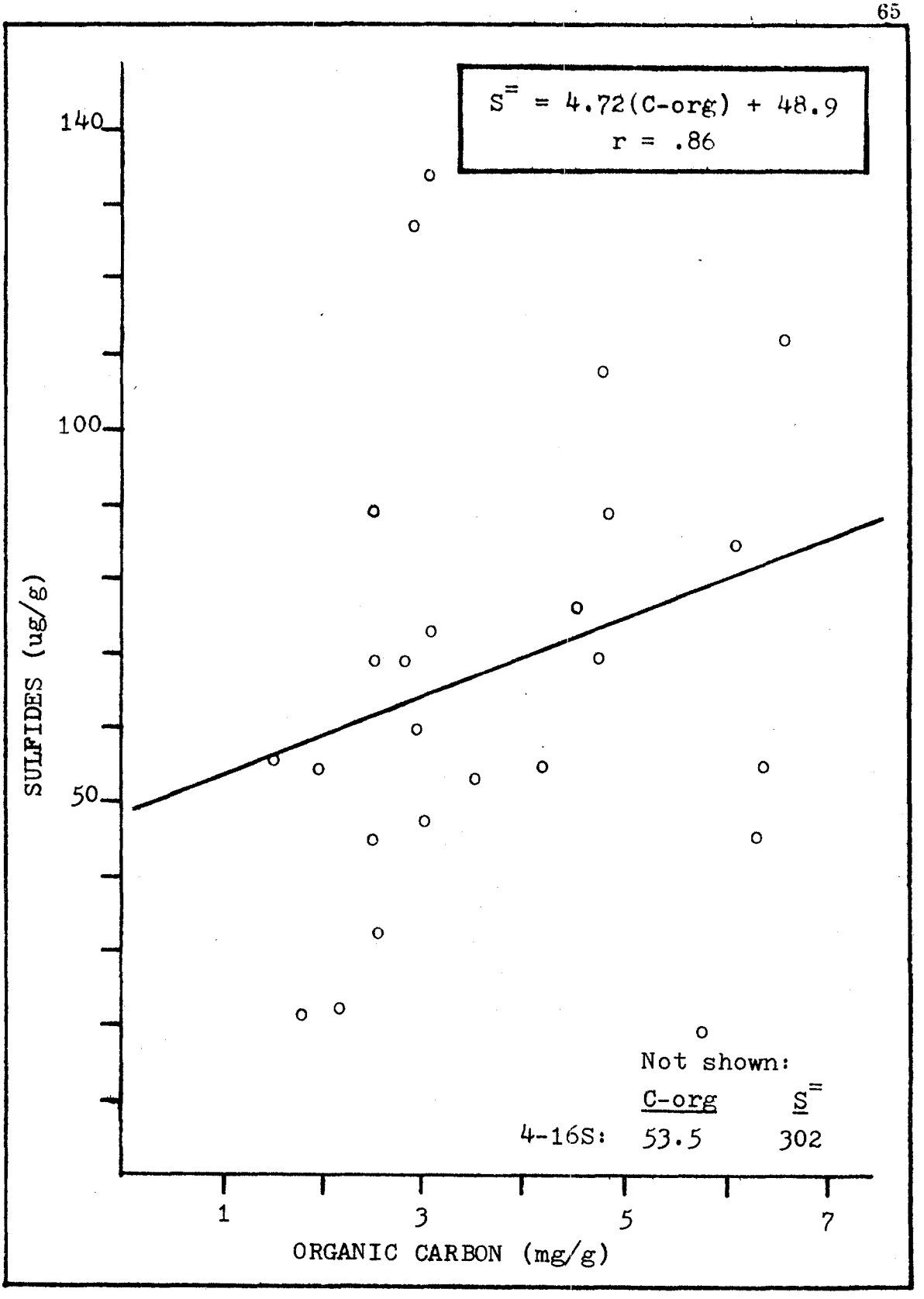


Figure 21. Organic Carbon vs Sulfides.

TABLE 7 SULFIDES (ug/g)

SITE	DEPTH	NATURAL	WATERWAY	OUTFALL	OTHER
1-2	1.6m	20.1			20.1
1-6	2.0	56.9	56.9		
1-8	.5	76.3			
1-11	2.0		73.4	73.4	
1-11S	.5			55.8	
1-15	2.0		47.0	47.0	
1-19	1.0	53.6			53.6
1-20	1.75	68.8	68.8		
1-23	1.0				44.8
1-26	.75	69.0			
1-29S	.5			59.6*	
(MEAN)		57.4	61.5	58.7	
2-1	.5	23.4		23.4	
2-1S	.75			18.1	
2-2	1.25	56.7		56.7	
2-9	1.3	42.0	42.0		
2-17	1.75	55.1	55.1		
2-24	1.0	127.			127.
2-30	.5	108.			
(MEAN)		68.7	48.6	32.7	
3-3	1.0	46.0			
3-7	1.75	68.4			
3-9	2.0	112.			
3-12	.75	88.9	88.9		
(MEAN)		78.8			
4-12	.25	89.3		89.3	
4-16	1.25	134.		134.	134.
4-16S	.25			303.*	
4-18	.5	84.7			
(MEAN)		103		112.	

* THIS SITE NOT COMPUTED IN THE MEAN FOR THIS AREA.
AVERAGE FOR BANANA CREEK (1-26 and 1-29S): 64.3 ug/g
AVERAGE FOR AREA AROUND BANANA RIVER
OUTFALL INCLUDING THE VALUE AT SITE 4-16S: 175 ug/g

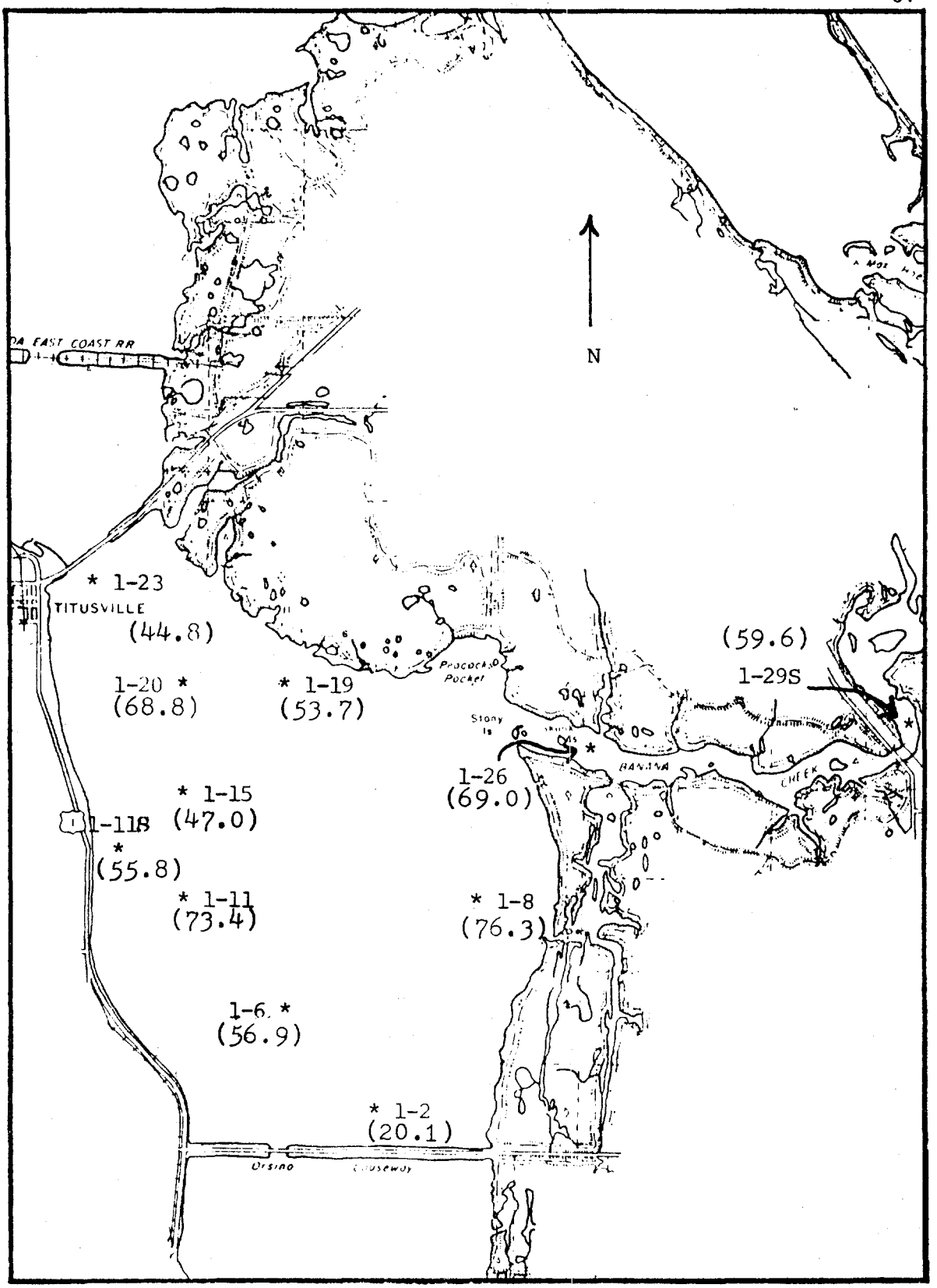


Figure 22. Sulfide values (ug/g) for Area 1.

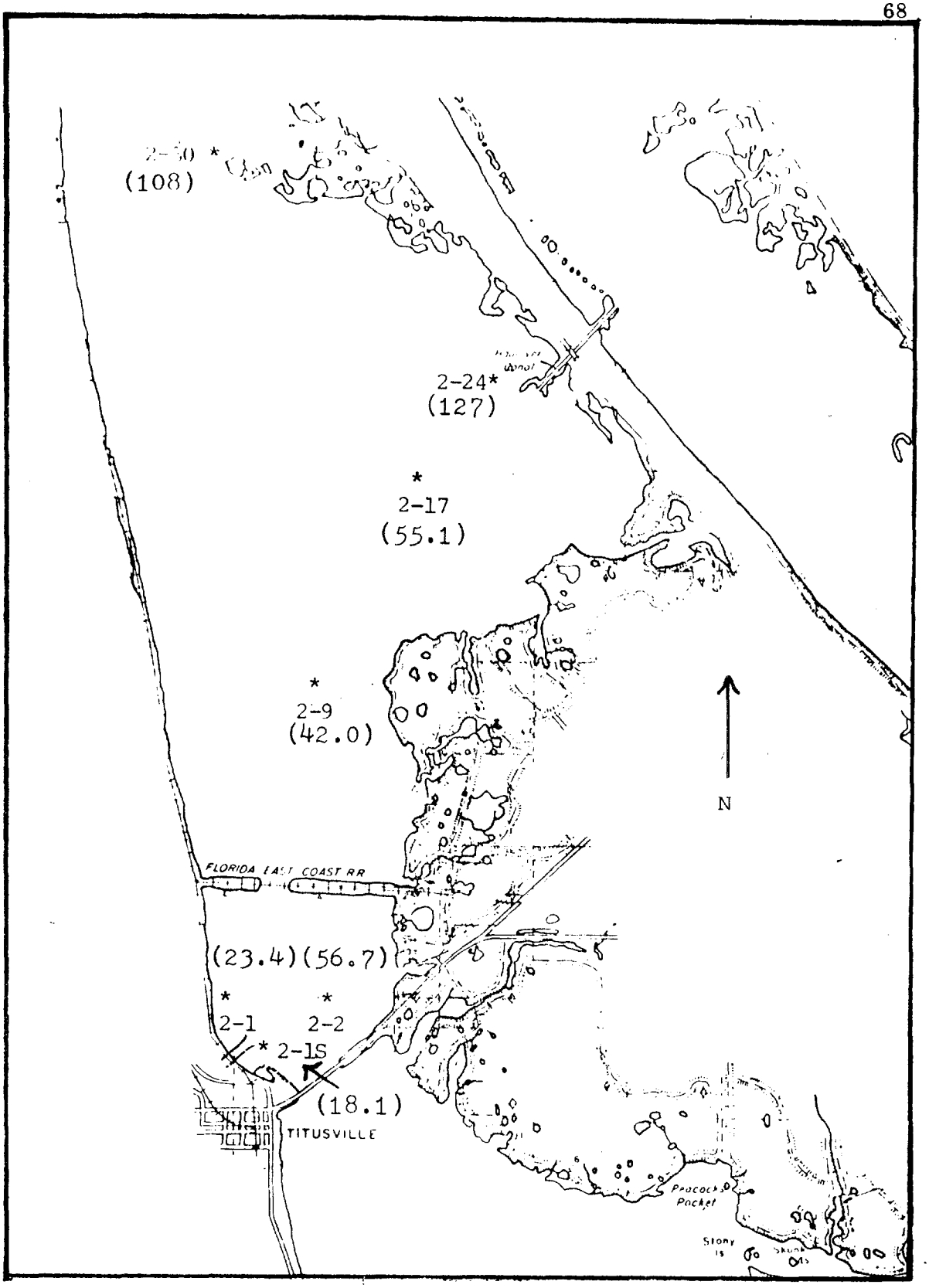


Figure 23. Sulfide values (ug/g) for Area 2.

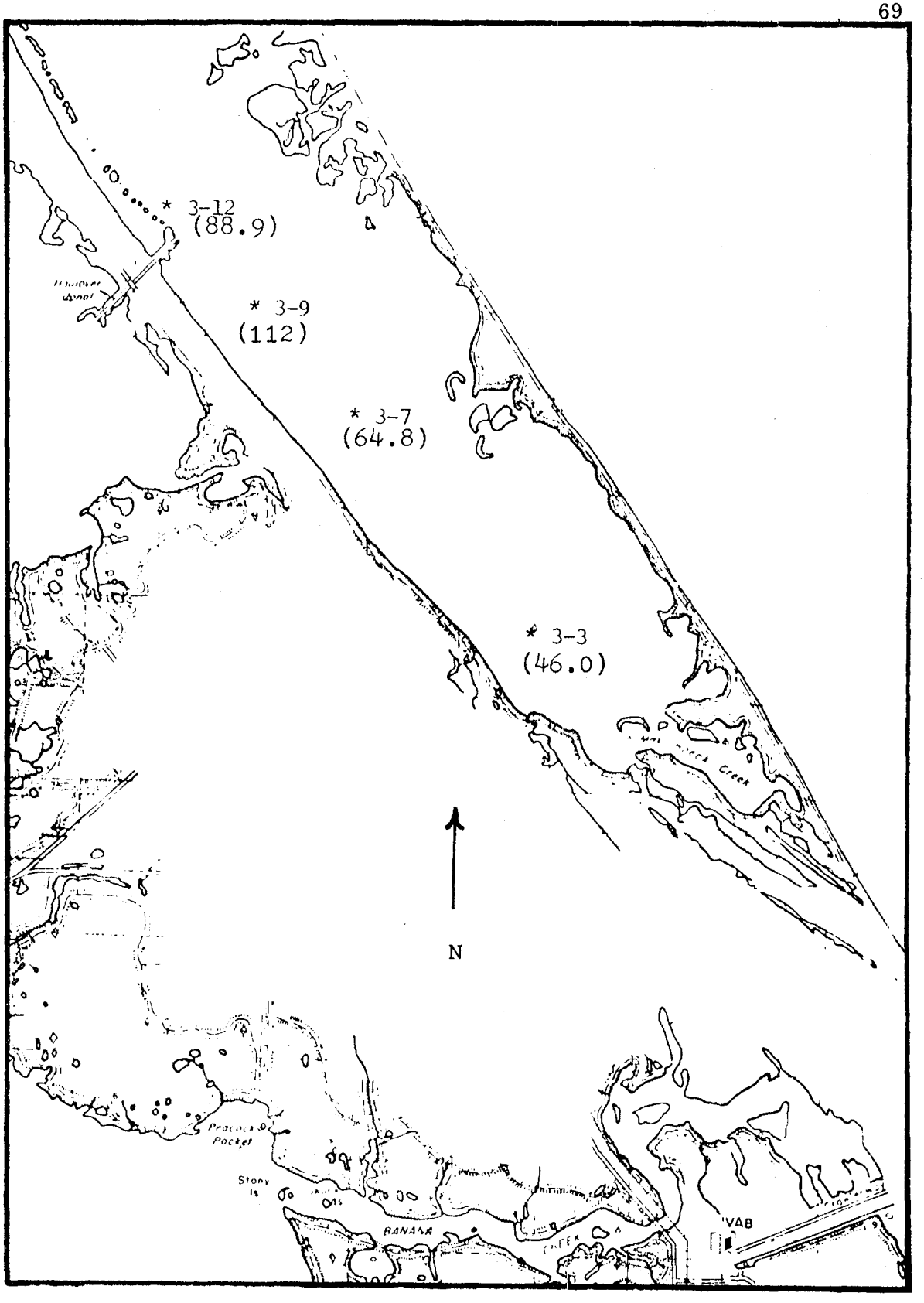


Figure 24. Sulfide values (ug/g) for Area 3.

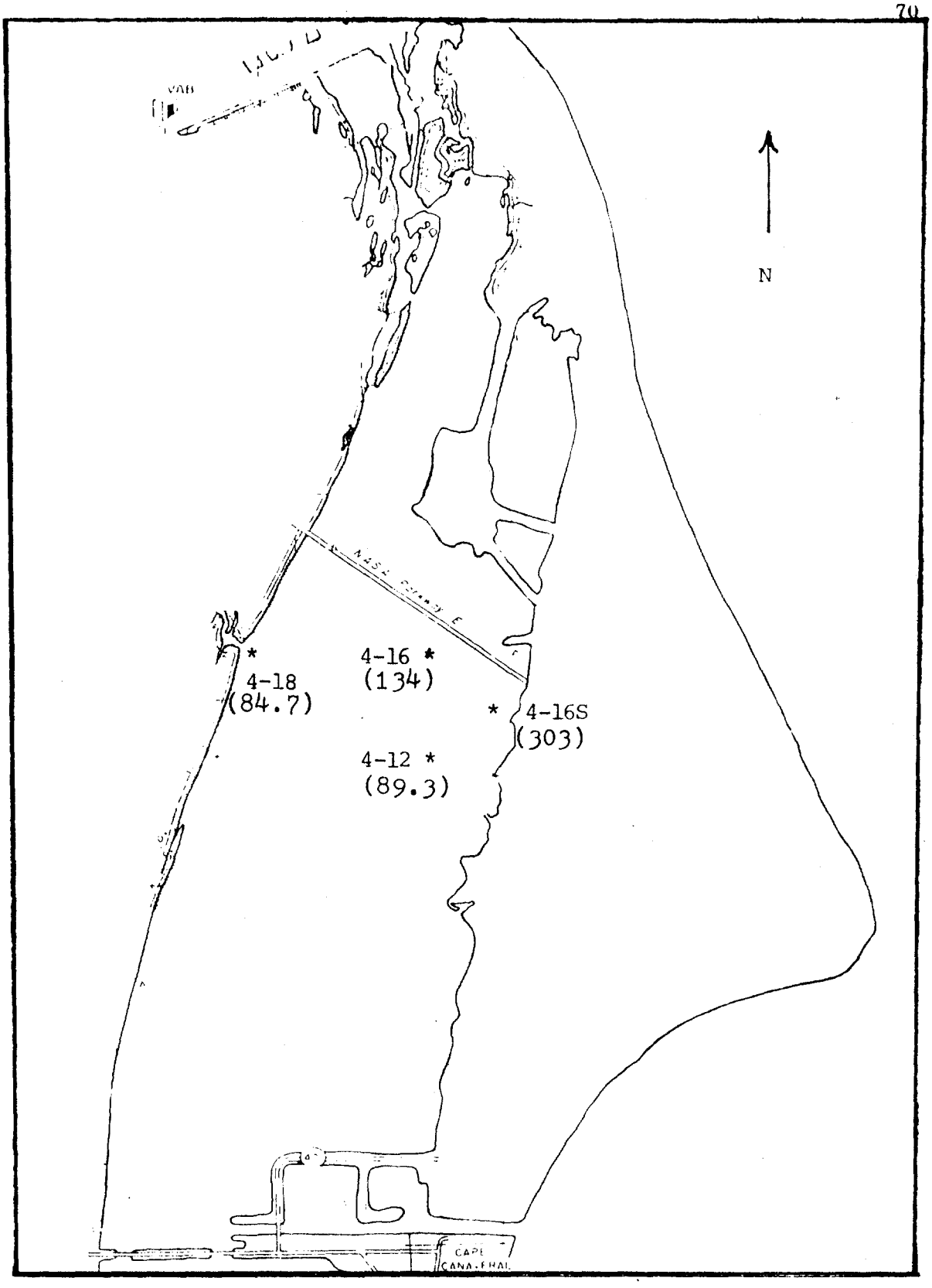


Figure 25. Sulfide values (ug/g) for Area 4.

an average value of 122 ug/g. Site 4-16 had the highest concentration of the natural areas with a value of 134 ug/g, while 4-12 and 4-18 came in about even at 89.3 ug/g and 84.7 ug/g respectively. The highest value for the lagoonal system was again recorded at 4-16S (303 ug/g) reaffirming the nutrient trapping effect so evident at this location.

In general it can be said that the higher sulfide concentrations in all areas were found in those locations where the currents and mixing effects of the water were likely to be least evident, such as in the deeper sites (1-11, 3-9), those near grass beds (1-8, 2-30, 3-12, 4-12), or where man made structures have reduced the circulation of the water (2-24, 4-16). The sulfide levels reported for the surface sediments are probably representative of the conditions deeper in the substrate, where the greatest concentrations of sulfides occur, but this conjecture should be tested by future researchers in order to determine the validity of surface sediment measurements for sulfide studies.

Carbon tied up as calcium carbonate ($CaCO_3$) is essentially removed from the nutrient cycling and is more important to the geological considerations of the sediment than it is to the biota. The carbonates found in the lagoonal system surrounding the Kennedy Space Center are almost exclusively in the form of pelecypod shell debris, and thus can serve as an indicator of past molluscan community assemblages. Carbonate values in the sediments ranged from a low of .8 mg/g at Site 4-18 to a high of 23 mg/g (2.3 %) at Sites 3-9 and 4-16S (see Figures 26 - 29). The Indian River Lagoon stood out as having the highest overall percentage of shell debris in the surface sediments, a finding verified by the grain size analyses run by Mendelsohn (1975).

When the natural sites of each area are grouped and averaged, it is possible to get some indication of the comparative nutrient quality of each. In Table 8 shown below, the various areas have been ranked from high to low in each of the major nutrient categories. While the small number of sample sites employed make it difficult to draw conclusions with a high degree of certainty, the results of the nutrient analysis performed in this research indicate that Area 4 has the highest overall concentration of nutrients in the sediments, followed in order by Area 3, Area 2, and Area 1.

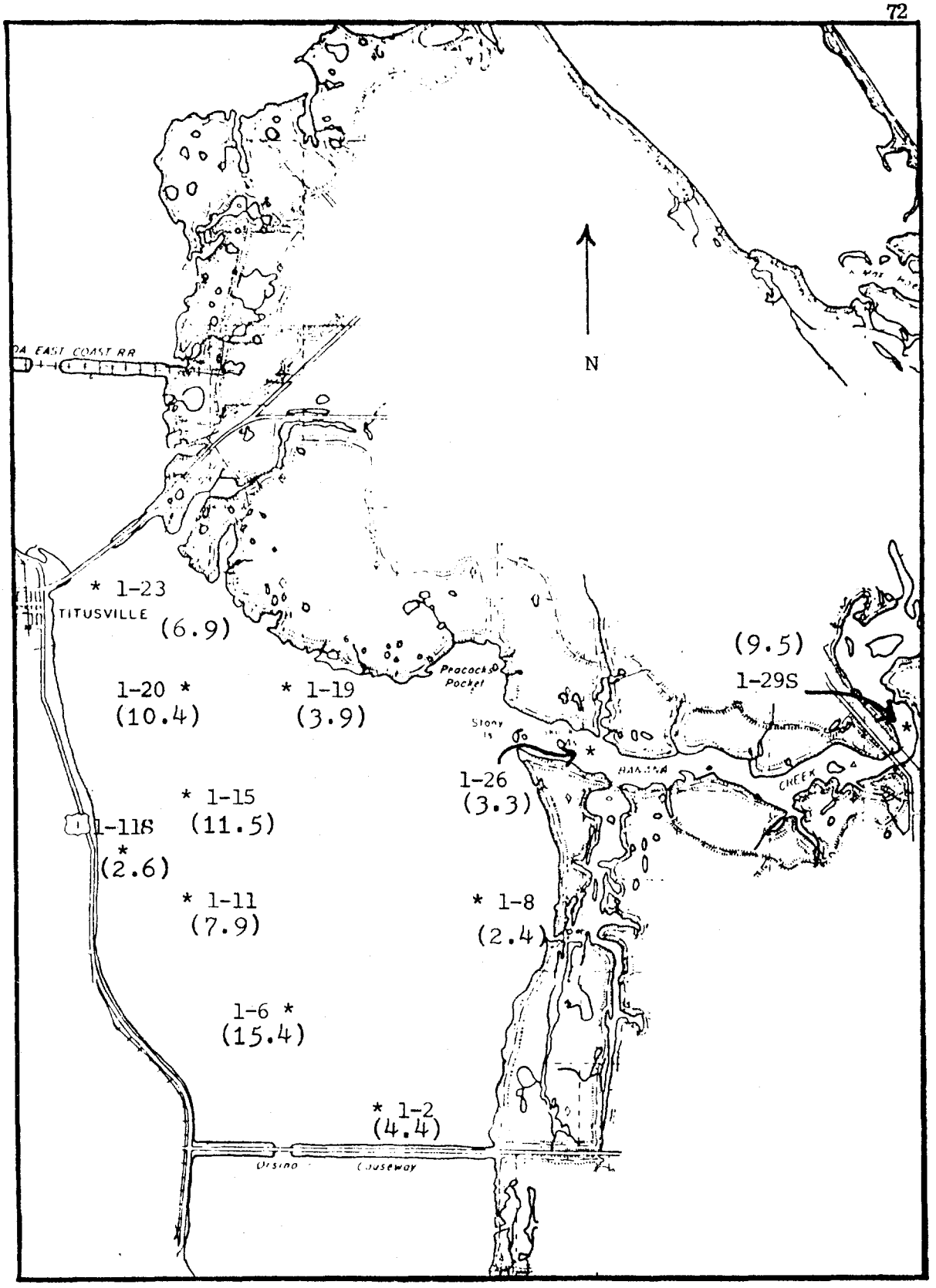


Figure 26. Carbonate Carbon values (mg/g) for Area 1.

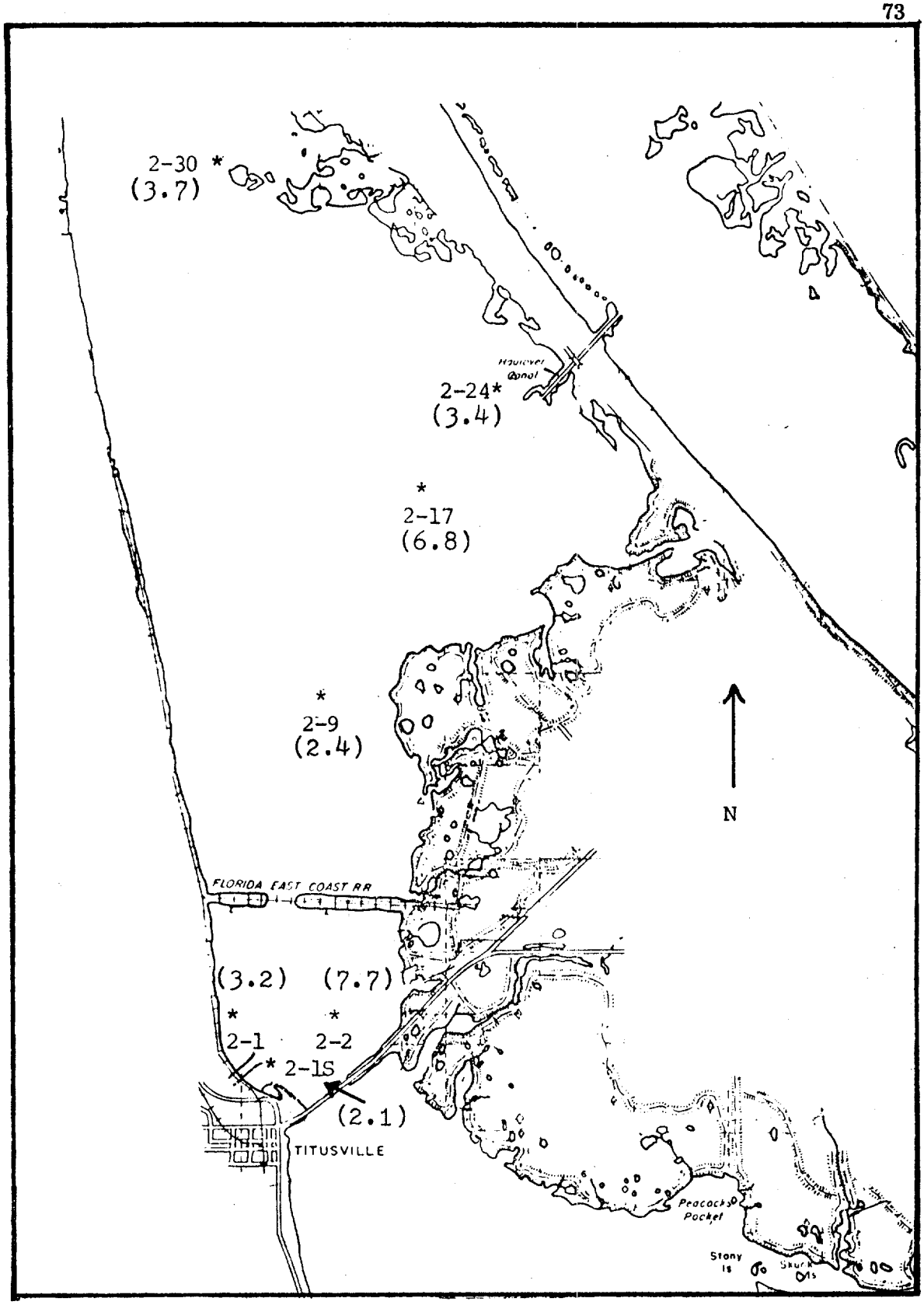


Figure 27. Carbonate Carbon values (mg/g) for Area 2.

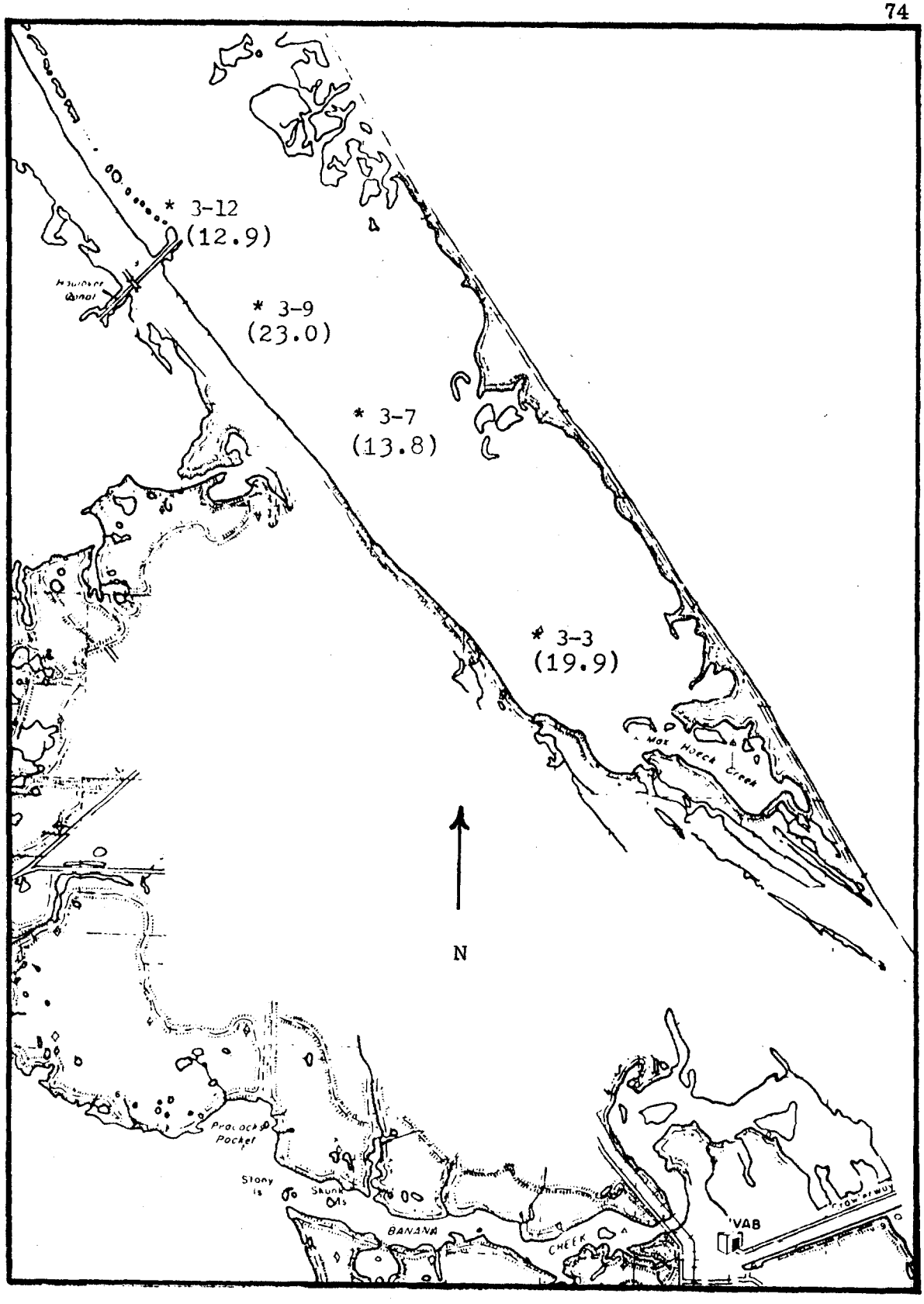


Figure 28. Carbonate Carbon values (mg/g) for Area 3.

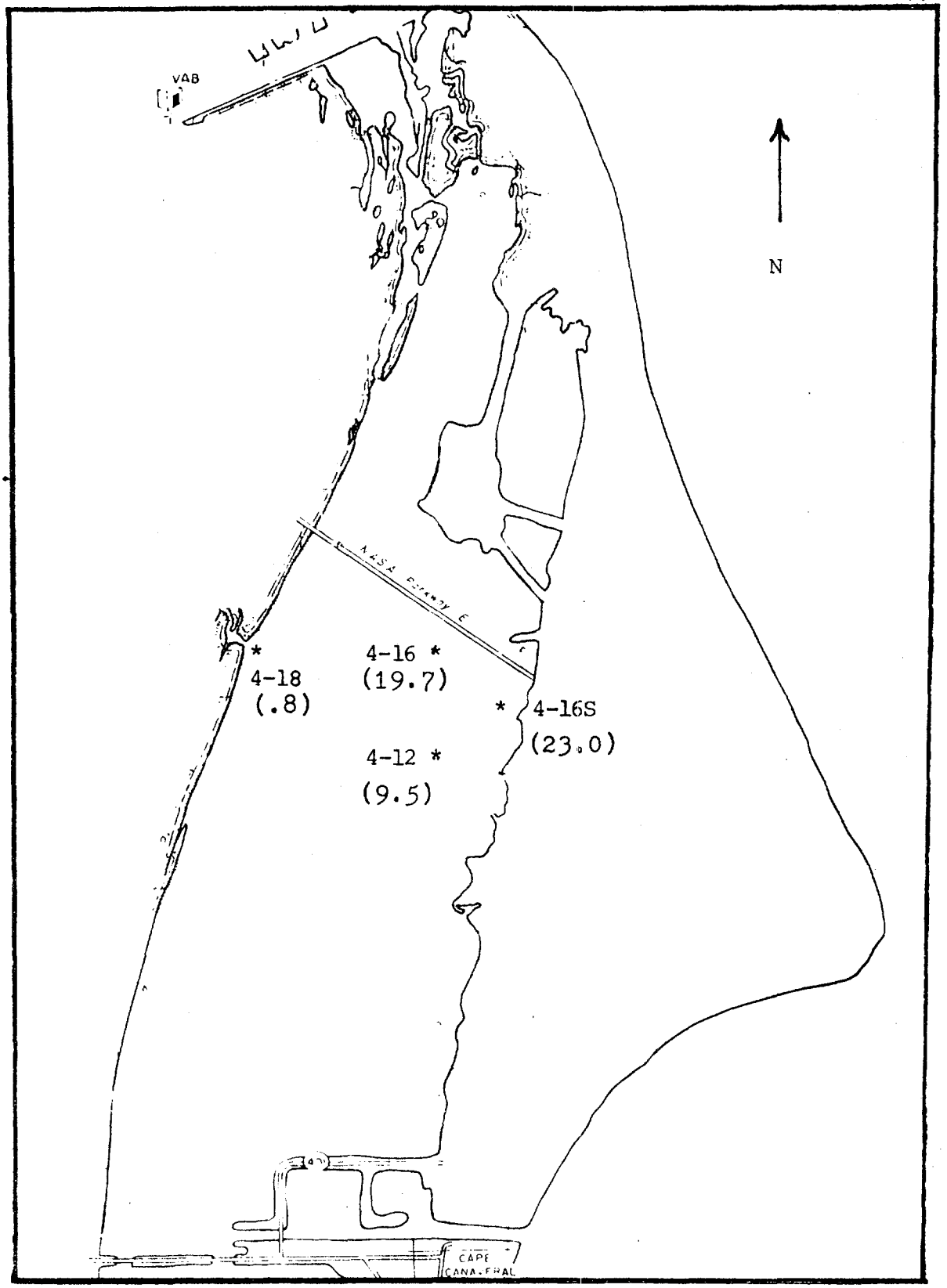


Figure 29. Carbonate Carbon values (mg/g) for Area 4.

TABLE 8

Ranking of Nutrient Concentrations Found
in Natural Sites by Study Area

	Area 1	Area 2	Area 3	Area 4
Organic C	1 pt	2 pt	4 pt	3 pt
Organic N	2 pt	3 pt	1 pt	4 pt
Total P	2 pt	1 pt	3 pt	4 pt
Sulfide	1 pt	2 pt	3 pt	4 pt
	6 pts	8 pts	11 pts	15 pts

Key:

4 pts = Highest average concentration

1 pt = Lowest average concentration

VII. CONCLUSIONS

The objective of this research was to assess the overall ecological quality of the lagoons surrounding the Kennedy Space Center by a study of the nutrient conditions as reflected in the sediments. The results of this research indicate that the influence of man on the lagoons has been of minimal consequence, and that cultural eutrophication is not evident at this time. The only area of concern was that in the immediate vicinity of Site 4-16S, where high concentrations of nutrients were found to be accumulating due to the effluent of the Air Force Base sewage treatment plant. It is recommended that this area should be investigated further, with special reference to the possibility of extending an effluent discharge pipe into the Banana River. Sediment analysis has shown that this procedure works well in this lagoonal system, as evidenced by the fact that the sediments taken from the immediate vicinity of the Titusville treatment plants discharge pipes showed no substantial accumulation of nutrients, and indeed often showed extremely low values when compared to the adjacent areas. The accumulation of nutrients at Site 4-16S has been shown by Tower (1975) to be paralleled by an accumulation of trace metals, and it is felt that this may present a potential problem area if left unchecked.

The influence of the Intracoastal Waterway on the sediment parameters was shown to be negligible, with values at the deeper sites near the waterway showing no substantial differences from values obtained in more natural areas.

The variation of nutrient levels from site to site does indicate that the sediments are not homogeneous throughout the lagoons, and that local influences are being felt. It would be necessary to collect much more data on the local circulation patterns and local biological communities in order to interpret variations on a site by site basis. This work is left for future researchers.

Baseline conditions have now been established for the concentrations of the major nutrients in the sediments surrounding Cape Kennedy. If the continued discharge of sewage effluents accumulates to levels that become unsatisfactory, these changes will be reflected by changes in sedimentary chemistry. At present, it seems that the input of nutrients is being satisfactorily handled by natural biological and chemical processes. If, on some future day, a returning space shuttle is forced to "splashdown" rather than "touchdown", the impact of this event can also be

measured with respect to sedimentary characteristics. It is hoped that this research will be of use to other investigators when they attempt to summarize the overall quality of this lagoonal ecosystem.

APPENDIX A

Techniques Used in the Analysis and Computation of Nitrogen and Phosphorus

The results of both nitrogen and phosphorus are reported as ug of nutrient ion per gram of dried sediment. As these analyses were made on wet sediments, it was necessary to make appropriate corrections of the laboratory results in order to report them as dry weight concentrations.

It was assumed that after the addition of the preservatives, the nutrient ions present in the sediments were actually contained in the pore water (Dr. J.A. Lasater, personal communication). The addition of the 10 mls. of preservative had the effect of diluting the concentrations in the pore water by a factor of

$$\frac{10+W_w}{W_w}$$

where 10 represents the weight in grams of the preservatives added (assuming that 10 mls. of preservative weighs 10 grams, an assumption verified by laboratory testing), and W_w represents the weight of the pore water of the collected sample in grams. With water content defined as the weight of the water divided by the weight of the solids, it becomes possible to determine the amount of water collected in the field sample by multiplying the wet weight of the collected sample by the water content of the sediments at that site as determined by Mendelsohn on his three co-site cores. Water content values were also measured on the wet sediments as they were taken from the sampling jar for laboratory analysis so as to measure the water content of the sediments as tested. This was done by taking a portion of the sediment and placing it in the reaction flask, and then taking a similarily extracted portion for water content analysis. By knowing the water contents of both the sample analyzed and the original sample, it becomes possible to convert wet results to dry weight results in the manner described below. It is assumed throughout that one g. H_2O is equivalent to 1 ml. H_2O.

Water content is defined as the weight of the water in a sediment sample divided by the weight of the solids (Lambe 1951).

$$W.C. = \frac{W_w}{W_s} \quad (1)$$

$$W_{total} = W_t = W_w + W_s$$

With the following algebraic manipulation:

$$W_w = (W.C.)\, W_s$$

$$W_t = (W.C.)\, W_s + W_s$$

$$= W_s(1 + W.C.)$$

$$W_s = \frac{W_t}{(1 + W.C.)}$$

the following useful formula is produced.

$$W_w = (W.C.) \frac{W_t}{(1 + W.C.)} \quad (2)$$

Allowing W_{wl} to represent the weight of the water in the sample analyzed in the lab, and W_{sl} and W_{tl} to similarly represent weights used in the samples as analyzed, then

$$W_{wl} = (W.C.) \frac{W_{tl}}{(1 + W.C._1)} \quad (3)$$

Dividing the amount of nutrient found in the testing procedure (lab result) by the amount of water contained in the analyzed sample produces the concentration of the nutrient species in the water of the analyzed sample, or:

$$\frac{\text{(lab result)}}{W_{wl}} = \text{concentration of nutrient in water analyzed} \quad (4)$$

Multiplying this result by the dilution factor $\frac{(10 + W_w)}{W_w}$ gives the concentration of the nutrient in the water of the field sediment:

$$\text{Concentration in water analyzed} \times \frac{(10 + W_w)}{W_w} = \text{Concentration in field sample} \quad (5)$$

Knowing the concentration in the field sample, and the weight of the water collected, it is possible to determine the total quantity of the nutrient collected in the field:

$$W_w \times \text{concentration in field water} = \text{total nutrient collected} \quad (6)$$

Dividing this by the weight of the solids collected gives the dry weight relationship:

$$\frac{\text{Total nutrient collected}}{W_s} = \text{nutrient/dry sediment} \quad (7)$$

Combining #3 through #7 produces the following formula for the calculation of dry weight relationships from wet weight results:

$$\frac{(\text{Lab result}) \times (10 + W_w)}{W_{wl} \times W_s} = \text{nutrient/dry sediment} \quad (8)$$

APPENDIX B

Supplemental Information
Summary of Mendelsohn's Results

TABLE I

Sediment Data

Site	pH	Eh(mv)	Eh(mv) Field	C.O.D. (% dry wgt.)	Vol. Sol. (% dry wgt.)	Water Content (%)
1-2	6.682	+144.2	ND	0.42	1.60	23.7
1-6	6.625	- 97.2	ND	0.87	2.97	29.8
1-8	6.710	+ 51.7	ND	0.55	1.37	24.8
1-11	6.641	- 66.2	ND	0.81	1.53	30.5
1-11S	6.664	- 26.7	- 40	1.05	1.03	22.1
1-15	6.554	-321.7	-300	1.29	2.63	39.0
1-19	6.572	-236.7	-310	0.77	1.43	25.9
1-20	6.539	-316.7	-370	1.18	3.53	47.4
1-23	6.755	- 90.0	-180	0.55	1.60	20.2
2-1S	6.682	-116.7	-280	0.49	1.73	31.5
2-1	6.551	- 53.3	-270	0.47	1.07	22.9
2-2	6.724	-216.7	-310	1.04	3.00	41.6
2-9	6.551	- 23.3	-100	0.53	1.17	32.3
2-17	6.488	-113.3	ND	1.31	2.40	43.1
2-24	6.501	-173.3	-250	0.78	1.67	34.2
2-30	6.496	-190.0	-180	0.75	2.10	40.5
3-3	6.635	-375.0	-360	1.14	6.07	43.0
3-7	6.625	-366.7	-330	0.97	3.67	42.0
3-9	6.647	-293.3	-340	2.31	6.33	71.5
3-12	6.625	-366.7	-350	0.78	4.03	43.8
1-26	6.533	-450.0	-410	1.08	2.60	46.2
1-29S	6.567	-570.0	-200	1.11	2.30	42.8
4-12	6.724	-290.0	-300	1.39	4.69	26.5
4-16	6.692	-320.0	-380	1.60	6.59	49.0
4-16S	6.767	-370.0	-330	12.82	19.44	188.7
4-18	6.718	-350.0	-490	3.37	2.99	50.4

ND - No Data Taken

TABLE 2

Bottom Water Data

Site	D.O.(ppm)	Salinity(ppt)	pH	Eh(mv)	Temp.(c)	Depth(m)
1-2	8.33	24	6.885	+114	18.5	1.60
1-6	9.20	25	6.818	+107.9	18.0	2.00
1-8	10.87	25	6.830	+169.9	22.5	0.50
1-11	8.83	26	6.880	+147.1	19.0	2.00
1-11S	7.87	30	6.624	+120	21.0	0.50
1-15	7.07	28	6.612	+ 85	27.0	2.00
1-19	8.07	32	6.602	+110	22.0	1.00
1-20	7.87	29	6.601	+ 60	28.0	1.75
1-23	7.67	33	6.604	+ 50	23.0	1.00
2-1S	11.27	30	6.702	+ 65	23.5	0.75
2-1	8.67	ND	ND	ND	24.0	0.50
2-2	7.73	28	6.730	+ 90	18.0	1.25
2-9	6.83	32	6.541	+170	27.0	1.30
2-17	6.27	35	6.514	+160	26.0	1.75
2-24	7.93	35	6.521	+150	28.0	1.00
2-30	7.90	35	6.508	+160	29.0	0.50
3-3	9.10	36	6.678	+ 40	28.0	1.00
3-7	8.47	35	6.639	+100	28.0	1.75
3-9	6.77	36	6.634	+105	27.0	2.00
3-12	7.43	34	6.665	+ 95	27.0	0.75
1-26	6.87	30	6.596	+ 90	30.0	0.75
1-29S	5.60	26	6.609	+ 60	28.0	0.50
4-12	8.80	25	6.783	+ 80	29.0	0.25
1-16	6.80	26	6.829	+ 85	26.0	1.25
4-16S	7.00	23	6.802	+ 82	28.0	0.25
4-18	3.60	25	6.788	+ 95	26.0	0.50

ND - No Data Taken

APPENDIX C

Laboratory Results

AVERAGES OF LABORATORY RESULTS - IN SIGNIFICANT FIGURES

SITE	$\%CO_3$	%C inorg	C-org mg/g	Sulfide ug/g	NH_3 ug/g	N-org ug/g	P-tot ug/g	P-dis ug/g
1-2	2.22	.44	1.84	20.1	1600	380	186	64.5
1-6	7.67	1.54	1.42	56.9	49	390	81	62.6
1-8	1.23	.24	4.55	76.3	1000	1500	281	128
1-11	3.97	.79	3.10	73.4	920	1300	142	64.3
1-11S	1.28	.26	1.97	55.8	1200	270	17.6	28
1-15	5.76	1.15	3.00	47.0	380	630	100	81
1-19	1.95	.39	3.52	53.7	1100	310	114	51.6
1-20	5.18	1.04	2.86	68.8	0	1100	419	107
1-23	3.34	.69	2.44	44.8	3000	1400	34	25.5
1-26	1.64	.33	4.81	69.0	1200	1000	258	67
1-29S	4.75	.95	2.98	59.6	890	1200	556	104
2-1	1.58	.32	2.11	23.4	2700	1600	65	62
2-1S	1.04	.21	5.67	18.1	1000	1500	193	87.3
2-2	3.83	.77	6.30	56.7	1500	2900	553	187
2-9	1.21	.24	2.51	42.0	1500	620	118	78.5
2-17	3.41	.68	4.04	55.1	2200	950	91	82
2-24	1.72	.34	2.80	127	940	1100	192	65

AVERAGES OF LABORATORY RESULTS - IN SIGNIFICANT FIGURES

SITE	$\%CO_3$	%C inorg	C-org mg/g	Sulfide ug/g	NH_3 ug/g	N-org ug/g	P-tot ug/g	P-dis ug/g
2-30	1.85	.37	4.78	108	1100	940	182	83.5
3-3	9.96	1.99	6.32	46.0	250	800	231	159
3-7	6.90	1.38	2.50	68.4	400	950	151	89.5
3-9	11.53	2.30	6.51	112	780	320	707	498
3-12	6.44	1.29	4.82	88.9	990	390	441	240
4-12	4.75	.95	2.52	89.3	470	820	1020	640
4-16	9.85	1.97	3.08	134	1400	1900	1130	809
4-16S	11.50	2.30	53.5	303	2800	14000	1540	763
4-18	.41	.08	6.06	84.7	480	1700	215	105

LABORATORY RESULTS - RAW FIGURES

SITE	%CO_3	%C inorg	C-org mg/g	Sulfide ug/g	NH_3 ug/g	N-org ug/g	P-tot ug/g	P-dis ug/g
1-2	2.79	.56	1.70	14.93	1831	685	199	65
	2.16	.43	1.98	25.28	2283	176	190	64
	1.70	.34			1966	324	168	
					554	342		
1-6	7.79	1.56	1.76	45.49	0	0	0	54
	8.01	1.60	1.07	68.24	148	942	130	51
	7.27	1.46			0	259	113	83
1-8	1.90	.38	4.55	73.99	1213	1199	253	143
	1.17	.23	4.55	78.66	1178	1832	406	153
	.61	.12			716	1376	185	89
1-11	4.65	.93	3.14	74.27	1046	1230	132	59
	3.87	.77	3.06	72.45	866	1782	142	74
	3.38	.68			865	910	151	60
1-11S	.45	.09	2.05	51.64	396	0	0	28
	2.38	.48	1.88	59.96	1987	546	53	26
	1.01	.20					0	30
1-15	6.31	1.34	3.08	29.85	0	631	100	81
	5.62	1.12	2.92	64.17	750	631		
	4.96	.99						
1-19	1.12	.22	3.47	44.44	1299	357	113	52
	2.78	.56	3.57	62.87	985	270	117	52
	1.98	.39					113	51
1-20	4.37	.87	2.88	74.63	0	1125	419	107
	5.70	1.14	2.84	62.99	0	1098		
	5.46	1.09						

LABORATORY RESULTS - RAW FIGURES

SITE	$\%CO_3$	%C inorg	C-org mg/g	Sulfide ug/g	NH_3 ug/g	N-org ug/g	P-tot ug/g	P-dis ug/g
1-23	3.42	.68	2.39	30.13	4404	1612	29	28
	2.86	.57	2.49	59.48	1585	1305	39	23
	3.75	.75						
1-26	1.53	.31	4.76	85.77	1504	619	258	67
	1.85	.37	4.85	52.24	869	1431		
	1.54	.31						
1-29S	4.52	.90	2.98	66.30	884	728	556	104
	4.51	.90	2.98	52.83	900	1630		
	5.23	1.04						
2-1	2.63	.53	2.06	15.56	4145	1707	65	62
	1.31	.26	2.15	31.31	1260	1556		
	.81	.16						
2-1S	1.06	.21	5.65	22.13	976	1406	174	97
	1.02	.20	5.68	14.07	1317	1989	227	81
					790	1085	179	84
2-2	4.79	.96	6.44	69.08	1440	2964	615	165
	3.68	.74	6.15	44.30	1816	2990	521	246
	3.02	.60			1392	2866	523	150
2-9	1.58	.32	2.43	44.44	1712	705	103	81
	1.16	.23	2.59	39.45	1274	525	133	76
	.90	.18						
2-17	2.90	.60	3.96	63.12	1046	963	113	81
	4.11	.82	4.12	47.15	3411	936	69	83
	3.23	.65						

LABORATORY RESULTS - RAW FIGURES

SITE	%CO_3	%C inorg	C-org mg/g	Sulfide ug/g	NH_3 ug/g	N-org ug/g	P-tot ug/g	P-dis ug/g
2-24	1.69	.34	2.58	123.93	989	813	186	69
	1.68	.34	3.01	130.02	900	1483	197	61
	1.79	.36						
2-30	1.55	.31	4.82	98.67	752	620	190	88
	1.80	.36	4.74	118.34	1536	1265	173	79
	2.20	.44						
3-3	9.80	1.96	6.22	45.11	0	778	231	130
	9.84	1.97	6.42	46.78	508	837		188
	10.25	2.05						
3-7	7.16	1.43	2.52	57.97	801	600	151	101
	7.07	1.41	2.48	78.85	0	1295		78
	6.48	1.30						
3-9	11.69	2.34	6.41	122.84	742	306	707	424
	11.44	2.29	6.60	101.36	827	341		572
	11.45	2.29						
3-12	6.81	1.36	4.69	94.55	902	372	441	293
	6.28	1.26	4.95	83.33	1076	443		187
	6.24	1.29						
4-12	4.82	.96	2.75	9108	549	679	1018	522
	4.59	.92	2.28	87.59	386	954		758
	4.84	.97						
4-16	10.96	2.19	2.98	140.01	903	2230	1127	728
	9.40	1.88	3.18	127.34	1944	1601		890
	9.18	1.84						

SITE	%CO_3	%C inorg	C-org mg/g	Sulfide ug/g	NH_3 ug/g	N-org ug/g	P-tot ug/g	P-dis ug/g
4-16S	10.94	2.19	54.81	285.12	2720	13441	1543	416
	11.68	2.34	52.19	320.01	2935	14504		1110
	11.88	2.38						
4-18	.41	.08	5.98	87.91	950	782	215	101
	.42	.08	6.14	81.48	0	2690		109
	.40	.08						

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Section IV, Article 13

Physical and Chemical Characteristics of the Sediments of the Lagoonal Waters Surrounding Kennedy Space Center, Florida

Stuart Mendelsohn

1975

PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE SEDIMENTS OF THE LAGOONAL WATERS SURROUNDING KENNEDY SPACE CENTER, FLORIDA

by

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B.S. in Ocean Engineering, Florida Institute of Technology, 1974

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1975

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Environmental Engineering

Physical and Chemical Characteristics of the Sediments of the Lagoonal Waters Surrounding Kennedy Space Center, Florida

---Major Advisor: Dr. D.D. Woodbridge

The investigation of the Indian River and Mosquito Lagoon, surrounding the John F. Kennedy Space Center, Florida, for possible pollution from local sewage treatment plants by analyzing their bottom sediments and the physical characterization of the sediments is the objective of this study. Using the chemical and physical data obtained from the dissolved oxygen, pH, oxidation-reduction potential (Eh), chemical oxygen demand (C.O.D.), volatile solids, water content and grain size, the marine sediments are studied.

The effect of two secondary sewage treatment effluents is examined along with areas disturbed by other factors. Some of the other factors having an effect on the bodies of water are land runoff, dredged sediments, and movements of the body of water itself.

The most important factors in the formation of a polluted body of water are the amount of oxygen available and the amount of mixing that occurs in the river or lagoon. Because of this, runoff from the

land and other sources of effluents can be more detrimental to a marine system than a treated sewage effluent.

This investigation has shown that effluents from the secondary treatment plants studied have no more of an effect on the waters than other factors in the area if their effluents are well dispersed with the receiving waters.

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INTRODUCTION

One way to investigate a body of water for possible pollution is to investigate its sediments. Using several chemical and physical tests on the sediments, much can be learned about what is going on in the marine environment and to see if it is being overloaded with organic matter. The chemical properties of bottom sediments reflect the nature of source sediments, the chemical nature and physical processes that characterize the water that overlies the bottom, and chemical and biochemical processes that take place within the sediments as they consolidate. (Nelson, 1972)

This study investigates what affect, if any, local sewage treatment plants have on the sediments and the chemical and physical characteristics of the sediments.

The lagoons being examined are important because of their proximity to the Kennedy Space Center and their use as a part of the Intracoastal Waterway System. These waters are saline due to having several inlets opening into the system (Figure 2) and also the locks located at Port Canaveral. There is also a considerable amount of fresh water entering the system from land drainage giving a brackish water typical of estuaries.

These bodies of water have been altered by man through land use and the construction of several bridge and causeway systems. Also, the construction of Haulover Canal has opened a connection between Mosquito Lagoon and the northern part of the Indian River. On the other hand, construction for the Kennedy Space Center has closed off

the natural connection of the Banana and Indian Rivers. The Canaveral Harbor and Barge Canal has opened another unnatural link between the Banana and Indian Rivers and the ocean.

The part of the Indian River being looked at in this study extends from the Orsino Causeway (NASA Parkway) to the Titusville Causeway (Area 1) to the north tip of the Indian River (Area 2). The Mosquito Lagoon was looked at over its length (Area 3). Also included are the Banana River north of the Bennett Causeway (Area 4) and Banana Creek (part of Area 1).

The nearest free connections to the ocean are the Ponce de Leon Inlet 25 miles to the north of the Mosquito Lagoon entrance to Haulover Canal, and Sebastian Inlet fifty miles to the south (Figure 2). This leads to the fact that there is little or no tidal influence.

These waterways are all very shallow. The deepest areas are the dredged areas of the Intracoastal Waterway which is dredged to 3.5 meters. The rest of the areas have water depths of 2 meters or less. Wind-induced currents and wind tides provide the major mechanism for movement and mixing of these waters. (Dill, 1974)

The two sewage treatment plants operated by the city of Titusville, located in areas 1 and 2, are secondary sewage treatment plants. They are activated sludge plants with an average daily flow of 1.2 million gallons and 4.2 million gallons, respectively, and a 90-95 per cent B.O.D. removal.

The treatment plants in the Banana River and the Banana Creek are both secondary treatment plants, however they treat industrial sewage. They are trickling filter plants, but the one in Banana Creek

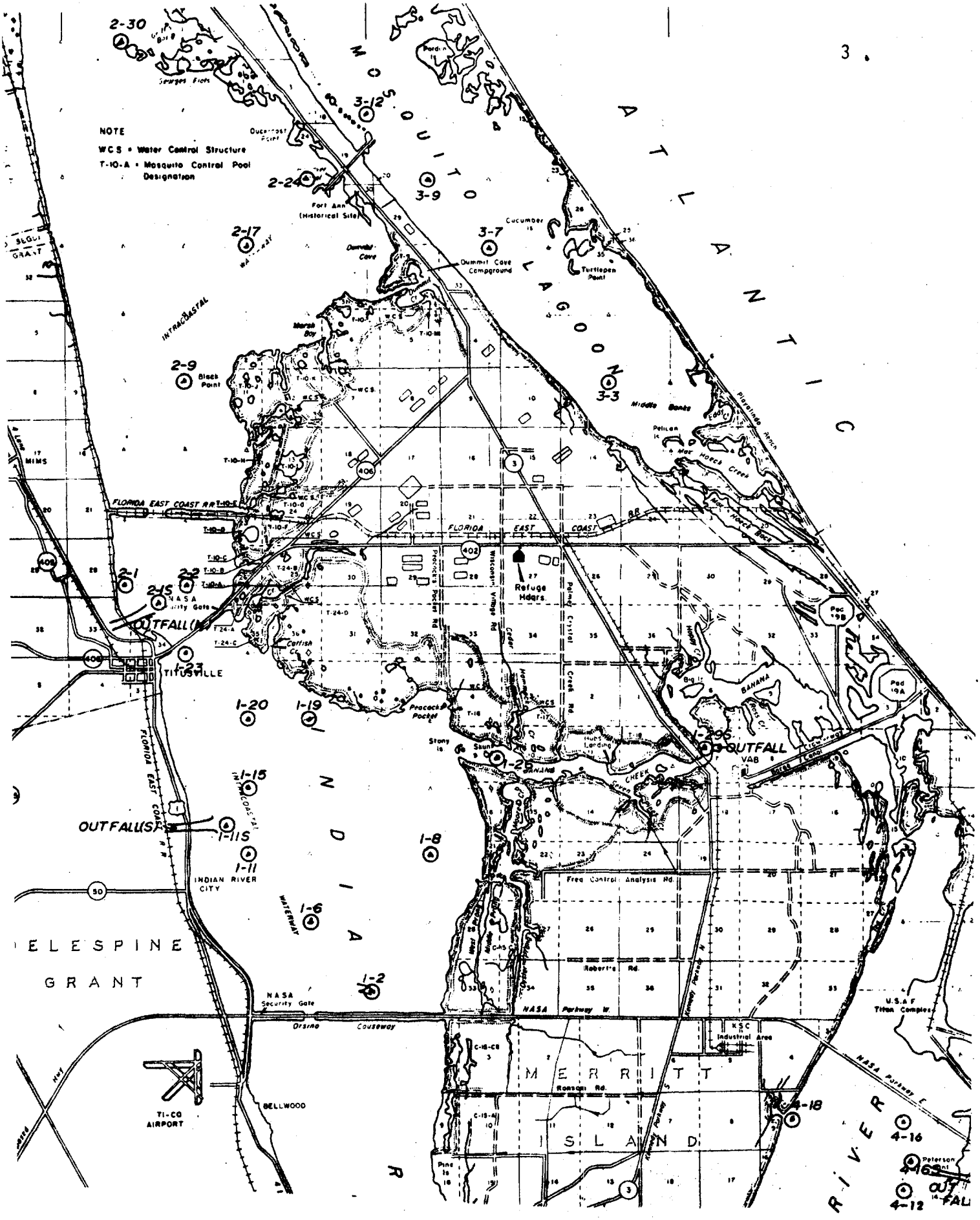
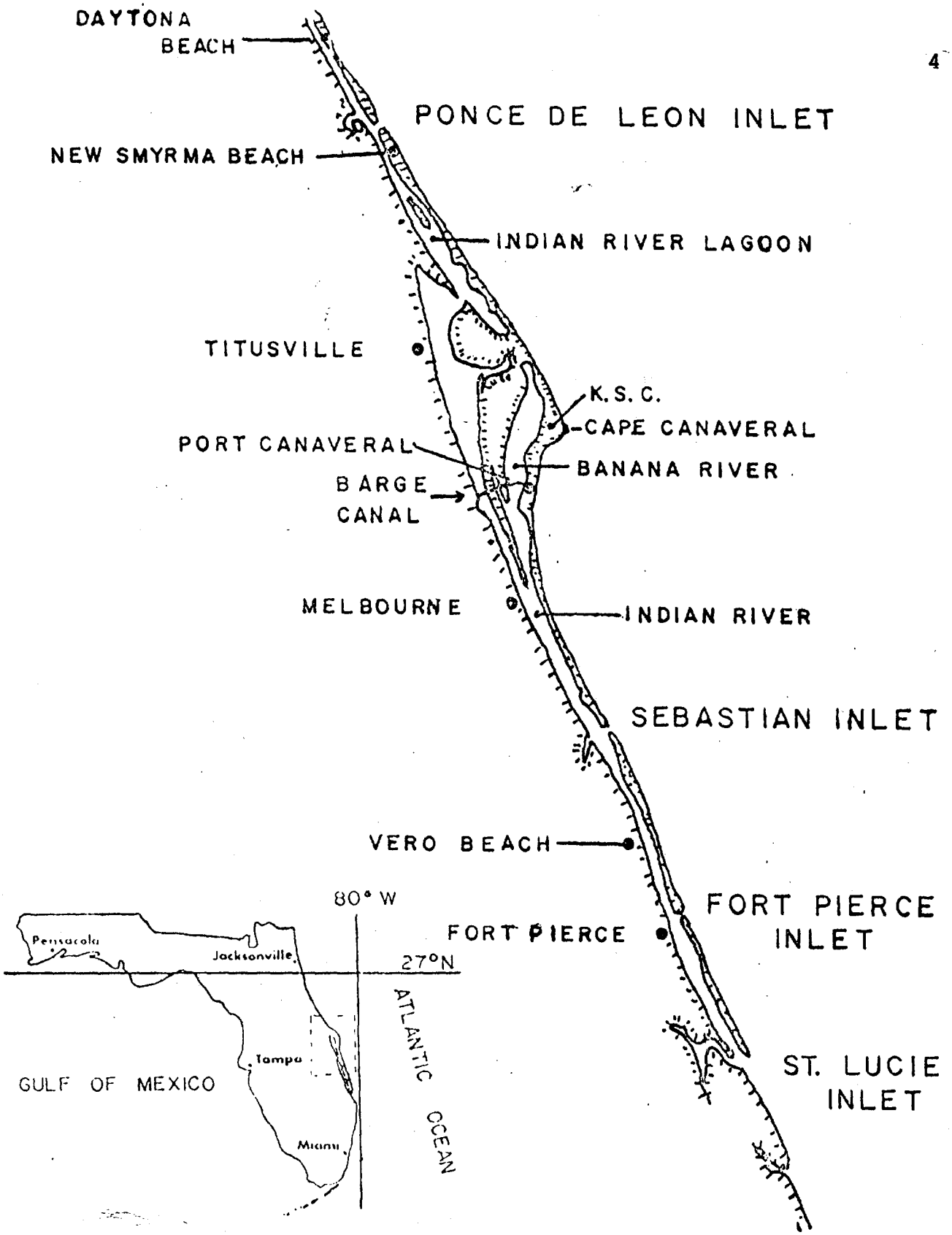


Figure 1
SITE LOCATION MAP



LAGOONS OF EAST CENTRAL FLORIDA

Figure 2.

also uses a polishing pond.

The abundance of algal nutrients in some secondary effluents can lead to profuse algal growths which would result in an increase in organic and suspended solids from the treatment plant. Even well-treated secondary effluents can contain refractory organic materials as measured by the chemical oxygen demand.

BACKGROUND

The dissolved oxygen (D.O.) is important to determine if there is oxygen available to the sediments for oxidation of organic matter. If the water were oxygen deficient, anerobic decomposition would occur. This is much slower than aerobic decomposition. Sediments with not enough oxygen become a reducing environment instead of an oxidizing one (Nelson, 1972). Atmospheric oxygen enters the water through the surface. This allows a river to be capable of eliminating a definite amount of organic matter by itself by having enough oxygen available in the water. This is called self-purification.

As one goes deeper into a body of water or as the body gets deeper, the sediments have less dissolved oxygen available since it is farther away from the surface interaction with the atmosphere. The D.O. decreases with depth (Yasso, 1965). The more isolated an area, the lower the bottom D.O. will be due to little mixing with the oxygen in the atmosphere and the surface waters.

The pH is a measure of acidity or alkalinity of the sediment. The pH of bottom sediments integrates a number of environmental variables including salinity, CO_2 dissolved in the pore waters, dissociated organic acids and bases, dissociated organic decomposition products such as ammonia, and dissociated clay minerals (Nelson, 1972).

The pH usually increases as the salinity goes up. It also is at its lowest where the bacterial action is at its maximum. As the grain size increases, the amount of organic matter usually decreases and therefore, the pH gets higher (Emery & Rittenberg, 1952). CO_2 lowers

the pH due to its ability of forming a slightly acidic solution, while ammonia raises it since it forms a basic solution.

The pH of most surface sediments is near that of the overlying water due to constant mixing due to the sediments retaining large amounts of water. A pH maximum occurs below the surface when sedimentation is rapid and implies that the large amount of organic matter is being decomposed by the micro-organisms at a fast rate, therefore producing ammonia due to the anaerobic decomposition (Nelson, 1974).

Throughout a 24-hour period, the pH increases during the daytime and decreases at night when there are plants present. This is due to the production of oxygen and the use of bicarbonate ion during the day by photosynthesis followed by the use of oxygen and the production of bicarbonate ion by respiration (Emery, 1969).

The Eh is probably one of the most important tests to learn the state of the sediments. The Eh of a system is an expression of its oxidizing or reducing intensity. A positive Eh will indicate a well oxygenated sediment usually poor in organic matter and in the oxidized state. A negative Eh usually indicates sediments rich in organic matter and in the reduced state (Zobell, 1946). The Eh of a sediment depends on 1) the rate and type of bacterial activity, 2) the amount and kind of organic matter, and 3) the rate of O_2 penetration into the sediment (Emery and Rittenberg, 1952). The controlling factor on Eh is the supply of oxygen with respect to the amount of organic matter to be decomposed or oxidized (Blatt, et al, 1972). "Negative Eh is associated with bacterial decay of organic matter and depletion of oxygen" (Nelsor, 1972). In a natural environment neither the Eh nor the pH is an independent

variable. The redox potential is particularly affected by the zone of maximum bacterial action. The zone of maximum bacterial action occurs at the zone of lowest pH which is usually at the sediment-water interface (Emery & Rittenberg, 1952). The surface sediments usually are positive and become negative just below the surface (Nelson, 1972).

The chemical oxygen demand (C.O.D.) test is an indicator of the quantity of oxidized compounds present in the sediments. This test is related to the amount of organic matter present. By definition, the C.O.D. is a measure of the oxygen equivalent of that portion of organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant.

The volatile solids content is an estimate of the organic material present in the sediments also. A correlation between total volatile solids and the chemical oxygen demand has been presented (Soule and Oguri, 1974). It is as follows:

$$T.V.S.\ (\%\ dry) = 1.32 + 0.98\ (C.O.D.\ \%)$$

The authors graph total volatile solids versus chemical oxygen demand for their sediments and do not arrive at this correlation. Their sediments were fine grained silts and clays. The Environmental Protection Agency has set up criteria for determining whether a dredged area is polluted. These are 6 per cent on a dry weight basis for volatile solids and 5 per cent on a dry weight basis for the C.O.D.

The water content is important in itself and because it is needed to obtain per cent dry weight values for several tests. Water content usually increases as the grain size decreases and as the amount of organic matter increases. Also, surface sediments exposed to scour

have low water content (Nelson, 1972).

Grain size is important because it helps give an idea of what is present in the sediments. Usually where sediment particles are the finest, the organic content is the highest and where they are the coarsest, the organic content is the lowest. In silt-free areas the coarseness of the particles provide much interstitial space favorable to interstitial biota which keep organic accumulations to a minimum. In finer sediments, filter feeders, which are important consumers of the organic supply, do not function well and are not as prevalent (Nelson, 1972).. Grain size also is important as to whether there is mixing to help oxidize the sediments. The finer particles are more cohesive and therefore more tightly bound so mixing is not as easily obtained.

The color of the sediments is a physical method for gaining an idea of the make up of the sediments. Differences in color are due to the following constituents: clay minerals, which make up the bulk of the fine-grained sediments, are olive colored; organic compounds which can yield dark gray or black colors; reduced ferrous-rich compounds yield gray-colored sediments. Land-derived ferric iron mixed with olive-colored soil may be responsible for the olive brown color in sediments. Sediments with thick oxidation layers are olive brown colored, while sediments with thin oxidation layers are grayish olive or olive (Nelson, 1972).

Surface sediments which are brown in color contain unreduced iron compounds with a slightly positive oxidation-reduction potential. When these sediments are suspended and redeposited due to water currents,

the reducing process must be started over again. Below the surface layer, reducing processes convert free iron compounds, and the sediments become olive gray (Nelson, 1972). When the surface sediments are dark gray in color, there usually is an excess of organic material present.

SAMPLING AND TESTING

The sites for investigation were selected in conjunction with Peffer (1975) to cover the Indian River and Mosquito Lagoon. The sixteen sites in the Indian River were selected in order to cover the area north and south of and in the area of two sewage outfalls (Figure 1). This would show what effect, if any, the two sewage treatment plants have on the river. Many sites were picked for their proximity to the Intracoastal Waterway. Also sites like 2-30, 1-8, and 3-7 were picked for their isolation from man's activity. Four additional sites have been selected in the isolated Mosquito Lagoon for use as a comparison. Single cores were taken in the Banana Creek and Banana River as background for Peffer (1975) and to gain a better picture of the area.

The data were collected over a four month period from the end of January to the end of May. During this time there was a lack of rain due to the annual dry season. For the most part the cores were collected from the south of area 1 to the northern tip of area 2 and then Mosquito Lagoon. The cores in area 4 were taken last. The samples were also taken between the hours of 10 a.m. and 3 p.m. during the day. The weather ranged from sunny and calm to stormy and windy. Since this study is looking at the sediments, these effects are considered minimal except for the temperature difference affect on the salinity and the water depth.

The sampling procedure was as follows: a small boat was positioned by using a hand bearing compass and anchored at the site using three anchors. While at each site, three cores were taken, except for the sites in Banana Creek and Banana River where only one core was

taken, and sealed to be brought back to the laboratory. Also, at each site the following information was taken from the water columns. dissolved oxygen, temperature, and water depth. Also, for use as a comparison with the laboratory data, the oxidation reduction potential was taken in the field using an Orion pH meter as described below. The sampling device used to take the cores was a two inch diameter polyvinyl chloride (PVC) hand corer. Samples were sealed in the field. However the water contents were probably affected by the inability to get a good seal for the core tubes. A water sample taken just above the sediment-water interface was also collected for most sites.

In the laboratory, the oxidation-reduction potential (Eh), pH and the water content were taken immediately on the surface sediments from every core. They were then resealed and stored in a refrigerator overnight to minimize the changing of the physical and chemical properties of the sediments. Also performed at this time was the test for pH, Eh, and salinity of the water sample collected. The pH and Eh were done as described below and the salinity was performed using an optical salinometer. Over the next couple of days, each core was extruded, described and tested for the chemical oxygen demand (C.O.D.) and its grain size. The volatile solids test was run on the dried sediments from the water content analysis. Also done on each core was an Eh profile of the top 30 centimeters when each was extruded.

The dissolved oxygen (D.O.) was taken on the water just above the bottom sediments. This test was done to see if there is oxygen available in the water for the sediments. A Y.S.I. meter and probe were used and the measurements done in situ.

The oxidation-reduction potential (Eh), which is the first test done upon getting the cores back to the laboratory, was performed using an Orion pH meter using a platinum electrode. The electrode was lowered into the core and immersed in the surface sediments before the cores were extruded. After extruding the core, at a later time, the Eh was read at four centimeter intervals down the core length to a depth of 30 centimeters.

Th pH, which is a measure of acidity or alkalinity of the sediment, is done using a Beckman pH meter with a glass electrode and a calomel reference electrode. This is the second test done immediately after the cores are returned to the laboratory again before they are extruded.

The next test done upon returning to the laboratory and before the cores are resealed and stored is the water content analysis. This is done by weighing a sample scooped from the surface sediments, drying in an oven at 105^{0} C for 24 hours and reweighing (Bowles, 1970).

After the cores were extruded, a physical description was done on each core including a color classification using the Munsell Color Chart (Appendix I). The chemical oxygen demand was then run as described by Standard Methods (p. 510-511) using a one gram sample, 25 mls. of potassium dichromate, 25 mls. of H_2SO_4 mixed with $AgSO_4$, and about one gram of $HgSO_4$. This was then heated and refluxed for two hours.

The volatile solids analysis was done also as described by Standard Methods (p. 534-535). It involved heating the dried sediments from the water content test to about 600^{0} C for one hour and reweighing. It is heated to 600^{0} C to drive off the volatile matter

and produce an ash residue.

The last test done was the grain size analysis since it is not affected by time. This was done as described in Bowles, 1970, using the following sieve numbers: 4, 10, 20, 40, 60, 100, 200.

All the tests were done on each core except the grain size analysis for which all three cores from a site were combined and treated together. The surface sediments were used for all analysis except the dissolved oxygen. The surface sediments consisted of approximately the top 10 centimeters or where the surface layer ended as seen by opening and describing the core. The combining of all three cores for a grain size analysis is done since the areas are not homogeneous and a representative sample is wanted.

PRESENTATION AND DISCUSSION OF DATA

The data presented are means for each site except the six sites for which only one core was taken. They are broken down into two groups: sediment data (Table 1), and bottom water just above the sediments data (Table 2). The complete data is presented in Appendix II. The grain size information and core descriptions are found in Appendix I.

The only site that shows an excess of organic matter and is above the EPA standards is 4-16S. This is one of the sites where only one core was taken, but the sediments of this area did not appear to be patchy. This site is right off a creek which has an industrial sewage treatment plant near its mouth. The effluent is not mixed as is the case in the two sewage treatment plant outfalls in areas 1 and 2. In addition to the poor mixing, there is a mangrove area obstructing the mouth of the creek further impeding mixing and aiding in the settling of the organic matter. No other site shows pollution by the EPA C.O.D. criteria, but three other sites, 3-3, 3-9 and 4-16, show that they contain greater than six per cent volatile solids. Two of these are in the isolated Mosquito Lagoon and one is near the poorly mixed effluent at site 4-16S. The EPA appears to be the only one which uses the C.O.D. and volatile solids as a pollution criteria.

The pH of the sediments showed little significant differences over the entire study. The salinity is seen to have little effect on the pH. The amount of organic matter present as indicated by the chemical oxygen demand (C.O.D.) and the total volatile solids tests also shows no effect. The Eh also is seen to have no effect (Figure 4).

TABLE I

Sediment Data

Site	pH	Eh(mv)	Eh(mv) Field	C.O.D. (% dry wgt.)	Vol. Sol. (% dry wgt.)	Water Content (%)
1-2	6.682	+144.2	ND	0.42	1.60	23.7
1-6	6.625	- 97.2	ND	0.87	2.97	29.8
1-8	6.710	+ 51.7	ND	0.55	1.37	24.8
1-11	6.641	- 66.2	ND	0.81	1.53	30.5
1-11S	6.664	- 26.7	- 40	1.05	1.03	22.1
1-15	6.554	-321.7	-300	1.29	2.63	39.0
1-19	6.572	-236.7	-310	0.77	1.43	25.9
1-20	6.539	-316.7	-370	1.18	3.53	47.4
1-23	6.755	- 90.0	-180	0.55	1.60	20.2
2-1S	6.682	-116.7	-280	0.49	1.73	31.5
2-1	6.551	- 53.3	-270	0.47	1.07	22.9
2-2	6.724	-216.7	-310	1.04	3.00	41.6
2-9	6.551	- 23.3	-100	0.53	1.17	32.3
2-17	6.488	-113.3	ND	1.31	2.40	43.1
2-24	6.501	-173.3	-250	0.78	1.67	34.2
2-30	6.496	-190.0	-180	0.75	2.10	40.5
3-3	6.635	-375.0	-360	1.14	6.07	43.0
3-7	6.625	-366.7	-330	0.97	3.67	42.0
3-9	6.647	-293.3	-340	2.31	6.33	71.5
3-12	6.625	-366.7	-350	0.78	4.03	43.8
1-26	6.533	-450.0	-410	1.08	2.60	46.2
1-29S	6.567	-570.0	-200	1.11	2.30	42.8
4-12	6.724	-290.0	-300	1.39	4.69	26.5
4-16	6.692	-320.0	-380	1.60	6.59	49.0
4-16S	6.767	-370.0	-330	12.82	19.44	188.7
4-18	6.718	-350.0	-490	3.37	2.99	50.4

ND - No Data Taken

TABLE 2

Bottom Water Data

Site	D.O.(ppm)	Salinity(ppt)	pH	Eh(mv)	Temp.(c)	Depth(m)
1-2	8.33	24	6.885	+114	18.5	1.60
1-6	9.20	25	6.818	+107.9	18.0	2.00
1-8	10.87	25	6.830	+169.9	22.5	0.50
1-11	8.83	26	6.880	+147.1	19.0	2.00
1-11S	7.87	30	6.624	+120	21.0	0.50
1-15	7.07	28	6.612	+ 85	27.0	2.00
1-19	8.07	32	6.602	+110	22.0	1.00
1-20	7.87	29	6.601	+ 60	28.0	1.75
1-23	7.67	33	6.604	+ 50	23.0	1.00
2-1S	11.27	30	6.702	+ 65	23.5	0.75
2-1	8.67	ND	ND	ND	24.0	0.50
2-2	7.73	28	6.730	+ 90	18.0	1.25
2-9	6.83	32	6.541	+170	27.0	1.30
2-17	6.27	35	6.514	+160	26.0	1.75
2-24	7.93	35	6.521	+150	28.0	1.00
2-30	7.90	35	6.508	+160	29.0	0.50
3-3	9.10	36	6.678	+ 40	28.0	1.00
3-7	8.47	35	6.639	+100	28.0	1.75
3-9	6.77	36	6.634	+105	27.0	2.00
3-12	7.43	34	6.665	+ 95	27.0	0.75
1-26	6.87	30	6.596	+ 90	30.0	0.75
1-29S	5.60	26	6.609	+ 60	28.0	0.50
4-12	8.80	25	6.783	+ 80	29.0	0.25
1-16	6.80	26	6.829	+ 85	26.0	1.25
4-16S	7.00	23	6.802	+ 82	28.0	0.25
4-18	3.60	25	6.788	+ 95	26.0	0.50

ND - No Data Taken

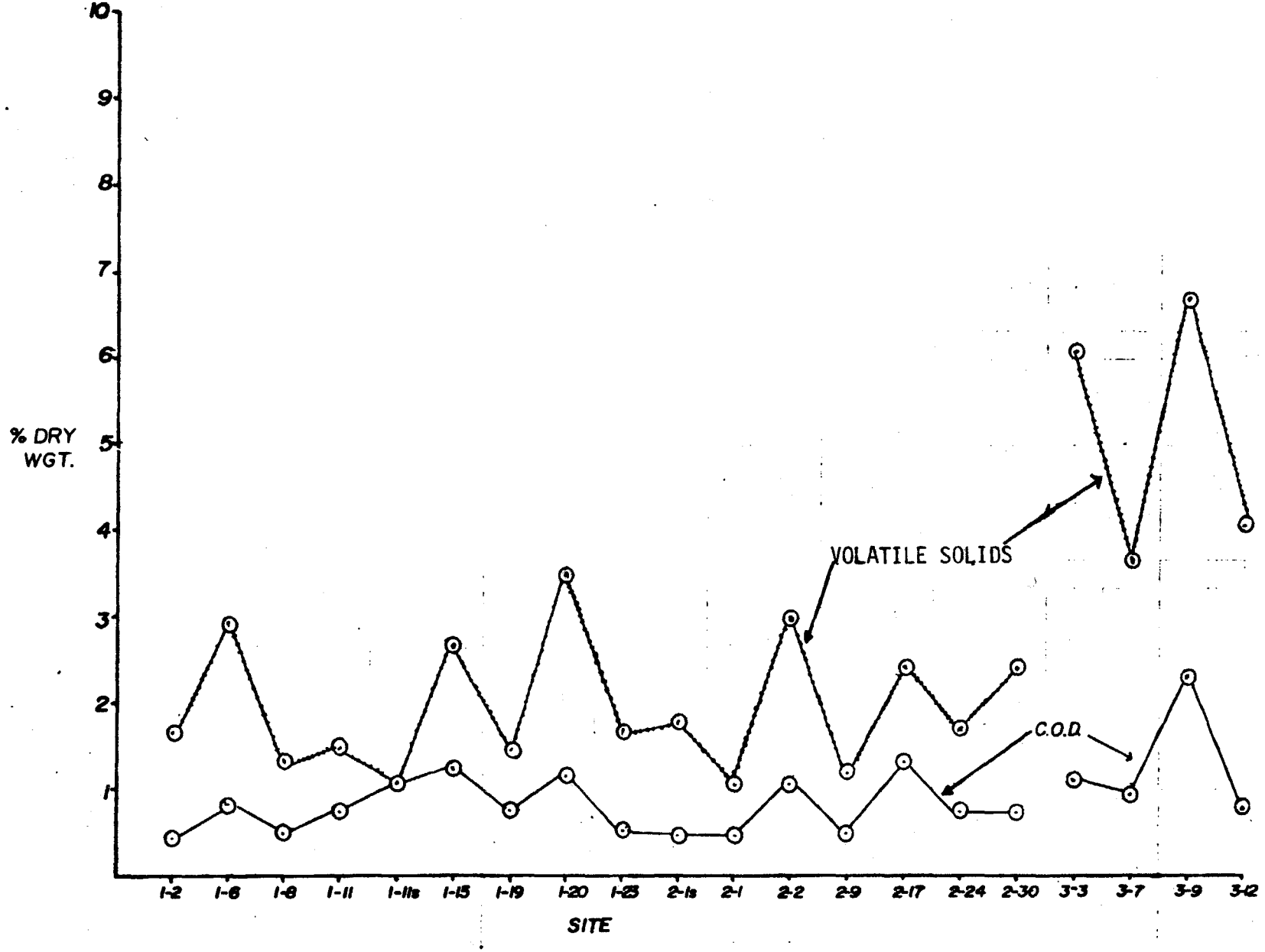


Figure 3
VOLATILE SOLIDS AND C.O.D. VS. SITE

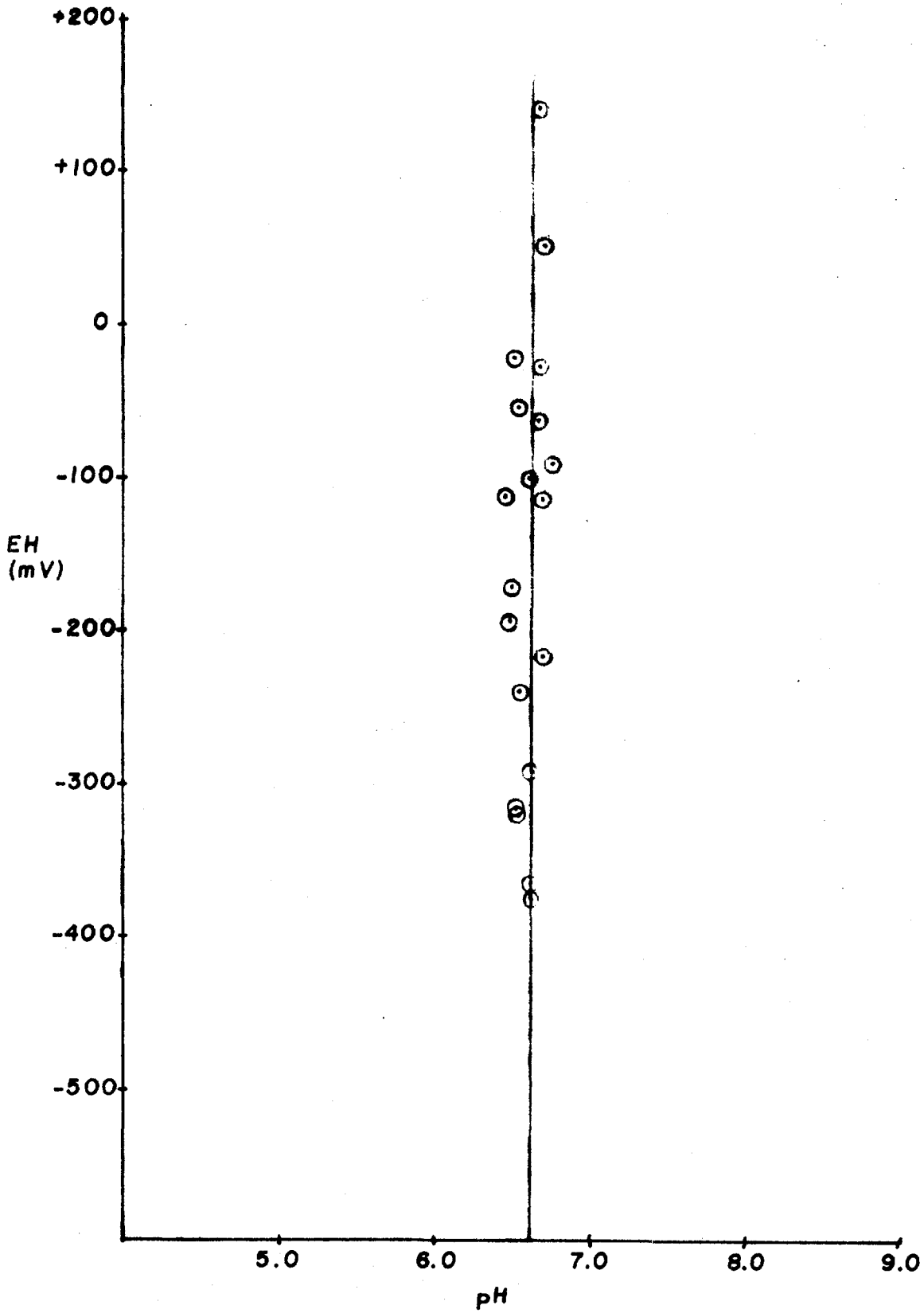


Figure 4
PH VS EH

The data in Figure 4 agrees with previous work done on marginal marine sediments (Baas Becking, et al., 1960). Figure 4 shows a close resemblance to this information and tends to characterize these sediments. Work done by Baas Becking, et al., was for 640 data points from around the world. Both show very little change in pH with Eh. The slight differences that are present in the pH data could be due to daily fluctuations from the photosynthesis cycle since the data was collected over the course of a day. The pH of the bottom water is seen to be for the most part just a little higher than the sediments just below them. They are very close as expected, however.

The dissolved oxygen (D.O.) showed some significant differences, but these were due to specific reasons and not the amount of organic matter present. All sites appear to have enough oxygen available to the sediments for decomposition of organic matter. The site with a low D.O. is 4-18. This value is due to the amount of Manatee grass decaying in those waters. The highest value at site 2-1S is due to two factors: 1) the high amount of plants growing there and 2) the day the data was taken it was stormy and the water was well mixed. This would affect the D.O. of the water, but not the sediments immediately. Another high value at site 1-8 was due to a more than average amount of green plants growing there. Most of the other differences in values is due to the daily fluctuations, the different weather conditions under which the data was taken, and the varying amount of green plants such as Cymodocea manatorum (Manatee grass) and Diplanthera (Shoalgrass).

The Eh is an important factor to the overall picture of the

sediments. The amount of mixing is important to Eh. The surface sediments are usually positive, but in most cases this layer was so thin that it was not measureable in this study or was lost in sampling. The grayish olive color is representative of thin oxidation layers (Nelson, 1972). There were significant differences of Eh between sites. Only two sites (1-2 and 1-8) were positive. This was due to a thicker than normal oxidation layer. One problem with the Eh data is the method of obtaining them. The values recorded in the laboratory did not always correspond with the values obtained in the field. This was partly due to the leakage problem previously mentioned. This allowed oxygen to get in and make some values less negative. Eh can be used to tell the state of the sediments with respect to whether they are being oxidized or reduced, but is not reliable enough to say that an area with an Eh of -500 mv is more reduced than one with -450 mv. It is seen that whenever the Eh is around -300 mv or below, the volatile solids are above 2.3 per cent, but the lowest Eh does not necessarily correspond with the highest volatile solids per cent. Once you go below the surface, the sediments become definitely negative and remain so down through the core often going to -500 mv.

The C.O.D. and the volatile solids together give an indication of how much organic matter is present. For the most part, the C.O.D. and volatile solids go up and down together with good correlation (Figure 3). The four highest in that figure are in Mosquito Lagoon and could be due to the isolation of the area. Since the area is more isolated, there is not much dispersion. As for the correlation presented in Soule and Oguri, 1974, the data obtained does not agree

with the given formula. A regression analysis was conducted with the result of the following equation:

T.V.S. (% dry wgt.) = -1.86 + 4.88 (C.O.D. % dry wgt.)

A graph of this data and that of the equation presented in Souza and Oguri, 1974, is seen in Figure 5. The equation presented by the above authors is an empirical formula arrived at by the Environmental Protection Agency. As seen by the data presented in this paper, this formula is not acceptable for all sediments.

A graph of sites versus volatile solids (Figure 6) is presented breaking down the graph into three parts. These are 1) sites near land (less than 2500 feet) 2) sites near center of river, (greater than 2500 feet), and 3) isolated sites near land in Area 3. This shows that there are more volatile solids near the center of the river than near the shore. This could be due to the fact that the volatile solids are usually finer grained and therefore are carried farther away from shore. The isolated area 3 sites are probably higher due to less motion of the water and the predominant Easterly wind in the area. The Intracoastal Waterway which is the deepest part of the lagoonal system, 3.5 meters, does not appear to have an affect on the amount of organic matter present in the sediments.

The water content, though not an exact value, showed an increase in most cases when the volatile solids increased (Figure 7). Also as the sediments got finer than normal, the water content increased.

A graph of Eh versus Volatile solids (Figure 8) shows that there appear to be limits that when reached have little affect on the Eh. For instance as the volatile solids go over about 3.5 per cent, the

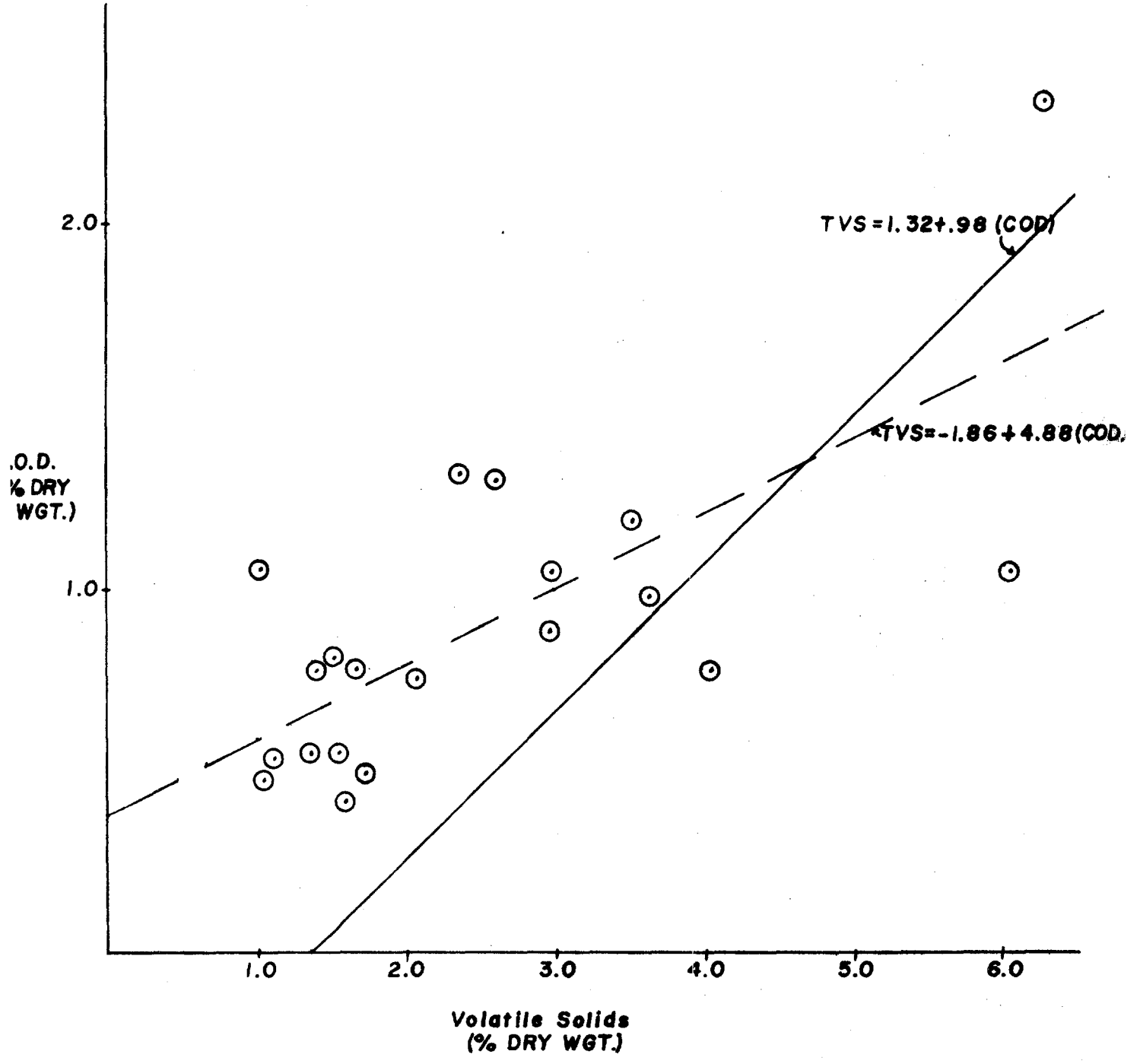


Figure 5
VOLATILE SOLIDS VS C.O.D.

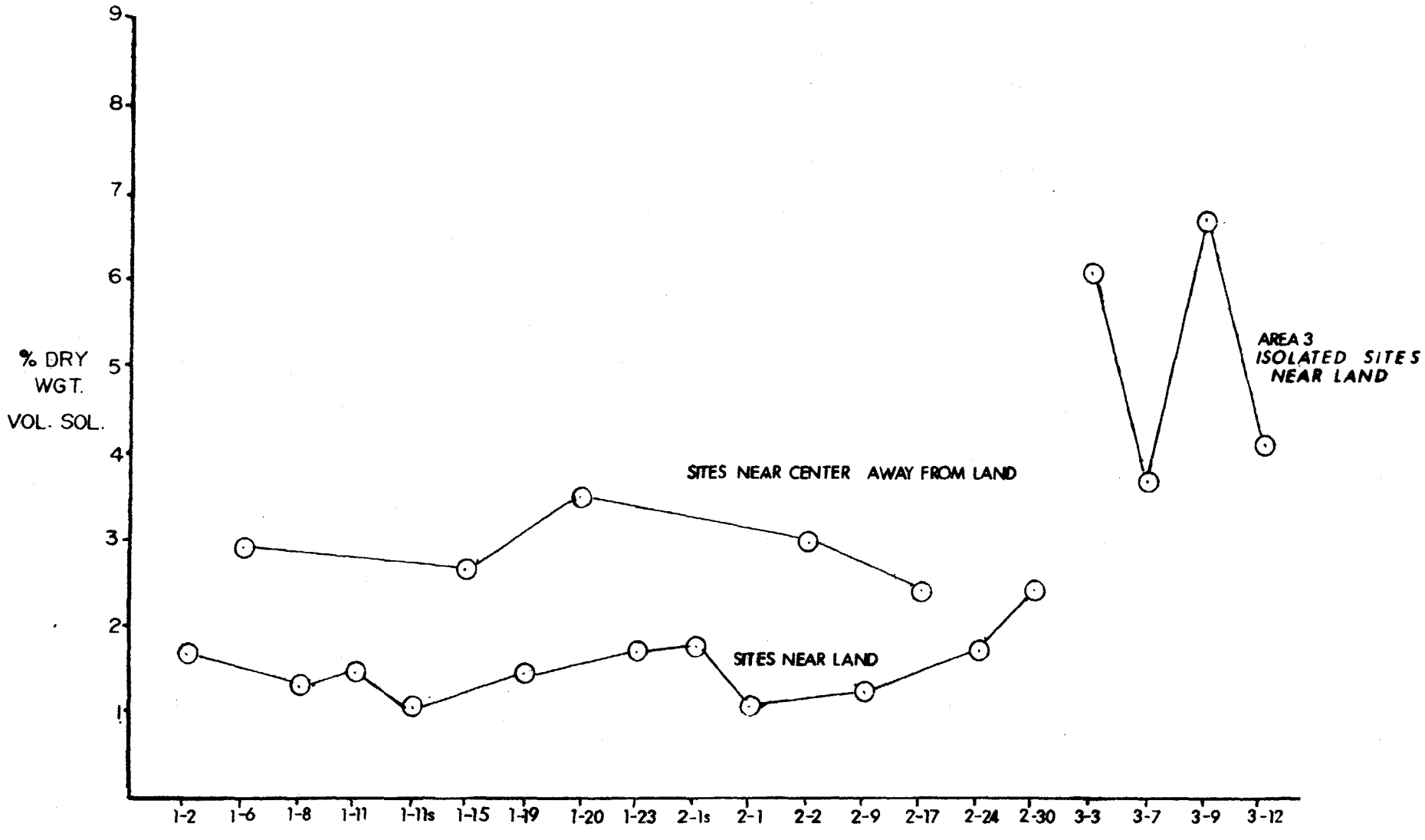


Figure 6
VOLATILE SOLIDS VS SITE LOCATION

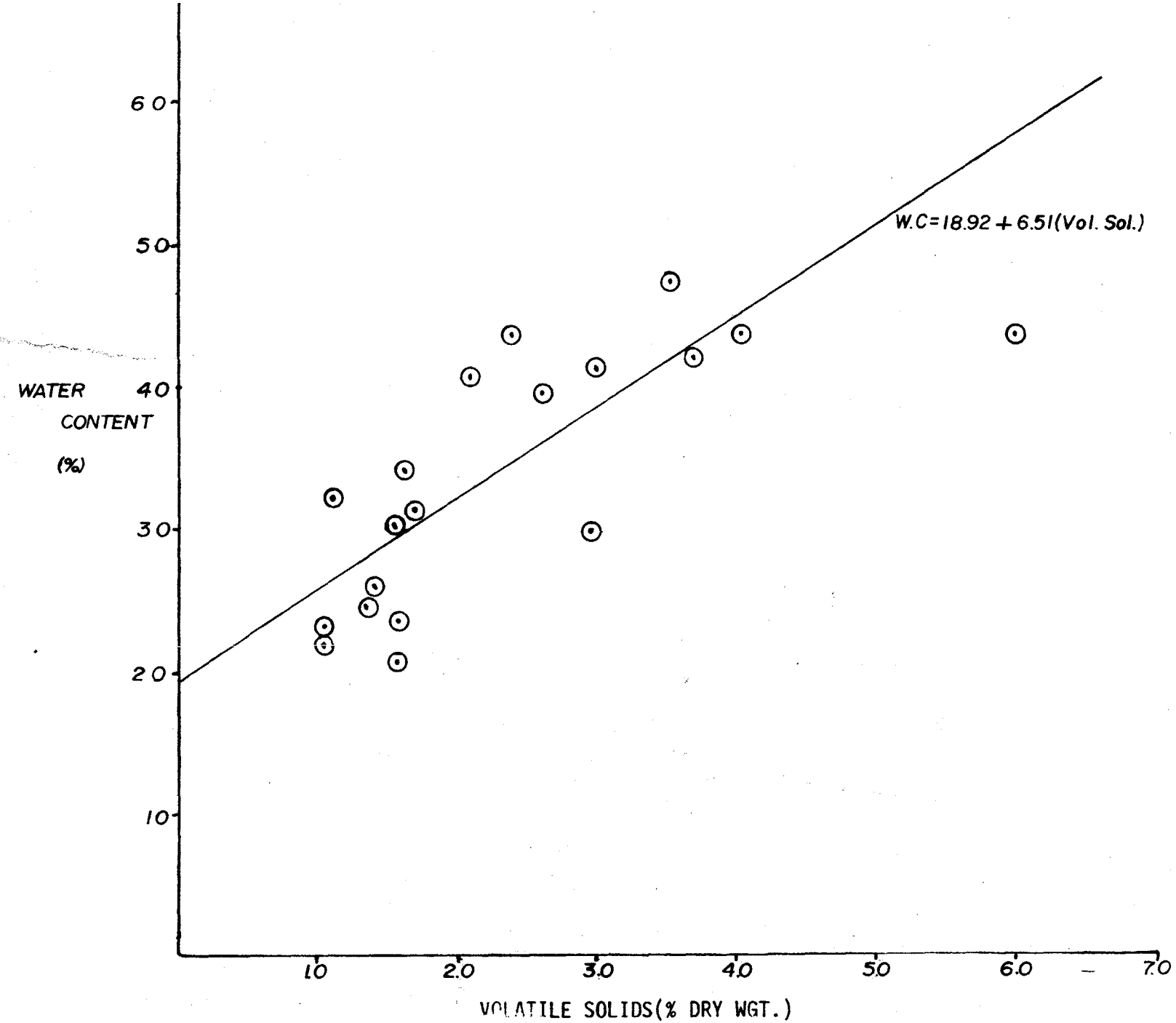


Figure
VOLATILE SOLIDS VS WATER CONTENT

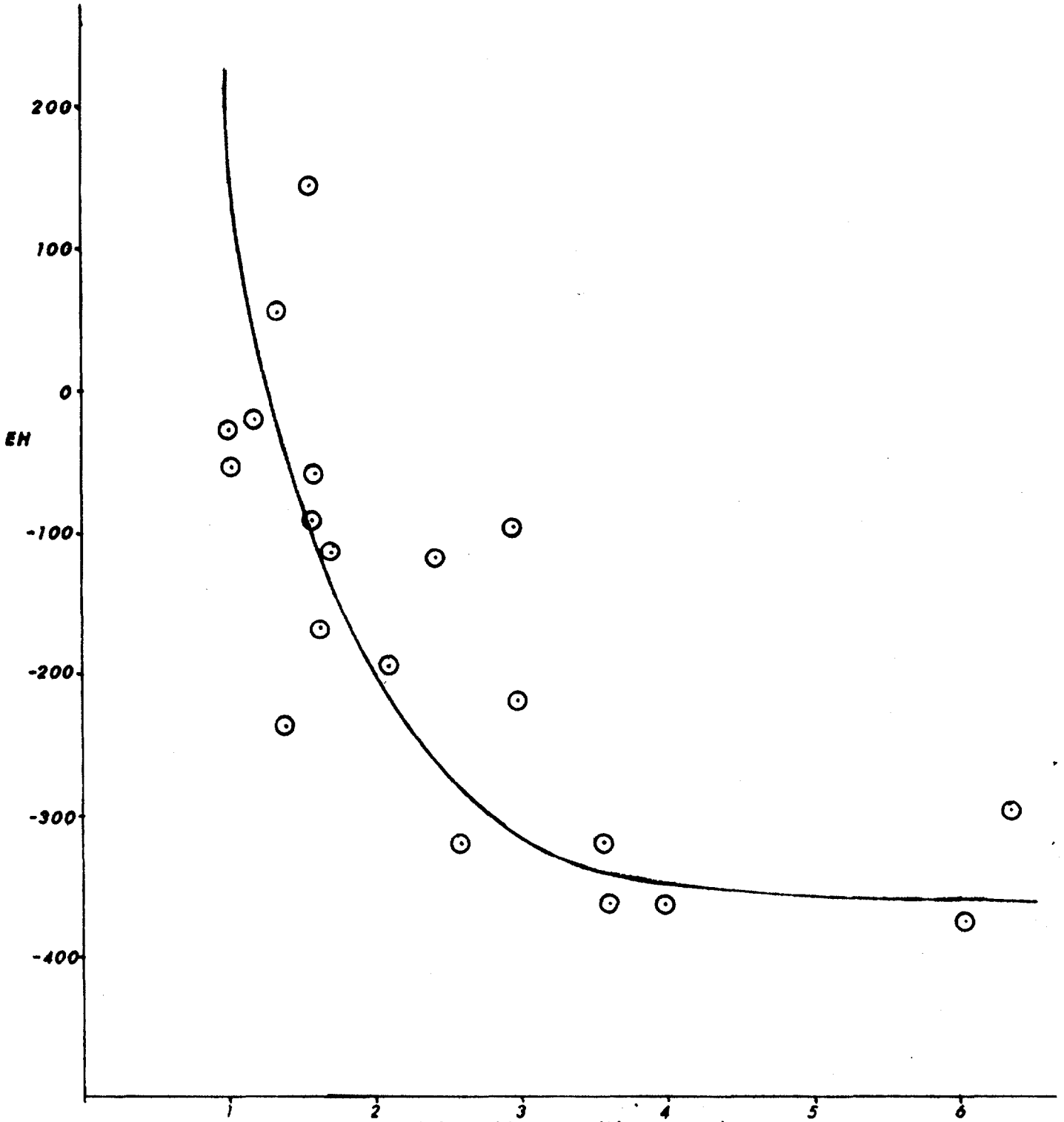


FIGURE 8
EH VS VOLATILE SOLIDS

Eh becomes more negative very slowly. As the volatile solids decrease below about 1.5 per cent, the Eh is seen to rise very quickly. This is to be expected since past a certain point, the sediments become overloaded with organic matter and a little more will not have an immediate affect. Also below a certain level there is not enough organic matter present to cause a reducing environment.

Most of the study area was shown to be non-homogeneous. Looking at the raw data (Appendix II) and the arithmetic means, this was evident. This is why using the means is the only way to get a representative idea of a particular site. The non-homogeneity though, caused some results to appear worse than they should. A good example of this is the volatile solids test from site 3-9 (Appendix II). For both the C.O.D. and the volatile solids test, if the sample selected has a clump of organic matter, the result would not be representative and would be much higher.

The sediments at all sites were seen to be fine uniform sands (Appendix I). The amounts of silts and medium sands varied, but in all cases was less than 10 per cent for each. The amount of silt was seen to increase a little when the amount of organic matter increased as is seen clearly by site 4-16S. Sediment color also shows that there is not an excess of organic matter present in the areas studied. The few sites with the black (5Y 2.5/1 and 5Y 2.5/2) do show patches of higher concentration of organic matter. The pale brown (10YR 6/3) found in some areas is probably wind-blown sand from the land. The olive gray, seen just below the surface in the reducing environment, is probably caused by the reduction of free iron compounds. (Nelson, 1972).

CONCLUSIONS AND RECOMMENDATIONS

The objective of this investigation was to look at what affect the two sewage treatment plants had on the Indian River. Although none of the variables looked at proved to be reliable parameters by themselves, it is seen from the data that the North and South Titusville sewage treatment plants do not have any more of a negative affect on the sediments of the river than other sources of pollution (Figure 3). The effluents from these two plants are dispersed well and handled by the river's natural self-purification process. In contrast, the core taken in area 4, where the dispersion is slight and flow is obstructed, shows a marked increase in volatile solids and chemical oxygen demand.

Other than the site near the outfall in area 4, the two points with the higher than normal volatile solids and therefore organic matter is in an isolated area, the Mosquito Lagoon. This points out that the major sources of organic pollution must be land runoff and natural sources and not treated sewage effluent. Also that the amount of movement in a body of water and the dispersion of organic matter are important as long as oxygen is available.

The Environmental Protection Agency equation presented in Soule and Oguri, 1974, for a relationship between volatile solids and C.O.D. is not necessarily true for all marine sediments. This is shown by the data presented in this study.

In future studies of this type it would be helpful if several other areas of study were looked at simultaneously to get a better

overall picture. These being the effluents from the treatment plants and the water above the sediments. Also it would be helpful if the dispersion of the effluents were studied such as how far and in what direction the effluents travel.

To help solve the problem in area 4, this author recommends the opening of the mouth of the creek in question by removing some mangrove trees or better yet extend the effluent pipe out so it empties directly into the river.

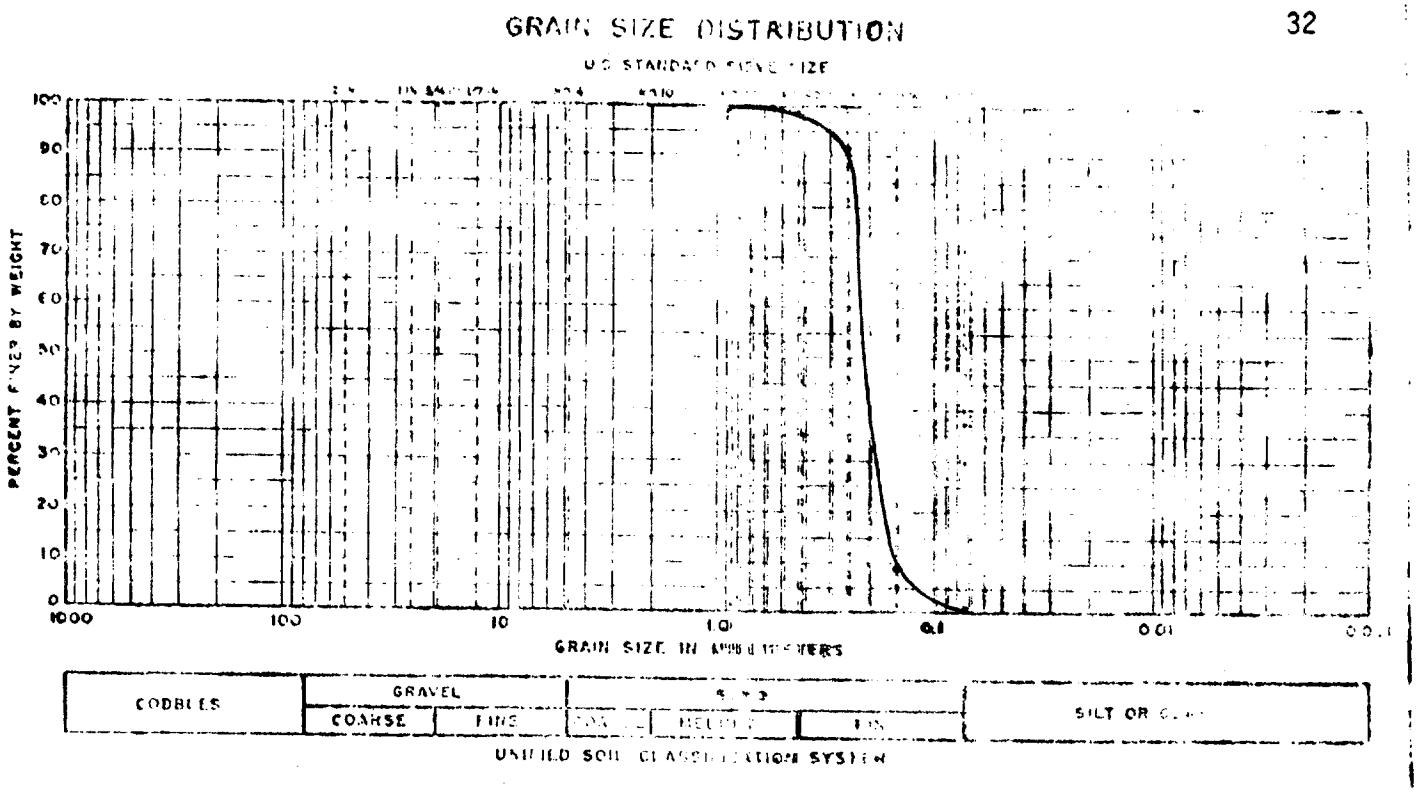
KEY TO GRAIN SIZE AND CORE DISCRIPTIONS

Color Code (Munsell)		
2.5	Y 6/2	Light Brownish Gray
5	Y 2.5/1	Black
5	Y 2.5/2	Black
5	Y 3/1	Very Dark Gray
5	Y 3/2	Dark Olive Gray
5	Y 3/3	Dark Olive
5	Y 4/1	Dark Gray
5	Y 4/2	Olive Gray (darker)
5	Y 5/1	Gray
5	Y 5/2	Olive Gray (lighter)
5	Y 5/3	Olive
5	Y 6/1	Light Gray to Gray
5	Y 6/2	Light Olive Gray
5	Y 7/1	Light Gray
5	Y 8/1	White
10	YR6/3	Pale Brown

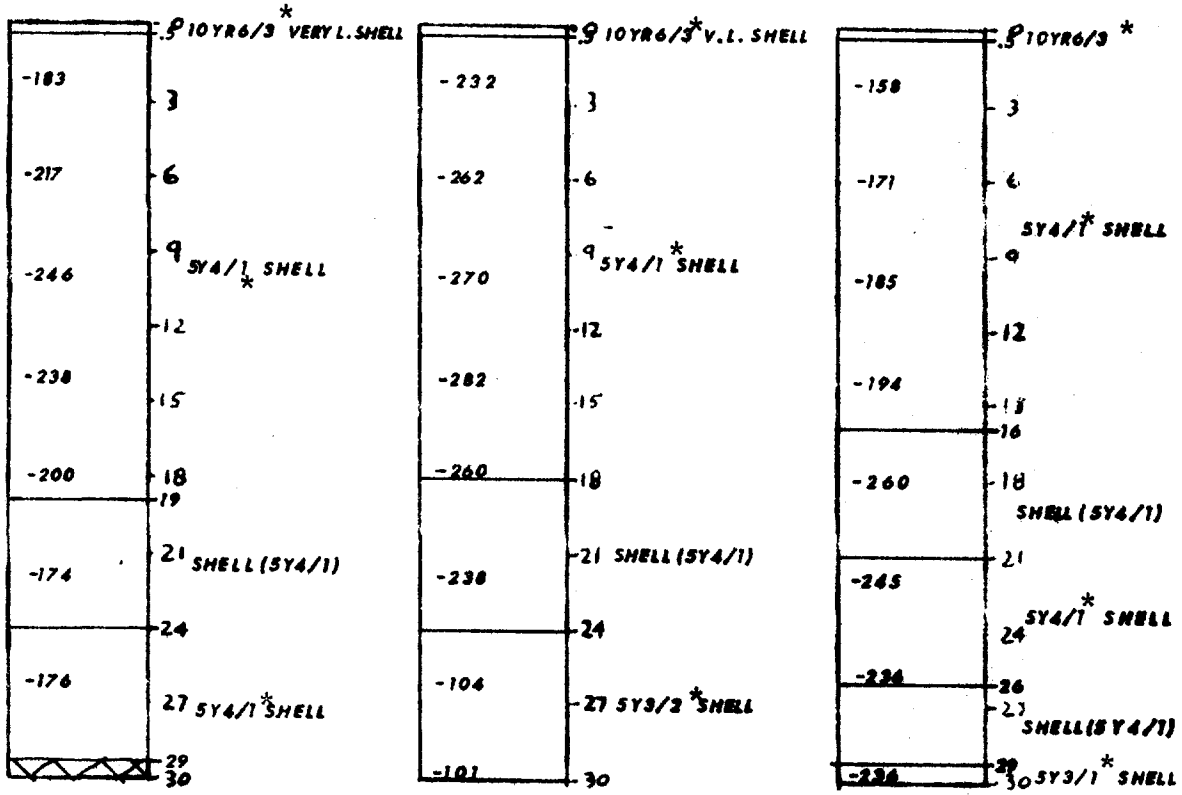
Soil Classification Code	
S	Sand
FS	Fine Sand
M	Silts
C	Clay
MS	Silty Sand
SM	Sandy Silt
L.SH	Little Shell

All sediments are a fine grained sand unless otherwise noted.

The numbers in the rectangle are the Eh values and the lengths are in centimeters.

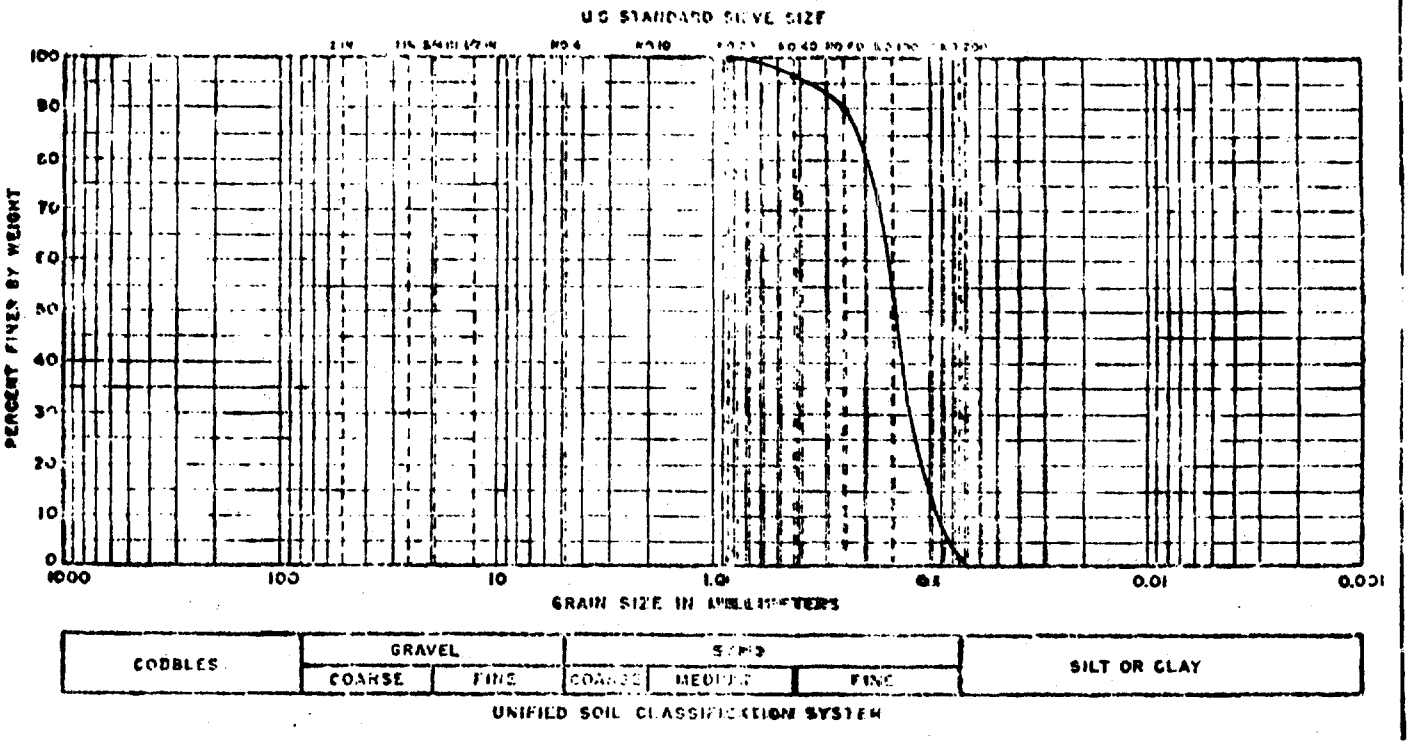

GRAIN SIZE DISTRIBUTION
U.S. STANDARD SIEVE SIZE
PERCENT FINER BY WEIGHT
100
90
80
70
60
50
40
30
20
10
0
1000
100
10
1.0
0.1
0.01
GRAIN SIZE IN MILLIMETERS
COBBLES
GRAVEL
COARSE
FINE
SILT OR CLAY
UNIFIED SOIL CLASSIFICATION SYSTEM

1-2


10YR6/3 * VERY L. SHELL
-183
3
-217
6
-246
9 5Y4/1 * SHELL
12
-238
15
-200
18
19
-174
21 SHELL (5Y4/1)
24
-176
27 5Y4/1 * SHELL
29
30
10YR6/3 * V.L. SHELL
-232
3
-262
6
-270
9 5Y4/1 * SHELL
12
-282
15
-260
18
-238
21 SHELL (5Y4/1)
24
-104
27 5Y3/2 * SHELL
-101
30
10YR6/3 *
-158
3
-171
6
5Y4/1 * SHELL
9
-185
12
-194
16
-260
18
SHELL (5Y4/1)
21
-245
5Y4/1 * SHELL
24
-236
26
SHELL (5Y4/1)
-236
30 5Y3/1 * SHELL

*Fine Sand

GRAIN SIZE DISTRIBUTION



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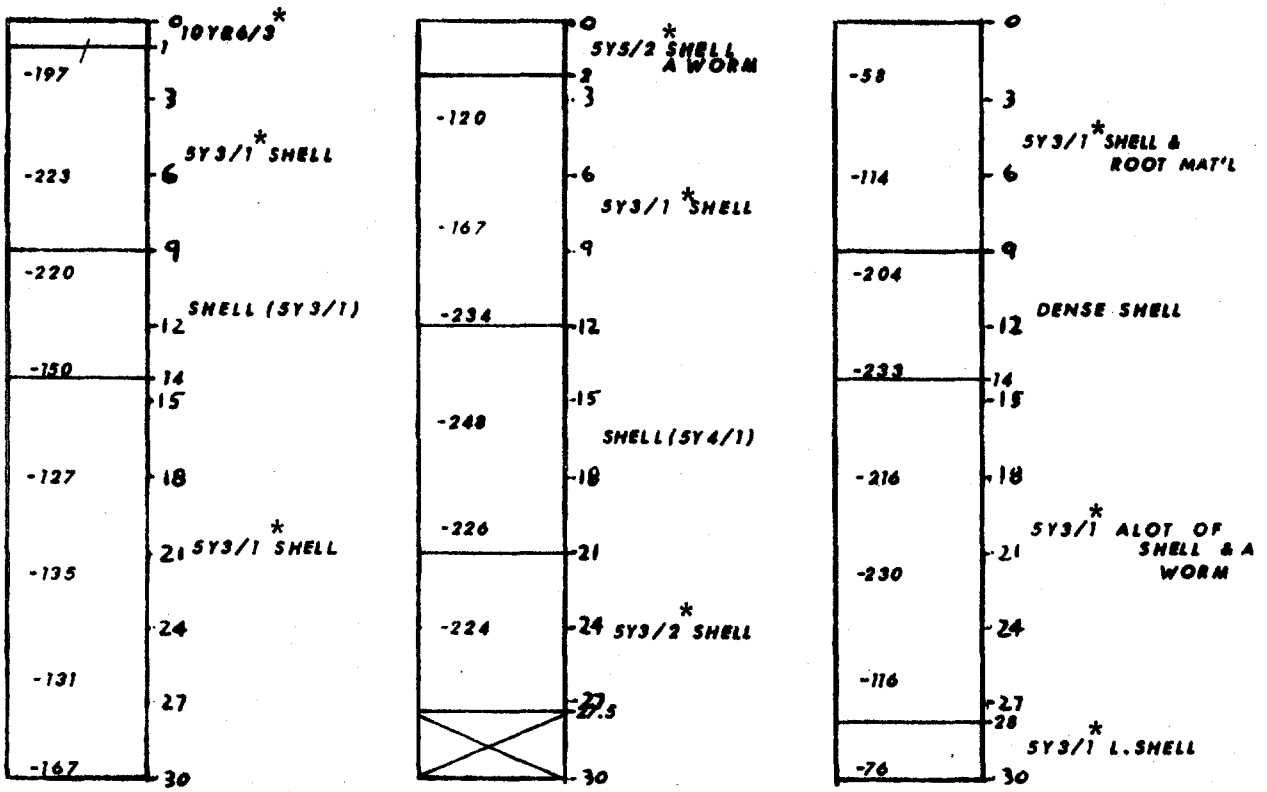
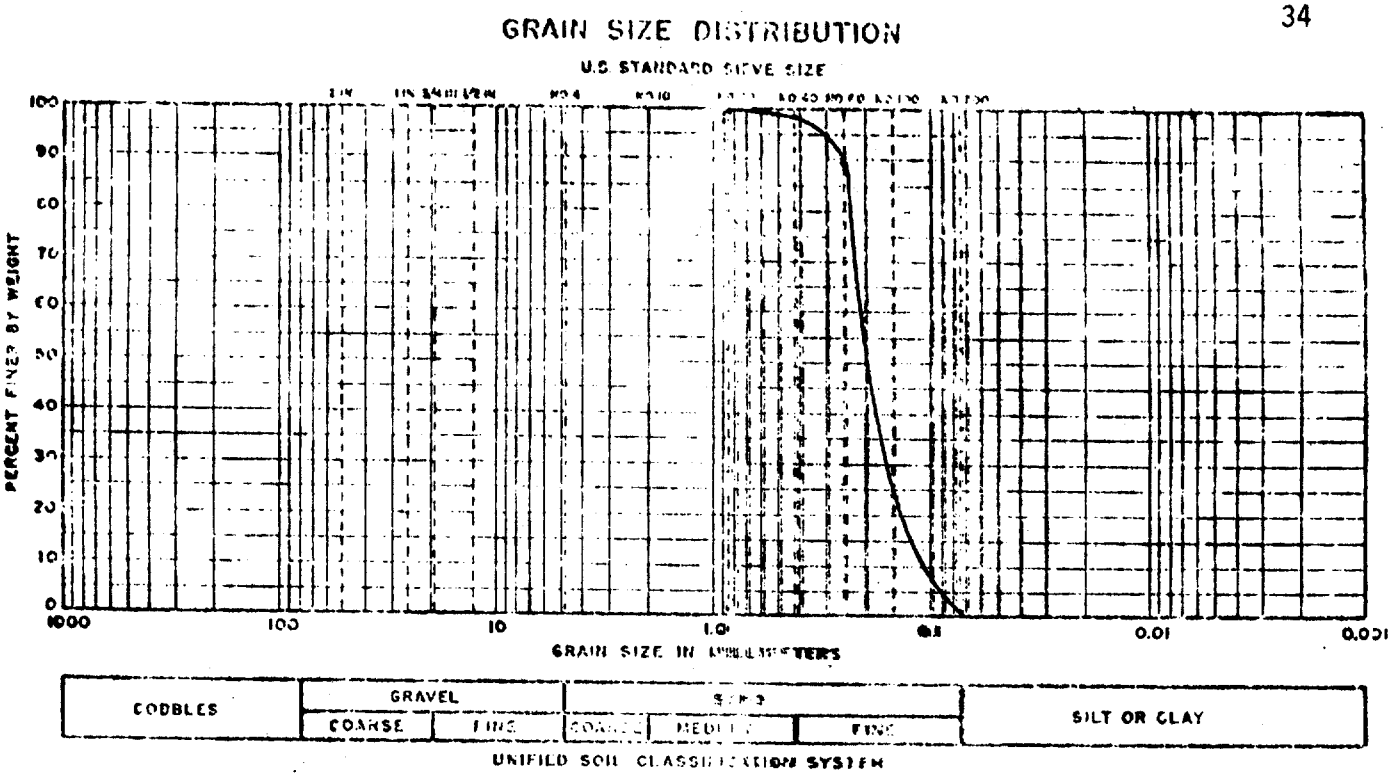


*Fine Sand



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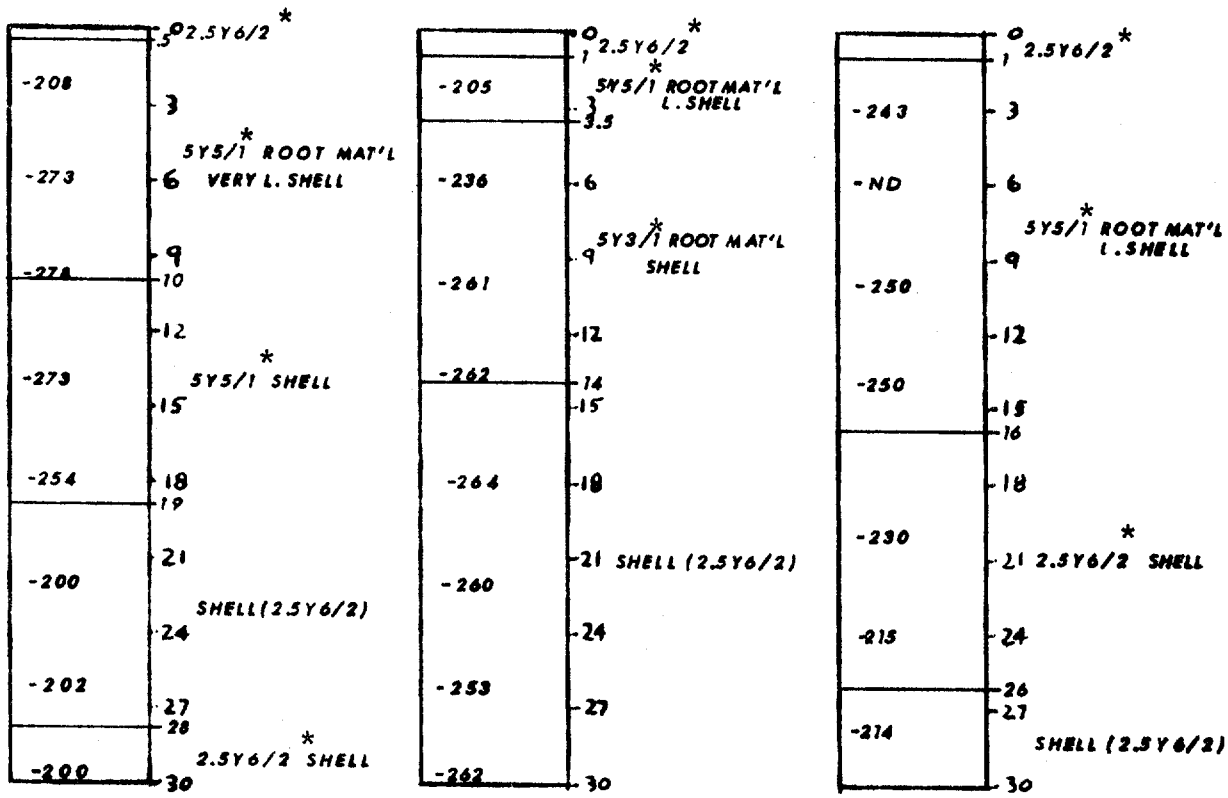
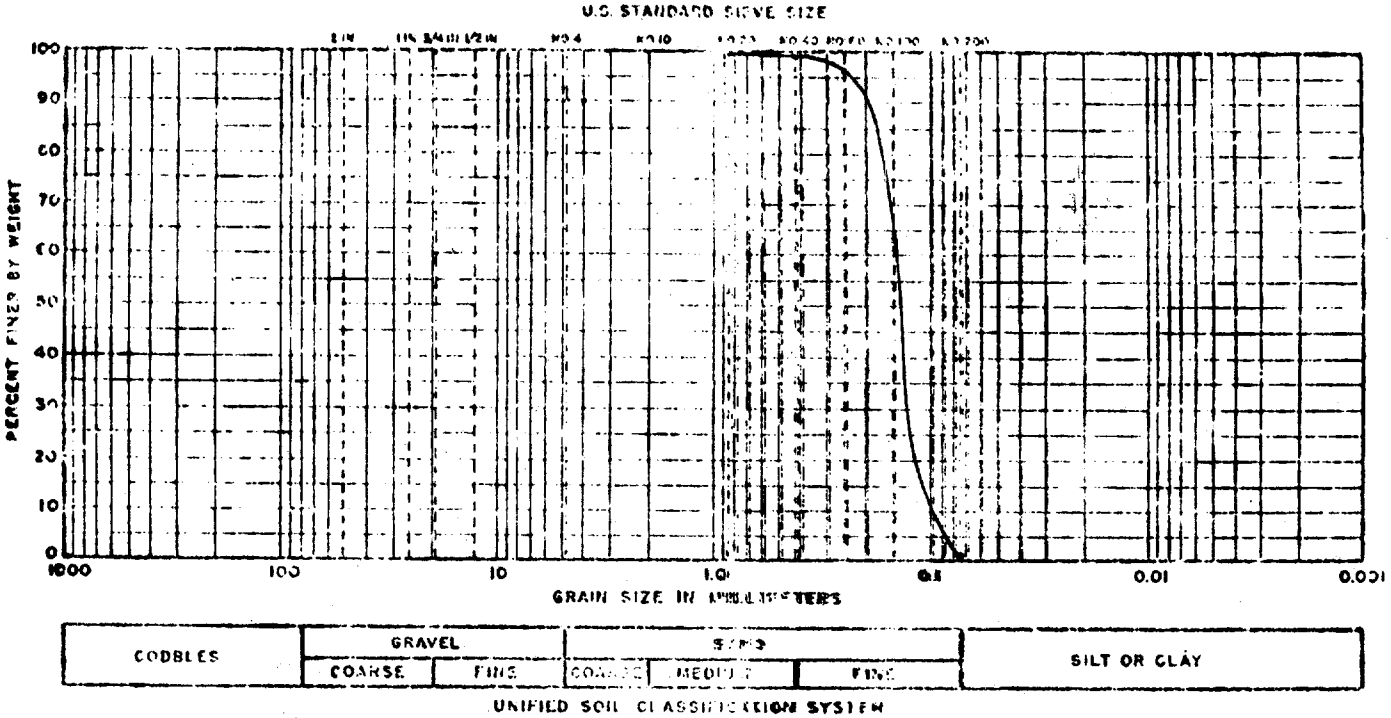


TRACE H_2S ODOR IN ALL 3 AT SURFACE

*Fine Sand

GRAIN SIZE DISTRIBUTION



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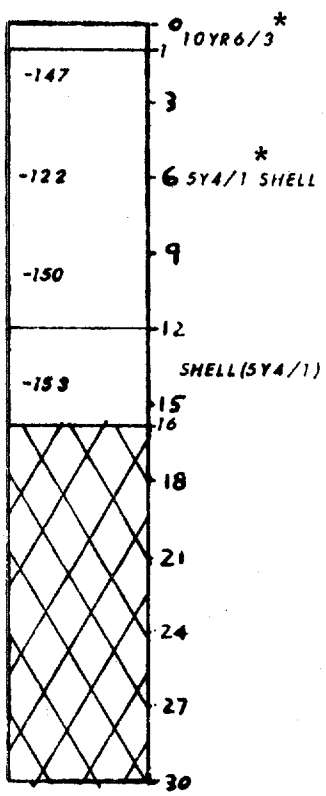

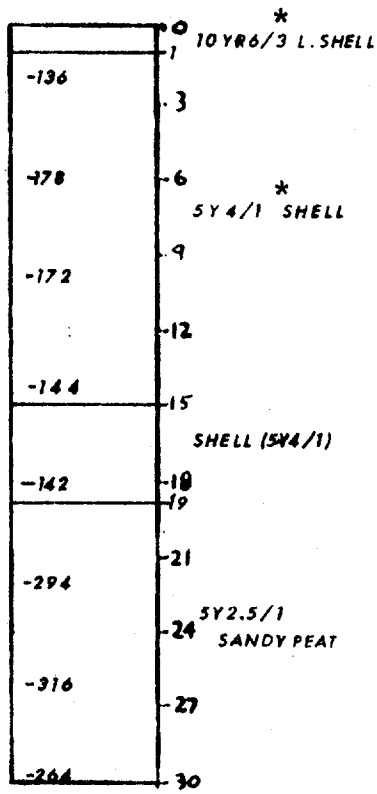

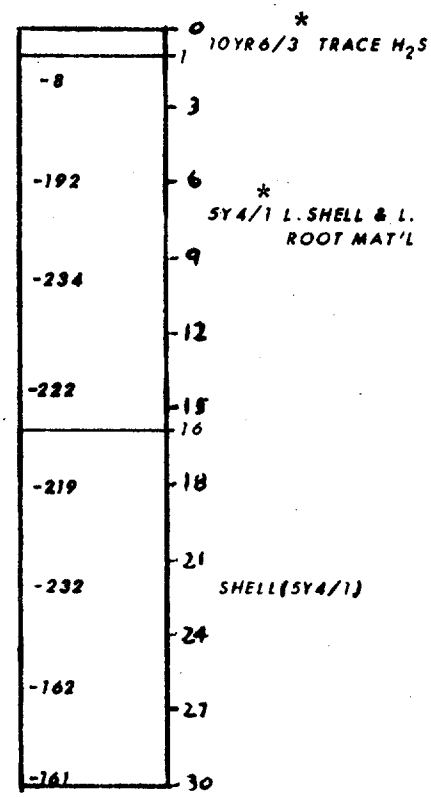

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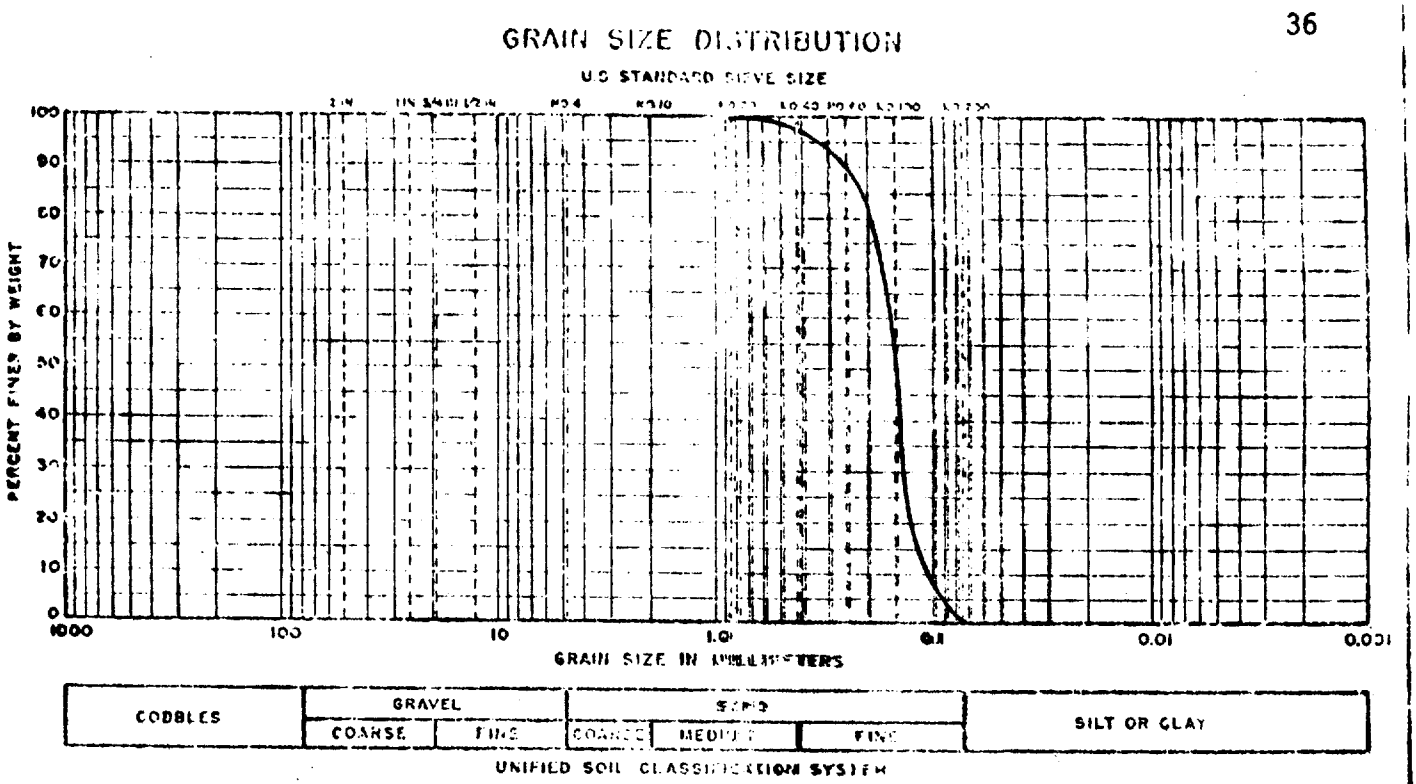

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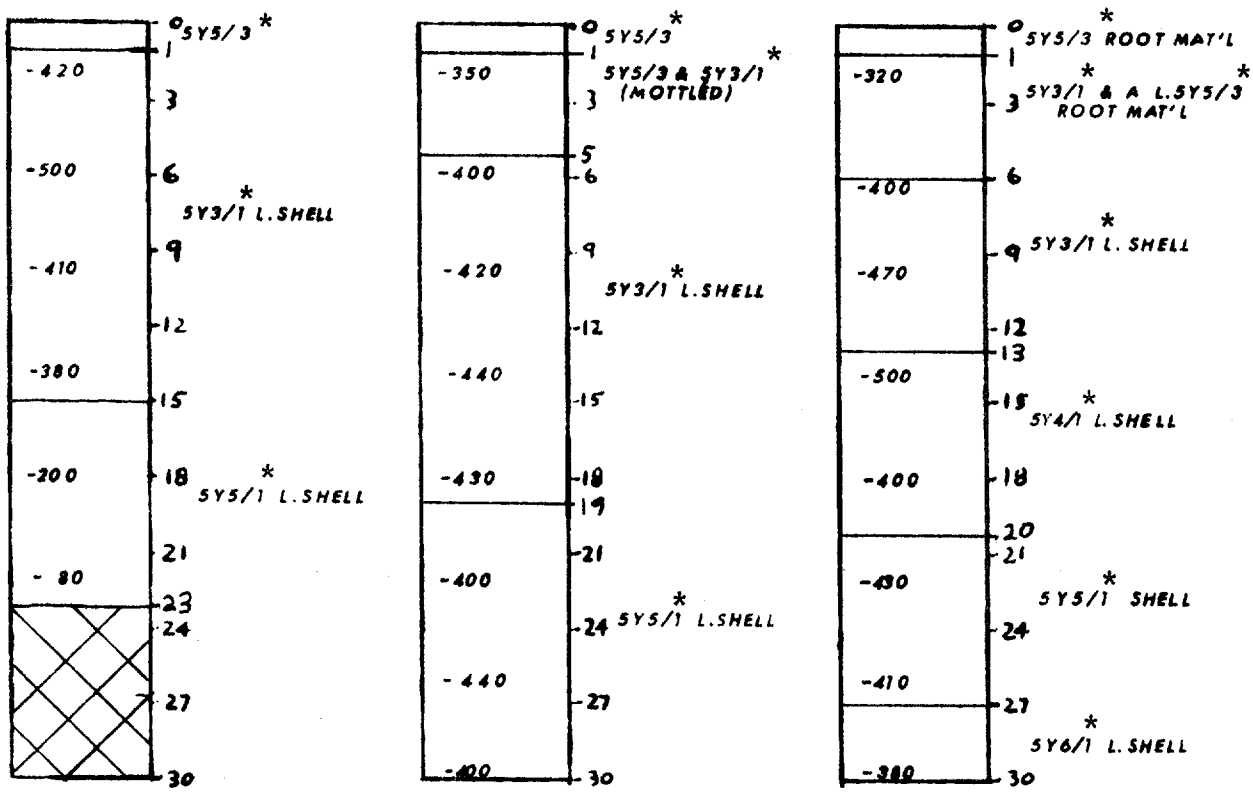
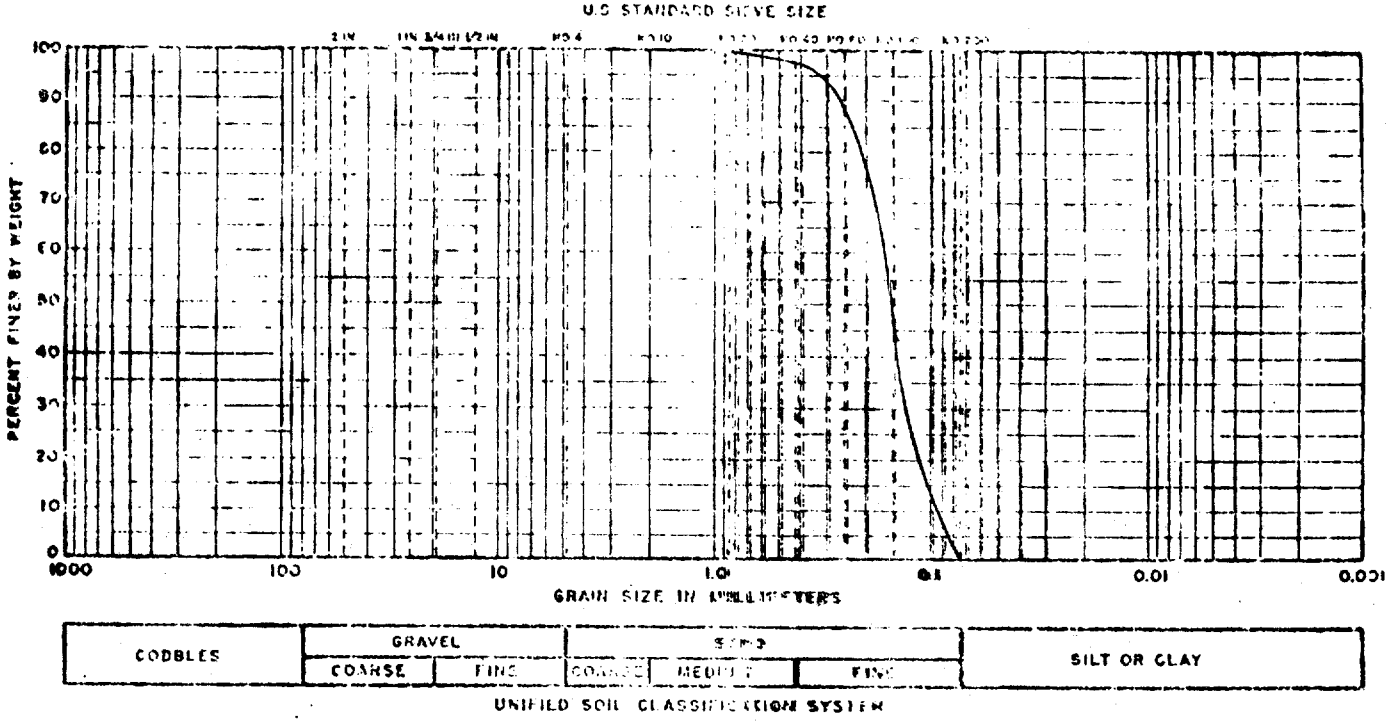


SLIGHT FISHY ODOR DETECTED NEAR SURFACE IN ALL 3

*Fine Sand

GRAIN SIZE DISTRIBUTION



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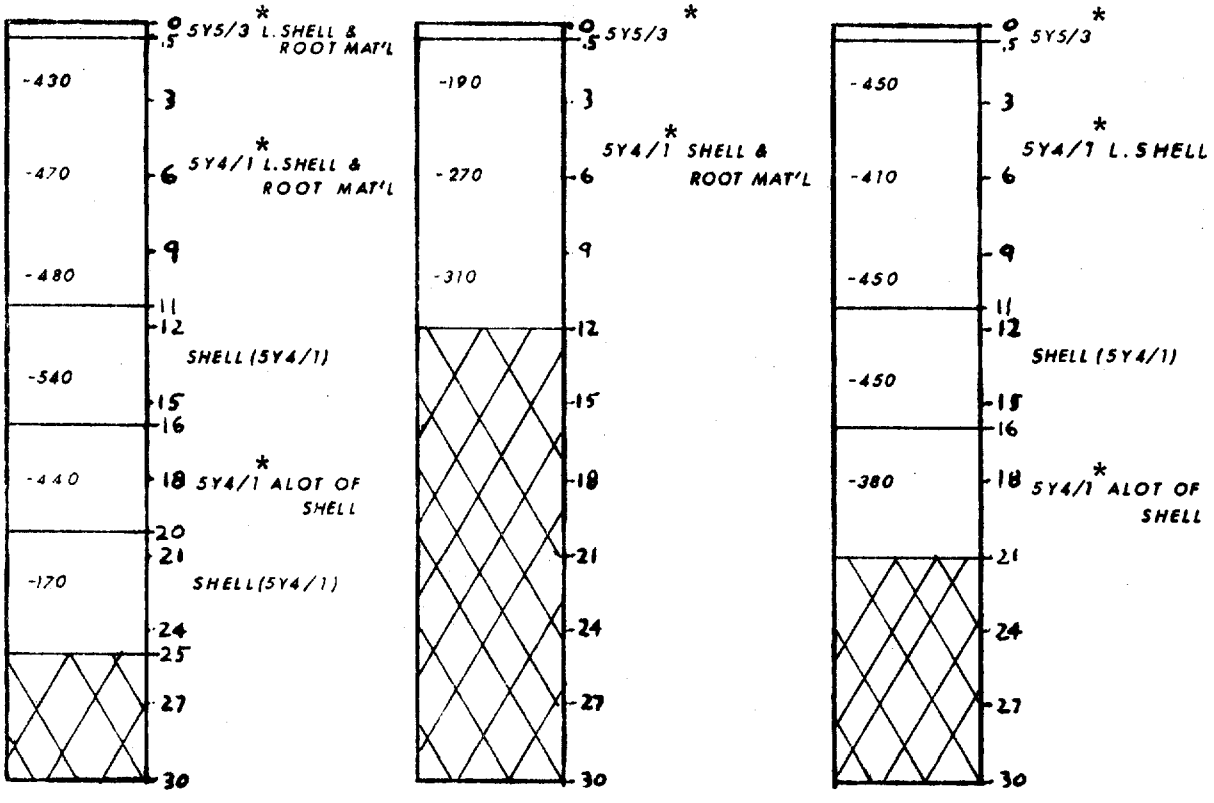
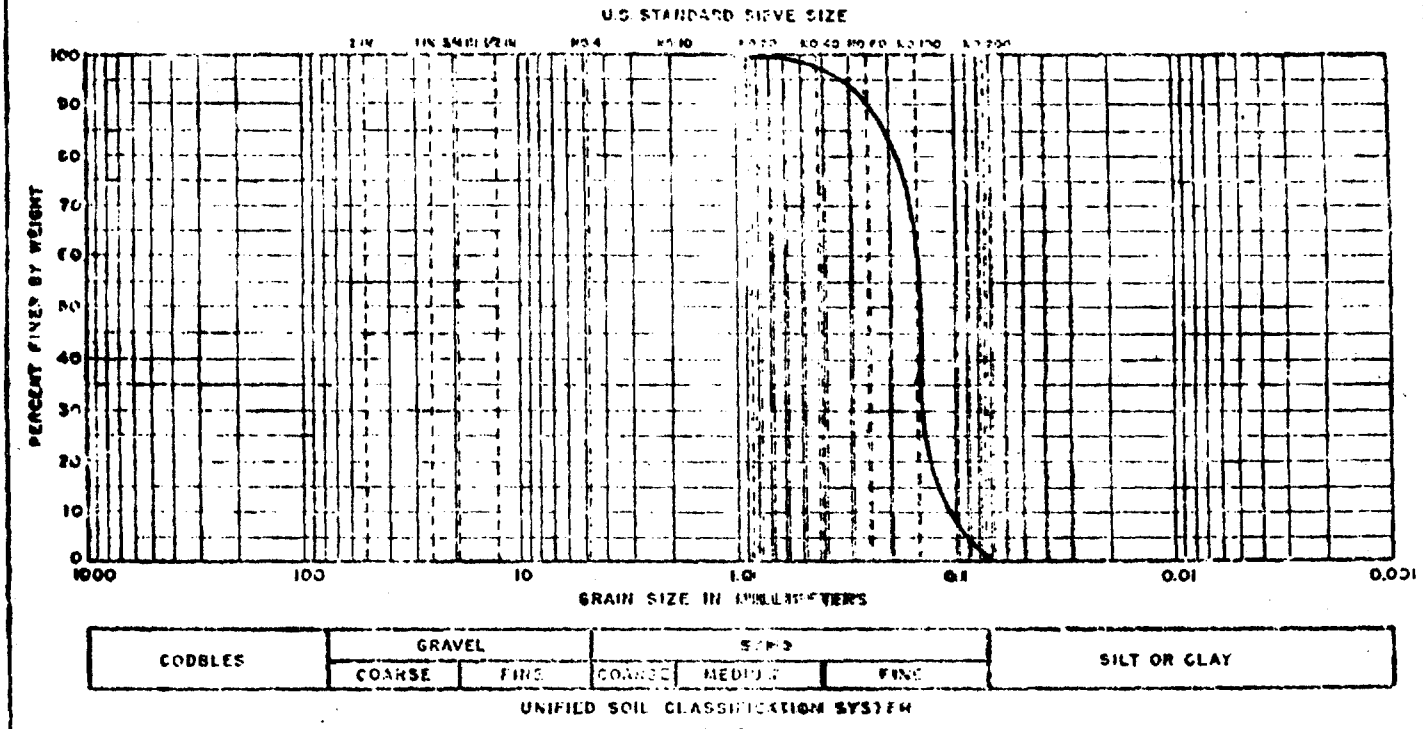


*Fine Sand

GRAIN SIZE DISTRIBUTION



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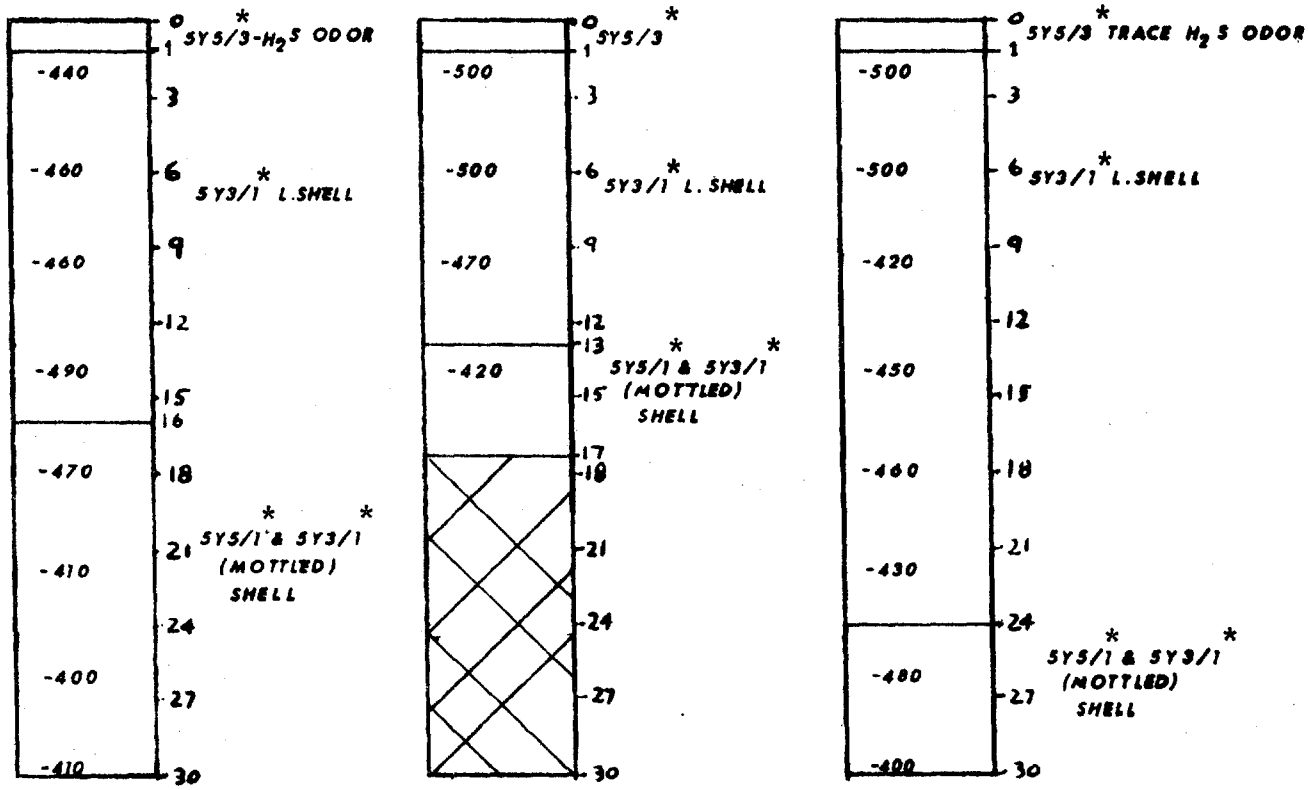

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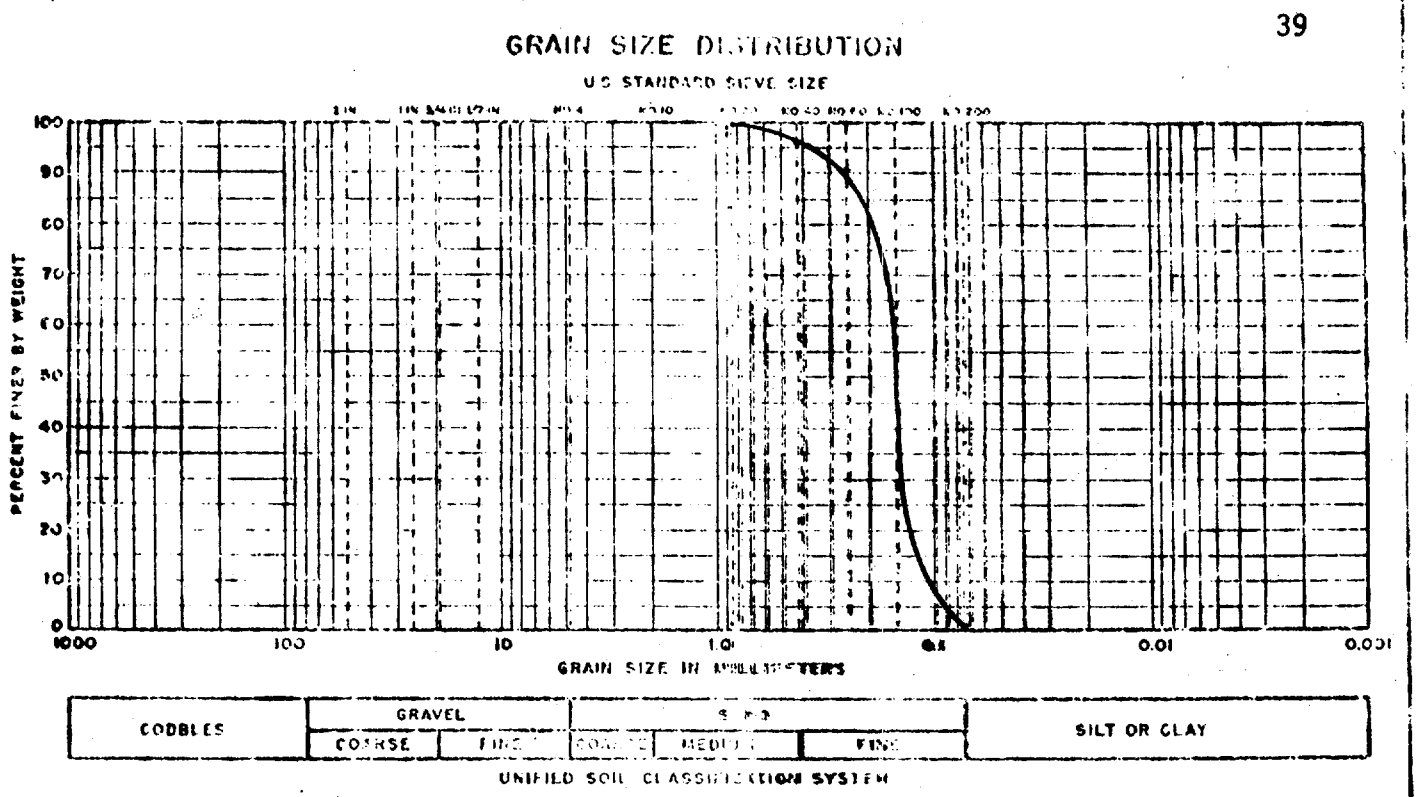

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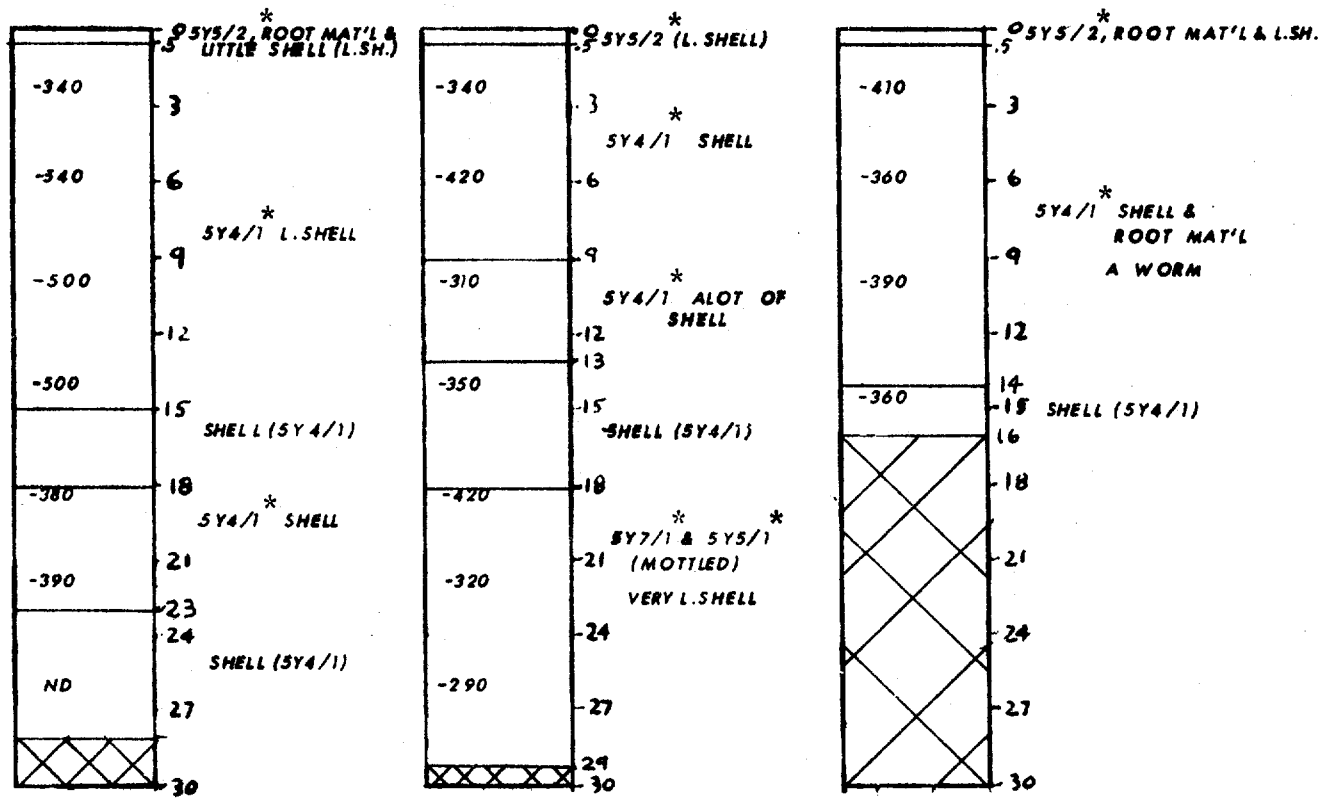

*Fine Sand

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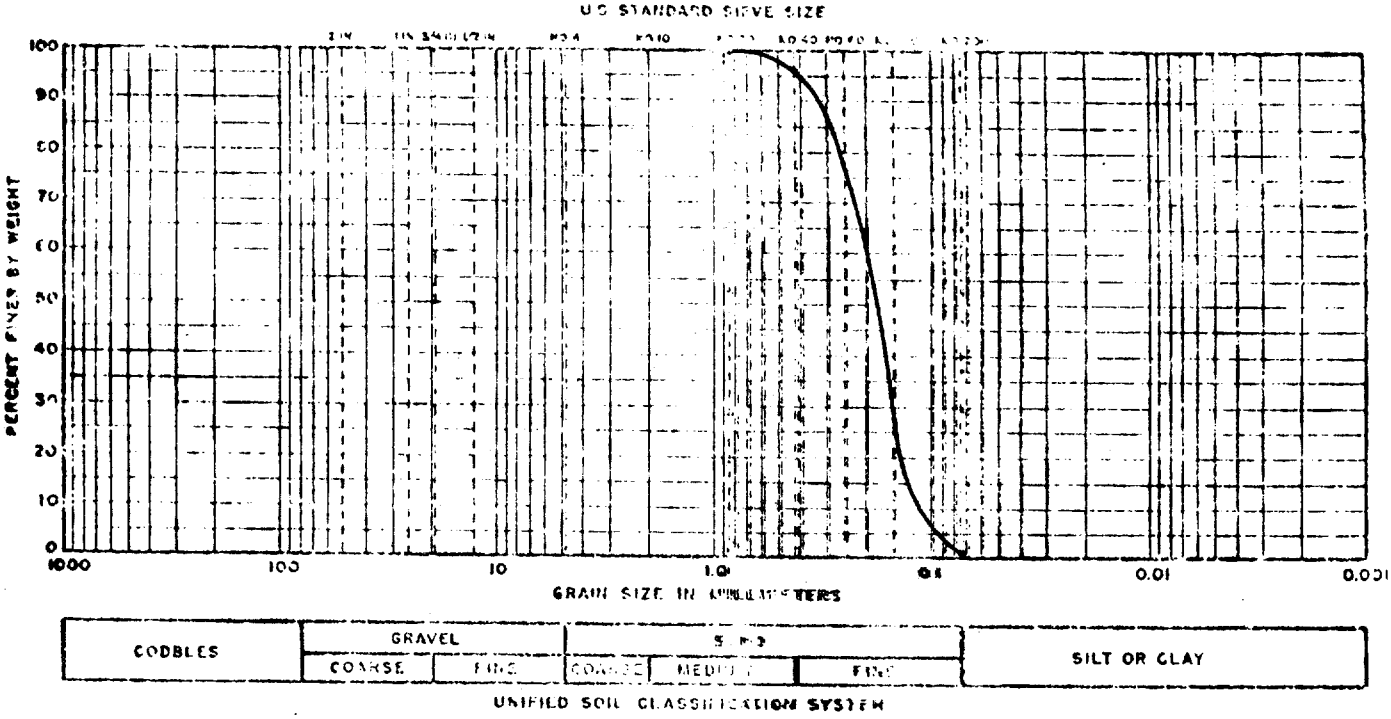

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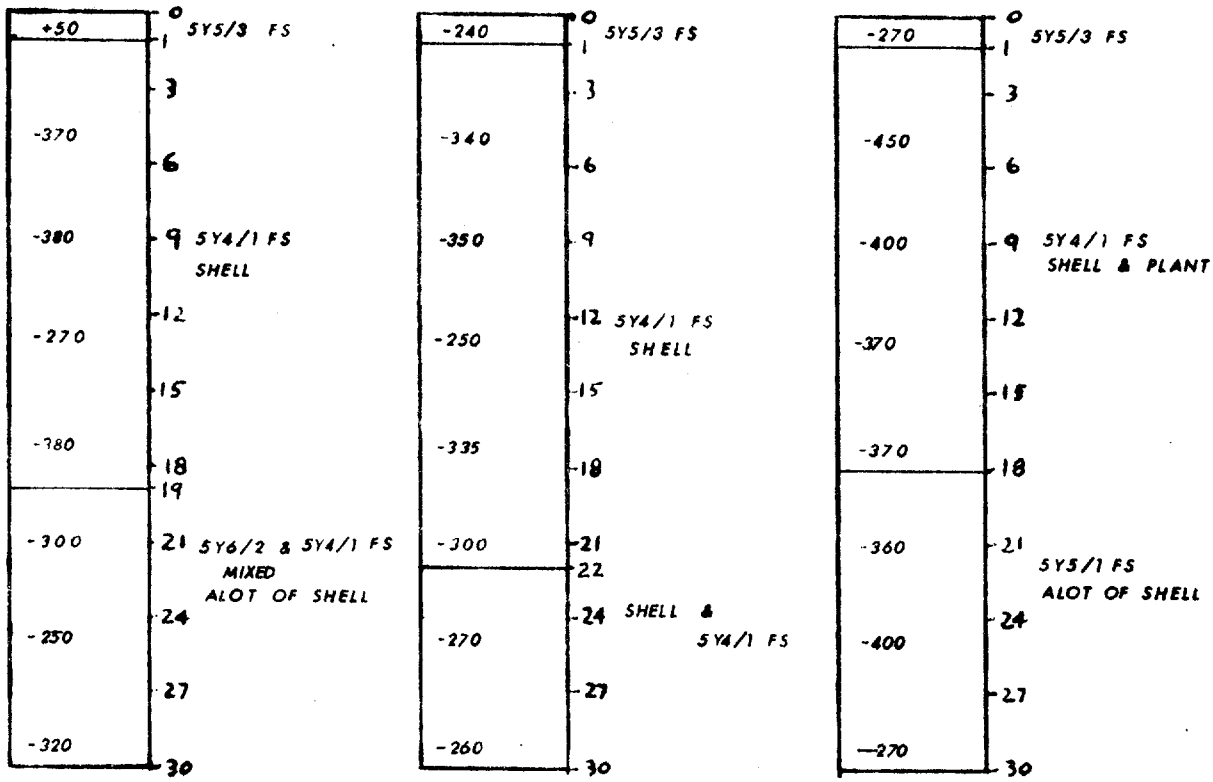

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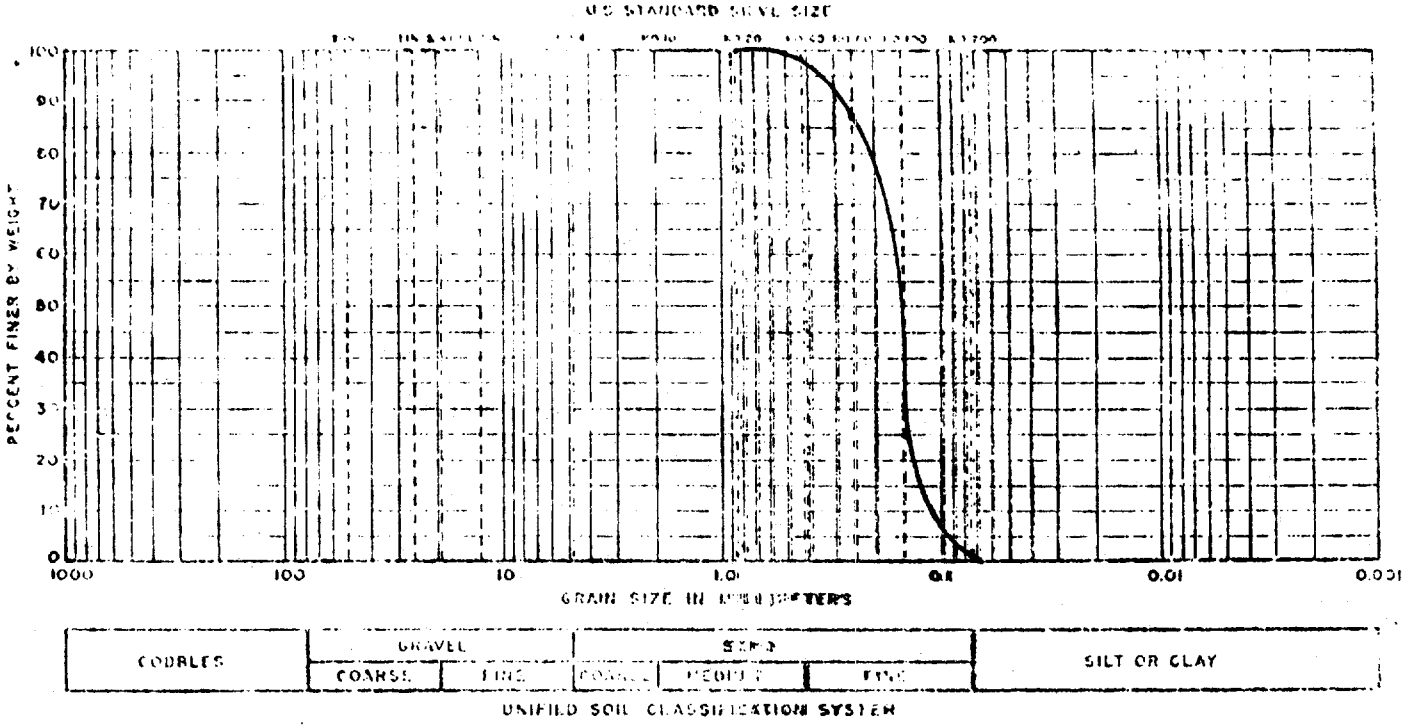

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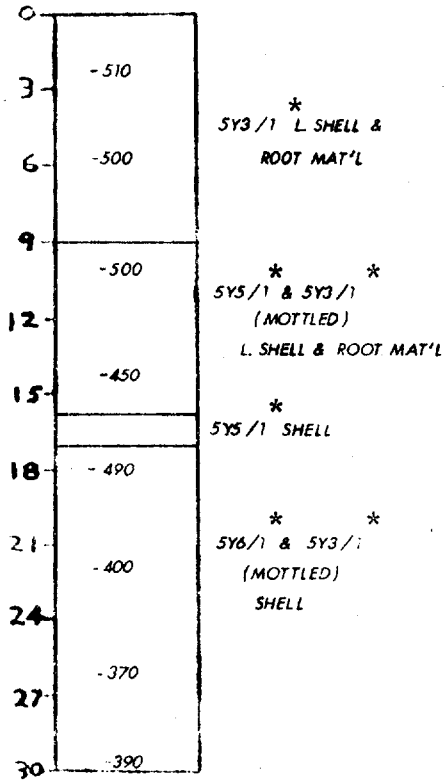
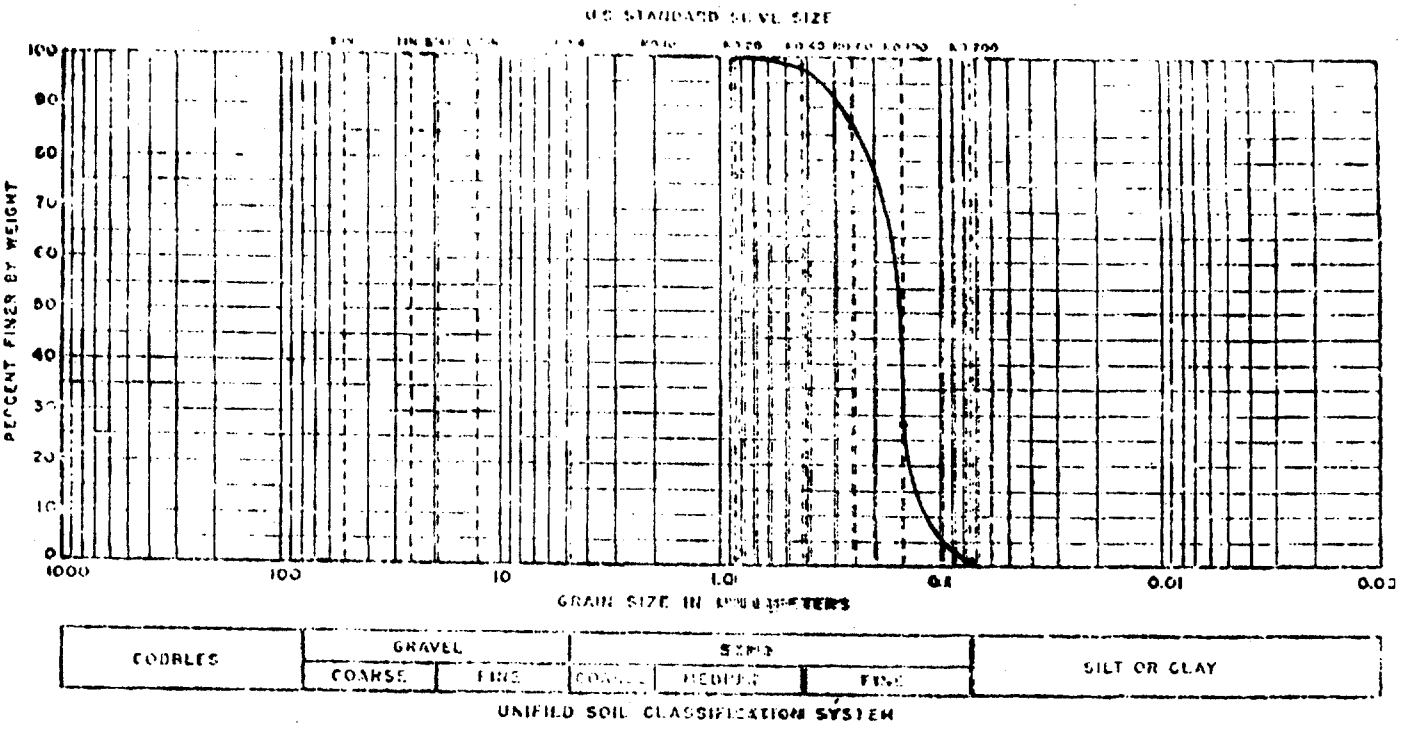


*Fine Sand

GRAIN SIZE DISTRIBUTION



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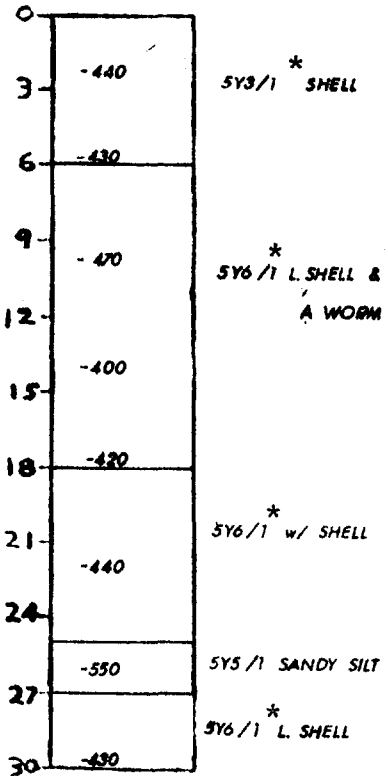
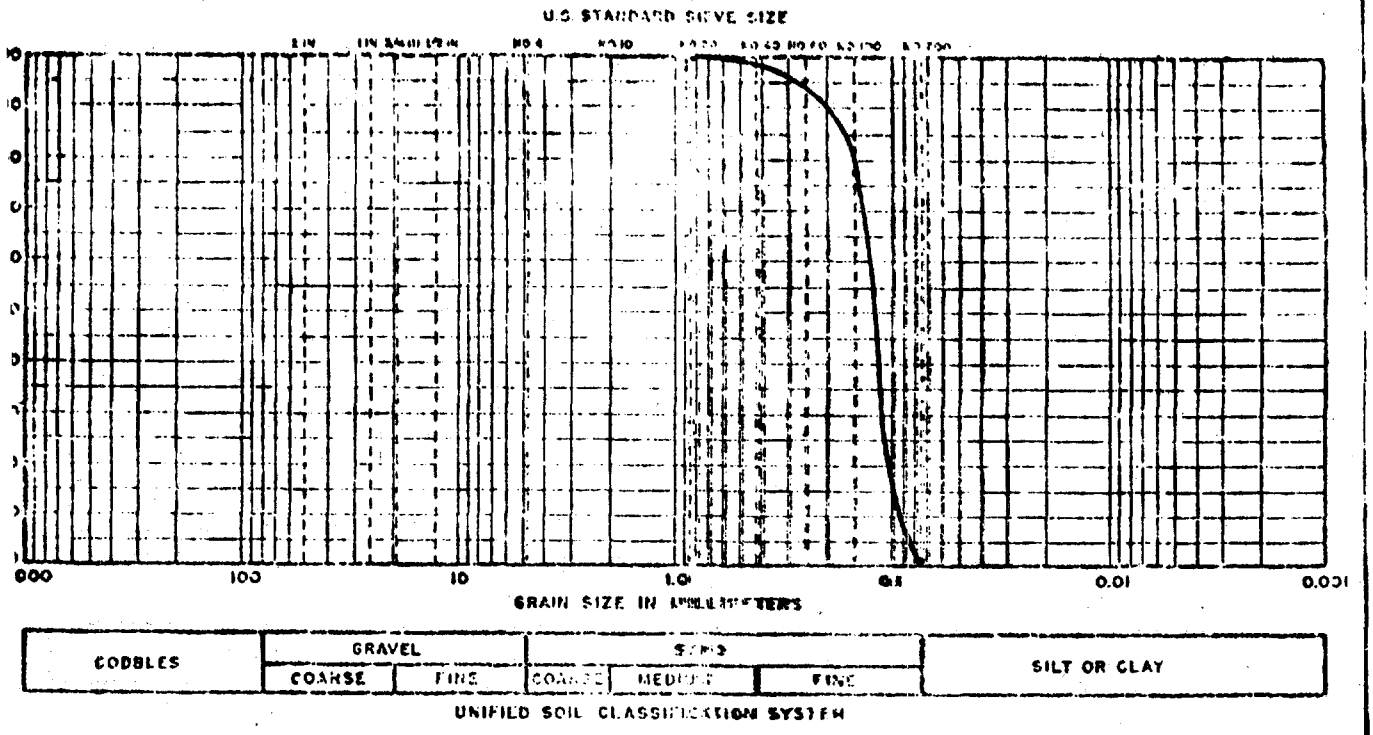


H_2S ODOR PRESENT

*Fine Sand

GRAIN SIZE DISTRIBUTION



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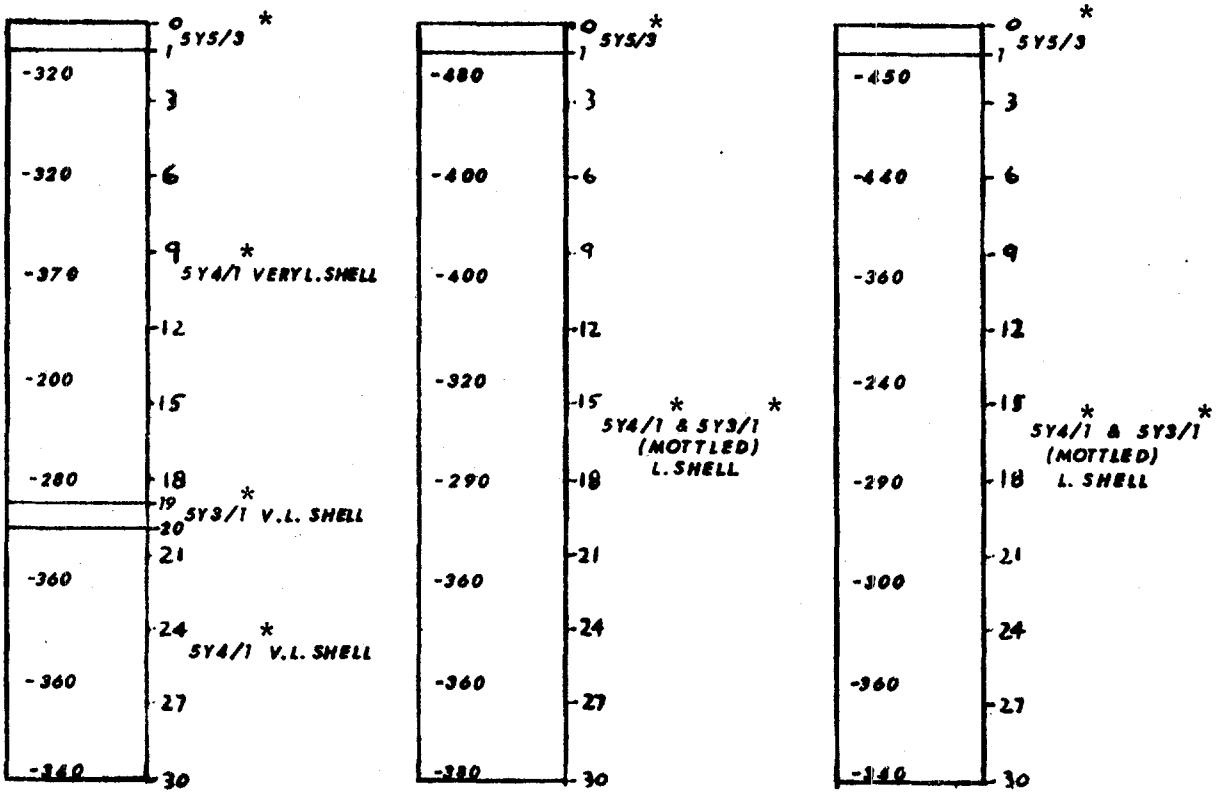
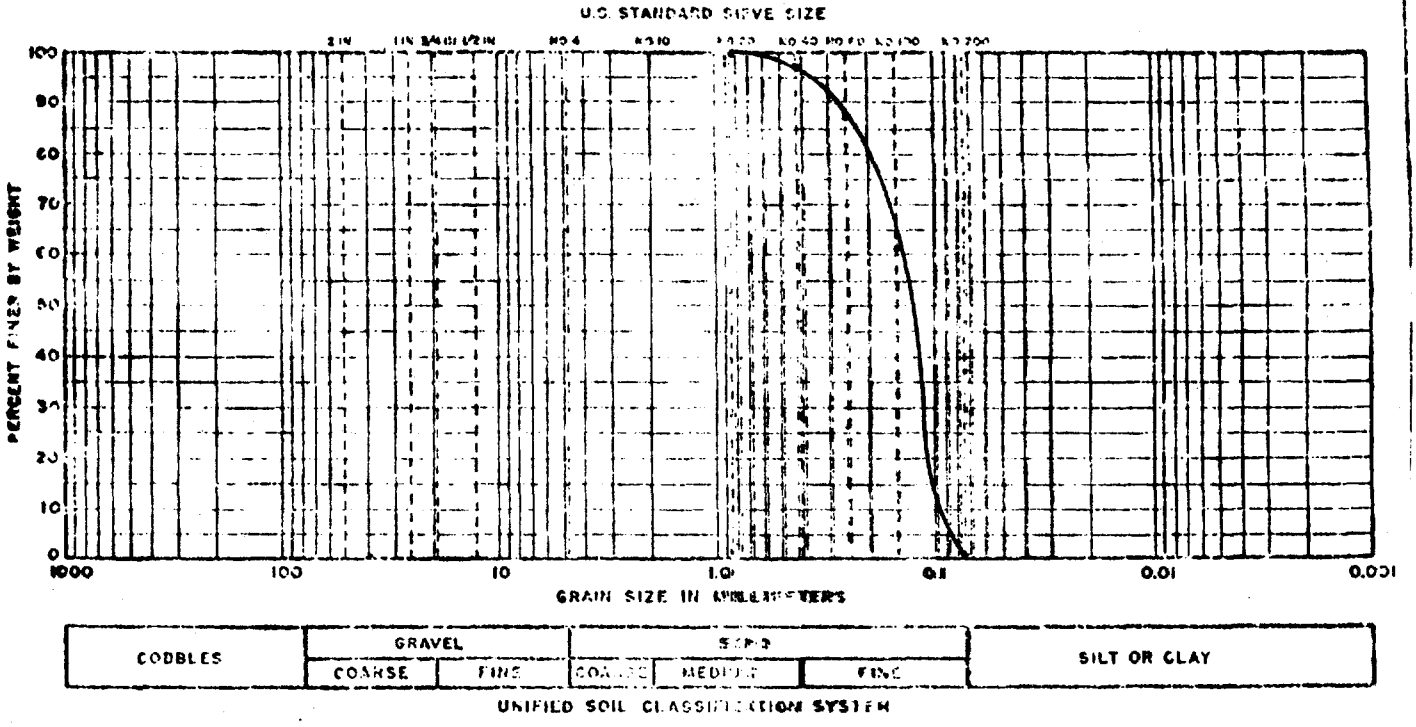
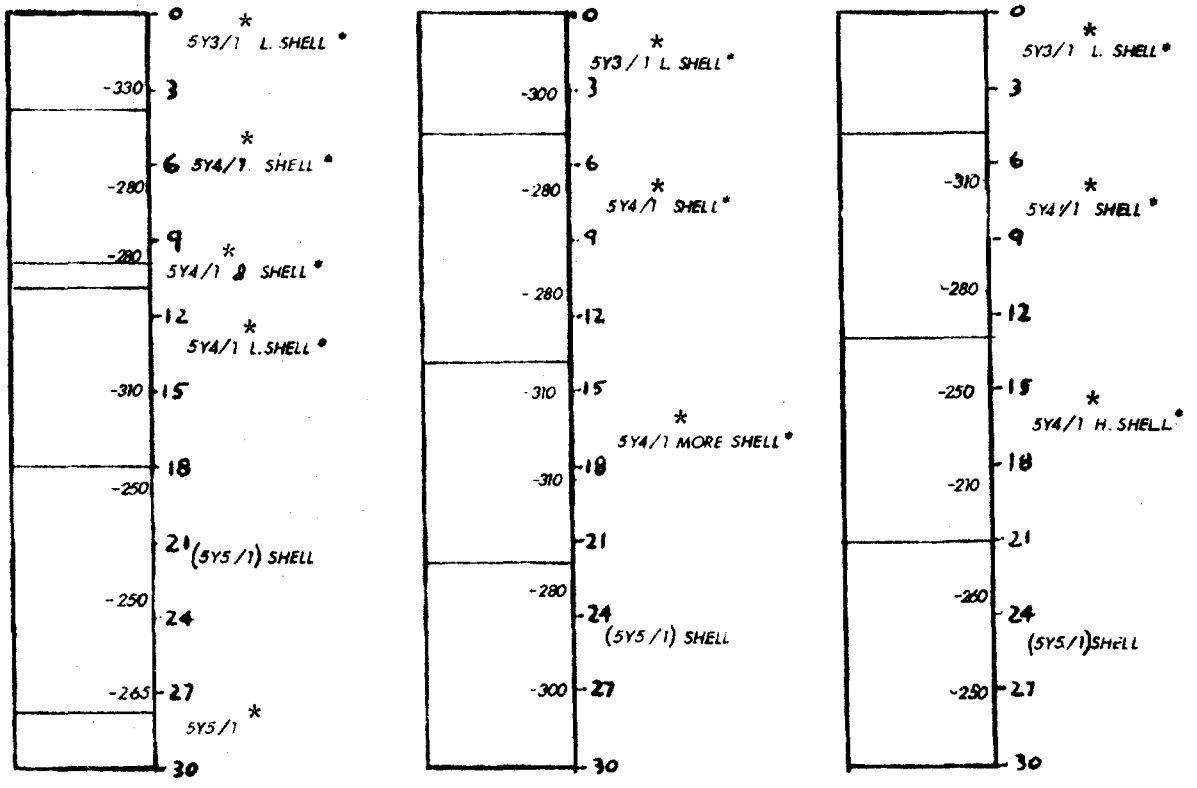


*Fine Sand

GRAIN SIZE DISTRIBUTION



2-Is

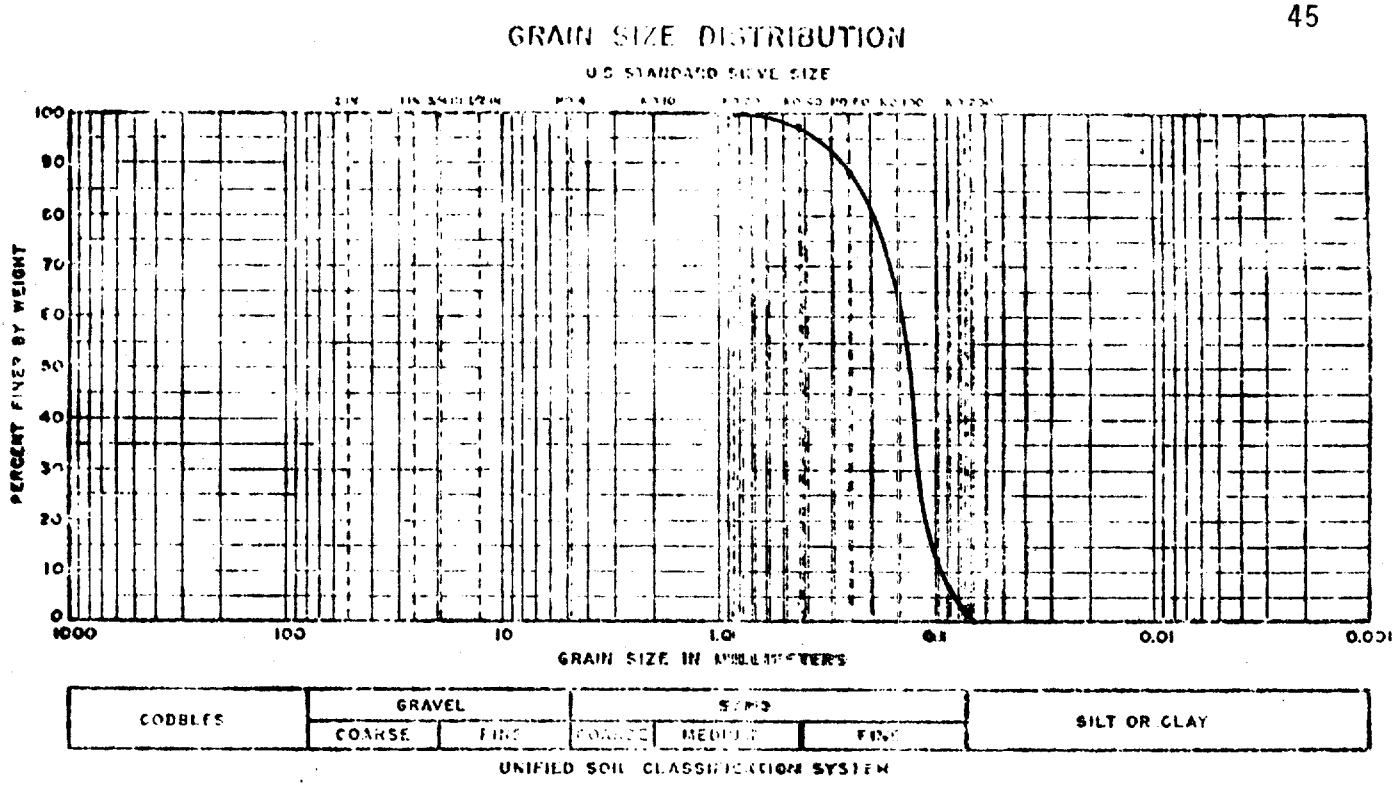


* MOTTLED WITH L. BLACK

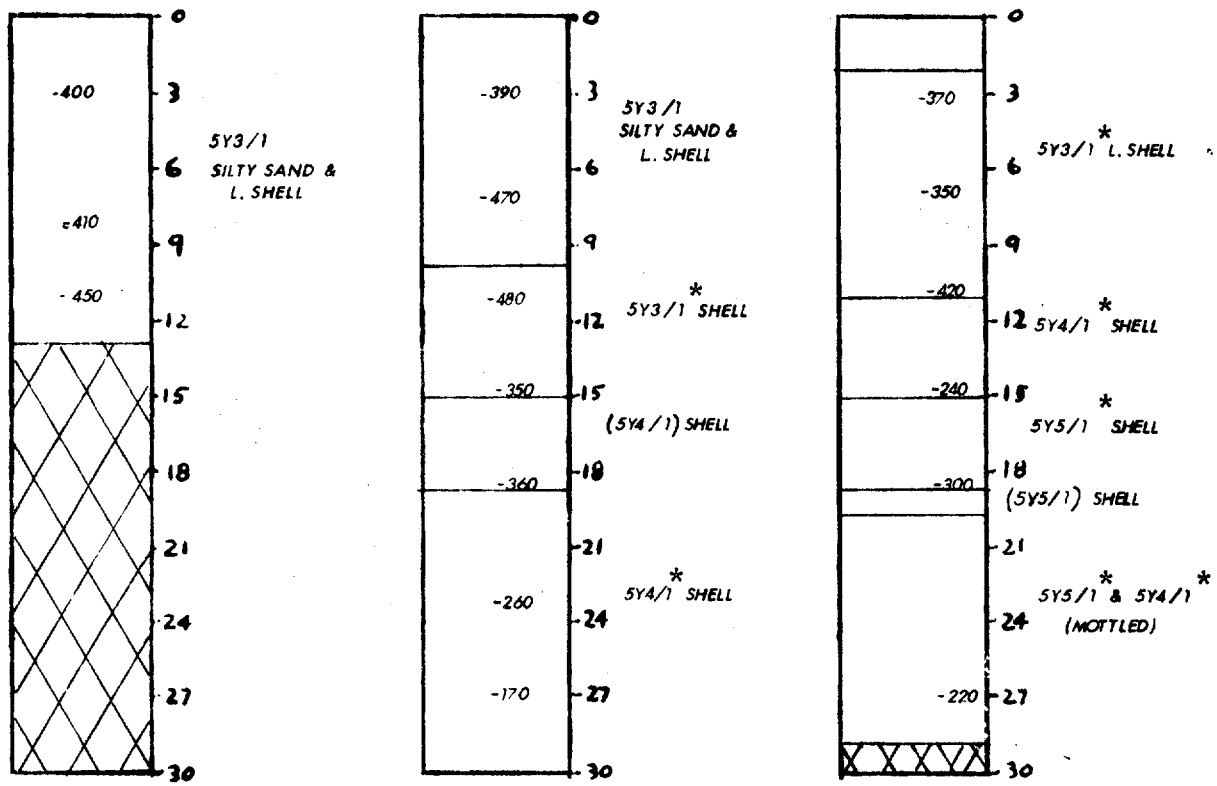
AT SURFACE - GREEN & RED PLANT

SLIGHT FISHY SMELL NEAR SURFACE

*Fine Sand

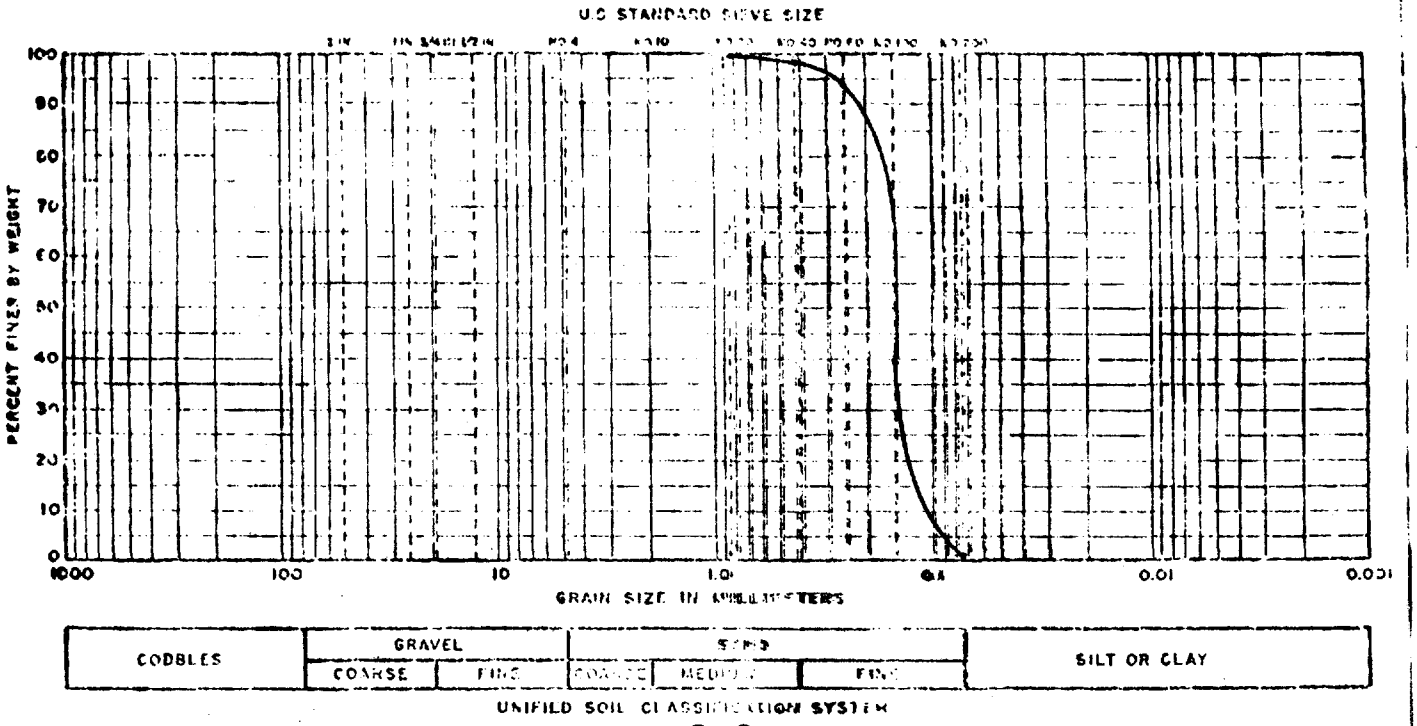

GRAIN SIZE DISTRIBUTION
U.S. STANDARD SIEVE SIZE
PERCENT FINER BY WEIGHT
100
90
80
70
60
50
40
30
20
10
0
1000
100
10
1.0
0.1
0.01
0.001
GRAIN SIZE IN MILLIMETERS
COBBLES
GRAVEL
COARSE
FINE
SAND
COARSE
MEDIUM
FINE
SILT OR CLAY
UNIFIED SOIL CLASSIFICATION SYSTEM

2-2


0
3
6
9
12
15
18
21
24
27
30
-400
-410
-450
5Y3/1
SILTY SAND &
L. SHELL
-390
-470
-480
-350
-360
-260
-170
5Y3/1
SILTY SAND &
L. SHELL
5Y3/1 SHELL
(5Y4/1) SHELL
5Y4/1 SHELL
-370
-350
-420
-240
-300
-220
5Y3/1 L. SHELL
5Y4/1 SHELL
5Y5/1 SHELL
(5Y5/1) SHELL
5Y5/1 & 5Y4/1
(MOTTLED)

*Fine Sand

GRAIN SIZE DISTRIBUTION



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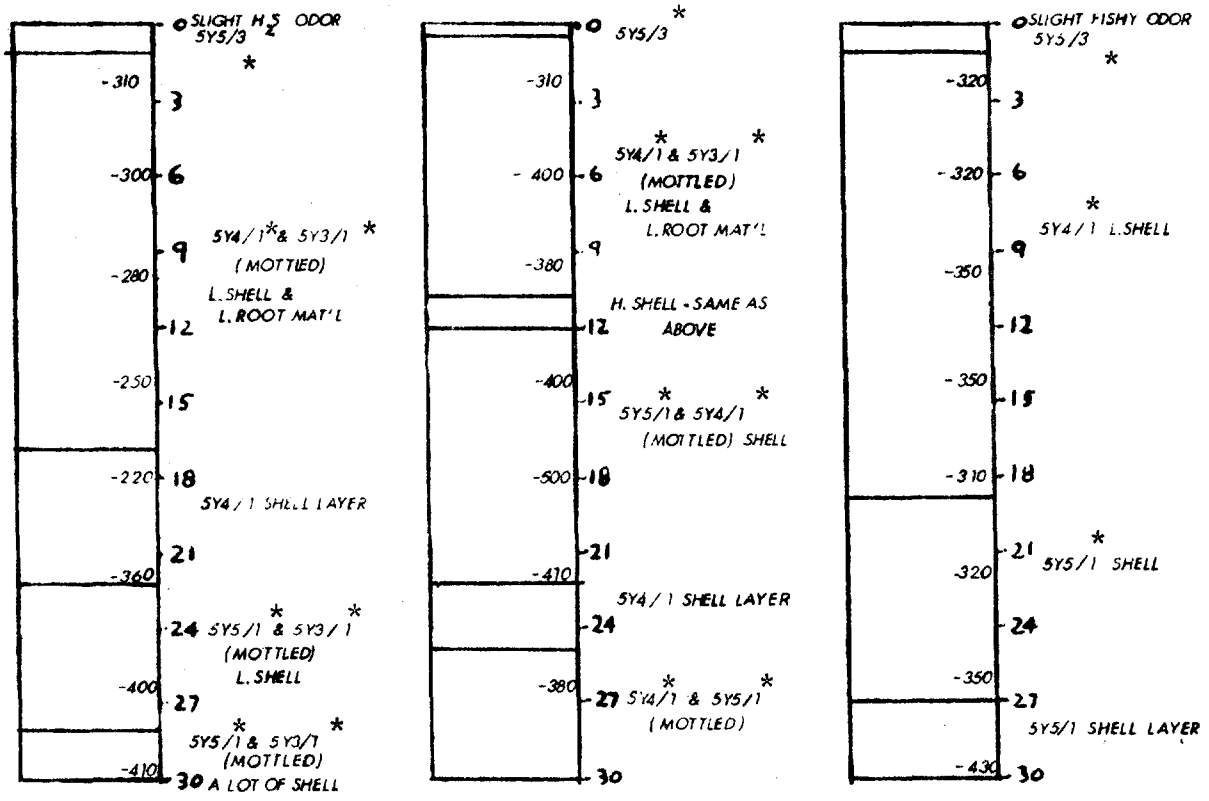
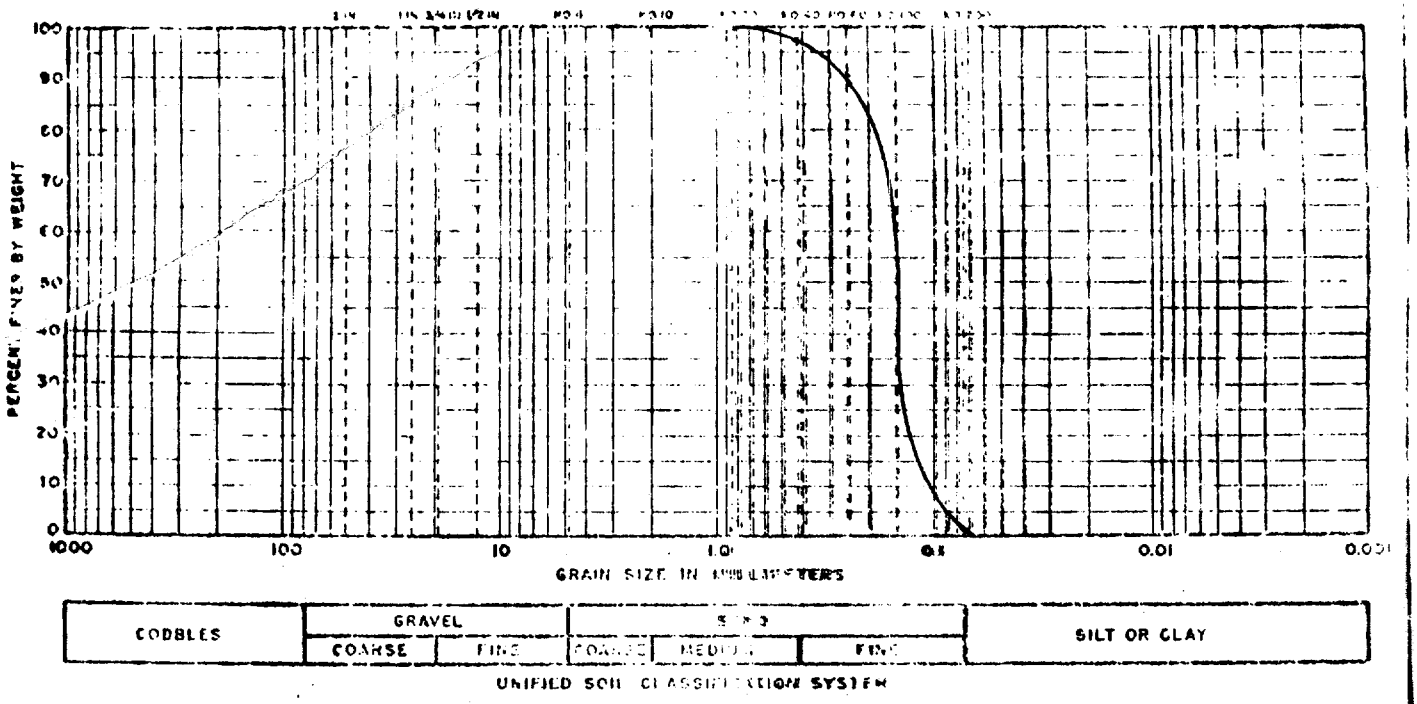


*Fine Sand

GRAIN SIZE DISTRIBUTION



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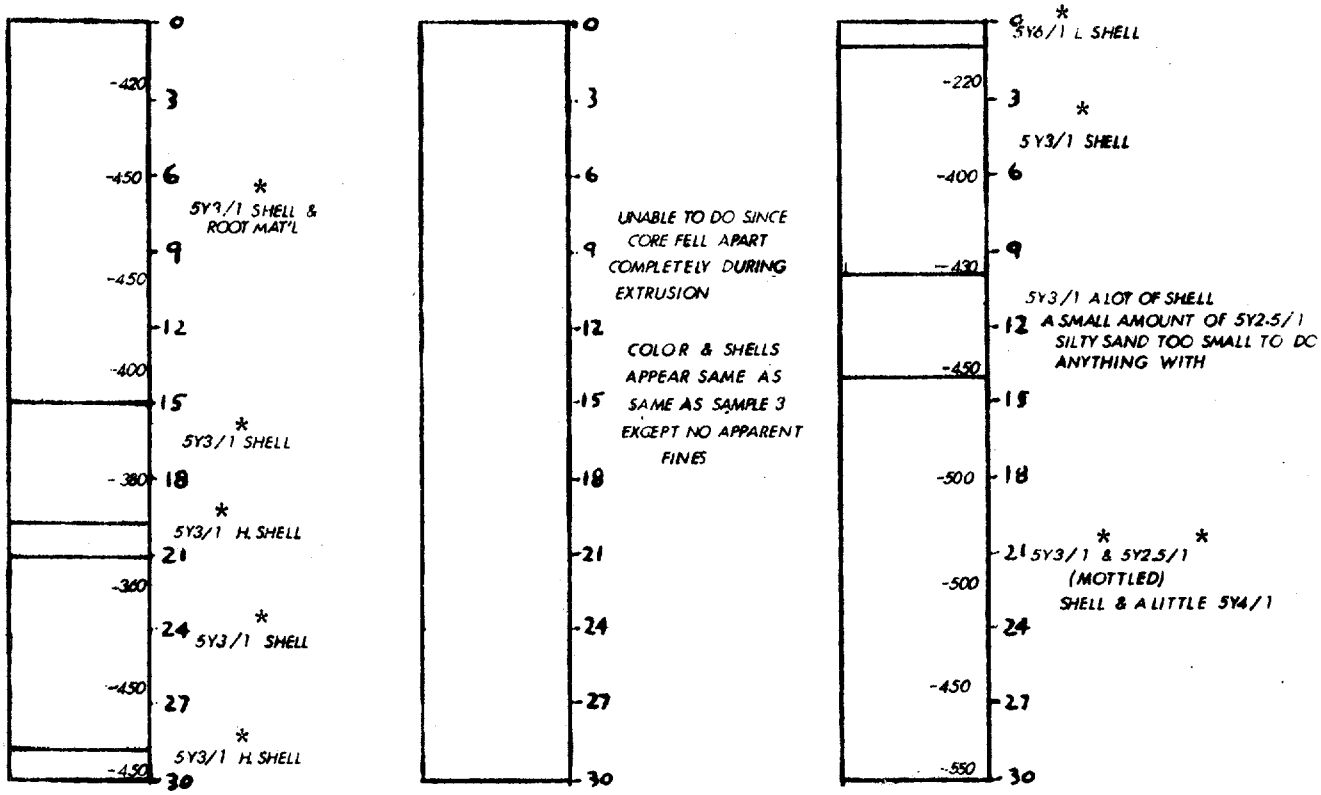
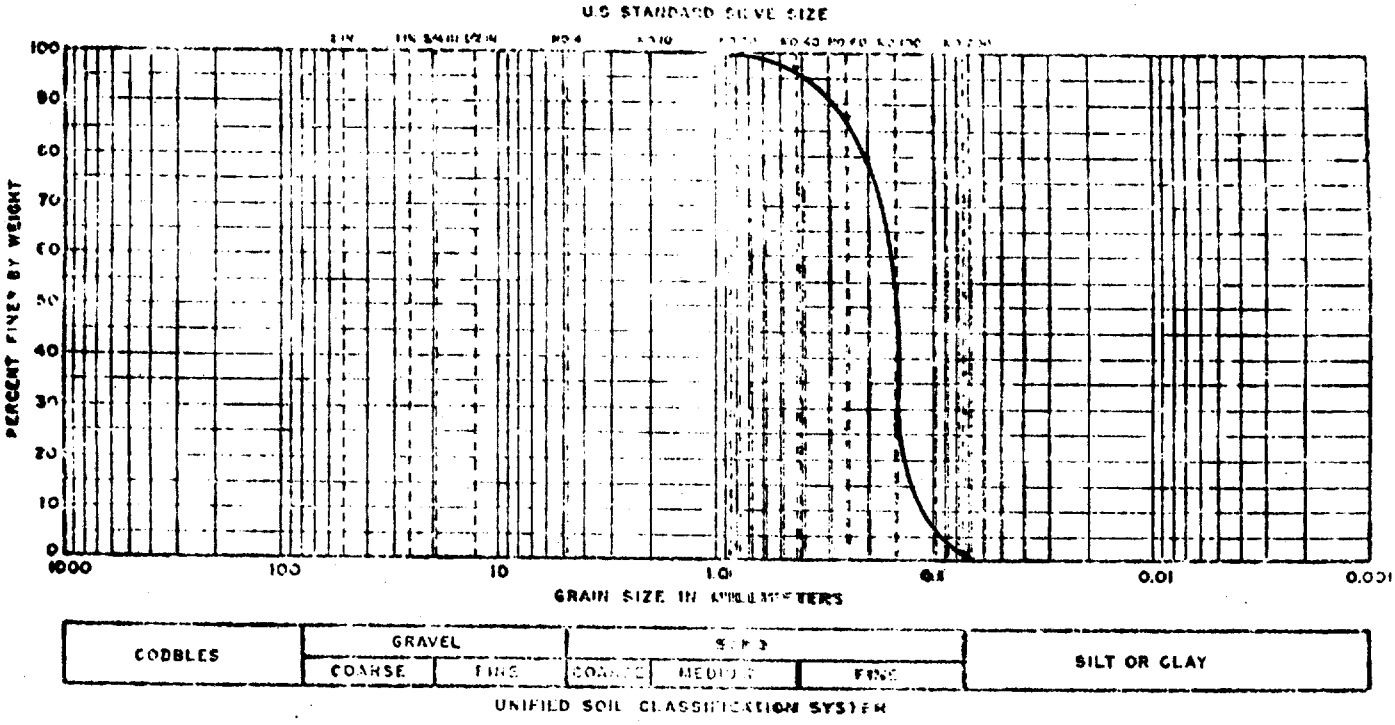


*Fine Sand

GRAIN SIZE DISTRIBUTION



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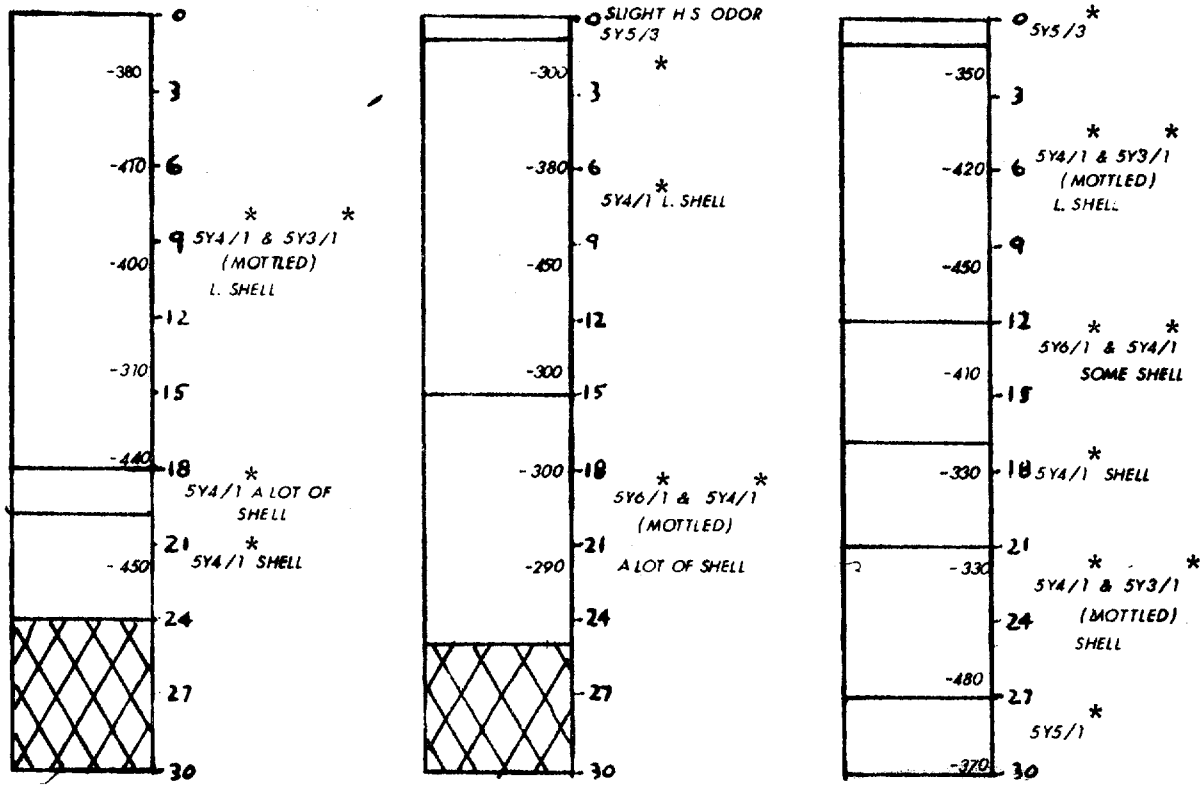
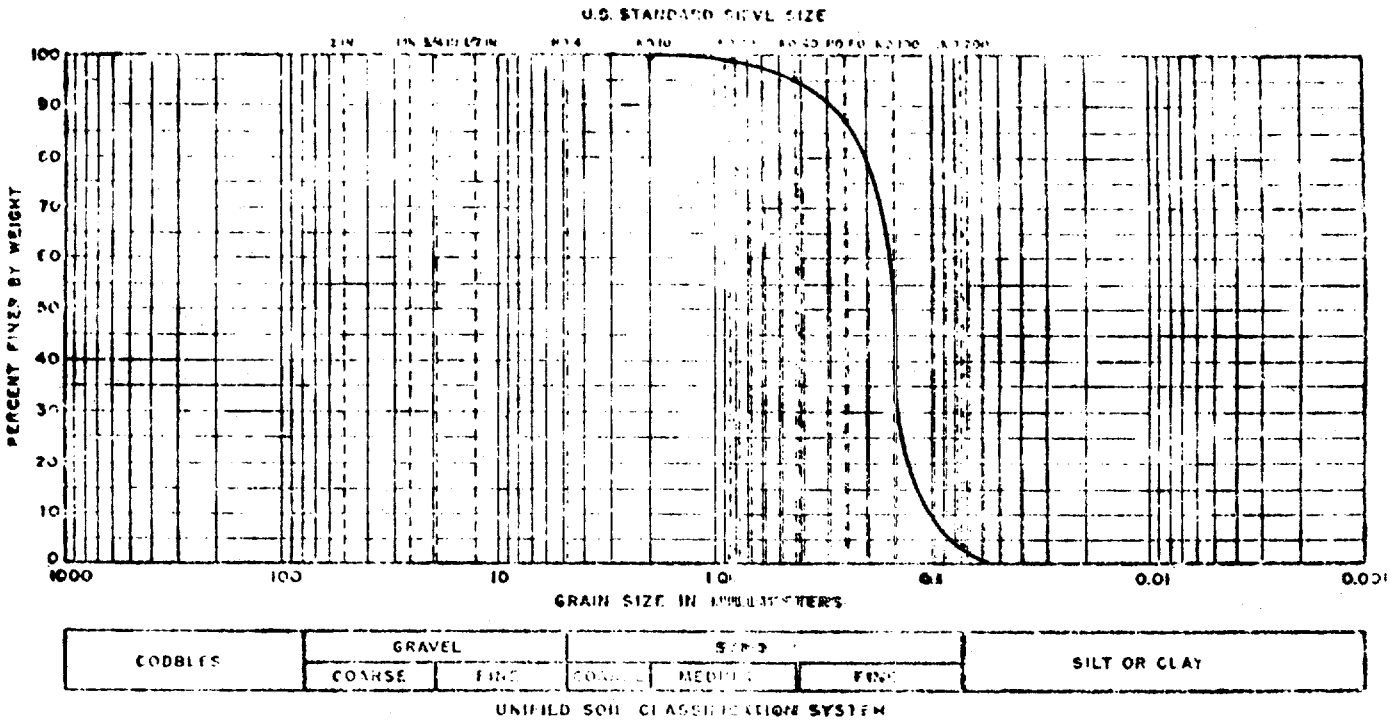


*Fine Sand

GRAIN SIZE DISTRIBUTION



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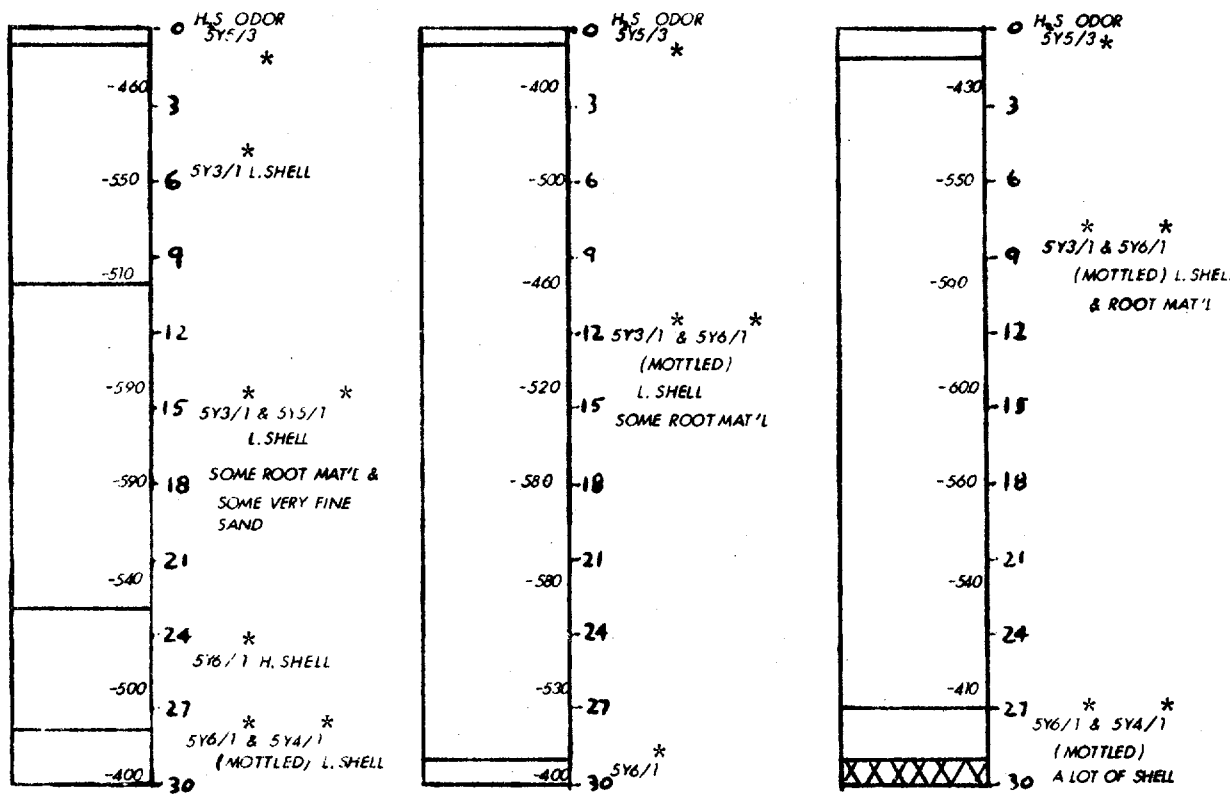
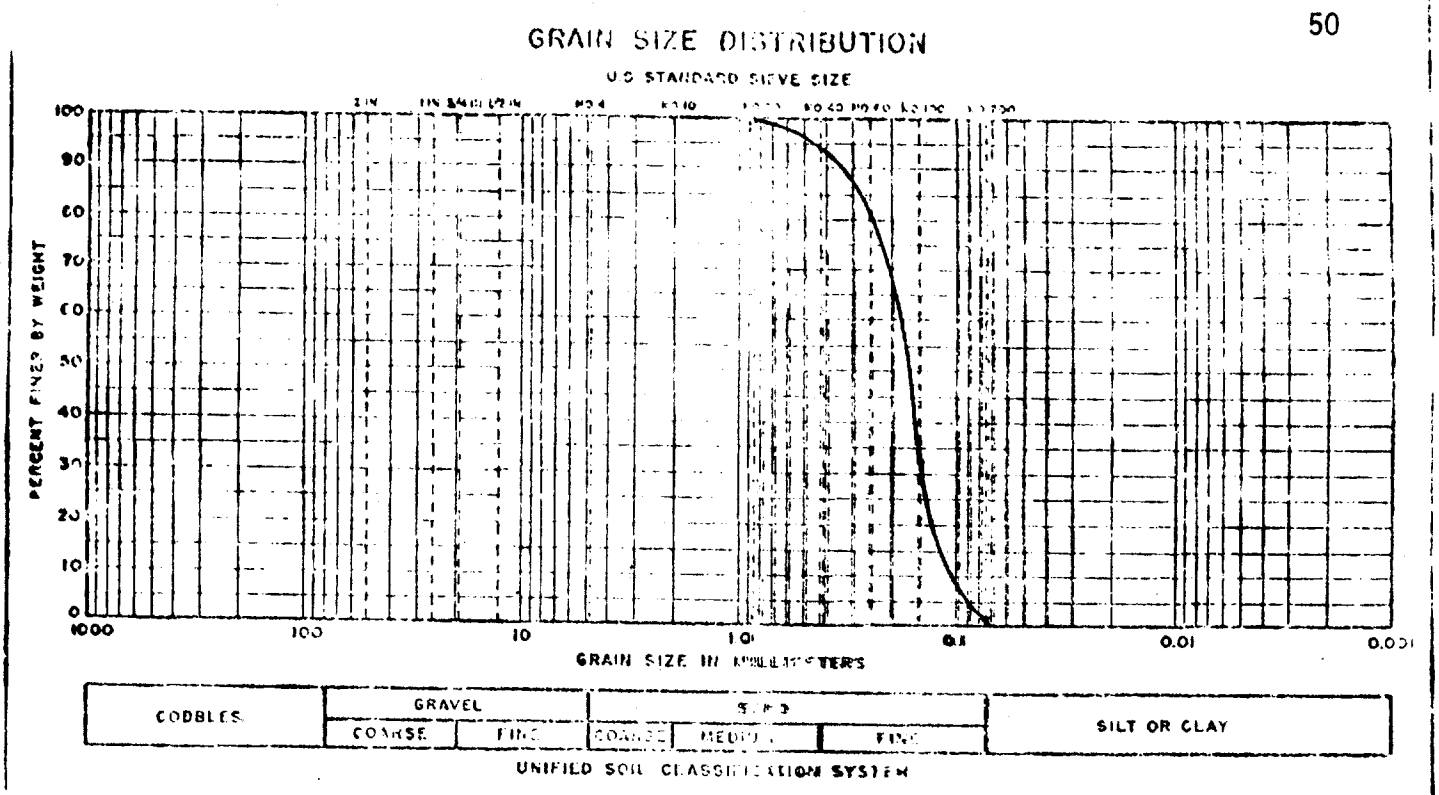
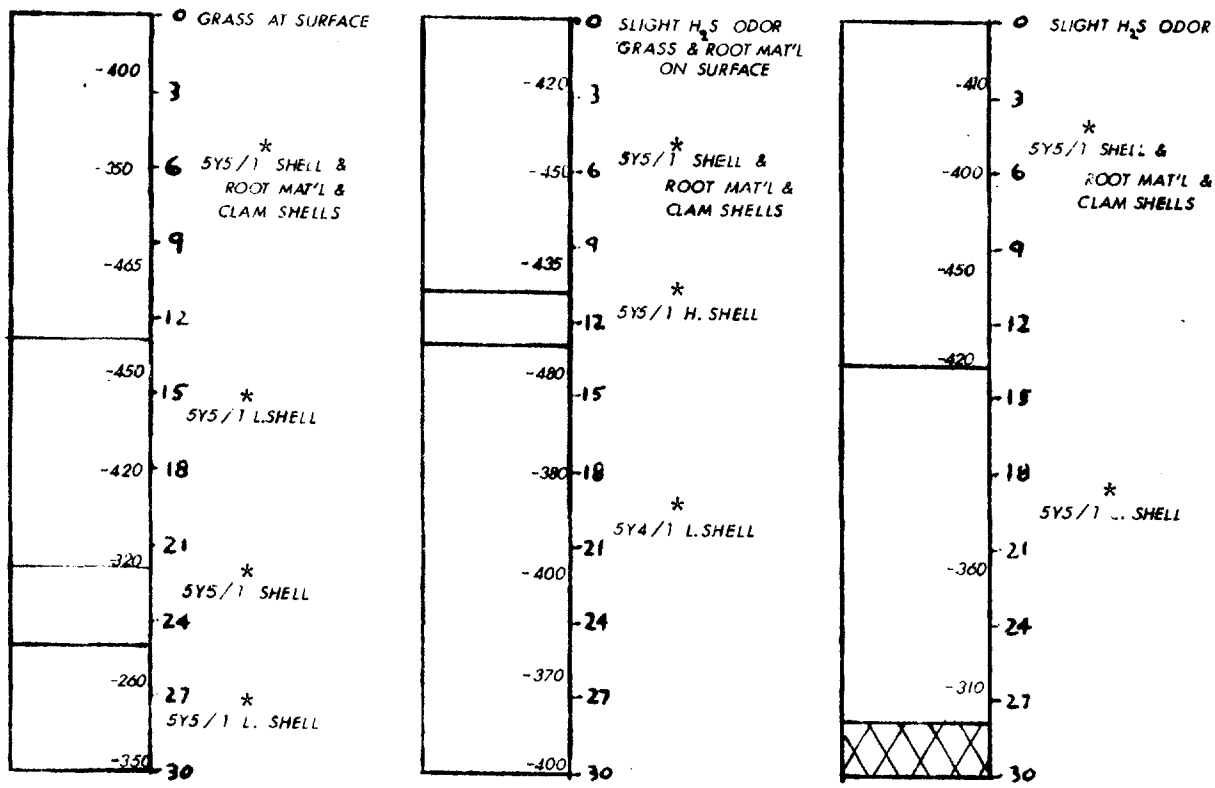


*Fine Sand

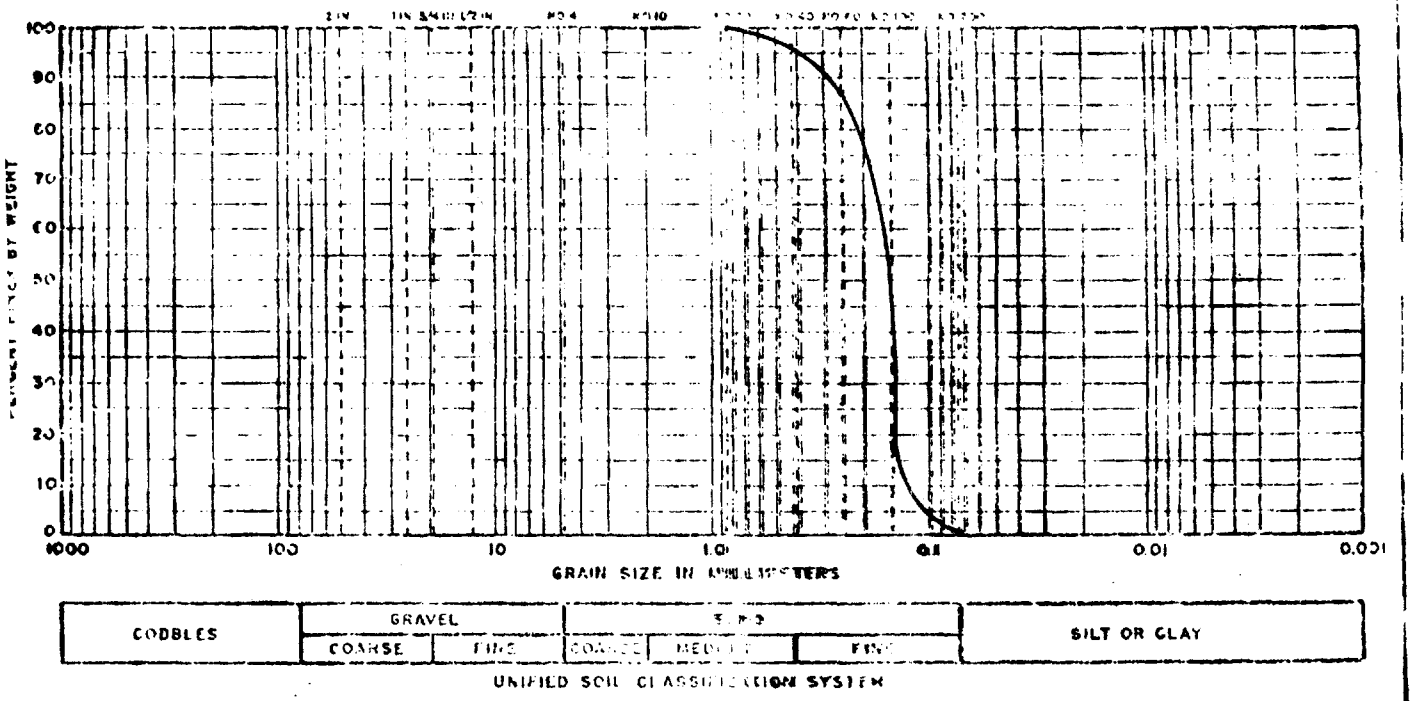

GRAIN SIZE DISTRIBUTION
U.S STANDARD SIEVE SIZE
PERCENT FINER BY WEIGHT
100
90
80
70
60
50
40
30
20
10
0
1000
100
10
1.0
0.1
0.01
0.001
GRAIN SIZE IN MILLIMETERS
COBBLES
GRAVEL
COARSE
FINE
SAND
COARSE
MEDIUM
FINE
SILT OR CLAY
UNIFIED SOIL CLASSIFICATION SYSTEM

3-3

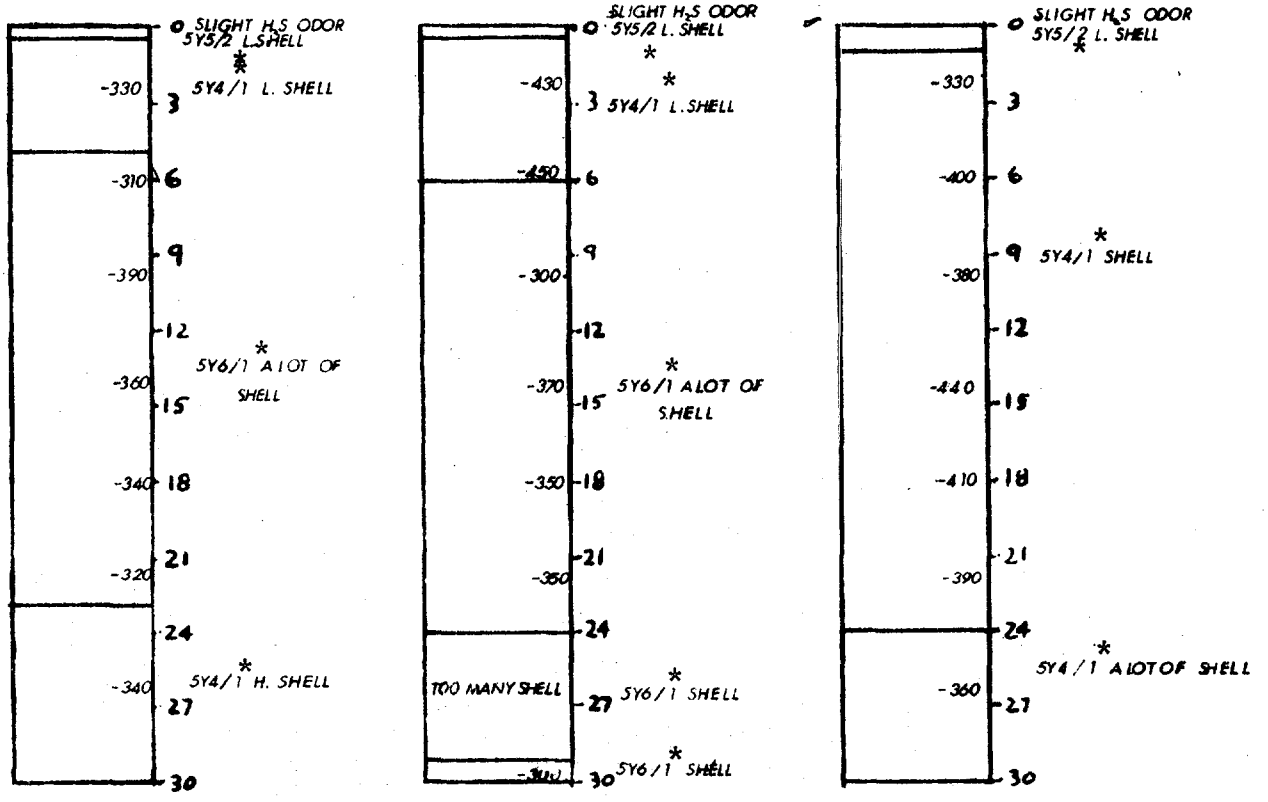

0 GRASS AT SURFACE
-400
3
-350
6
5Y5/1 * SHELL & ROOT MAT'L & CLAM SHELLS
9
-465
12
-450
15
5Y5/1 * L.SHELL
-420
18
21
-320
5Y5/1 * SHELL
24
-260
27
5Y5/1 * L. SHELL
-350
30
0 SLIGHT H_2S ODOR GRASS & ROOT MAT'L ON SURFACE
-420
3
-450
6
5Y5/1 * SHELL & ROOT MAT'L & CLAM SHELLS
9
-435
12
5Y5/1 * H. SHELL
-480
15
-380
18
5Y4/1 * L.SHELL
21
-400
24
-370
27
-400
30
0 SLIGHT H_2S ODOR
-410
3
5Y5/1 * SHELL & ROOT MAT'L & CLAM SHELLS
-400
6
9
-450
12
-420
15
18
5Y5/1 * .. SHELL
21
-360
24
-310
27
30

*Fine Sand

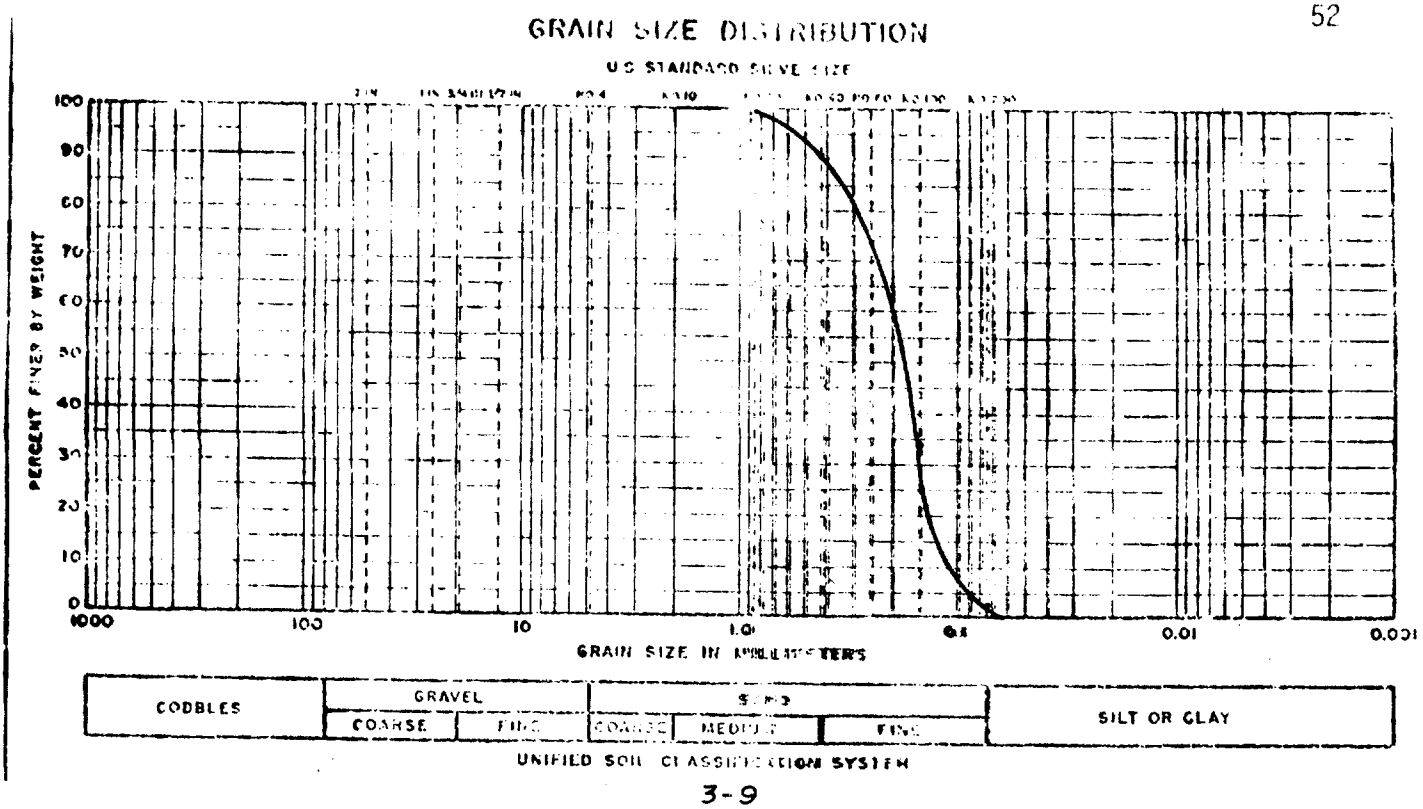
GRAIN SIZE DISTRIBUTION



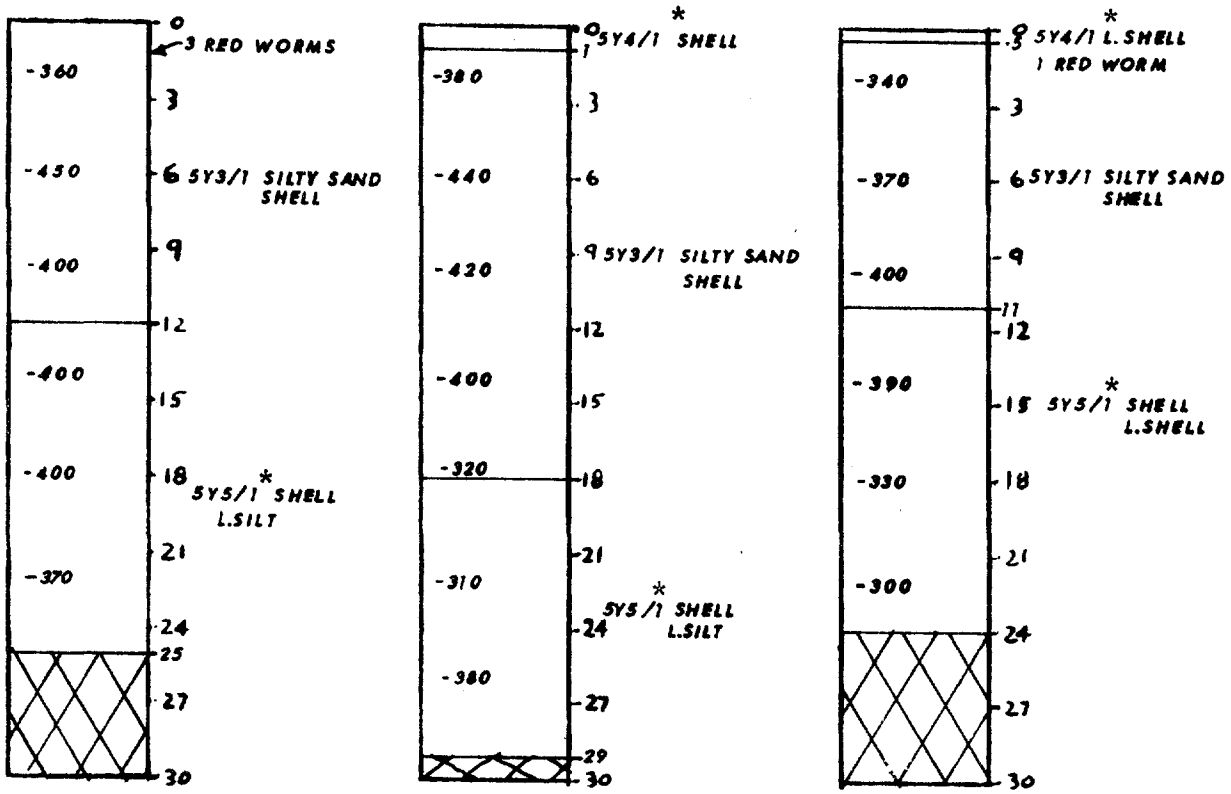
3-7



*Fine Sand

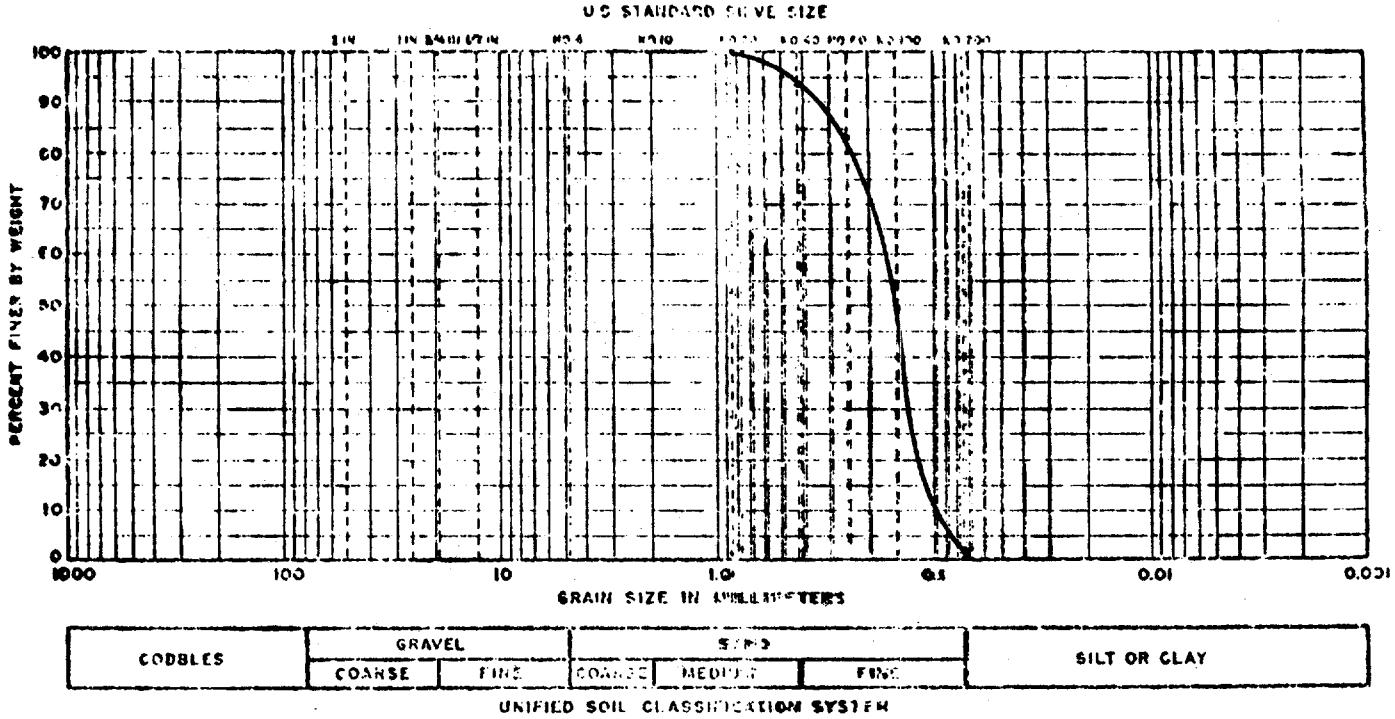

GRAIN SIZE DISTRIBUTION
U.S. STANDARD SIEVE SIZE
PERCENT FINER BY WEIGHT
100
90
80
70
60
50
40
30
20
10
0
1000
100
10
1.0
0.1
0.01
0.001
GRAIN SIZE IN MILLIMETERS
COBBLES
GRAVEL
COARSE
FINE
SAND
COARSE
MEDIUM
FINE
SILT OR CLAY
UNIFIED SOIL CLASSIFICATION SYSTEM

3-9

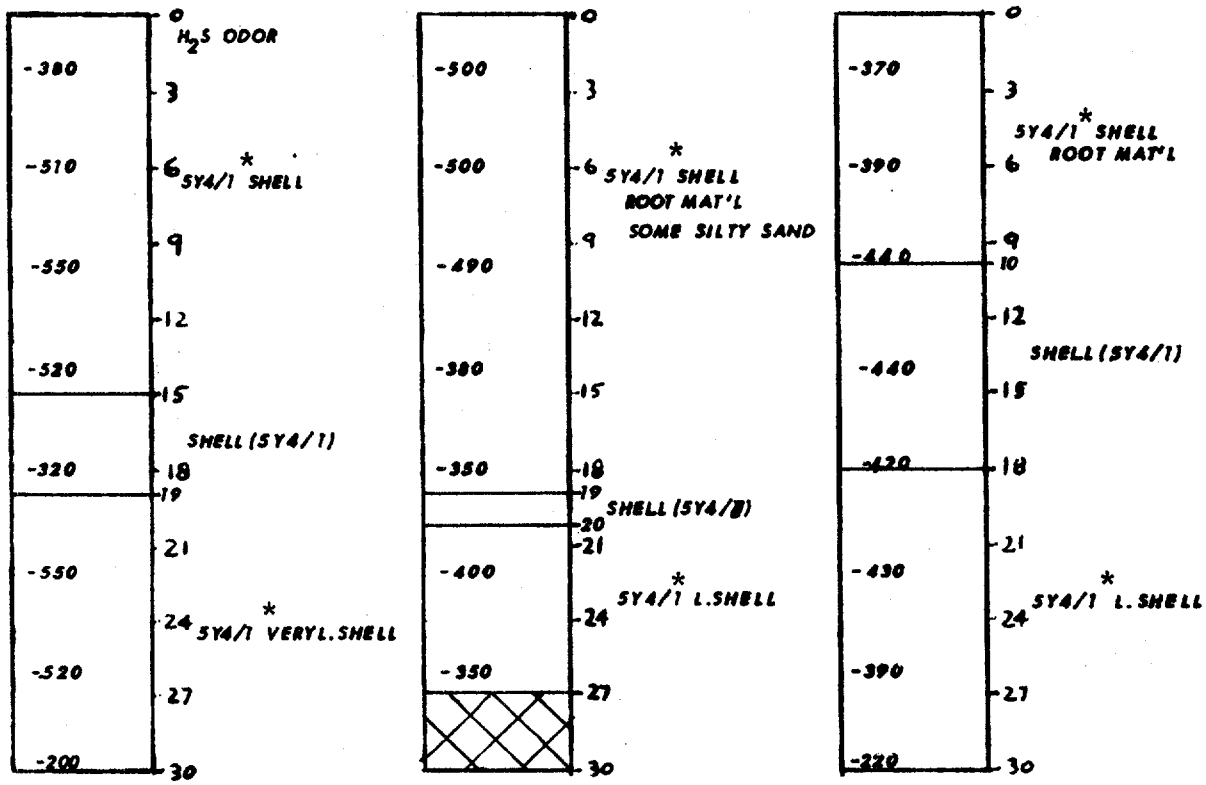

0
3 RED WORMS
-360
3
-450
6 5Y3/1 SILTY SAND SHELL
-400
9
12
-400
15
-400
18 5Y5/1* SHELL L.SILT
-370
21
24
25
27
30
0
1 5Y4/1 SHELL
-380
3
-440
6
-420
9 5Y3/1 SILTY SAND SHELL
12
-400
15
-320
18
21
-310
24 5Y5/1* SHELL L.SILT
-380
27
29
30
.5 5Y4/1 L.SHELL
1 RED WORM
-340
3
-370
6 5Y3/1 SILTY SAND SHELL
-400
9
11
12
-390
15 5Y5/1* SHELL L.SHELL
-330
18
21
-300
24
27
30

*Fine Sand

GRAIN SIZE DISTRIBUTION

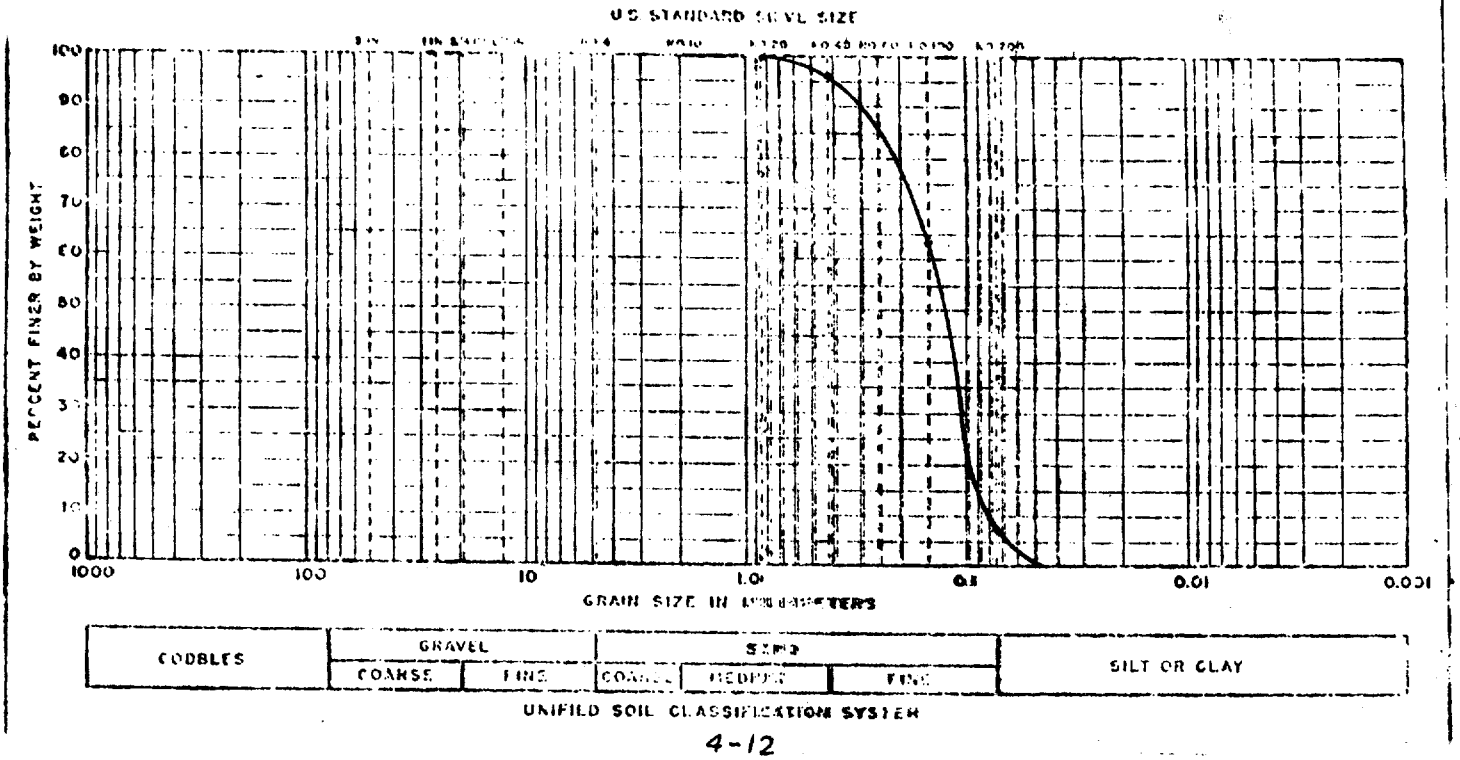


3-12

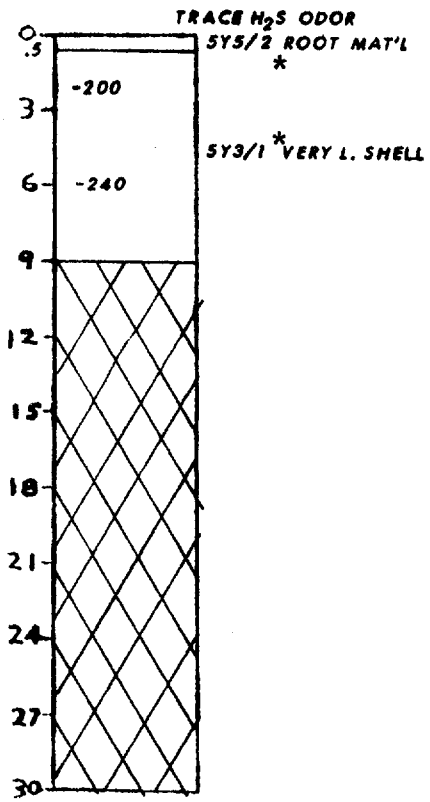


*Fine Sand

GRAIN SIZE DISTRIBUTION

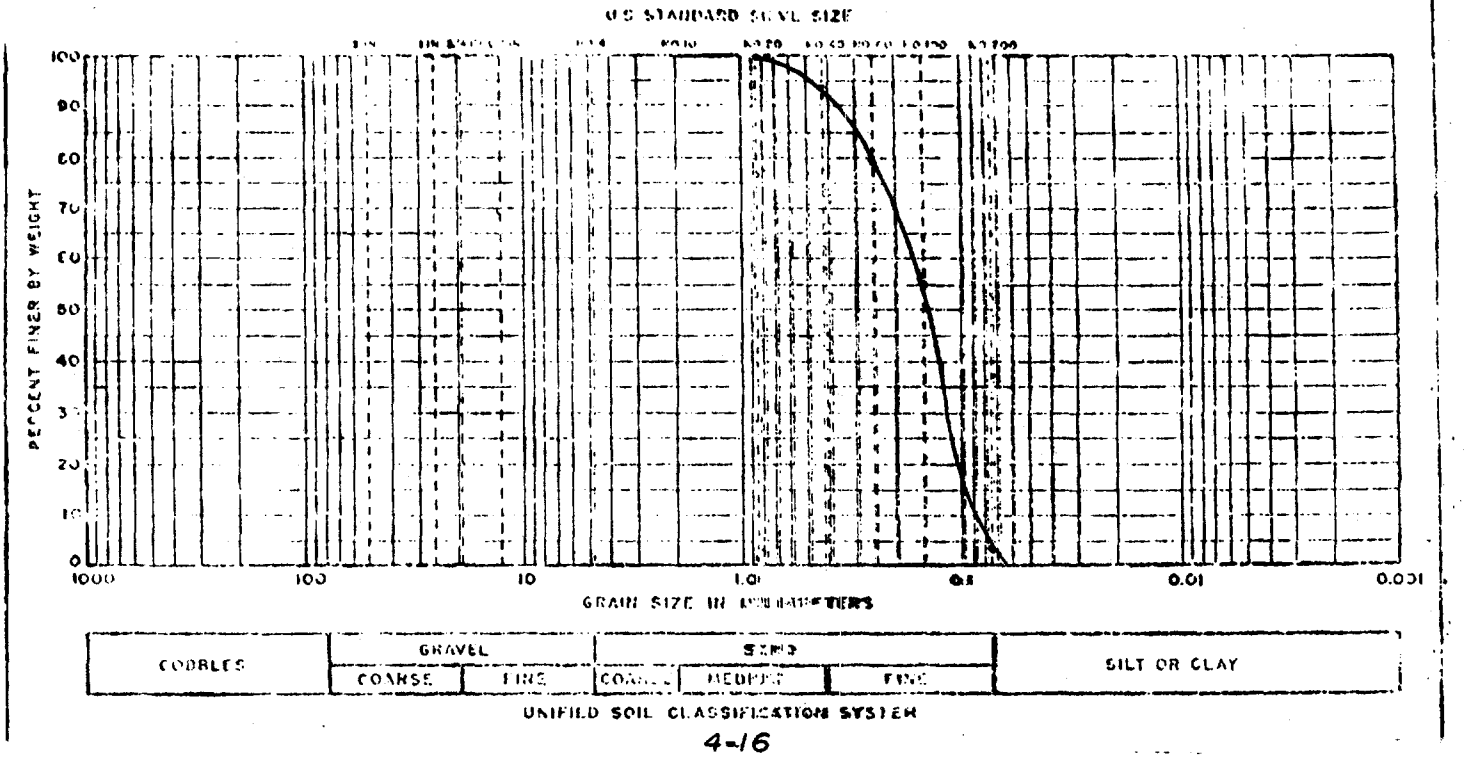


4-12



*Fine Sand

GRAIN SIZE DISTRIBUTION



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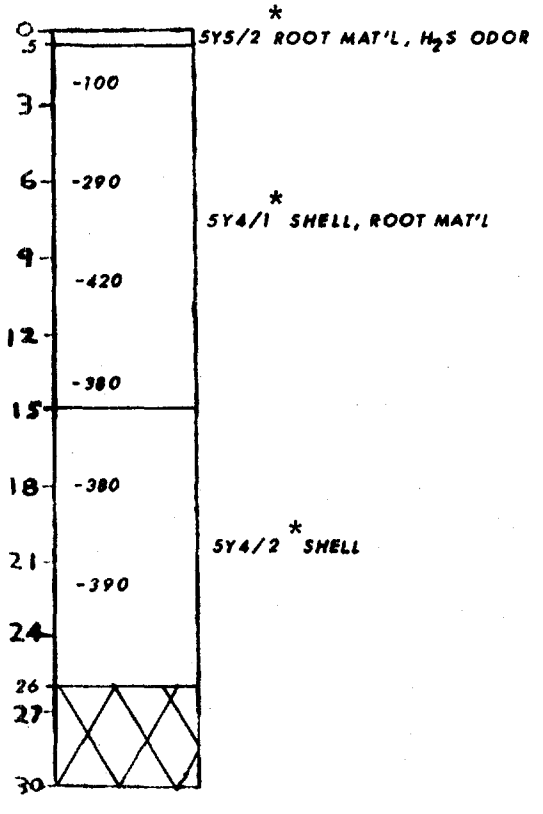
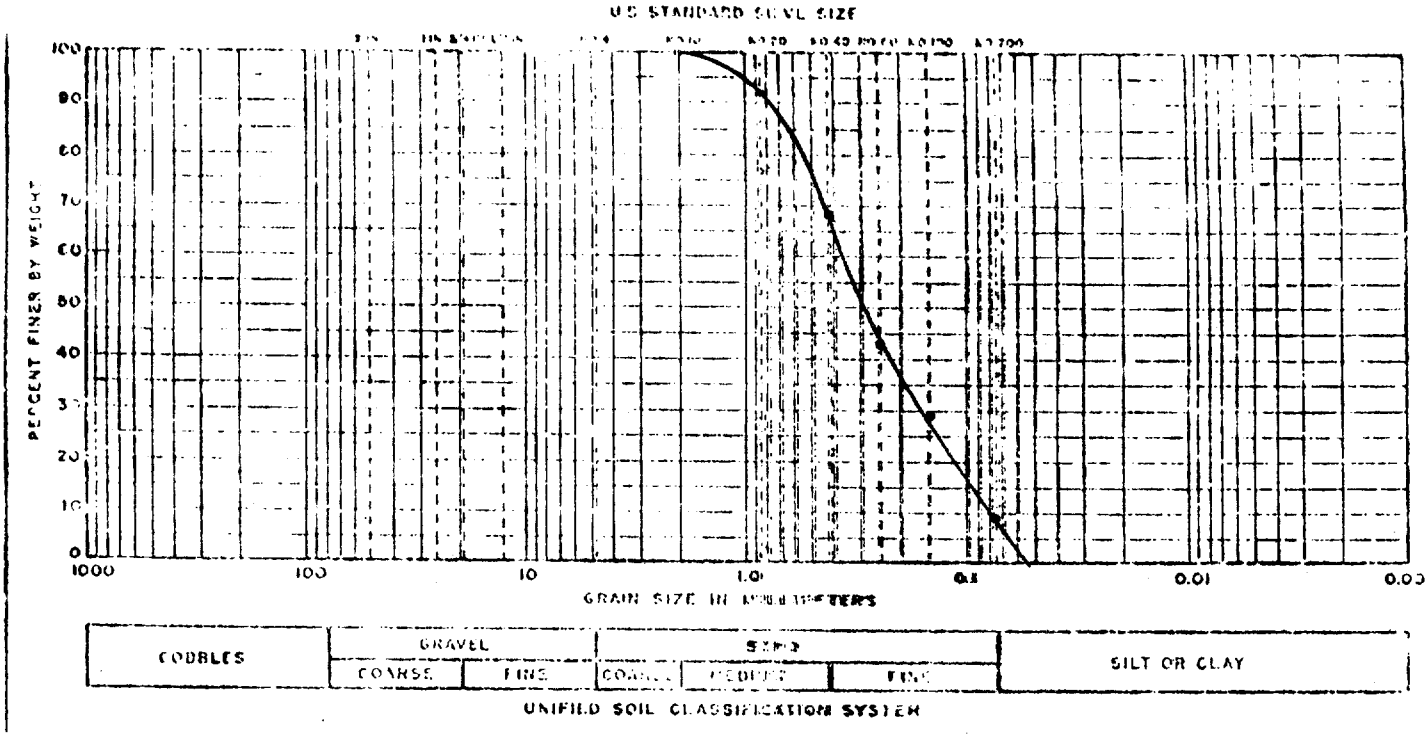
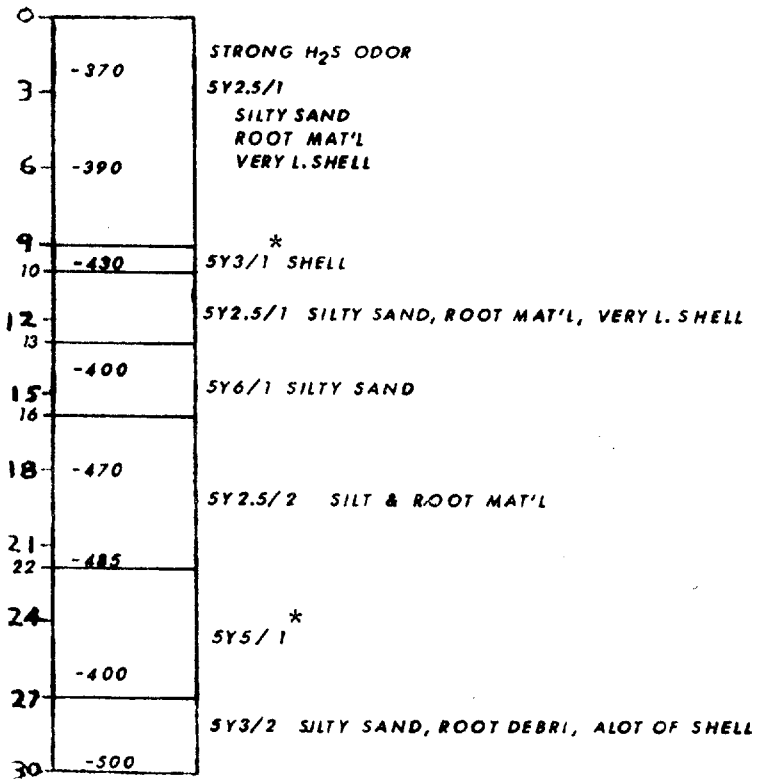


*Fine Sand

GRAIN SIZE DISTRIBUTION

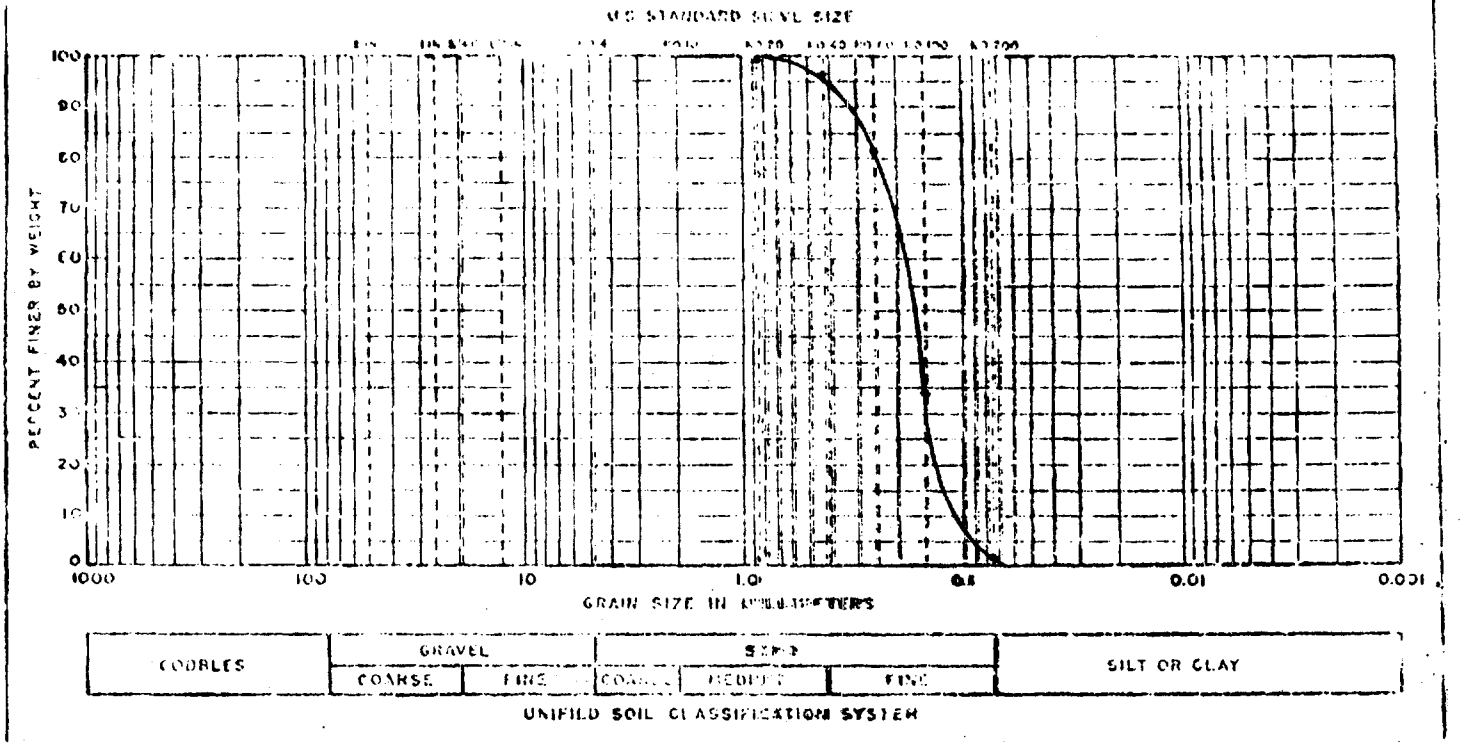


4-16S

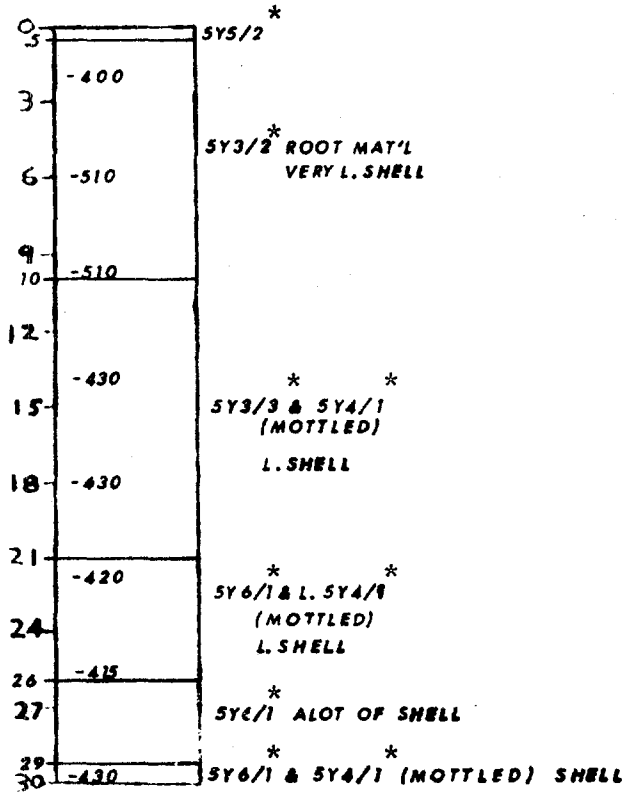


*Fine Sand

GRAIN SIZE DISTRIBUTION



4-18



*Fine Sand

Test	1-2			1-6			1-8			1-11			2-15			2-2			1-115			1-19			1-23			2-1		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Dissolved Oxygen mg/L	8.5	8.3	8.2	9.5	9.1	9.0	11.0	11.2	10.4	10.0	8.0	8.5	11.0	11.6	11.2	8.2	7.6	7.4	7.9	7.7	8.0	8.2	8.1	7.9	7.6	7.4	8.0	8.4	9.0	8.6
$\bar{y}$	8.33			9.20			10.87			8.83			11.27			7.73			7.87			8.07			7.67			8.67		
pH	6.745	6.675	6.625	6.668	6.610	6.598	6.746	6.693	6.740	6.685	6.656	6.612	6.696	6.687	6.663	6.723	6.731	6.719	6.675	6.622	6.695	6.579	6.570	6.568	6.868	6.657	6.740	6.592	6.586	6.565
$\bar{y}$	6.682			6.625			6.710			6.641			6.682			6.724			6.664			6.572			6.755			6.551		
Eh mv	204.6	140.3	90.8	117.3	+91.8	-82.6	29.6	74.2	51.4	+65.8	-62.0	-70.8	-70.0	-180	-100	-280	-300	-150	+10	-30	-60	-170	-240	-300	-60	-70	-140	-50	-50	-60
$\bar{y}$	+144.2			-97.2			+51.7			-66.2			-116.7			-216.7			-26.7			-236.7			-90.0			-53.3		
% dry wt Chemical Oxygen Demand ppm	0.42			0.87			0.55			0.81			0.49			1.04			1.05			0.77			0.55			0.47		
	2553	3234	4340	5702	6127	8340	4425	4340	4435	6893	6042	5782	5140	2249	3855	8193	6827	7133	5372	6340	9835	4552	9185	3920	5791	4958	4420	4582	2926	3414
$\bar{y}$	3376			6723			4400			6212			3748			7384			8182			5852			4389			3631		
Volatile Solids % dry	1.6	1.6	1.6	1.8	3.2	3.9	1.0	1.2	1.9	1.1	1.8	1.7	1.7	2.1	1.4	3.0	2.9	3.1	1.0	1.1	1.0	1.2	1.9	1.3	1.9	1.5	1.4	1.2	0.9	1.1
$\bar{y}$	1.60			2.97			1.37			1.53			1.73			3.00			1.03			1.43			1.60			1.07		
water content $\frac{W_w}{W_s} \times 100$ %	27.3	22.6	21.2	29.0	25.7	34.6	24.3	22.6	27.5	30.7	33.3	27.4	30.5	32.4	26.6	42.3	46.2	36.2	21.5	24.4	20.5	23.1	28.9	23.6	18.5	19.8	21.2	22.2	22.9	22.8
$\bar{y}$	23.7			29.8			24.8			30.5			31.5			41.6			22.1			25.9			20.2			22.9		

	2-9			2-17			2-30			2-24			1-15			1-20			3-3			3-7			3-9			3-12		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Dissolved Oxygen	6.8	7.0	6.7	6.5	6.3	6.0	8.0	7.8	7.9	7.6	8.0	8.2	7.0	6.8	7.4	8.4	8.0	7.2	9.0	9.4	8.9	8.7	8.4	8.3	7.0	6.5	6.8	7.0	7.8	7.5
mg/L	6.83			6.27			7.90			7.93			7.07			7.87			9.10			8.47			6.77			7.43		
pH	6.572	6.564	6.538	6.491	6.482	6.492	6.489	6.513	6.496	6.478	6.530	6.494	6.583	6.559	6.556	6.536	6.542	6.540	6.632	6.632	6.640	6.627	6.615	6.634	6.644	6.645	6.652	6.622	6.640	6.613
	6.551			6.488			6.496			6.501			6.559			6.539			6.635			6.625			6.647			6.625		
Eh	+50	-40	-80	-200	-60	-80	-200	-180	-190	-230	-140	-150	-390	-210	-375	-230	-390	-330	-350	-390	-385	-370	-390	-340	-320	-270	-290	-370	-370	-360
mV	-23.3			-113.3			-190.0			-173.3			-321.7			-316.7			-325.0			-366.7			-293.3			-366.7		
% dry	0.53			1.31			0.75			0.78			1.29			1.18			1.14			0.97			2.31			0.78		
Chemical Oxygen Demand	5771	3576	2682	10404	8778	8209	7152	4145	4633	5039	3739	8616	9022	9185	9428	10160	6177	7640	6561	10530	6885	4941	11826	3645	11583	16200	12855	6642	5494	3726
ppm	4010			9130			5310			5798			9212			7992			7992			6804			13446			5454		
Volatile Solids	1.3	1.1	1.1	2.8	2.2	2.2	2.3	2.1	1.9	1.5	2.0	1.5	2.8	2.6	2.5	3.3	3.8	3.5	5.2	6.2	6.8	4.4	3.8	2.8	5.5	4.3	9.2	2.9	5.5	3.7
% dry	1.17			2.40			2.10			1.67			2.63			3.53			6.07			3.67			6.33			4.03		
water content	28.9	42.7	25.9	46.2	41.0	42.2	47.2	38.1	36.1	42.6	30.2	29.8	36.2	38.1	42.6	58.5	42.4	44.3	40.3	46.1	42.7	46.6	43.6	40.8	73.8	70.7	71.1	44.8	45.0	42.4
%	32.3			43.1			40.5			34.2			39.0			47.4			43.0			42.0			71.5			43.8		

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Section V, Article 14

A Study of the Circulation in the Lagoons Encompassing the Kennedy Space Center

Richard Evon Dill

A STUDY OF THE CIRCULATION IN THE LAGOONS ENCOMPASSING THE KENNEDY SPACE CENTER

by

Richard Evan Dill

B.S. in Engineering, United States Naval Academy, 1967

Submitted to the Graduate Faculty

in partial fulfillment of

the requirements for the degree of

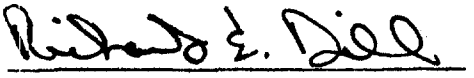
Master of Science

in

Physical Oceanography

Florida Institute of Technology

1974



ABSTRACT

Advisor Signature

A STUDY OF THE CIRCULATION IN THE LAGOONS ENCOMPASSING CAPE CANAVERAL, FLORIDA

Richard Dill, M.S.
Florida Institute of Technology, 1974

The hydrodynamics of the Indian and Banana Rivers and Mosquito Lagoon, surrounding the John F. Kennedy Space Center, Florida, is the object of this study. Data gathered from surface current measurements made with simple current crosses are compared with measurements of the wind field over each lagoon under varying meteorological conditions.

Steady-state and time dependent mathematical models are developed and predicted current velocities are compared with measured values. Extensive discussion is given to the previous work of other investigators in attempting to determine values for such ill-known quantities as eddy viscosity coefficients, dynamic roughness length, wind drag coefficient and bottom stress.

The circulation in these shallow lagoons appears to result from a combination of wind stress and slope currents. Tidal and Coriolis forces seem negligible. Calculations of theoretical surface current velocities under pure wind stress conditions compare reasonably well with measured current velocities. However, recommendations are made concerning specific areas of requisite future investigation.

ACKNOWLEDGEMENTS

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The author gratefully acknowledges the many valuable suggestions and comments made by Dr. Pieter S. Dubbelday.

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INTRODUCTION

Man's interest in and use of estuaries has been well established in the past decades. With much of the world's transport done by ships and its many industrial complexes requiring access to coastal water bodies, population growth has thus increased tremendously near coastlines. More than forty-five per cent of the populace of the United States and seven of the world's ten largest urban areas are situated in coastal areas. With the increasing use of estuarine waters for a multitude of purposes, it has become vital for environmental protection and for the assessment of the proper use of these waters to understand more completely the physical and biological processes related to these nearshore waters.

In the past, the major interest in estuaries has been primarily biological, resulting in a notable lack of literature on specific estuary circulation processes. An even more apparent lack exists of synoptic field measurements in testing the accuracy of theoretical predictions of natural circulation phenomena. This disparity of field work has apparently been mainly due to a lack of proper funding because of various economic factors. The main factor is the high cost involved in obtaining an accurate, detailed description of such a large body of water, while another factor is the seemingly low, short-term return of such an expensive study. To date, there have only been a handful of detailed studies done on various estuaries; notably, the Chesapeake Bay and its tributaries (Pritchard (Lauff,

1967), Hansen and Rattray, 1966); Alaskan, Canadian and Norwegian fjords (Rattray and Saelen (Lauff, 1967)); the Columbia River, USA (Hansen, 1965); and the Mersey Estuary, England (Hansen and Bowden (Lauff, 1967)). It will later be seen that none of these estuaries exhibit the same characteristics as those under consideration in this paper.

DEFINITION AND CLASSIFICATION

The most commonly accepted definition of an estuary from a dynamic viewpoint has been expressed by Pritchard (Lauff, 1967): "An estuary is a semi-enclosed coastal body of water which has free connection with the open sea and within which seawater is measureably diluted with fresh water derived from land drainage." It should be noted that this definition limits the estuary to the landward limit of salinity intrusion, thus possibly not including the entire body of water under consideration. Also note that Pritchard sought to imply that the tide was always a driving force when he included the "free connection" restriction (Kinsman, 1965b). There are further definitions based on geomorphology and biological considerations, which give rise to the question of the difference between a lagoon and an estuary. For example, Webster's Dictionary defines a lagoon as: "A shallow sound, channel, pond or lake near or communicating with the open sea."

Caspers (Lauff, 1967) has distinguished between these two types of water bodies based on biological considerations. He states that a stable body of brackish water is a lagoon, whereas a basin that shows periodic changes in the mixing of fresh and marine waters is an estuary. Although this definition relies on the analysis of a hydrological feature, e.g. the instability of salinity, it is precisely this stability, or lack thereof, which determines an estuary's biological features. The environmental conditions in the brackish water lagoon are relatively stable, whereas the euryhaline conditions of an estuary restrict the population of organisms to only those that are adaptive to fluctuating environmental conditions.

Johnson (1919) has gone as far as differentiating estuaries from lagoons by the influences of geological coastline development. Emery (Lauff, 1967) states that lagoons are typical of areas where continental shelves and coastal plains are wide and nearly flat because lagoons have been long-conceived as being caused by the marine deposition of offshore bars in areas of low relief. Estuaries, on the other hand, are related to continental shelves and coastal plains that are narrow and of high relief, mainly because they are formed by drowned river valleys, glaciers and other tectonic processes.

Estuaries have been classed using various systems. Pritchard (Lauff, 1967) classified estuaries by geomorphology as follows:

1. Coastal plain estuaries (drowned river valleys) are of gently sloping bottoms, whose depths uniformly increase towards the mouth (having been cut by erosion), and often show a dendritic pattern. Examples: Chesapeake Bay, USA and the Thames, Southampton Water and Mersey Estuary in England.

2. Fjords, characterized by U-shaped cross sections, have deep water, steep sides, and sills of terminal glacial deposits at their mouths. Examples: Sogne Fjord, Norway; Silver Bay, Alaska and Alberni Inlet, British Columbia, Canada.

3. Bar-built estuaries, which have been the result of marine deposition of offshore bars that have risen above sea level, are characterized by being elongated parallel to the coast, having extensive lagoons, large width to depth ratios, reduced tidal influence, and usually several inlets providing exchange with the open sea. Examples: Pamlico Sound, North Carolina; Vellar Estuary, India and the Laguna Madre, Texas.

4. Tectonically produced estuaries primarily compose this category, which serves to include all those estuaries that do not fit easily elsewhere, but specifically include those produced by faulting, subsidence and volcanic activity. Example: San Francisco Bay, California, USA.

A classification system based on the salinity distribution of an estuary has also been formulated (Pritchard, 1955, Pritchard and Bowden (Lauff, 1967)). It should be noted, however, that this system is only applicable for coastal plain and fjord estuaries, thus excluding entirely bar-built estuaries. The four main types of estuaries are delineated according to their degree of salinity stratification as follows:

1. Highly stratified estuaries, in which the river flow dominates the circulation, thus producing a bottom "salt wedge" of seawater, are mixed only near the fresh water-salt water interface by turbulent entrainment. Examples: Mississippi and Vellar estuaries.

2. Fjord estuaries are also highly stratified, exhibiting a deep saline bottom layer which is due to a restriction in circulation caused by the shallow sill. Mixing is usually limited to the upper layer only, again with entrainment as the major cause. Examples: Sogne Fjord and Silver Bay, Alaska.

3. Moderately stratified estuaries (partially mixed) have greater mixing which is caused by a larger tidal flow that results in increased turbulence. Most coastal plain estuaries are of this type, exhibiting a gradual increase of salinity seaward and with depth. Example: Chesapeake Bay.

4. Vertically homogeneous estuaries (which are usually subdivided into laterally inhomogeneous and sectionally homogeneous) result from

extreme tidal mixing. Examples: Delaware Bay and Mersey Estuary

It should be noted that these classification systems are attempting to facilitate a better definition of estuarine circulation and to organize and classify these natural water bodies into specific groups. In so doing, several problems have risen at the expense of solving other difficulties inherent in the classification systems. For example, several classifications may apply to the different regions of the same estuary and various authorities have had to modify the previous classifications to fit their particular water body. In one specific instance, Overland (1972) places the bar-built, wind-dominated estuary into category (4) above, to be classified as a vertically and laterally homogeneous estuary. This can be seen as an attempt in expanding this classification system to include the wind-dominated estuary which may exhibit little or no tidal mixing.

Lastly, Ippen and Harleman in 1961 (Dyer, 1973) developed an expression, termed the stratification number, which classifies an estuary by the amount of energy lost by the tidal wave relative to the energy used in mixing the water column. Hansen and Rattray (1966) have also developed a stratification-circulation diagram which utilizes two dimensionless parameters in characterizing estuaries. Like most classification systems, theirs neglects the importance of wind effects on circulation, which must be accounted for in shallow estuaries, especially of the bar-built type.

AREA OF STUDY

The lagoonal estuaries under consideration form one of the principal water resources of east central Florida on the Atlantic Coast of the United States. Their proximity to the Kennedy Space Center and use as an integral portion of the Intracoastal Waterway System add to their importance. This lagoonal system, consisting of Mosquito Lagoon (or Indian River Lagoon) to the north, the Indian River to the west and the Banana River to the south, has open connection with the Atlantic Ocean via four inlets and the locks at Port Canaveral (see Figure 1). Thus, these waters are saline, but there is a significant amount of fresh water entering the lagoonal system from land drainage to give them the brackish water typical of estuaries. They are all typical of the bar-built estuaries of the Southeastern United States and Gulf of Mexico coastline.

Man's activities have significantly affected the character of these water bodies, converting them from a group of casually related lagoons into a series of segmented, interacting estuaries. Even if we ignore the changes caused by land urbanization, the construction of nineteen bridge and causeway systems crossing these lagoons have greatly segmented these water bodies. Moreover, the construction of Haulover Canal has established direct communication between Mosquito Lagoon and the northern extreme of the Indian River, whereas the construction of the railroad line to the Kennedy Space Center and the Saturn V Crawlerway have completely severed the natural connection of the Banana and Indian Rivers. Additionally, the Canaveral Harbor and Barge Canal have provided yet another unnatural link between the Banana and Indian Rivers and the ocean, although

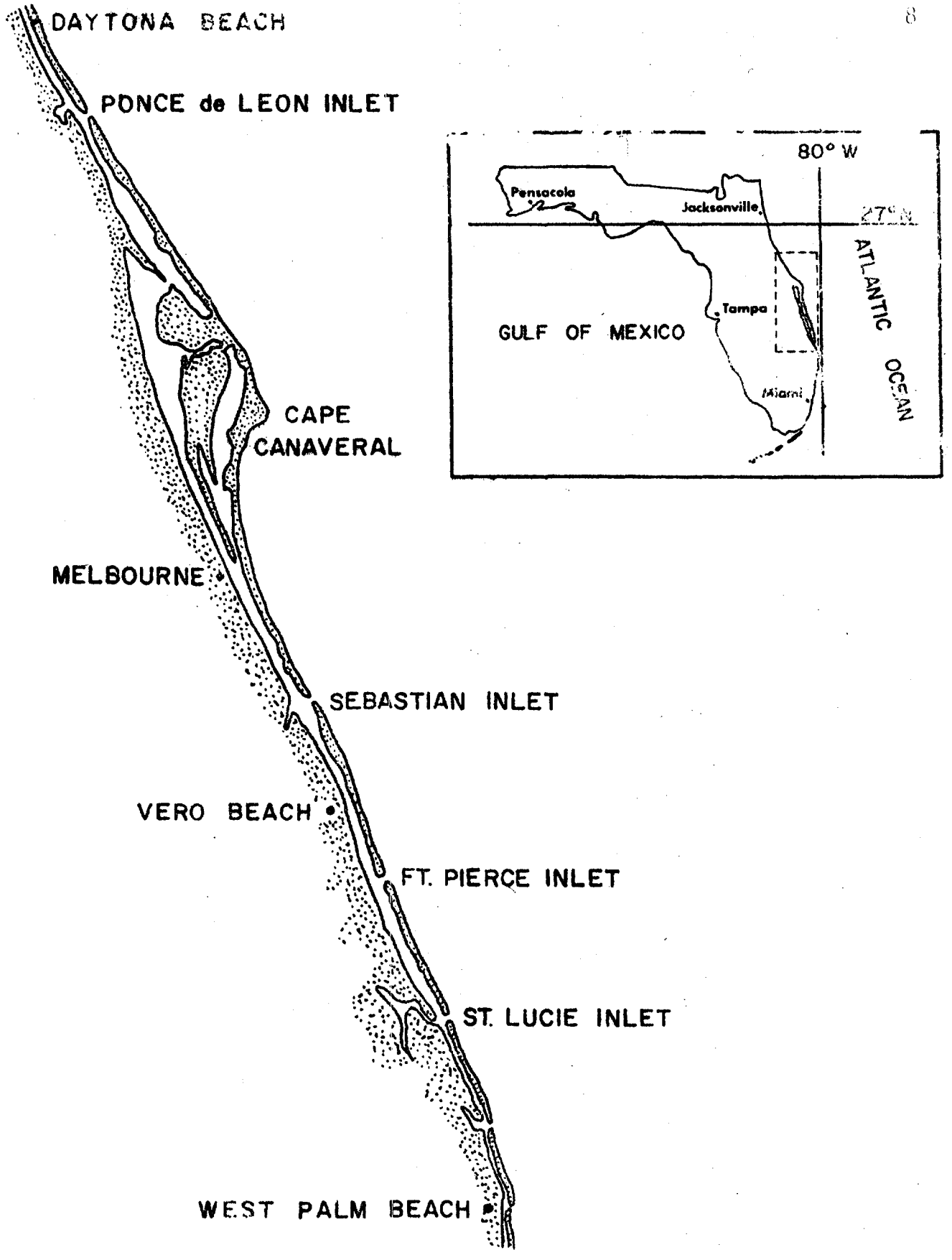


FIGURE 1. Lagoons of East Central Florida

this is not a completely free connection due to the presence of locks. The man-made inlet at Sebastian also provides another important river to ocean connection.

For this study, these waters were divided into four major areas, based upon geographical considerations (refer to Figure 2). Area I is the Indian River between the Orsino Causeway (NASA Parkway) and the Titusville Causeway (Hwy. 402), including Banana Creek to the east as far as its connection with State Road #3. Area II is the Indian River north of the Titusville Causeway. Area III is Mosquito Lagoon, although sampling was limited to the southern area from Haulover Canal to the extreme south tip of the lagoon. Area IV is that part of the Banana River north of the Bennett Causeway (Hwy. 528 and A1A) and Port Canaveral Harbor to its northernmost point near Pad 39A of the Kennedy Space Center.

These lagoonal estuaries are free of any tidal influence to an accuracy of 0.30 centimeters as reported by the Intracoastal Waterway Chart (845-SC) and by personal communication with Mr. C. Thurlow of NOAA's Tidal Branch, Washington, D.C. This appears quite justifiable if it is noted that the closest free connection to the sea to the south is Sebastian Inlet at fifty miles (80 km) distant. Furthermore, any tidal effects of Ponce de Leon Inlet, twenty-five miles (40 km) to the north of the Mosquito Lagoon entrance to Haulover Canal, are damped by the narrowness of the only connecting deep link which is the dredged Intracoastal Waterway channel. Because over 50% of Mosquito Lagoon is less than two feet deep, it acts a final inhibitor of possible tidal effects.

These bar-built estuaries are all very shallow. The greatest depths are the dredged areas (see Figure 3), especially the Intracoastal

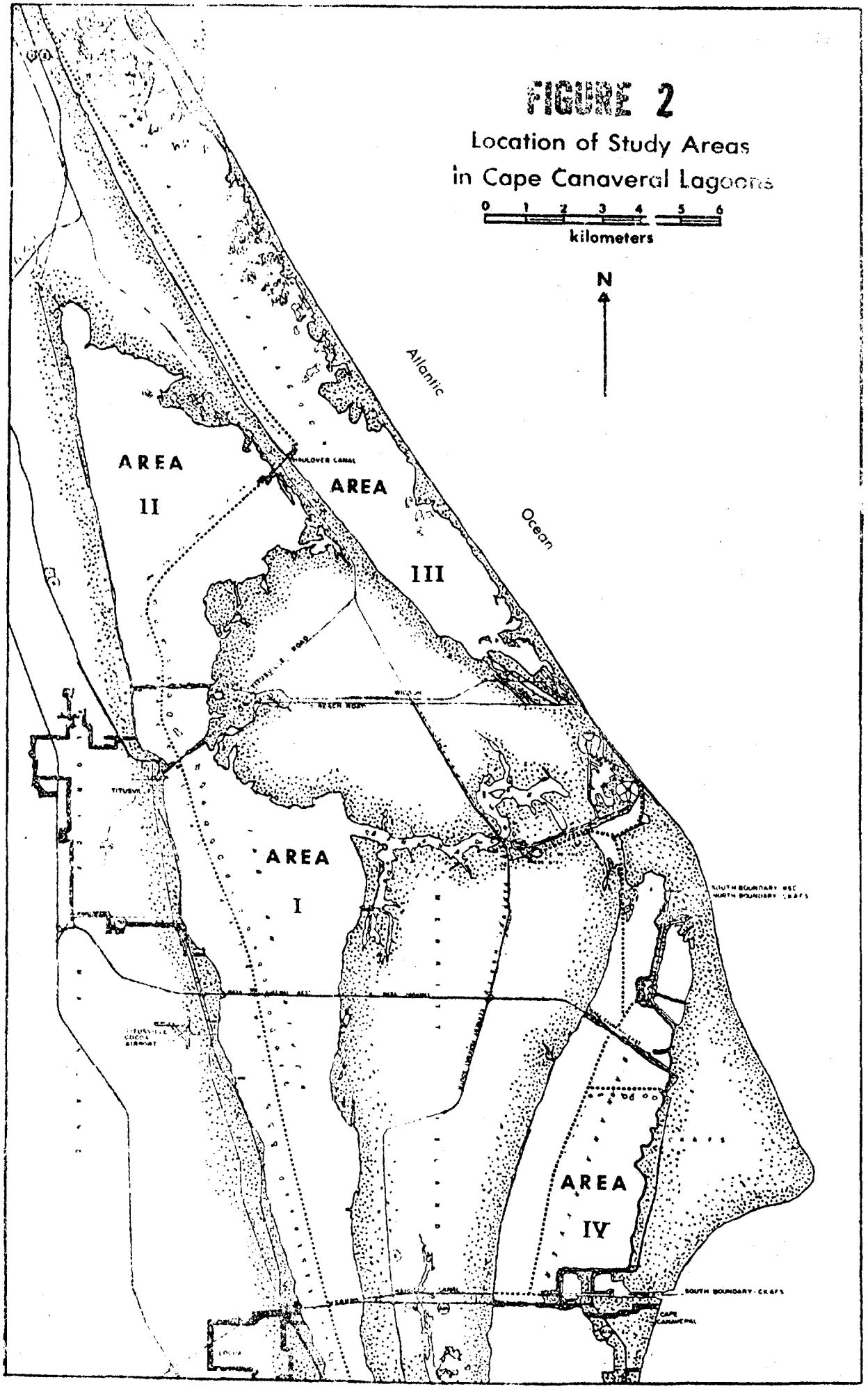


FIGURE 2
Location of Study Areas
in Cape Canaveral Lagoons
0 1 2 3 4 5 6
kilometers
N
Atlantic
Ocean
AREA
II
AREA
III
AREA
I
AREA
IV

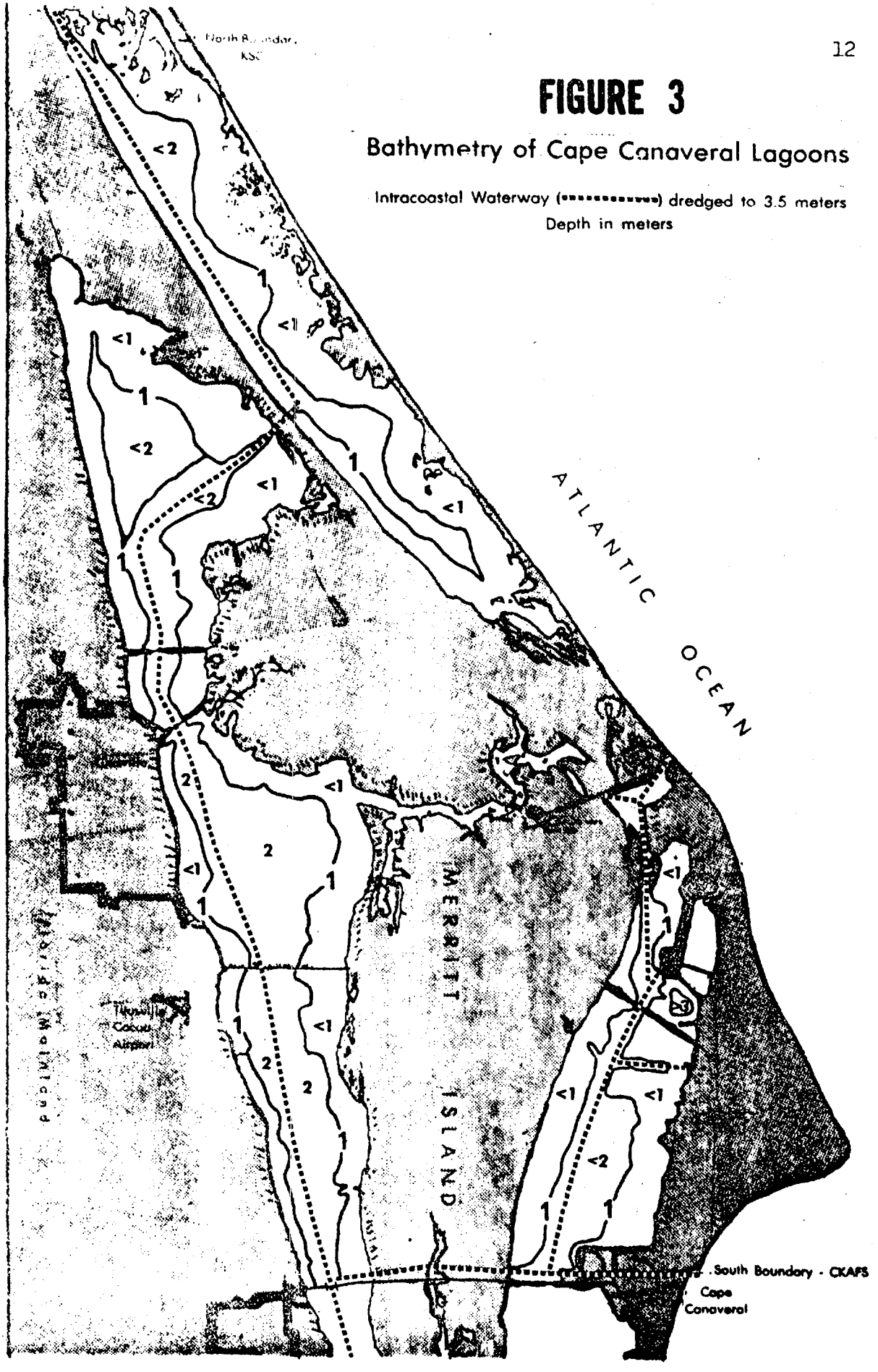
Waterway channel which is reportedly dredged to about three and one-half meters, but has been sounded by the author to depths of at least six meters. Nevertheless, most of each lagoon has water depths equal to two meters or less. The presence of bottom growth, especially long grasses, over most of the observed bottom, impedes water flow and further increases frictional effects. These grasses may reach heights of one-half of a meter from the bottom.

W. M. Cameron and D. W. Pritchard (1963) have stated that "the relatively great width and small depth of such systems [bar-built estuaries] permit wind-induced currents and wind tides to provide the major mechanism for movement and mixing of these estuarine waters. No adequate dynamic description of this type of estuary has yet been produced, and, in fact, this type of estuary has probably received the least systematic attention." With this in mind, the hydrodynamic sampling of the four study areas was undertaken as related in the next section.

FIGURE 3

Bathymetry of Cape Canaveral Lagoons

Intracoastal Waterway (▪▪▪▪▪▪▪▪▪▪▪▪) dredged to 3.5 meters
Depth in meters



DESCRIPTION OF FIELD WORK

The sampling was carried out in conjunction with an Ecological Baseline Study of the Kennedy Space Center environs, performed by Florida Institute of Technology under NASA Grant No. 10-015-008. It was limited to certain restrictions as dictated by the modus operandi of the biological sampling requirements. However, sites were chosen with regards to covering the entire area and special sites were occasionally adaptable to the normal sampling schedule.

It was felt desirable that the measurements should be taken within as short a time span as possible, in order to formulate an accurate picture of the current field of any lagoon at any "instant" in time. Thus, two to four small boats were used in sampling one area at a time. This meant that it normally took two to three hours to completely sample any one area, especially when the biological sampling was heavy. In this way any variations in wind magnitude and direction were held to a minimum as much as possible. However, it should be noted that many cases arose of the wind shifting velocity considerably throughout the sampling period.

The sampling procedure was as follows. The small boat was securely anchored at the designated sampling point (which is usually located through a combination of visual reference to landmarks and experience gained by having previously sampled the area). The current velocity was measured in a Lagrangian fashion using aluminum crosses suspended one-half meter below a plastic bottle half-filled with water. The current crosses were four inches high and had two 36-inch perpendicular vanes (see Figure 4). The crosses were hand-released from a point downcurrent of the boat

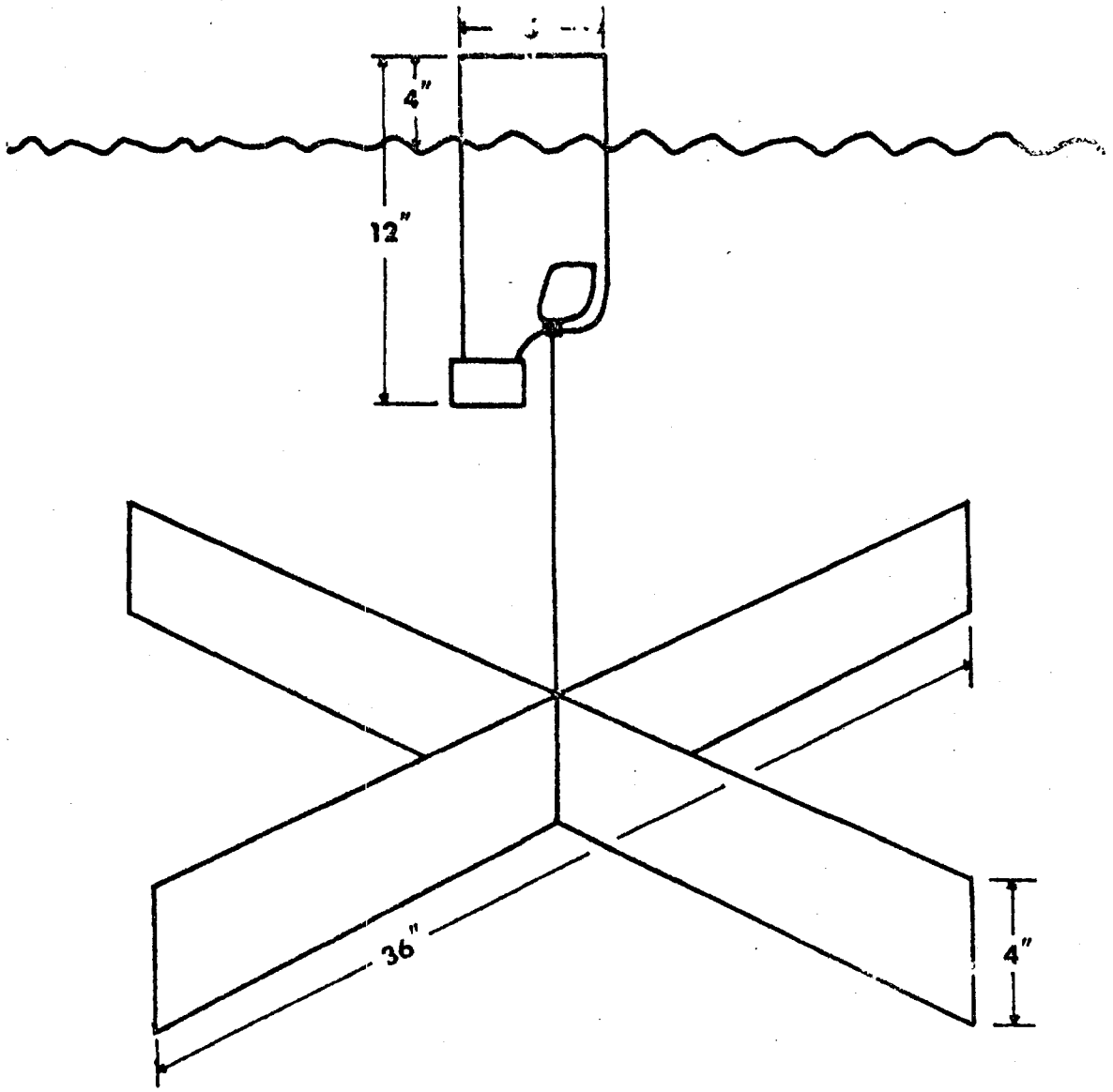


FIGURE 4. Current Cross

and the time noted. Meanwhile, the wind magnitude was measured (in mph) at a standing height of one to two meters above the water using a hand-held wind meter (pocket tube type manufactured by Dwyer Instruments, Inc. of Michigan City, Indiana). The wind direction was measured using a hand-held compass. After approximately five minutes had elapsed from the time that the current cross was placed in the water (during which time the biological sampling was normally done), the current cross direction was noted using the compass and its distance from the release point measured (in feet) with a field range finder (manufactured by Edmund Scientific Company of Barrington, New Jersey). The total elapsed travel time was also noted simultaneously with the distance measurement. Thus, the speed of the current could be calculated using its known travel time and distance. Finally, the air and water temperatures were taken and any unusual meteorological conditions noted, such as rain, erratic wind shifts and gustiness, etc. The current cross was retrieved and the boat moved on to its next sampling site. The average on-station time was about fifteen minutes per sample site for an experienced crew. After sampling all sites, the data were gathered from the boat crews, tabulated, reduced and plotted as seen in Charts 1 A-T of the Appendix.

Among the many procedures that had to be modified, the following are most noteworthy. The unrestricted lateral movement of the boat on its anchor became very apparent when more experience was gained in sampling. Although the boat lay generally with its bow into the wind, it would swing as much as thirty degrees to either side, thus giving false current velocity readings. This problem was solved by using a second anchor from the stern in keeping the boat tautly secured between two points.

It was also found that the best distance at which to measure the cross is between 20-40 feet, mainly due to the inherent characteristics of the optical rangefinder. Due to the fact that it involves the use of a logarithmic scale, any slight error in measuring over 40 feet is compounded by this scale in producing inaccuracies as large as 20% of the total distance.

It was determined that the best way in which to measure wind direction was to face into the wind and measure the direction perpendicular to the wavelets and ripples. Although the wave crests are not necessarily perpendicular to the wind, this does give a good approximation. Direction in very light winds was determined by holding up a piece of tissue and noting its movement.

THEORETICAL CONSIDERATIONS

The set of equations expressing the basic principles of circulation in an estuary are the well-known Navier-Stokes conservation of momentum equations for viscous flow of an incompressible fluid. In their more common form, they are called the hydrodynamic equations of motion and, when coupled with the continuity equation (mass conservation equation) and the proper boundary conditions and assumptions, they may be made mathematically tractable for solving several special circulation phenomena. It is stressed, however, that in their pure form, they are presently unsolvable due to the fact that they are nonlinear, partial differential equations with non-constant and poorly understood coefficients. Because these equations have been previously derived many times, only a cursory explanation of them will be given herein before proceeding to make further simplifications as applicable to the estuaries under consideration.

The mass continuity equation is derived from the fact that the change in mass in a fixed volume of fluid must be balanced by a corresponding change in density within the volume. Explicitly, this is

$$\frac{d\rho}{dt} + \rho\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}\right) = 0, \qquad (1)$$

where ρ = density
t = time
u,v,w are velocities in the x,y,z directions respectively.

This can be further simplified for the case of an incompressible fluid for which $d\rho/dt = 0$. Since the compressibility of water is very small, the continuity equation can be approximated by

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0. \qquad (2)$$

This is a statement that the flow field is non-divergent. Note that, even if the density of a fluid particle is varied by changes in salinity and temperature, equation (2) is assumed valid (the Boussinesq approximation).

The equations of motion state that the acceleration of a fluid particle is proportional to the sum of the applied forces. Assuming a left-handed coordinate system with the z-axis positive downward and the z = 0 plane coinciding with the undisturbed free water surface, the instantaneous equations are, for incompressible flow,

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} + w\frac{\partial u}{\partial z} = -\frac{1}{\rho}\frac{\partial P}{\partial x} + fv + \frac{\mu}{\rho}\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}\right), \quad (3)$$

$$\frac{\partial v}{\partial t} + u\frac{\partial v}{\partial x} + v\frac{\partial v}{\partial y} + w\frac{\partial v}{\partial z} = -\frac{1}{\rho}\frac{\partial P}{\partial y} - fu + \frac{\mu}{\rho}\left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} + \frac{\partial^2 v}{\partial z^2}\right), \quad (4)$$

and the pressure force assumed hydrostatic in the vertical yields

$$0 = -\frac{\partial P}{\partial z} + \rho g. \quad (5)$$

where u, v, w, ρ, t are as previously defined
p = pressure
g = gravitational acceleration
f = Coriolis parameter = $2\omega \sin \phi$
where ω = angular velocity of the earth
ϕ = latitude
μ = the dynamic molecular viscosity coefficient.

In equations (3) and (4) the first term on the left of the equal sign is the time rate of change of momentum at a specific location (also called the local time derivative). The next three terms are the non-linear field acceleration terms expressing the advection of momentum. The first term to the right of the equal sign is the pressure force term; the next term is the Coriolis term which is due to a rotating earth; and the

last term is a viscous frictional term.

These equations are mathematically intractable without further assumptions (note that incompressible flow was already assumed; that is, $d\rho/dt = 0$). Although most of the assumptions and simplifications can be reasonably supported, there are some compromises made simply in order to be able to apply implicit mathematical solutions. It should be noted, however, that the object of this is not an attempt to seek specialized solutions of the equations of motion as pertaining to the estuaries under study. Rather, it is an effort to use mathematical analysis to obtain a more complete conception of the circulation phenomena that were actually observed and measured.

The first assumption is that any horizontal velocity shears are so small as compared to the total field of motion that they can be neglected. Pritchard has noted that the inertial terms are small as compared to the pressure force and eddy stress terms (Kinsman, 1965b, p. 69). This allows the nonlinear field advective terms to drop out. Note that there is no measurable tidal motion necessitating inclusion as an external driving force, which is contrary to the conditions found in most coastal plain and fjord estuarine types where tidal effects are most apparent in forming stratified flow and resultant velocity shears.

The next assumption is to neglect the viscous force terms in the horizontal direction. It has been stated by Pritchard that the only viscous force term of significance is the vertical one (Kinsman, 1965b, p. 68). Although this assumption is admittedly weak, most authorities have also had to make it in attempting any solution to the equations of motion. Neumann and Pierson (1966, p. 412) state that: "In general, the

mean quantities vary most rapidly in the vertical direction, so that these theories are mostly concerned with the vertical fluxes of momentum..." Overland (1972) also states this more firmly with the following discussion concerning estuarine modeling:

> **The present limit of models neglects the longitudinal and vertical variations of salinity and reduces the three-dimensional system to one or two dimensions by spatial averaging. In principle, this limits prototypes to tidal rivers and vertically homogeneous estuaries with weak horizontal salinity gradients. If they [the estuarine models] are applied to estuaries where there are velocity shears and substantial concentration variations within the averaging interval, as in a partially-mixed estuary, there is an effective diffusion [diffusivity] increase due to the spatial or temporal averaging.**

Note that the three lagoons in this study appear to fit Overland's vertically homogeneous prototype. Charts 2 A-H of the Appendix show the weak horizontal salinity and temperature gradients and the strong vertical homogeneity exhibited in each estuary (note: data was taken by the author).

A further assumption is that the Coriolis force term, which accounts for the inertial effects of a rotating frame, is negligible for these water bodies. However, this is to be expected if direct application is made of V.W. Ekman's theoretical results for drift currents in a homogeneous ocean (see Neumann and Pierson, 1966, pp. 194-5). He proved that,

when the ratio between the water depth (d) and the depth of "frictional influence" (D) is very small, the Coriolis parameter may be neglected. Using the following equation,

$$D = \pi \sqrt{\frac{A_z}{\rho \omega \sin \phi}}, \qquad (6)$$

D is found equal to about 50 meters in middle latitudes, assuming an average value of the eddy viscosity coefficient (A_z) equal to 100 gm/cm-sec and a density of one gm/cm^3. Note that A_z is an eddy viscosity coefficient which will be explained in the following paragraph. With an average depth of two meters in the Cape Canaveral estuaries, d/D = 0.04, and Ekman's criterion thus easily allows us to discard the Coriolis parameter.

An important modification in reducing the hydrodynamic equations to a more solvable form is to replace the viscous force coefficient (μ) by an eddy viscosity coefficient (A_z). This is an attempt to account for energy exchanges due to turbulent effects such as velocity shearing stress (also variously called Reynold's stresses). Much literature has been devoted to these "Austausch" coefficients, their meaning, theory and physical measurement, hence no attempt is made herein to fully explain these terms in detail. One may refer to the following references for a more complete description than given here: Sverdrup, Johnson, and Fleming (1942), Roll (1965), Neumann and Pierson (1966) and the TRACOR Report (1971). Suffice it to say that this coefficient attempts to include the macroscopic effects of turbulence. Therefore, its value is usually very much greater than the molecular coefficient of small-scale motions, μ, which is on the order of 0.01 gm/cm-sec.

In an effort to clarify the Austausch coefficient, L. Prandtl introduced a hypothetical, characteristic mixing length (ℓ). This has an analogy to the mean free path used in the kinetic theory of gases in that it represents the distance that a fluid particle travels normal to the flow until it has exchanged its given property with the surrounding fluid particles. The Austausch coefficient is defined in terms of this as

$$A_z = \rho \ell^2 \left| \partial \bar{u} / \partial z \right| \quad \text{gm/cm-sec}, \qquad (7)$$

where $\bar{U}$ = the mean velocity in the direction of flow.

Another important aspect of this eddy viscosity coefficient is that it appears to spatially vary, especially with depth. Various estimates and measurements have shown that the value of this coefficient is greater in the turbulent wind- and wave-agitated surface layers than in the deeper layers. Its value also increases with increasing wind speed (Neumann and Pierson, 1966, p. 195). Nevertheless, for our purposes we will assume that A_z remains constant, again to simplify the mathematics. Any physical validity that we can offer for making this assumption is very weak, especially since so little is actually known about this coefficient. One should note, however, that the shallow depths encountered in these estuaries may give rise to almost constant vertical eddy coefficients due to thorough mixing along the entire water column by the wind. Again, the temperature and salinity profiles shown in Charts 2A-H of the Appendix show this vertical homogeneity. Further proof of this can be personally witnessed in one of the more polluted areas of these estuaries on a windy day. It is then that the foul-smelling hydrogen sulfide layer near the

bottom (caused by excessive decomposition) is brought to the surface by thorough mixing.

There have been various numerical values given for the eddy viscosity coefficient; all are based on empirical formulas. Sverdrup, et al. (1942) presents the following table, in which formulas derived by Thorade (1914), Ekman (1905) and Fjeldstad (1929) appear to be the most plausible for our shallow, wind-dominated estuaries. Note that Fjeldstad's formula implies that the eddy viscosity coefficient decreases toward the bottom in relatively shallow water, a conclusion so demonstrated by Sverdrup in 1929 (Neumann and Pierson, 1966, p. 196).

Locality	Layer	A_z in g/cm/sec	A_z derived from	Authority
All oceans	surface	[a] $A_z = 1.02\ W^3$ (W <6m/sec) $A_z = 4.3\ W^2$ (W >6m/sec)	Thickness of upper homogeneous layer	Thorade, 1914 Ekman, 1905
North Siberian Shelf	0 to 60 m	0–1000	Tidal currents	Sverdrup, 1926
North Siberian Shelf	0 to 60 m	10–400	Tidal currents	Fjeldstad, 1936
North Siberian Shelf	0 to 22 m	[b] $385\left(\frac{z+0.1}{22.1}\right)^{3/4}$	Wind currents	Fjeldstad, 1929
North Sea	0 to 31 m	75–1720	Strong tidal currents	Thorade, 1928
Danish waters	0 to 15 m	[c] 1.9–3.8	All currents	Jacobsen, 1913
Kuroshio	0 to 200 m	[d] 680–7500	All currents	Suda, 1936
Japan Sea	0 to 200 m	150–1460	All currents	Suda, 1936
Off San Diego, Calif	near bottom	[e] $93(z + 0.02)$	Tidal currents	Revelle and Fleming, ms.

[a] W = wind velocity in m/sec.
[b] z = distance from bottom in meters.
[c] Very great stability.
[d] Very strong currents.
[e] z = distance from bottom in meters. Formula valid between $z = 0.2$ and $z = 1.3$ m.

TABLE 1. Numerical values of the eddy viscosity coefficient (A_V) as derived from measurements of various investigators (from Sverdrup, et al., 1942, p. 482).

It will later be shown that many of the coefficients calculated from these various formula do not give similar values for the same wind speed, although Figure 5, taken from Neumann and Pierson (1966), shows otherwise.

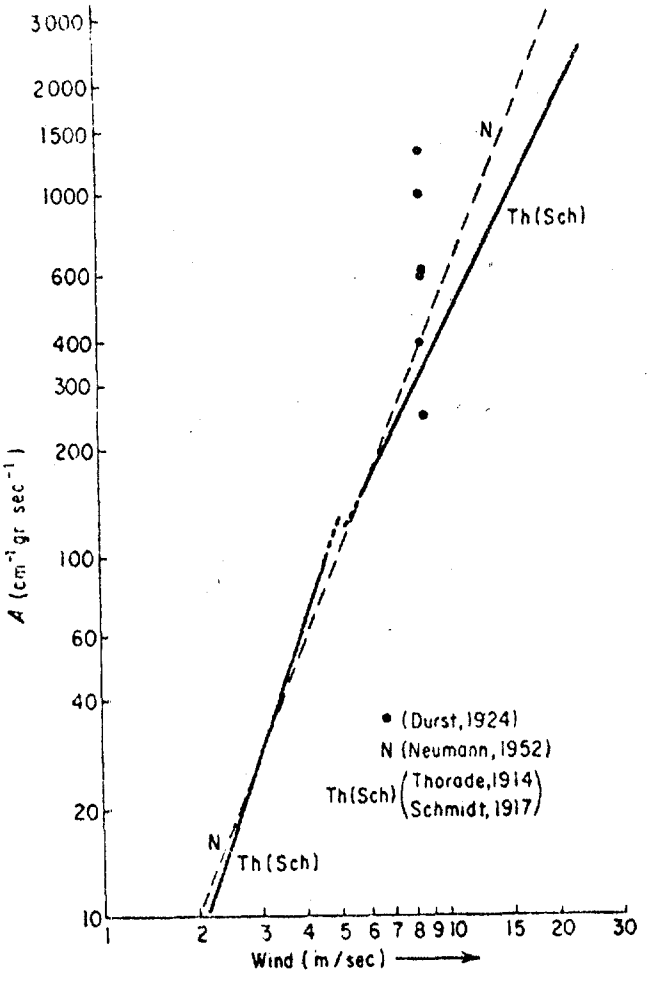


FIGURE 5. Comparison of surface eddy viscosity coefficients obtained as a function of wind velocity using different methods (from Neumann and Pierson, 1966, p. 211).

Neumann and Pierson (1966) also present the following values for A_z as a function of wind speed. The first set of values were derived by Neumann in 1952 from estimates of the energy balance in waves in a fully developed, wind-generated sea. The second set of values were derived by Schmidt in 1917 from Thorade's drift current observations in 1914. Note that the heights of the wind speed measurements are not specifically given, although it is assumed that they were taken at the commonly-used ten meter height. Inferences should be made to the following TABLE 2.

TABLE 2. Comparative values of the eddy viscosity coefficient as a function of wind speed

Wind speed (m/sec)	1	3	4	5	6	7	8	10	14	15	18	20
A (gm/cm-sec) *	-	-	58	-	161	-	332	577	1350	-	2520	-
A (gm/cm-sec) **	(1)	28	-	110	-	220	-	430	-	1000	-	1750

*derived by Neumann (Neumann and Pierson, 1966, p. 195)
**derived by Schmidt (Neumann and Pierson, 1966, p. 210)

Now that the general assumptions have been made, the equations of motion have been reduced to the following set:

$$\frac{\partial u}{\partial t} = -\frac{1}{\rho}\frac{\partial P}{\partial x} + \frac{A_z}{\rho}\frac{\partial^2 u}{\partial z^2}, \tag{8}$$

$$\frac{\partial v}{\partial t} = -\frac{1}{\rho}\frac{\partial P}{\partial y} + \frac{A_z}{\rho}\frac{\partial^2 v}{\partial z^2}, \tag{9}$$

$$0 = -\frac{\partial P}{\partial z} + \rho g. \tag{10}$$

These equations express the fact that the current structure in our estuaries appears primarily the result of a combination of two forces. A drift current is caused by the wind stress on the water surface and a slope current is caused by the pileup of the water by the wind on the downwind side of the estuary. This appears to be a quite reasonable assumption, but the present forms of these equations still remain intractable for explicit solutions and cannot be further simplified without irreparably distorting the physical representation of the circulation phenomena present. However, it would do well to try and solve these equations for each effect; that is, first for a pure drift current and then for a steady-state drift and slope current, in order to get a better insight into the dynamics involved in the problem. A further comparison with the measured data may then help us

to add more to our intuitive picture of what is taking place in the circulation in these estuaries (see Analysis of Results section).

Pure Drift Current Solution

In this solution it is assumed that the only driving force is the wind stress applied to the water surface and the frictional coupling between the water layers. Any horizontal pressure gradients are assumed nonexistent, which would most probably be the actual state in real time at t = 0 (no wind) and the water body in a complete state of rest. Thus, equations (8), (9) and (10) are further reduced to

$$\frac{\partial u}{\partial t} = \frac{A_z}{\rho} \frac{\partial^2 u}{\partial z^2} . \tag{11}$$

$$\frac{\partial v}{\partial t} = \frac{A_z}{\rho} \frac{\partial^2 v}{\partial z^2} . \tag{12}$$

$$\frac{\partial P}{\partial z} = \rho g . \tag{13}$$

When a constant wind begins to blow in the positive x-direction, a wind stress τ_s is exerted on the water surface. The following boundary conditions apply:

(i) $A_z \frac{\partial u}{\partial z} = -\tau_s \quad : z = 0$

(ii) $u(d, t) = 0 \quad : t \geq 0$

(iii) $u(z, 0) = 0 \quad : 0 < z < d$

where τ_s = surface wind stress in the x-direction
A_z = Austausch coefficient
d = total water depth.

We can see that the equation of motion in the x-direction (11) has a solution in the form of $u(z,t) = U(z) + U_o(z,t)$ where $U(z)$ is time independent and $U_o(z,t)$ is time dependent. Dealing with only the time independent solution, that is $\partial u/\partial t = 0$, we find

$$\frac{d^2U}{dz^2} = 0 \tag{14}$$

Integrating this yields a solution $U + C_1 z + C_2 = 0$ where C_1 and C_2 are constants of integration. Applying the boundary conditions we find as a final steady-state solution

$$U(z) = \frac{\tau_s}{A_z}\left|d - z\right| \tag{15}$$

This is the expression to be later used in comparing some computed current values to those actually measured (see TABLE 4). It should be noted that the total solution, after addition of the time dependent part, is (as also found by Schneider, 1972)

$$U(z,t) = \frac{\tau_s}{A_z}(d-z) + \sum_{n=0}^{\infty} e^{-\lambda_n \frac{A_z}{\rho} t} A_n \cos\left[\left(\frac{2n+1}{2}\right)\frac{\pi z}{d}\right] \tag{16}$$

where $\lambda_n = \left[\left(\frac{2n+1}{2}\right)\frac{\pi}{d}\right]^2$

$$A_n = +\frac{2}{d}\int_0^d \frac{\tau_s}{A_z}(d-z)\cos \lambda_n^{1/2} z \, dz$$

A_n may be explicitly evaluated as

$$A_n = \frac{2d\tau_s}{A_z \lambda_n}$$

Steady-State Drift and Slope Current Solution

The solutions for a steady-state current as produced by a steady wind drift current have been derived many times. Ekman was the first to solve for this special case, but included the Coriolis term. It is essentially similar to computations for the piling up of water against coastlines

by storm and hurricane surge (Bretschneider, 1966). For our solution, it is assumed that a steady wind has blown continuously in the x-direction, thus piling up the water at the far shore while lowering the water level at the near shore until equilibrium conditions have been attained.

For this steady-state condition ($\partial u/\partial t = 0$) the one-dimensional equations of motion become

$$0 = -\frac{1}{\rho}\frac{\partial P}{\partial x} + \frac{A_z}{\rho}\frac{\partial^2 u}{\partial z^2}, \tag{17}$$

$$0 = -\frac{\partial P}{\partial z} + \rho g. \tag{18}$$

The slope of the water surface in the positive x-direction is

$$\tan\beta = +\frac{dz}{dx} = -\frac{\partial P/\partial x}{\partial P/\partial z}. \tag{19}$$

Assuming this water slope to be a very small angle with the horizontal, $\tan\beta \rightarrow \beta$ and therefore,

$$\frac{\partial P}{\partial x} = -\beta\frac{\partial P}{\partial z}. \tag{20}$$

Substituting this result into equation (17) yields

$$\frac{A_z}{\rho}\frac{\partial^2 u}{\partial z^2} = -\frac{\beta}{\rho}\frac{\partial P}{\partial z}, \tag{21}$$

and simultaneous solution of this with equation (18) yields

$$\frac{A_z}{\rho}\frac{d^2 u}{dz^2} = -g\beta. \tag{22}$$

Upon integration of this equation twice with respect to z, the solution takes the form

$$\frac{A_z}{\rho}u(z) = -\frac{\beta g z^2}{2} + C_1 z + C_2. \tag{23}$$

The two boundary conditions again are

$$(i)\quad A_z \frac{du}{dz} = -\tau_s : \quad z = 0,$$

$$(ii)\quad u(z) = 0 : \quad z = d.$$

We now invoke stationarity, which means that we can correctly assume that an equilibrium condition has been reached. This implies that all of the water that is being pushed towards the far end of the estuary by the wind is somehow returning, in order to keep an equilibrium between forces. This means that the net current thoughout the entire water column must be equal to zero, or the water would continue to pile up higher and higher as long as the wind continued to blow. Mathematically, this stationarity is expressed as $\int_0^d u\,dz = 0$. Applying this and our boundary conditions to equation (23) we find that one of the results is Ekman's equation for a stationary slope in an enclosed sea with no Coriolis; that is,

$$\beta = -\tfrac{3}{2}\,\frac{\tau_s}{\rho g d}. \tag{25}$$

As the final slope and wind drift current equation, we find that

$$\frac{A_z}{\tau_s d}\,u(z) = \frac{3}{4}\left(\frac{z}{d}\right)^2 - \left(\frac{z}{d}\right) + \frac{1}{4}. \tag{26}$$

This equation implicitly contains an interesting current feature. It predicts that in the top one-third of the water column, the current flows in the direction of the wind motion. However, this flow is reversed in the bottom two-thirds of the water column (refer to the following Figure 6).

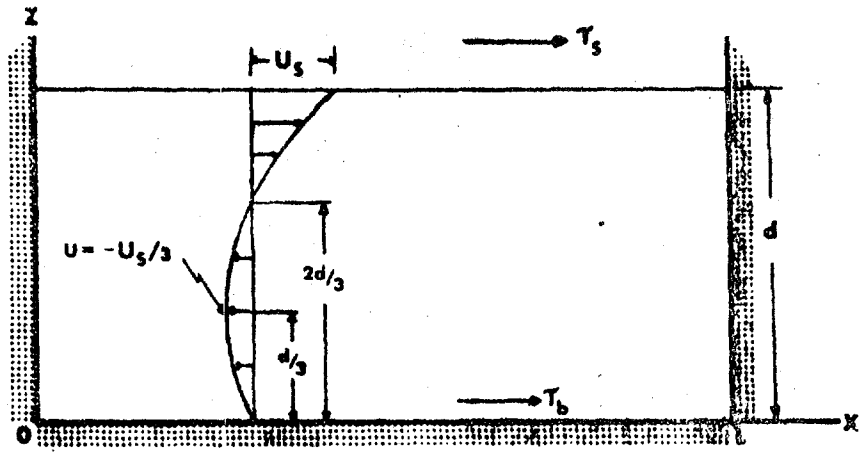


FIGURE 6. Representation of the velocity distribution over the water column due to a combination of wind stress and slope current forces (adapted from Van Dorn, 1953, p. 252).

These same results have been theoretically determined by Keulegan in 1951 (Van Dorn, 1953), Van Dorn (1953) and Hidy and Plate (1966). This can be seen as a very real situation when considering the fact that the surging water must have some return flow if the estuary is to remain in equilibrium. Otherwise, the estuary would literally overflow its banks. Quite analogous to this is the well-known mechanism of water pile-up due to ocean waves breaking on a shoreline and the subsequent return of water to the offshore area through a seaward-flowing rip current system, which, in small surf, usually lies along the bottom on beaches with flat bottom topography. One should refer to TABLE 4, Comparison of Results, in comparing various computed values of U(z) from equation (15) to those of the pure wind drift solution and typical measured values.

Additional Developments

It presently appears out of the reach of rigorous mathematical analysis to formulate implicit solutions to the time-dependent equations of motion as expressed by equations (8), (9) and (10). In summarizing the developments discussed in the preceeding pages, we have found the current velocity as a function of depth and time for a pure wind drift current, and the velocity, as a function of depth only, for a combination of wind drift and slope currents. Implicit analytical techniques have not yet been developed (or, at least, publicized) that aid in solving these equations for the current velocity as a function of depth and time (as minimum requirements) for a combination slope and wind current.

However, by no means should one assume that there are no solutions to this problem. Non-exact numerical solutions have been obtained for tidal estuaries using finite-difference methods coupled with the necessary use of high-speed, electronic computers. The computers are necessary in handling the large amount of data and calculations necessary. These methods, involving finite-difference applications of explicit, implicit and characteristics techniques, require division of the water body into a finite number of segments based on geometry and a knowledge of initial and boundary conditions. Several specific parameters such as depth and eddy viscosity coefficients must be known functions also. However, this is a vast subject in itself and, although it appears no wind driven estuaries have been the subject of such techniques, good treatments of this subject are found in the TRACOR Report (1971) and Dronkers (1964). The equations of motion and continuity must be integrated over one or more of the spatial

and temporal parameters for use with these numerical solutions.

First, the equation of continuity (1) can be integrated from the water surface (ζ) to the bottom (h). With the use of Leibnitz' Rule and invoking the following kinematic boundary conditions for the rigid bottom and side boundaries and for the surface condition,

(i) $$w(h) = u(h)\frac{\partial h}{\partial x} + v(h)\frac{\partial h}{\partial y},$$

(ii) $$w(\zeta) = u(\zeta)\frac{\partial \zeta}{\partial x} + v(\zeta)\frac{\partial \zeta}{\partial y} + \frac{\partial \zeta}{\partial t}.$$

(note: the addition of the $\partial\zeta/\partial t$ term includes the movement of the surface with time)

we find that the vertically integrated general continuity equation has the form of

$$\frac{\partial}{\partial x}\int_{\zeta}^{h} \rho u\, dz + \frac{\partial}{\partial y}\int_{\zeta}^{h} \rho v\, dz + \frac{\partial}{\partial t}\int_{\zeta}^{h} \rho\, dz = 0. \qquad (27)$$

Starting from the Boussinesq form of continuity (2), and introducing the "instantaneous" depth, H (i.e. the total water depth as a function of time, or $H = h - \zeta$), the form of the continuity equation is

$$\frac{\partial}{\partial x}\left(H\bar{U}\right) + \frac{\partial}{\partial y}\left(H\bar{V}\right) + \frac{\partial H}{\partial t} = 0, \qquad (28)$$

where $\bar{U}$ and $\bar{V}$ are vertical averages of velocities U and V

In one dimension this equation can be written as

$$\frac{\partial H}{\partial t} + \bar{U}\frac{\partial H}{\partial x} + H\frac{\partial \bar{U}}{\partial x} = 0 \qquad (29)$$

We can neglect the $\bar{U}\partial H/\partial x$ term because the ratio of the $\bar{U}\partial H/\partial x$ and $H\partial\bar{U}/\partial x$ terms is of the order $\frac{\Delta H}{H}$, which is usually $\ll 1$.

In a similar fashion; the equations of motion can be vertically integrated. Starting with the hydrostatic equation (5), and integrating

over the instantaneous water depth, H, as before, we find

$$P = P_{atm} + \int_{\zeta}^{z} \rho g \, dz . \tag{30}$$

where P = pressure
P_{atm} = atmospheric pressure.

Integration of the simplified equation of motion (8) is a more difficult matter. With the use of Leibnitz' Rule again, we find that the first term of equation (8); that is, $\int_{\zeta}^{h} \partial u/\partial t \, dz$, is approximated by $H \partial \bar{U}/\partial t$, where $\bar{U}$ is assumed approximately equal to $U(\zeta)$. Integration of the pressure force term and use of equation (30) yields the following expression

$$\frac{1}{\bar{\rho}} \int_{\zeta}^{z} \frac{\partial P}{\partial x} dz = \frac{H}{\bar{\rho}} \frac{\partial P_{atm}}{\partial x} - \rho g H \frac{\partial \zeta}{\partial x} + \int_{\zeta}^{h} \int_{\zeta}^{z} \frac{\partial \rho}{\partial x} g \, dz, \tag{31}$$

where $\bar{\rho}$ = the spatially averaged density, (Boussinesq approximation)

Note that the three terms on the right hand side of the equation are the pressure forces caused by differences in atmospheric pressure, sea surface slope, and density gradients respectively. Except for situations of large atmospheric pressure differences caused by such severe meteorological disturbances as hurricanes and higher density gradients than those typically exhibited in Charts 2 A-H, the surface slope term dominates the equation.

Integration of the viscous stress term in equation (8) yields

$$\int_{\zeta}^{h} \frac{A_z}{\rho} \frac{\partial^2 u}{\partial z^2} = \frac{A_z}{\rho} \frac{\partial u}{\partial z} \Big]_{\zeta}^{h} = \frac{\tau_s - \tau_b}{\bar{\rho}} \tag{32}$$

where τ_s = surface (wind) stress
τ_b = stress due to the bottom .

Note that now the wind stress appears in the equation, as well as the bottom stress. The latter is further discussed in the next section. Thus, the vertically integrated equation of motion (8) has become

$$H \frac{\partial \bar{U}}{\partial t} = g \frac{\partial \zeta}{\partial x} + \frac{1}{\bar{\rho}} (\tau_s - \tau_b) . \tag{33}$$

Thus, numerical solutions may be determined for U = U(x,z,t) and h = h(x,t), because we have two equations (29, 33) with two unknowns.

Bottom Stress

The integrated equations of motion necessitate inclusion of bottom stress, not unlike the wind stress parameter. Pritchard (TRACOR Rep. 1971)uses a bottom boundary friction term in the form of

$$\tau_b = \frac{g u (u^2 + v^2)^{1/2}}{C_h^2}, \qquad (34)$$

where C_h = Chezy coefficient,

which appears to be considered a satisfactory inclusion to the equations of motion by authorities such as Harleman, Rattray and Leendertse. Other authors simply consider the bottom friction to be some significant percentage of the wind stress. As an example, Ekman (1905) states that, depending on the conditions, the bottom stress (τ_b) equals from zero to one-third of the wind stress (τ_s) at the surface (from Sverdrup, et al., 1942, p. 490). However, some authors state that the majority of available evidence supports the assumption that the bottom stress is negligible. Bretschneider (1966) reports that, from Lake Okeechobee, Florida studies done by the U.S. Army Corps of Engineers, the ratio of $\tau_b / \tau_s = 0.1$. Van Dorn (1953) also found in controlled experiments on an artificial pond that the bottom stress was negligible within the accuracy of his instrumentation (0.1 dyne/cm^2). Pritchard has elsewhere stated (Kinsman's Notes, 1965b) that he used the bottom stress results of Lesser (1951) in computing his own figures in the work he did on the James River. Sample calculations

using the equations and values for z_o as given by Lesser, coupled with random data points from our lagoons, yields τ_b / τ_s ratios on the order of 0.1 also. In addition to this supporting evidence, Deacon and Webb (1962) report that results from measurements made by Francis in 1951 and 1954, Keulegan in 1952, and Hellstrom in 1953, also indicate that τ_b may be neglected.

With this is mind, bottom stress was neglected in the theoretical considerations of the Cape Canaveral lagoons. Nevertheless, it should be understood that this is not necessarily a valid interpretation. Factors of obvious influence such as the extreme shallowness over much of the lagoons and the presence of bottom algae and grasses have unknown effects. In any case, one would expect a significant increase of the bottom stress term for both of these factors. Lastly, it is of interest to note that Farrer (1958) reported, from wind-tide studies of hurricane effects on Lake Okeechobee, Florida, that the bottom stress appeared to significantly increase near the boundaries where the bottom is sloping and considerably rougher than near the center of the lake where the depth is constant.

Wave-induced Currents

Another effect to consider is that of the waves on the current. It has been shown through considerable research that, generally, there is a net mass transport of water by wave action. It is considered a matter of fact that there is always some mass transport due to the translating "open" orbits of the water particles during the passage of a wave (Johnson and Wiegel, 1959). However, determination of the direction of the net transport appears to be yet another source of disagreement. Some

researchers have observed that the tractive force of the wind on the water surface drags the water particles in the direction of the surface drift considerably faster than the normal mass transport due to normal wave action without wind. This was most notably observed in photographs taken of marked water particles under the influence of wind waves in a laboratory flume by Johnson and Rice in 1952 (Wiegel, 1964, p. 224).

An opposing group of researchers have experimentally verified the predictions of Longuet-Higgins' theory for null net transport. This theory has two outstanding features. It both predicts the fact that, in relatively shallow water, the velocity along the bottom is always in the direction of wave propagation and that the transport is in the opposite direction of the advancing waves.

The findings of many investigators have tended to prove one or the other of these two theories. In order to better illustrate by example the contradictory nature of both theories, the following Figures 7, 8 and 9 are presented from Johnson and Wiegel (1959) and Wiegel (1964).

In order to show a general order-of-magnitude for a wave-induced current, as predicted by Figures 7 and 8, in comparison to a measured wind current taken from our data, some estimated values will be used for wave height. It is emphasized that wave heights were not strictly measured, but a general idea was gained from the accumulation of many on-site observations of wave height with simultaneous measurements of wind and current velocities. Thus, generally speaking, it can be estimated that a one foot (30 cm) wave height in our lagoons will be related to a ten-meter wind speed of at least 8 m/sec and a drift current of 5-8 cm/sec. From Figure 8, a one foot wave height produces on the order of a 0.02 ft/sec

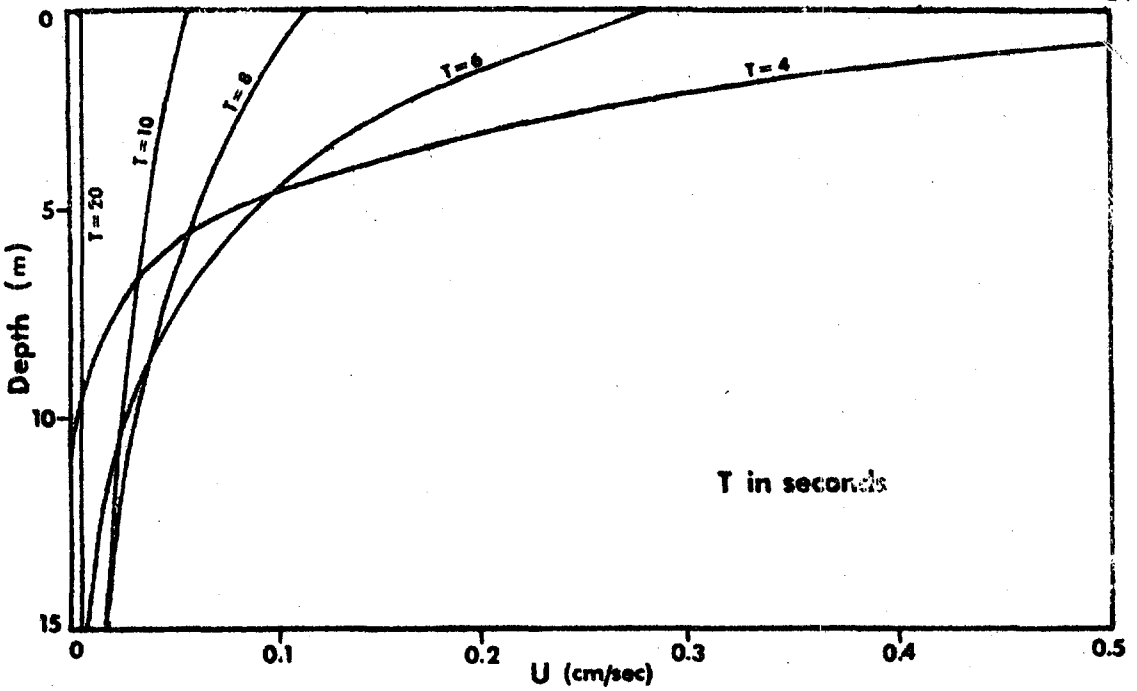


FIGURE 7. Velocity of mass transport at various depths as a function of wave period for a wave one foot high (from Beach Erosion Board 1942).

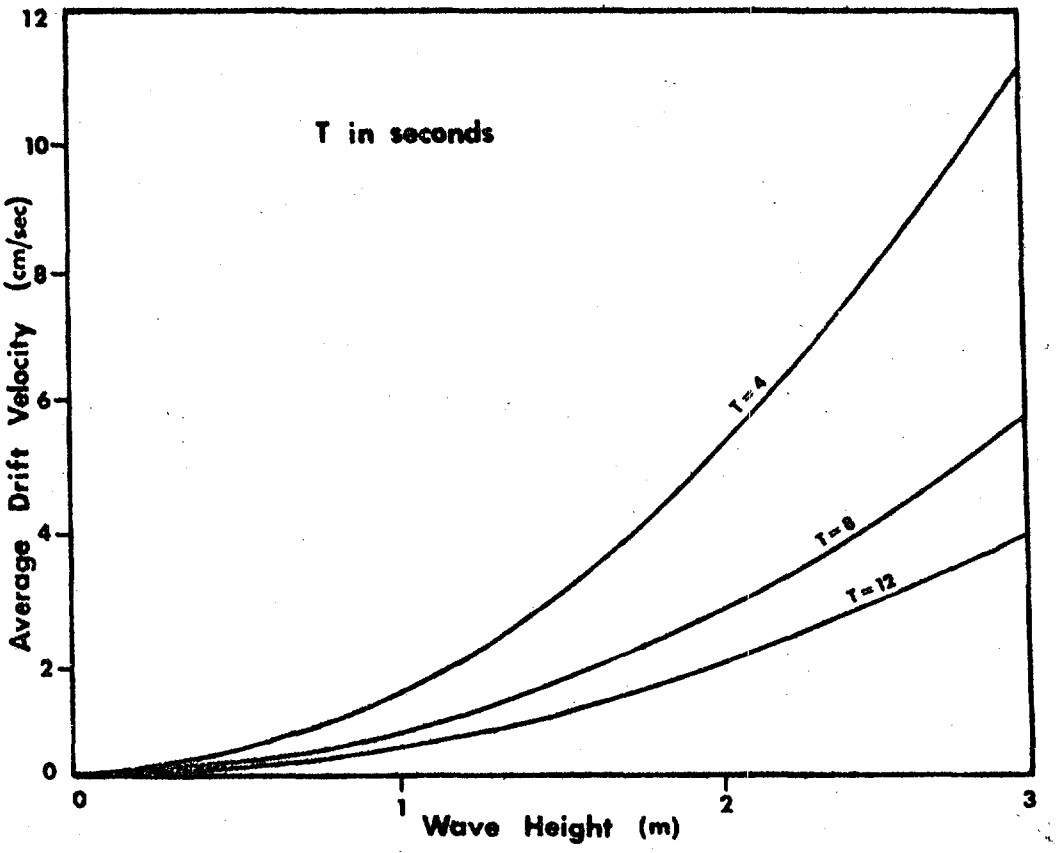


FIGURE 8. Average drift velocity as a function of wave height and period for the region between the water surface and a depth of 50 feet (adapted from Johnson and Wiegel, 1959).

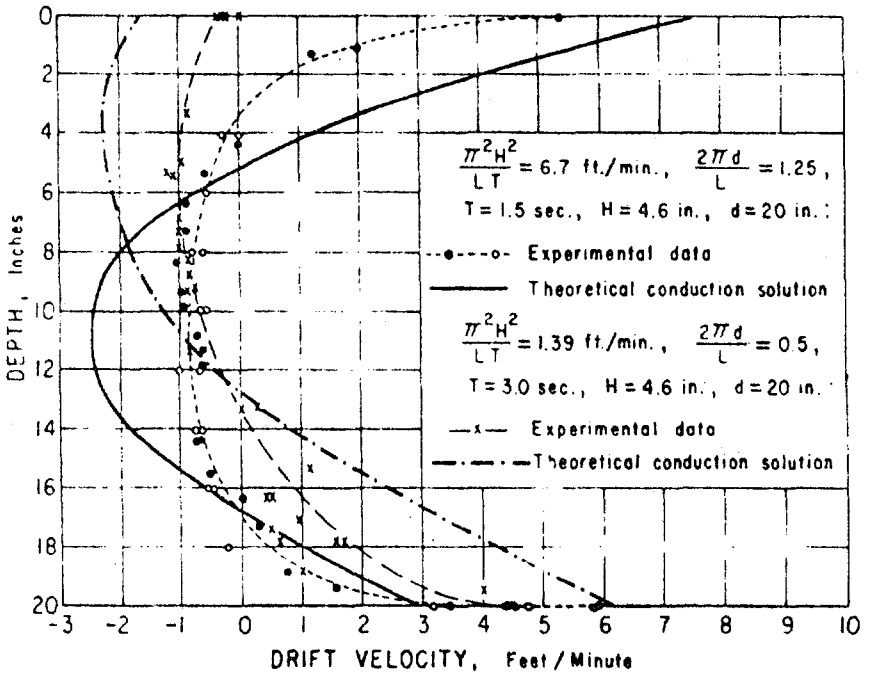


FIGURE 9. Comparison between measured and theoretical (null net transport) velocity profiles in water of uniform depth by Russell and Orsorio, 1958 (from Wiegel, 1964, p. 39).

(0.04 cm/sec) current, which appears insignificant compared with the wind induced current. Thus, for our present analysis, the effect of wave induced currents has been considered negligibly small. However, by no means should one be convinced that this is an infallible assumption. The present body of evidence simply appears to be far too limited in the justification of any definitive conclusion.

Time Constants

In order to gain a general idea of the times involved for a pure wind drift or slope current to develop, a first-order approximation can be made by inspection of the appropriate equations. As previously developed,

The equation of horizontal motion for a pure wind drift current is

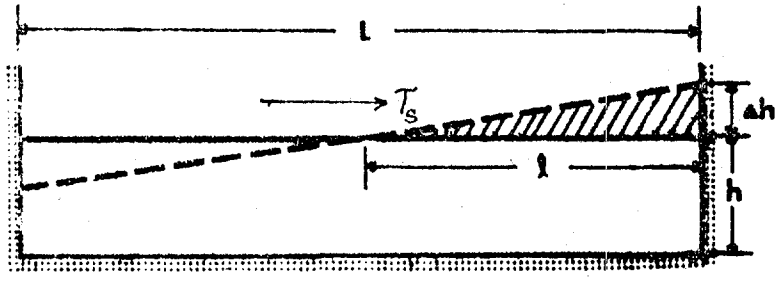
$$\frac{\partial u}{\partial t} = \frac{A_z}{\rho} \frac{\partial^2 u}{\partial z^2} . \qquad (11)$$

From this we find a time constant of

$$T \simeq \frac{\rho d^2}{A_z} , \text{ (compare with (16)).}$$

Substituting into this equation average values of d = 1.8 m and A_z/ρ = 100 cm^2/sec, we find that a steady-state wind drift current can develop in a time on the order of 5 minutes. Current observations made with respect to time by the author in the Cape Canaveral lagoons indeed indicate that the time factor in generating wind drift currents can be on the order of only several minutes. More will be state about this little-known subject in the ANALYSIS OF RESULTS section.

Determination of the time constant for a pure steady-state slope current may come through examination of the problem from a more intuitive basis. Using the notation shown in the below figure, we can assume that the total water transport by the wind is equal to the amount of water piled up on the down-wind shore of the water body (as represented by the crosshatched area).



As shown by the preceeding figure, we are able to express this relationship as

$$S = (Uh)T = \tfrac{1}{2}\Delta h \ell = \tfrac{1}{4}\Delta h L, \qquad (36)$$

where S represents the total transport, assuming a width of unity. In relating this directly to our wind force (since Δh was not measured, but the wind velocity was), we use the relationship for the slope, β,

$$\beta = \frac{\Delta h}{L/2} \quad \text{or} \quad \Delta h = \frac{\beta L}{2}, \qquad (37)$$

where we know from equation (25), for a stationary slope,

$$\beta = \frac{3\tau_s}{2\rho g h}. \qquad (25)$$

Thus, we find a time constant of

$$T \simeq \frac{3\tau_s L^2}{16 U \rho g h^2}. \qquad (38)$$

Substitution of average values of τ_s = 2 gm/cm-sec^2, L = 17 km, and U = 10 cm/sec, and use of the previously assumed values, gives an order-of-magnitude time factor of one hour for the generation of a pure slope current. Note, that for these values, Δh (the set-up) $\sim$ 12 cm.

Another consideration while examining transient responses of our lagoons to the wind is to compute the expected seiche period for each lagoon. This has been done by various authors for a variety of water body shapes and, for our problem, we will use the results computed for a shallow water, constant depth water body whose length is greater than its width. Using specialized forms of the equations of motion and continuity, one arrives at a form of the wave equation which appears as the following,

$$\frac{\partial^2 u}{\partial t^2} = -gh\frac{\partial^2 u}{\partial x^2}. \qquad (39)$$

From this, the period for a standing wave (i.e. a seiche) is

$$T \simeq \frac{2L}{\sqrt{gh}}. \qquad (40)$$

Using values of h = 1.8 m and L = 11 km (length of Area I) to 22 km (length of Area III), we find a seiche period of approximately 1.5 hours for Area I to 3 hours for Area III. For reference, the period of the fundamental seiche in Lake Okeechobee, Florida (of near circular shape with a diameter equal to 50 km) is about 6 hours, as reported by the U.S. Army Corps of Engineers (1955). Although these approximated values seem of no immediate importance, they may help us better understand and evaluate the ever-changing circulation patterns of the Cape Canaveral lagoons.

Nothing more conclusive can be postulated beyond these approximations because there simply has been very little field work done on this aspect of circulation phenomena. Although Van Dorn (1953) appears to have completed the most recent work on transient responses of a water body to changing wind force and set-up, it is doubtful whether his work can be extrapolated to the larger scale of our lagoons. It is of interest to note, however, that he measured a set-up that decreased to 6 per cent of its previous height within only 12 minutes after a sudden wind shift (seiche period equals approximately 2 minutes).

One other notable development of a time-dependent wind drift solution has been presented by Lamb (1945, p. 590) and McCormack and Crane (1973, pp. 161-3), among others. The velocity distribution, U(z), is found, assuming laminar flow in the water, as a function of the wind drift

velocity at the surface, U_s. The equation is a well-known similarity solution having the form

$$\frac{U(z,t)}{U_s} = 1 - \frac{2}{\sqrt{\pi}} \int_0^{\Theta} e^{-\theta^2} d\theta, \tag{41}$$

where $\Theta = z/\sqrt{4\nu t}$, z is the water depth below the surface, ν is the kinematic viscosity, and t is time. This equation has been plotted by Wiegel (1964) and is reproduced in Figure 10 below. The initial equation to be solved is almost identical to equation (11), with the only change being a replacement of the factor A_z/ρ by ν.

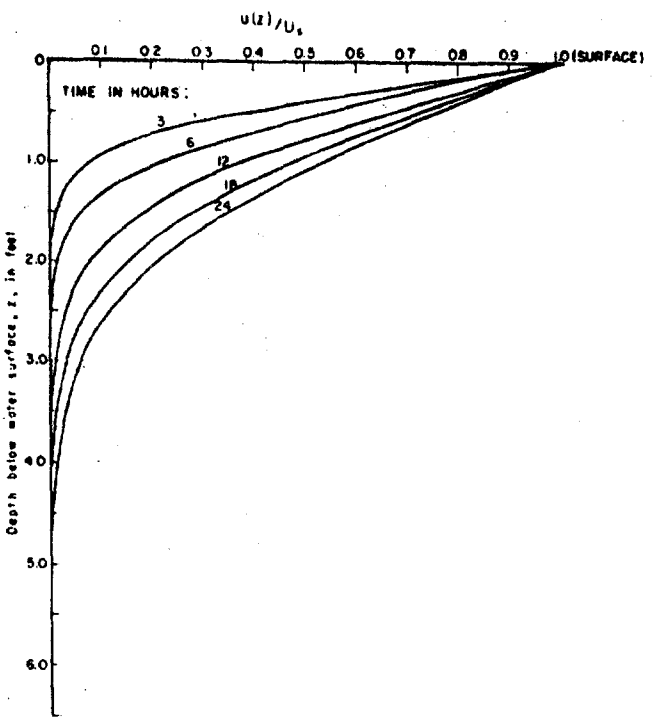


FIGURE 10. Development of a wind drift current due to viscosity as a function of time (from Wiegel, 1964, p. 317).

However, it should be kept in mind that the neglect of surface slope effects and other important parameters such as the eddy viscosity, ultimately distort the true representation of the circulation in our lagoons. Yet, Figure 10 does give us a partial idea of the transient responses of current to wind. Nevertheless, this subject of transient responses of wind currents remains the least known aspect of wind driven circulation phenomena.

It will be shown in the next section how these theoretical results compare with the actual in situ observations. This is no small task due to the fact that there are many problems encountered with methods of data taking, standardization of results with previously published ones, and computation of such ill-known factors as the wind stress, wind resistance coefficient and, of course, the eddy viscosity coefficient. Nevertheless, all of these problems will be emphasized in an effort to grasp a better concept of the future work necessary in the study of the hydrodynamics of these estuaries.

ANALYSIS OF RESULTS

An initial quick glance at the raw data (Charts 1 A-T) can tell us a great deal when compared with the results of other investigators. Previous work by Van Dorn (1953) in a pond, Keulegan (1951), Van Dorn (1953) and Shemdin (1972) in the laboratory, have showed the surface wind drift to be about 3% of the wind speed under turbulent conditions. Further laboratory measurements by Wu (1968) substantiate a linear (with depth) surface current profile that is 3-5% of the free stream wind velocity, U_∞ (note: it was assumed that this maximum wind velocity excludes boundary effects due to the water surface and the laboratory walls or roof). Noble (1965) states that a good "rule of thumb" is that the surface current is of the order of 1% of the wind speed, while a comprehensive study by Stommel in 1954 (Wiegel, 1964) shows a range of 3.5-5.0%. Another study by Carruthers in 1951 (Johnson and Wiegel, 1959), off the southeast coast of England, showed drift speeds of about 2% of the wind speed. However, since it is well known that the wind drift decreases rapidly with depth, and Carruthers' measurements were made at approximately 10 feet below the surface, this may account for his smaller ratios of wind drift to wind speed as compared with Stommel's values.

The data obtained in the Cape Canaveral lagoons shows no such strict correlation. However, it should be kept firmly in mind that parameters such as variable depth, irregular shape and bottom topography, and possible effects of variable bottom stresses, rain, land runoff and other factors, probably substantially effect the circulation in our lagoons. On the other hand, the results of the above investigations were usually

obtained either in the closely-controllable conditions of the laboratory or in locations such as the open ocean where consideration of shallow depth, boundary effects and other variables is not necessary. Thus, one cannot justifiably expect exact correlation of our results for ratios of current speed to wind speed to those of the previously mentioned investigators. Table 3 shows some representative examples, chosen at random. Ratios of measured wind velocity to current speed vary from 0.28% (Site 1-9 on 07/24/73) to 1.8% (Site 1-6 on 08/21/73), based on a ten-meter wind height. Although it can generally be seen that the plotted current vectors coincide with the same basic direction of the wind vectors, the magnitudes of these vectors simply don't relate to wind speed as clearly. For example, examination of the wind field over Area I on March 19 (Chart 1 A of the Appendix) shows that the current may be strong when the wind is weak and, conversely, the current may be weak when the wind is strong (compare Sites 1-3, 1-20 and 1-23 to Sites 1-11, 1-15, and 39).

Further insight may be gained by comparing differences in measured current fields as related to the same basic wind fields during different sampling periods. For instance, in comparing the results of Area I on March 19 (Chart 1 A) to those in the same area on August 8 (Chart 1 F), we see that the wind fields are approximately the same, yet the current fields differ greatly, especially in magnitude. However, one may also find examples of separate current fields that compare very favorably to each other under similar wind fields (compare Area II Charts 1 I to 1 K). A more intense examination of the collected data only provides an increased affirmation of the intuitive feeling that the most influential factor in the development of a current field from a given wind field is

Date	Area - Site No.	Wind Speed (M/SEC)	Current Speed (CM/SEC)	Ratio
July 24, 1973	1-20	6.5	4.7	1:138
	1-9	8.1	2.3	1:352*
	1-13	9.7	4.6	1:210
July 18, 1973	2-22	8.1	10.2	1:79
	2-25	9.7	9.2	1:105
	2-26	9.7	3.9	1:249
July 19, 1973	3-6	3.25	4.7	1:69
	3-7	4.9	5.1	1:96
	3-10	8.1	4.7	1:172
July 26, 1973	4-3	4.9	8.5	1:58
	4-14	6.5	3.2	1:203
	4-17	7.3	2.5	1:292
	4-36	4.9	4.3	1:114
August 8, 1973	1-6	3.25	4.0	1:81
	1-9	5.7	4.6	1:124
	1-20	5.7	3.8	1:150
August 13, 1973	3-3	5.7	4.3	1:133
	3-7	4.9	4.8	1:102
	3-12	8.1	4.7	1:172
August 16, 1973	4-3	4.0	6.8	1:59
	4-10	5.7	6.6	1:86
	4-17	4.9	6.9	1:71
August 21, 1973	1-6	1.7	3.1	1:55**
	1-14	2.4	3.7	1:65
	1-22-S	3.25	5.5	1:59
August 22, 1973	4-10	4.0	3.8	1:105
	4-11	3.25	5.4	1:60
	4-13	5.7	4.1	1:139
	4-17	3.25	2.5	1:130

*Highest ratio - current = 0.28% of wind speed
**Lowest ratio - current = 1.80% of wind speed

TABLE 3. Representative examples of wind speed to current speed ratios in the Cape Canaveral Lagoons.

that of time. In order to predict the current field with certainty, it is not enough to merely know the present velocity of the wind. Rather, one must also have a complete knowledge of the time factors involved; that is, the duration of the wind and some of the transient conditions that prevailed before the onset of the present state.

It is difficult to explicitly show this time dependence directly from the data in Charts 1 A-T, but a general feel for the phenomena may be obtained through the following comparisons of some of these data, coupled with knowledge of the previous transient wind conditions. Due to the fact that, in several instances, the data from all four areas was collected on succeeding days, the author was able to directly measure the result of changing wind conditions, although much extrapolation is necessary from area to area and day to day.

For instance, on June 20 (Chart 1 I-Area II), a light wind and weak current from the south were measured (note: the wind was light and variable on the preceeding day also). That afternoon the wind shifted to the southeast and increased intensity. By the following day (June 21 - see Chart 1 O of Area III) the wind was moderately strong from the northeast and the current was beginning to flow in the direction of the wind.

As a second example, on July 18 (Chart 1 J-Area II), the wind was light and variable in the morning (shown in Sites 2-1 through 2-19 and 2-23, 2-24) causing small, variable currents. This wind changed to a steady, moderate, easterly wind by early afternoon, which caused a radical increase in the current velocities (refer to Sites 2-20 through 2-27 except for 2-23 and 2-24). However, by midmorning of the following day (see Chart 1 P-Area III), the weather pattern had shifted to a typical

"Northeaster" storm condition and the current, which had previously been flowing northwest in Area III due to the previous day's wind pattern (refer to Sites 3-12 and 3-15 which were the first to be sampled that day), reversed direction and began to flow southerly and follow the wind.

As a final example, on August 1, the wind was blowing strongly from the south after being observed to be light and variable on the preceeding day. Measurements recorded in Chart 1 E (Area I) were taken in the late morning. Note that the strength of the current did not match the strength of the wind. However, on the following day (Chart 1 L - Area II), the southerly wind had now strengthened and the current (again measured in the late morning) had increased considerably. This specifically shows the importance of the function of the wind duration on the current.

Wind Stress Calculations

One of the difficulties in the comparison of the measured results with theoretical calculations and the results of other investigators lies in correcting the wind data to that of the wind speed at a "standard" ten-meter height (U_{10}). "Standard" is loosely used here because a thorough literature survey revealed that most wind and current investigations have used any height that is most convenient to their equipment and facilities.

The wind speed above a wavy surface has been long represented by the well-verified logarithmic wind profile (also called the "law of the wall") over a rough boundary. That is, it is represented by the

following equation,

$$U(z) = \frac{U_*}{K} \ln \left[\frac{(z + z_o)}{z_o} \right], \qquad (42)$$

where $U_* = \sqrt{\tau_s/\rho}$ = wind friction velocity
k = von Karman constant = 0.4
z = height of measurement
z_o = dynamic roughness length.

This profile has been verified by at least fourteen investigators (see Roll, 1965, Table X, pp. 126-7). There are two difficulties directly encountered when using this formula in converting measured wind speeds to other heights. The problems lie in choosing the values for U_* and z_o, both of which appear to be poorly defined.

The roughness length (z_o) is construed as that height at which the mean wind velocity is equal to zero. However, in turbulent marine conditions the mean wind velocity is not equal to zero at any height due to boundary layer separation and eddy formation caused by the hydrodynamically-rough, wavy surface. Thus, a better physical interpretation of the roughness length is as a parameter denoting the scale of these turbulent eddies. In this manner it represents the effects of the boundary on the mean air flow. This parameter has been frequently determined using simultaneous windspeed measurements at different heights over varying wave conditions. Nevertheless, it remains a point of debate among authors as to what factors z_o is dependent upon, how to best represent it, and what are typical values of z_o. Roll (1965) and Kraus (1972) give a more complete description of the many contradictory statements regarding the variation of this parameter with the characteristics of the air flow. However, Figure 11 gives an indication of the discrepancies encountered. Note that the

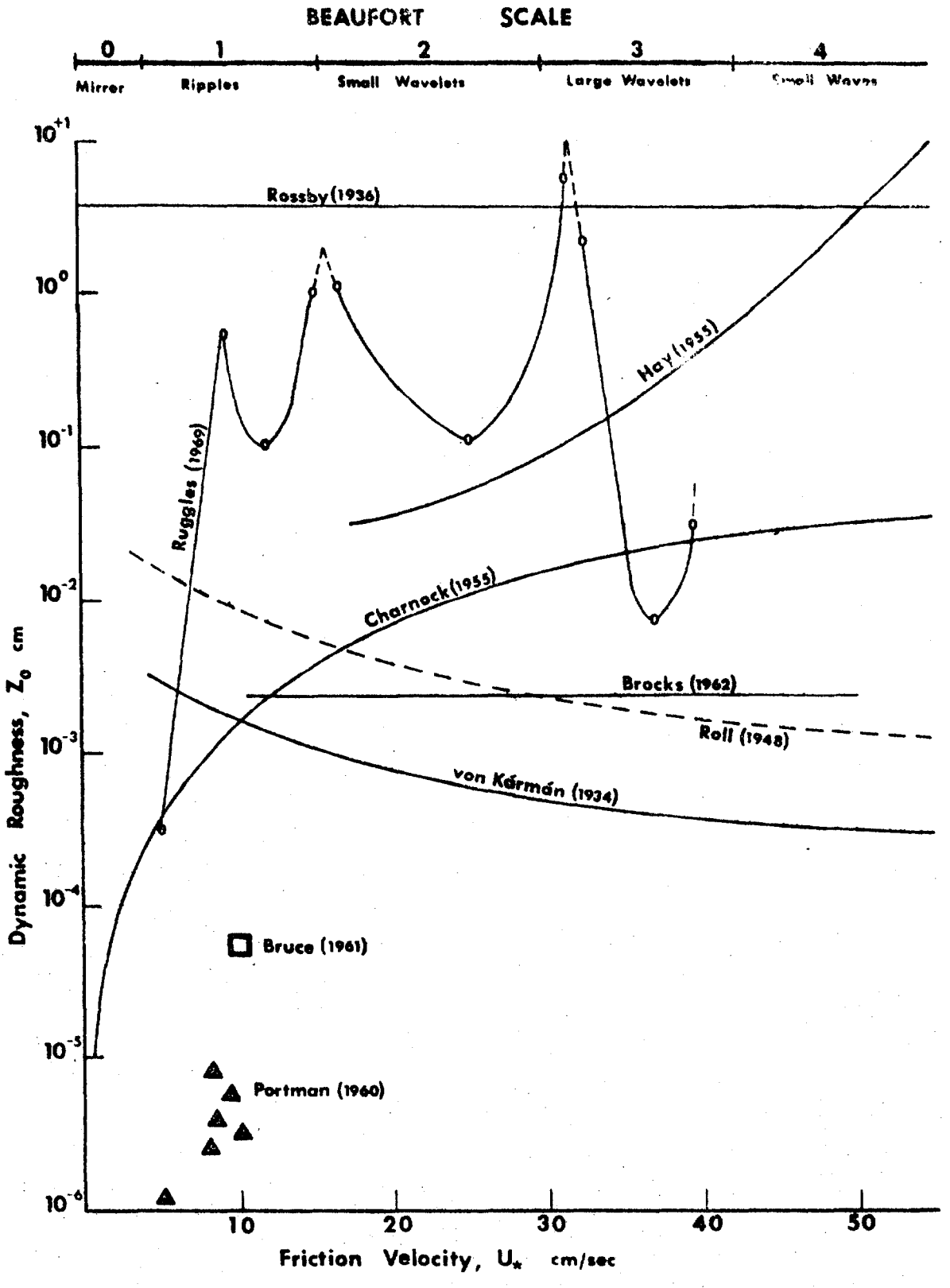


FIGURE 11. Summary of investigations of dynamic roughness as a function of friction velocity and Beaufort Wind Scale (adapted from Roll, 1965, p. 139 and Ruggles, 1969, pp. 41 and 49).

unusual peaks in Ruggles' data, which have also been observed by Wu (1969), coincide with divisions in the Beaufort wind scale as found in Kinsman (1965a). This scale is an adoption of natural wind speed divisions selected on the basis of the differing appearance of the ocean surface by seamen. It is also of interest to note that Ruggles considers the marked peak at $U_* = 32$ cm/sec ($U_{10} = 8.5$ m/sec) to be representative of the Kelvin-Helmholtz shear instability as predicted by Munk (1947). This instability criterion predicts that a transition from laminar to turbulent flow occurs for winds around 7-9 cm/sec.

With these conflicting values for z_o in mind, the chosen value of a constant z_o was 0.6 cm. This value was chosen because it appears to be a best fit constant for Ruggles' data and because C.-G. Rossby (1936) has stated: "The roughness parameter corresponding to steady, moderate to strong winds seems to be in the vicinity of 0.6 cm...," a value lying intermediate between one calculated by Prandtl in 1932 and another by Sverdrup in 1936 (Munk, 1947). Rossby arrived at this value by applying wind profile formulae developed by him and Montgomery in 1935 to measurements made by Wust in 1920 (Sverdrup, et al., 1942, p. 489). In conclusion, Wu (1969) observed values of $z_o = 0.01$-0.1 cm for $U_{10} = 2$-5 m/sec and $z_o = 0.1$-1.0 cm for $U_{10} = 5$-10 m/sec.

The next problem lies in dealing with the wind friction or shear velocity, U_*, defined as

$$U_* = \left(\frac{\tau_s}{\rho_a}\right)^{1/2}, \tag{43}$$

where τ_s = wind shearing stress
ρ_a = density of air.

The physical significance of U_*, according to Roll (1965, p. 133), is that it represents the difference between the velocity of a specified fluid particle and that of its new surroundings, after having traveled the distance of one mixing length. Reference should be made to the previous section and equation (7) for a description of the mixing length, ℓ.

Again, considerable differences of opinion are encountered in discussion of the relationship of the friction velocity to other parameters such as wind speed, dynamic roughness and wave profiles. Roll (1965) and Kraus (1972) again provide more detailed accounts of the theoretical considerations involved. In the interest of simplifying the problem, the following relationship has been accepted as valid for our calculations.

$$U_* = 0.04 U_{10}. \tag{44}$$

This has been verified by Ruggles (1969) using simultaneous vertical measurements of wind speed over an open ocean site. Kraus (1972) estimated a constant coefficient of 0.05 vice 0.04. It should be noted that literature on the friction wind speed as related to measured wind speeds over water appears quite sparse.

With these two unknowns now resolved, at least temporarily, U_* can now be calculated directly using equation (42) and our measured wind speeds taken at an average standing height of 1.5 m above the water surface. From this, the standard ten-meter wind speed can be calculated using equation (44). The objective in obtaining this ten-meter wind height is to be able to calculate the actual stress on the water as exerted by the wind. This shearing stress is usually expressed in terms of the wind

at a ten-meter height as

$$\tau_s = \rho_a C_d (U_{10})^2 , \qquad (45)$$

where C_d = dimensionless resistance (drag) coefficient.

It should be noted that the work of some authors suggests that this stress term is proportional to U^n where n is a number other than two.

Choosing a reasonable value for the drag coefficient, C_{10}, is difficult because of its direct dependence on the poorly-defined parameters, U_* and z_o (note: The subscript 10 denotes that this is for a wind speed at a ten meter height). There is much literature concerning this coefficient; all have specific contradictory results. The only agreement is that C_{10} is a coefficient whose value is on the order of 10^{-3} for air-water interactions. Figure 12 gives an overall idea of the present state of dissent. Wilson (1960) compiled the results of forty-seven investigators and found that the mean value of C_{10} is 2.37×10^{-3} with a standard deviation of 0.56×10^{-3} for wind speeds greater than 10 m/sec (mean equal to 20 m/sec). For winds with speeds less than 10 m/sec (mean equals 5 m/sec), the average value of C_{10} is 1.47×10^{-3} with a standard deviation of 0.83×10^{-3}. In attempting to establish greater accuracy, Roll (1965) took Wilson's results, expanded them with the results of more recent studies, and evaluated the data on the basis of the methods used in estimating C_{10}. Briefly, the five methods of measuring used are: 1) wind profile, 2) geostrophic wind departure and 3) the eddy correlation methods for use in air; and 4) sea surface tilt and 5) the surface film methods for use in the water. Detailed discussions of this coefficient are given by Roll (1965), Wilson (1960, Deacon and Webb

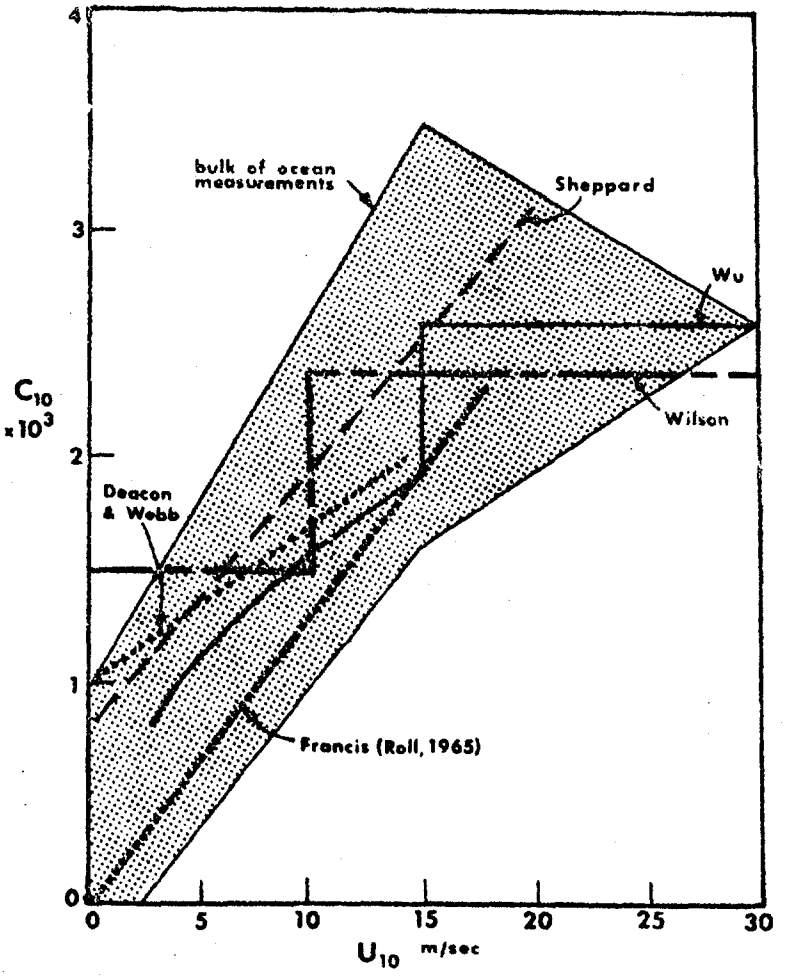


FIGURE 12. Variation of wind resistance coefficient with wind velocity (adapted from Silvester, 1970).

(1962), Hidy and Plate (1966, Neumann and Pierson (1966), Wu (1969) and Kraus (1972).

The value chosen for C_{10} to be used in our calculations is 1.5×10^{-3}. This is based not only on Wilson's and Roll's results for light winds, but also on measurements done by Deacon in 1962 and Brocks in 1959 and on values derived by Van Dorn (1953), which were obtained with great accuracy ($\pm 5 \times 10^{-7}$) under well-controlled, but natural, conditions in an

artificial pond. However, by no means should this resistance coefficient be viewed as a well-defined parameter, even though much research has been devoted to it. Very little is presently understood about the influence of atmospheric stability, rain, wave form drag, fetch, wind gustiness and other variables on this parameter.

Now that a value for C_{10} has been singled out, we may calculate values of τ_s to be used in the evaluation of our data. Table 3 A of the Appendix shows some typical values for various wind speeds. These values appear to correlate with those of other investigators (Sverdrup, et al., 1942, p. 491; Shemdin, 1972; and Van Dorn, 1953).

Accuracy of Measured Data

Before making a comparison of the actual current velocities measured in the lagoons to computed theoretical current values, it is necessary to know the magnitude of errors which may be introduced in the data collection process.

There is room for much error in the measurements of wind magnitude because the Dwyer Wind Meter measures wind speed directly and is thus subject to the wind's random fluctuations. When the meter is held vertically facing the wind, the direct force of the wind on a hole in the rear of the meter pushes a small ball inside the meter up along a scale. Although the wind meters were proved accurate to within 15% of the measured wind velocity by Jen (1974), the inaccuracies involved in trying to determine the mean wind during a short period of time may be as high as 50% of the mean wind speed. This is especially evident in gusty conditions when, for example, the readings may fluctuate between 2-10 mph. It becomes more a matter of

experience, accumulated after many hours on the lagoons, in estimating the true mean speed of the wind. Of course, there may also be much spatial deviation in wind velocity due to interference by land boundaries. However, in a final analysis of the data for the wind field over an entire area (see Charts 1 A-T), one can get a good idea of the mean wind velocity.

Deviations in measuring wind direction are not such a problem. The use of a closely-gradated compass is all important, but the estimated standard deviation is as high as 5°, mainly because this measurement depends on the stability of the wind direction. As previously noted, concurrent observations of wavelets helps in this measurement because it has been shown by several investigators that the wave crests customarily line up normal to the wind direction, at least for wind speeds less than 6 m/sec (Hidy and Plate, 1966). It is in these lighter winds that one meets with more difficulty in measuring wind direction, so this observational technique is of great help.

The current measurements have several aspects that may inherently produce errors. This is due to the fact that the current is not directly measured. Notwithstanding any other types of errors, the first two months of data (March and June, 1973) should be considered to contain current measurements with only fair accuracies. This is because we had not yet made use of a double anchor mooring system in preventing lateral movement of the small boats, which was previously discussed in the field work description section. Also previously discussed in the field work description section are the errors inherent in the field range finder's logarithmic scale for any readings greater than 40 feet. For readings of less than 40 feet, accuracies with less than 5% error may be obtained. The determination

of the direction of the current cross is probably the most accurate measurement ascertained, having a standard deviation of only 2° at the most.

Another source of possible error in the current measurements is in the design of the current cross system. It should be designed so that the force exerted by the wind on the float is relatively small compared to the force exerted by the current on the vanes. For measurements made at deeper levels, one must also be concerned about the force exerted on the float by the surface drift current as compared to that of the current at the depth of the cross, especially in the presence of strong velocity shears (Knauss, 1963). In the present case, however, the cross essentially measured surface current because it was never deeper than 0.5 m below the surface. Thus, we need only be concerned with the wind force on the float (reference may be made to Pritchard and Burt (1951) and Cook (1970) for additional developments). In an attempt to lessen the effects of this wind coupling, the float was always filled with water, whenever possible, to lessen its profile above the surface. However, in rough, choppy water, more of the float had to be out of the water in order to be able to clearly follow the drogue's motion.

The forces on the float and current cross are given as

$$F_f = \frac{1}{2} C_f \rho_a A_f (U_f)^2 \tag{46a}$$

$$F_c = \frac{1}{2} C_c \rho_w A_c (U_c)^2 \tag{46b}$$

where F_f and F_c are the forces on the float and the current cross, U_f and U_c denote the velocities of the surface wind on the float and of the current on the cross respectively, A_f and A_c are the effective cross-sectional

areas of the float and cross upon which these velocities act, C_f and C_c are non-dimensional drag coefficients for the float and cross, and ρ_a and ρ_w are the densities of air and water.

A well-designed drogue system is one in which the ratio of F_f/F_c is very small. Using tabulated values of $C_c = 1.75$ and $C_f = 0.75$ (from Meyers, et al., 1969) and computed values of $A_f = 129$ cm^2 (20 in^2) and $A_c = 1123$ cm^2 (174 in^2) (see Figure 4), for a representative value of $U_f = 0.5$ m/sec (from a wind velocity of $U_{10} = 10$ m/sec), it can be found that the force of the wind on the float will not exceed 5% of the current force on the cross. This indeed shows that this possible source of error from the wind on the float is negligible. It should be noted that the value of 0.5 m/sec for a wind speed at only a few centimeters above the surface is an uncertain value which is simply an order-of-magnitude estimate based on the logarithmic wind profile.

Comparison of Results

In comparing the measured currents to those predicted by the theory, reference is made to Table 4, Comparison of Results. Note that the measured values used in this table are the same as those in Table 3, p. 46. In the last three columns of this table are values of current speed; the first value is the current actually measured, the second is the current as predicted by the steady-state wind and slope current solution, equation (26), and the third value is the theoretical velocity calculated from the steady-state pure drift current solution as expressed by equation (15). For ease of reference these equations are reproduced below:

$$U(z) = \frac{\tau_s}{A_z}(d - z) \qquad (15)$$

$$\frac{A_z}{\tau_s d} U(z) = \frac{3}{4}\left(\frac{z}{d}\right)^2 - \left(\frac{z}{d}\right) + \frac{1}{4} \qquad (26)$$

As can be easily seen, the current velocities predicted by equation (26) appear nowhere close to the magnitudes of the respective measured currents. Notwithstanding current deviation due to unknown factors (such as bottom topography), these discrepancies could be explained as resulting from the use of improper values of A_z, τ_s or depth; any of which would produce large inaccuracies. Naturally, one would be prone to interpret these inconsistent values as the result of improper initial assumptions in the simplifications of the equations of motion. That is, possibly terms were disregarded that should have been included. One of the major factors that, most probably, has a large effect in distorting the predicted current behavior is the choosing of a constant eddy coefficient, rather than a variable A_z (which would decrease with depth).

Nevertheless, we can see that the values calculated using equation (15) for a pure wind drift current, appear to correlate much better with our measured current values. At least, they are of the same order of magnitude as the measured values, even though they appear to predict, in all cases, smaller current velocities than those measured. However, this does tell us that the values of τ_s and A_z are, to a limited degree, correct. It should be remembered, though, that the values predicted by equation (15) are asymptotic values because there is no time-dependence involved. Thus, if anything, these theoretical values should always be greater than those measured. This is because the maximum steady-state conditions are implied by the theoretical approach, whereas the actual measured values are probably not those for a fully-developed, steady-state

circulation pattern.

One should not be drawn into an erroneous conclusion that, because the predicted values for a pure wind drift current correlate considerably better with our collected data than do the predicted slope current values, there is much more dependence of the actual current directly on the wind stress rather than on the resulting surface slope. This may or may not be the case, but it should be realized that the solutions found for our theoretical equations are only very crude attempts to approximate the actual circulation phenomena present. Thus, their usefulness and veracity may only be extended to a certain point, beyond which further application and reliance will only lead to mistaken conclusions.

Nevertheless, we have additionally seen that the current direction is closely related to the wind direction. Although this point has been discussed more completely in the first part of this section, one can gain an immediate feel for the correlation between wind and current direction through a rapid survey of the data presented in Charts 1 A-T of the Appendix. Also of note is the discussion of transient responses of current to the wind in the Time Constants section and the supportive examples from the measured data which are presented in this section. In summary, it has at last been reasonably demonstrated that the current in our lagoons is a function of the wind field over each lagoon.

TABLE 4 Comparison of Results

Site	Date	U(z)	U_{10} (1)	A_n (2)	A_s (3)	τ_s (4)	Water Depth (d)		Measured velocity	Slope (5) velocity	Wind Drift (6) velocity
Units.....		m/sec	m/sec	g/cm-sec	g/cm-sec	g/cm-sec^2	ft	m	cm/sec	cm/sec	cm/sec
1-2	7/24/73	3.6	6.52	50	181	0.79	8	2.4	4.7	0.29	3.0
2-25	7/18/73	5.4	9.78	130	408	1.79	5	1.5	9.2	0.00	1.4
3-6	7/19/73	1.8	3.26	10	35	0.20	6	1.8	4.7	0.11	1.5
4-10	8/16/73	3.1	5.61	40	193	0.59	4	1.2	6.6	-0.07	1.0
1-6	8/21/73	0.9	1.63	5	5.4	0.05	6	1.8	3.1	0.05	1.3
1-14	8/21/73	1.3	2.35	8	11.6	0.10	6	1.8	3.7	0.07	1.6
4-17	8/22/73	1.8	3.26	10	35	0.20	6	1.8	2.5	0.11	2.6

NOTES:

(1) U_{10} calculated from $U_{10} = 25\ U_*$

where $U_* = \dfrac{k_o\ U(z)}{\ln\left(\frac{z}{z_o}\right)}$ $k_o = 0.4$, $z_o = 0.6$ cm, $z = 1.5$ m

(2) A_n taken from Neumann & Pierson, 1966, p. 210

(3) A_s taken from Sverdrup, et al., 1942, p. 494

$A_s = 1.02\ W^3$ $W<6$ m/sec
$A_s = 4.3\ W^2$ $W>6$ m/sec

(4) $\tau_s = \rho_a C_{10} (U_{10})^2$

where $\rho_a = .00125$ gm/cm^3
$C_{10} = .0015$

(5) V_{slope} calculated from Equ. (36)

where $z = 0.5$ m
$A_z = A_n$

(6) $V_{wind\ drift}$ calculated from Equ. (15)

where $z = 0.5$ m
$A_z = A_n$

FUTURE WORK

Now that we have a fuller insight into the circulation phenomena of wind driven estuaries, the specific future work needed to pin down some of the less-understood aspects in the Cape Canaveral lagoons becomes clearer. A listing of recommended possible future investigations follows:

1. Apply finite-difference methods of solution to time-dependent equations of motion using synoptic observations over a single lagoon.

2. Make simultaneous measurements of current velocities as a function of depth. This will provide insight into the vertical velocity profile shown in Figure 6. This will most probably require the use of a pressure-stabilized float as a measuring device.

3. Measure currents (as a function of depth) near boundaries, especially the upwind and downwind boundaries and near bridge and causeway systems. This will determine the effects of boundaries upon the circulation structure.

4. Examine and measure wind stress, bottom stress and related parameters (e.g. z_o, C_d, etc.).

5. Measure the effects of evaporation and precipitation and estimate the total area water budget.

6. Perform numerical analysis of the collected data using a computer in order to discover any hidden correlations unforeseen in this present study.

APPENDIX

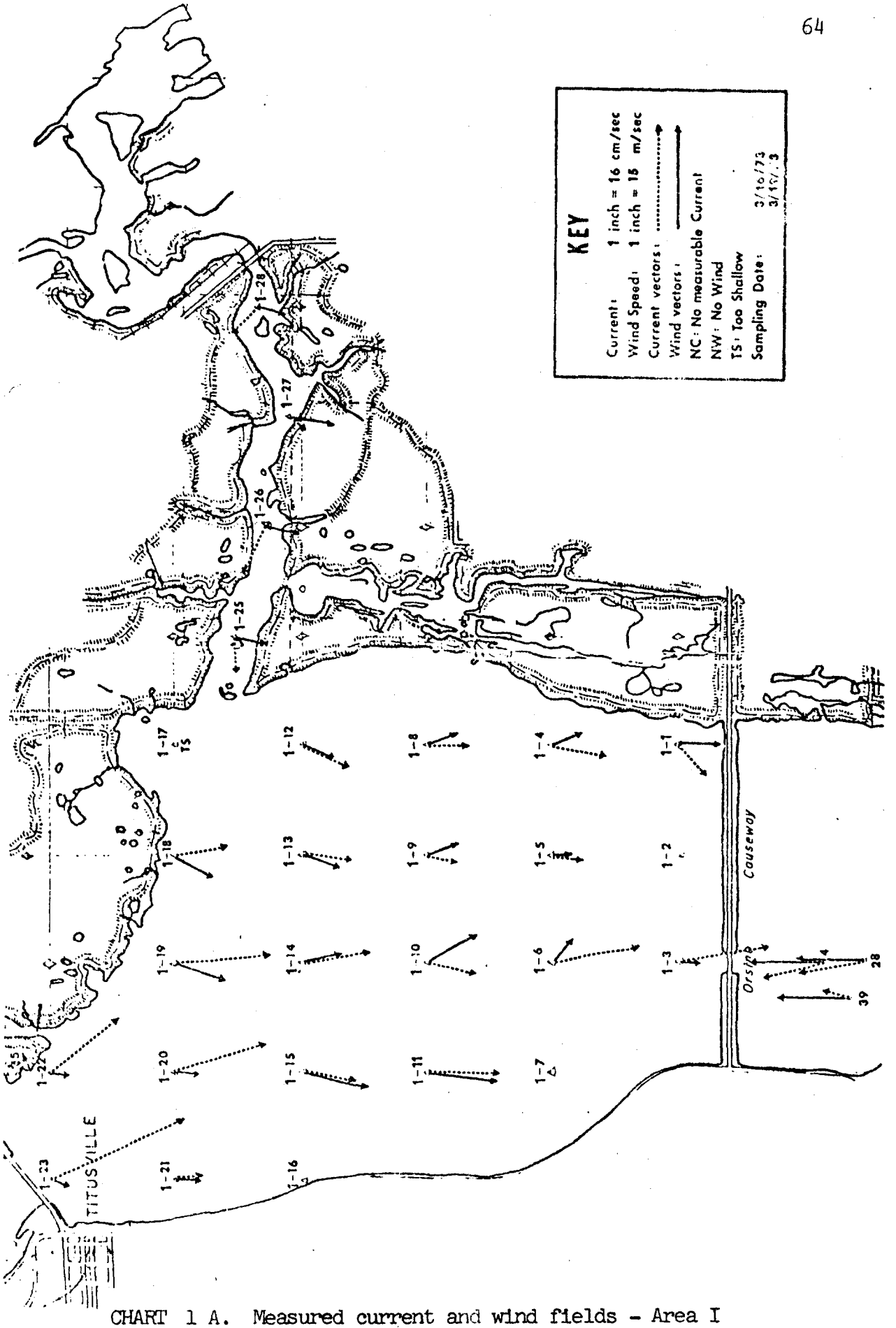


CHART 1 A. Measured current and wind fields - Area I

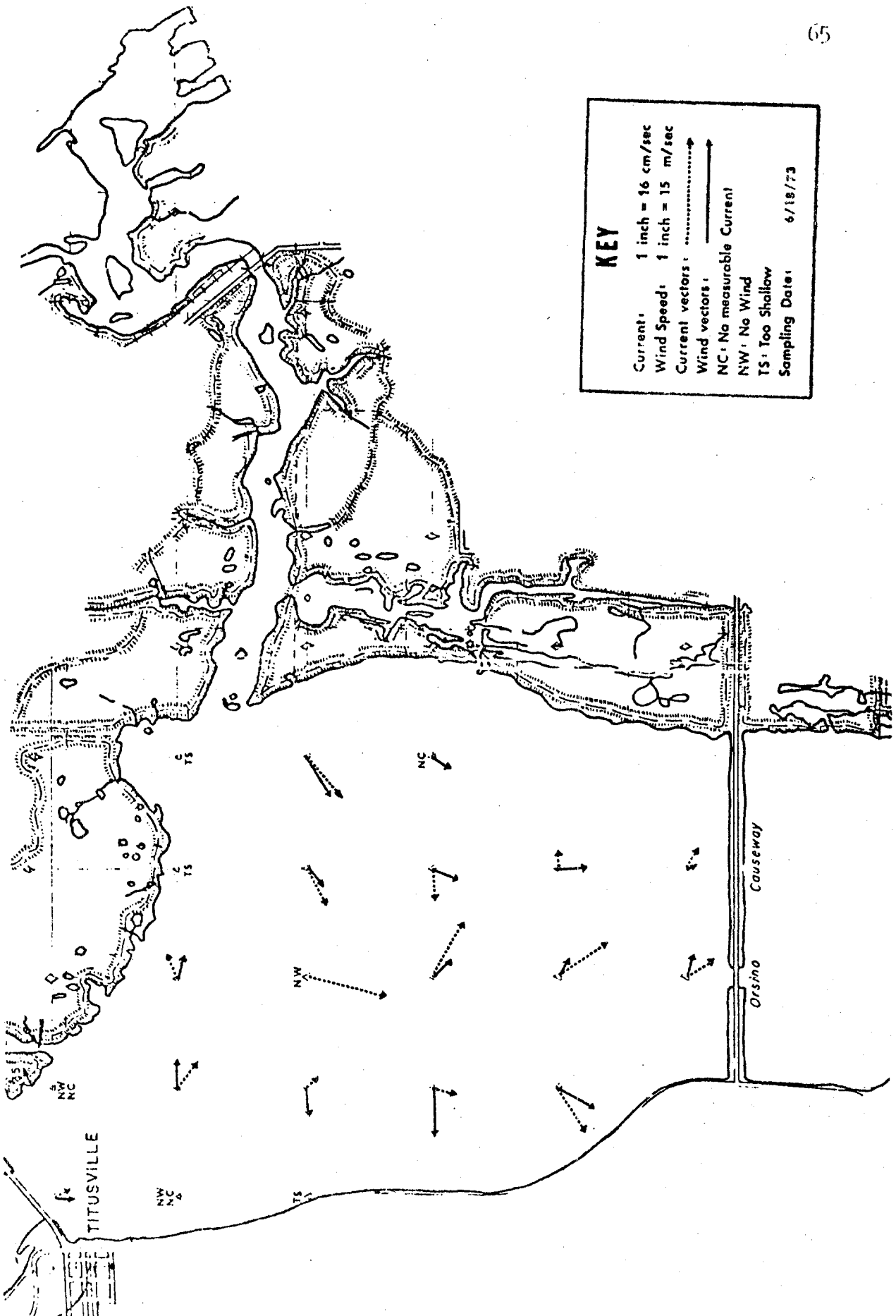


CHART 1 B. Measured current and wind fields - Area I

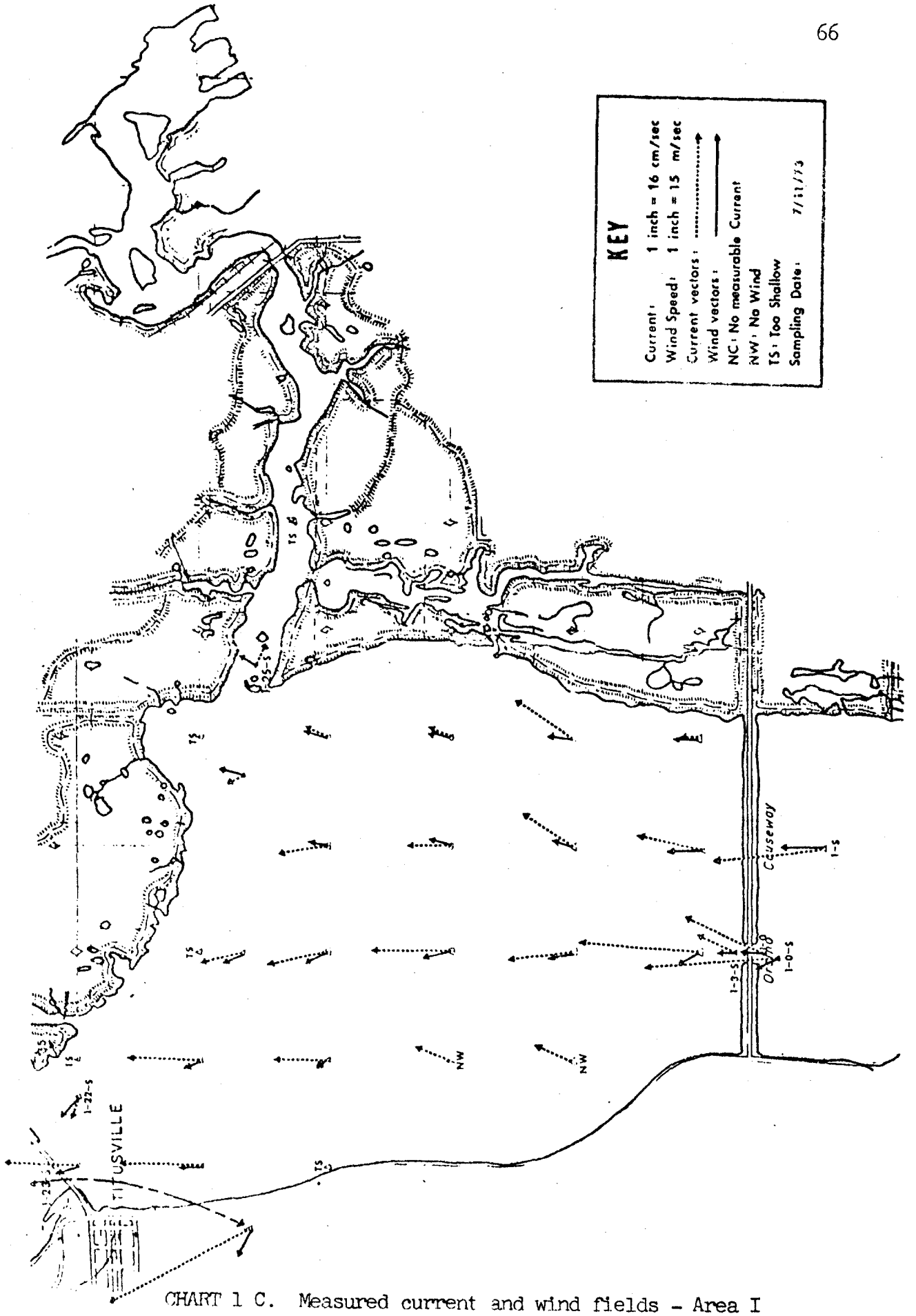


CHART 1 C. Measured current and wind fields - Area I

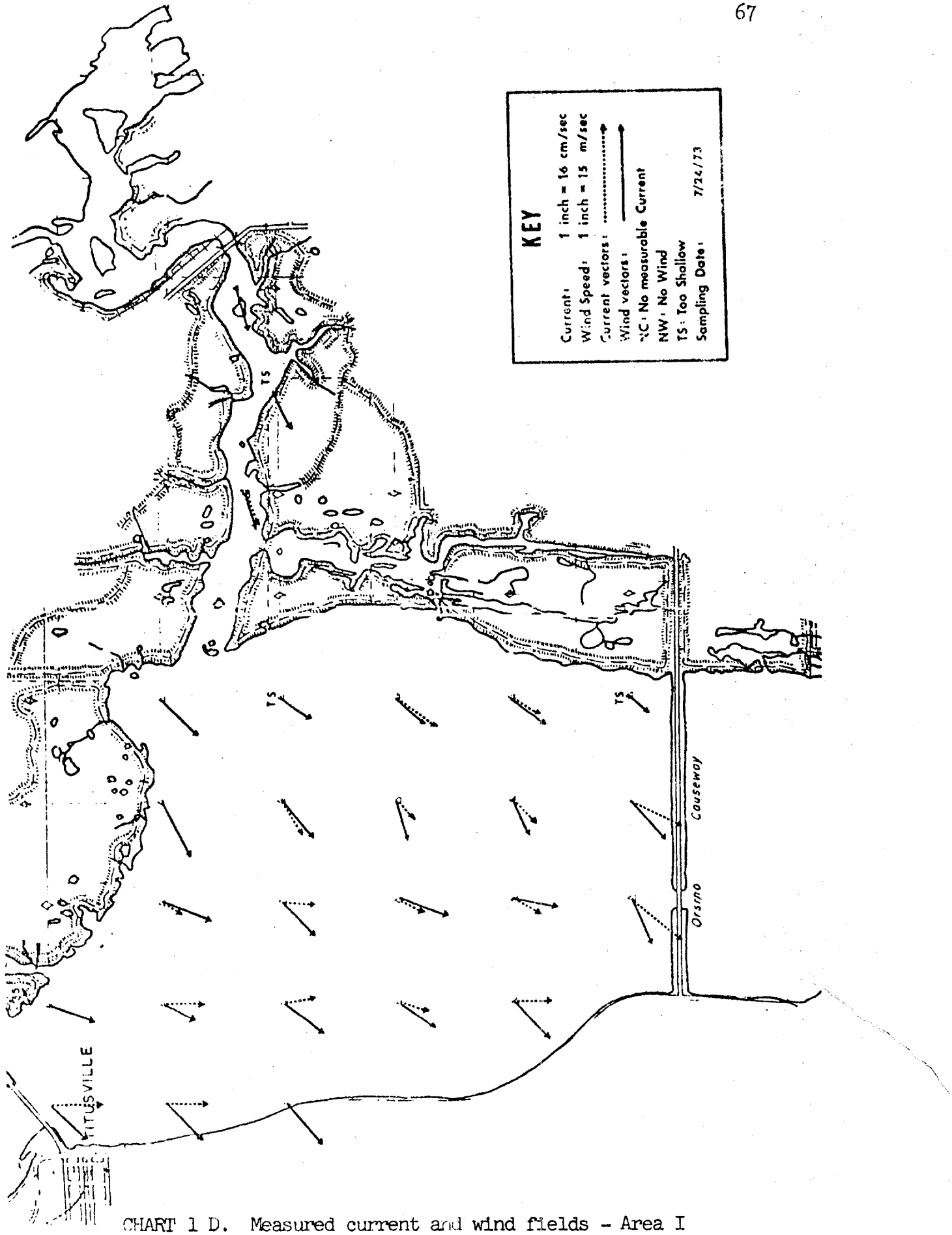
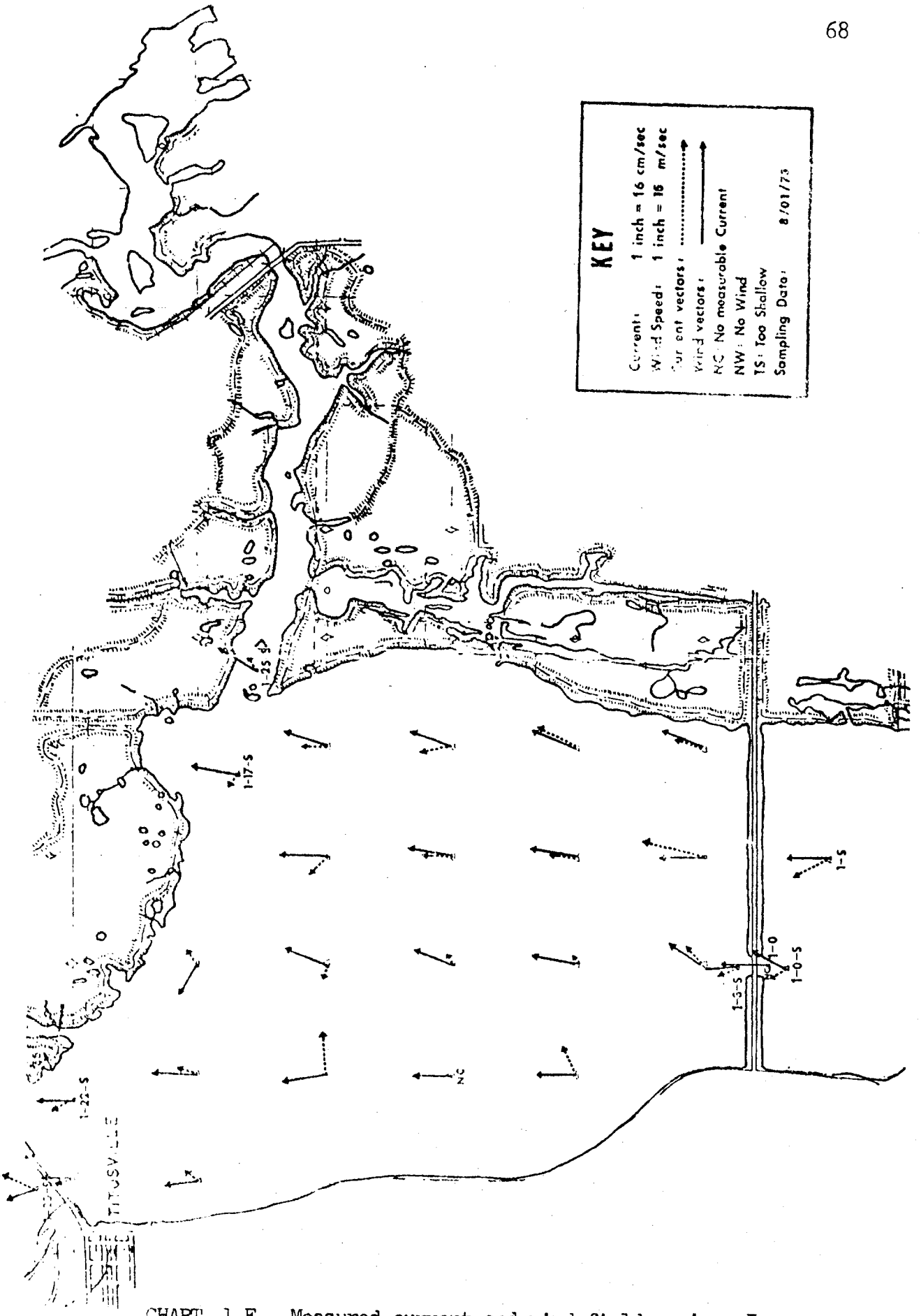


CHART 1 D. Measured current and wind fields - Area I



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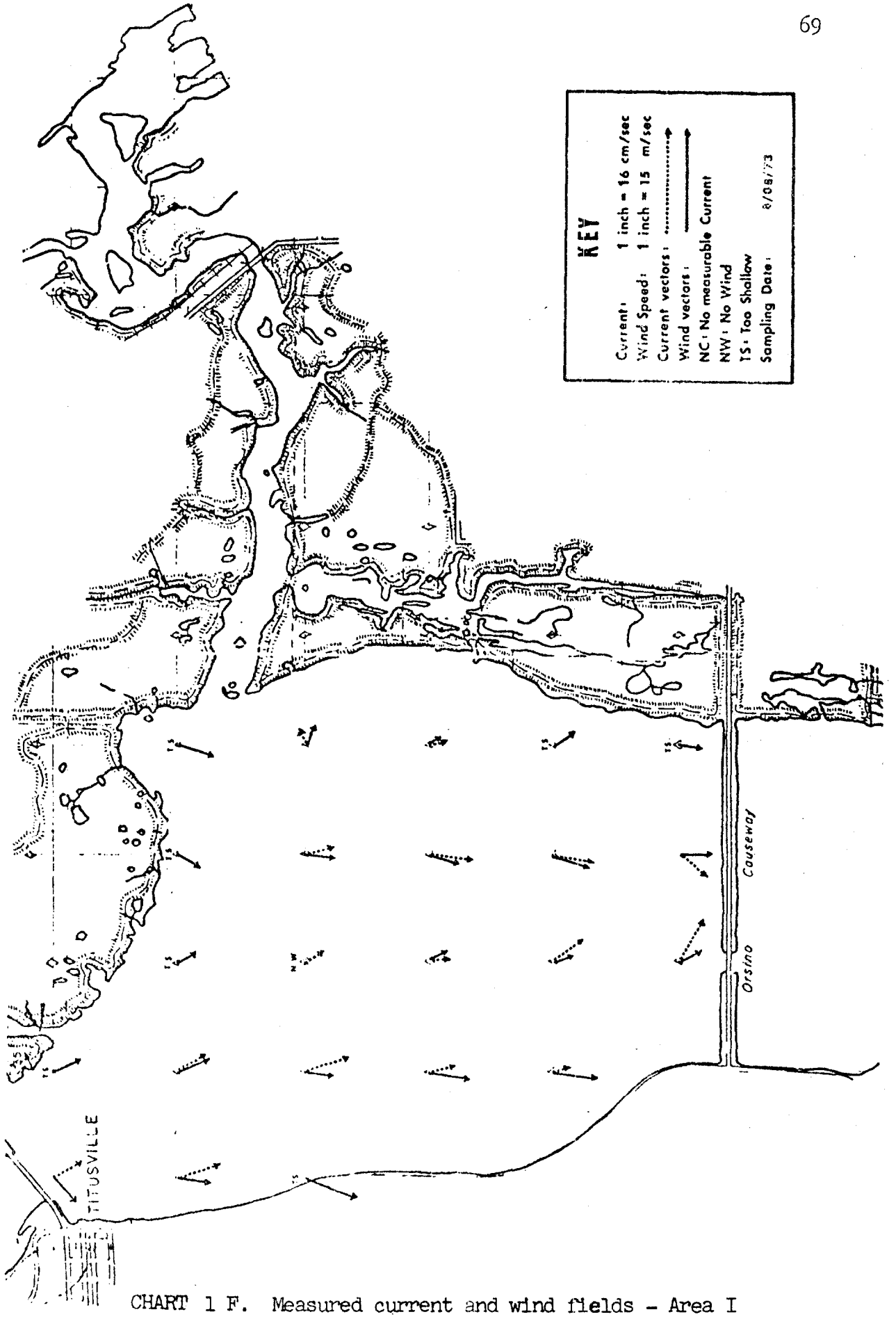


CHART 1 F. Measured current and wind fields - Area I

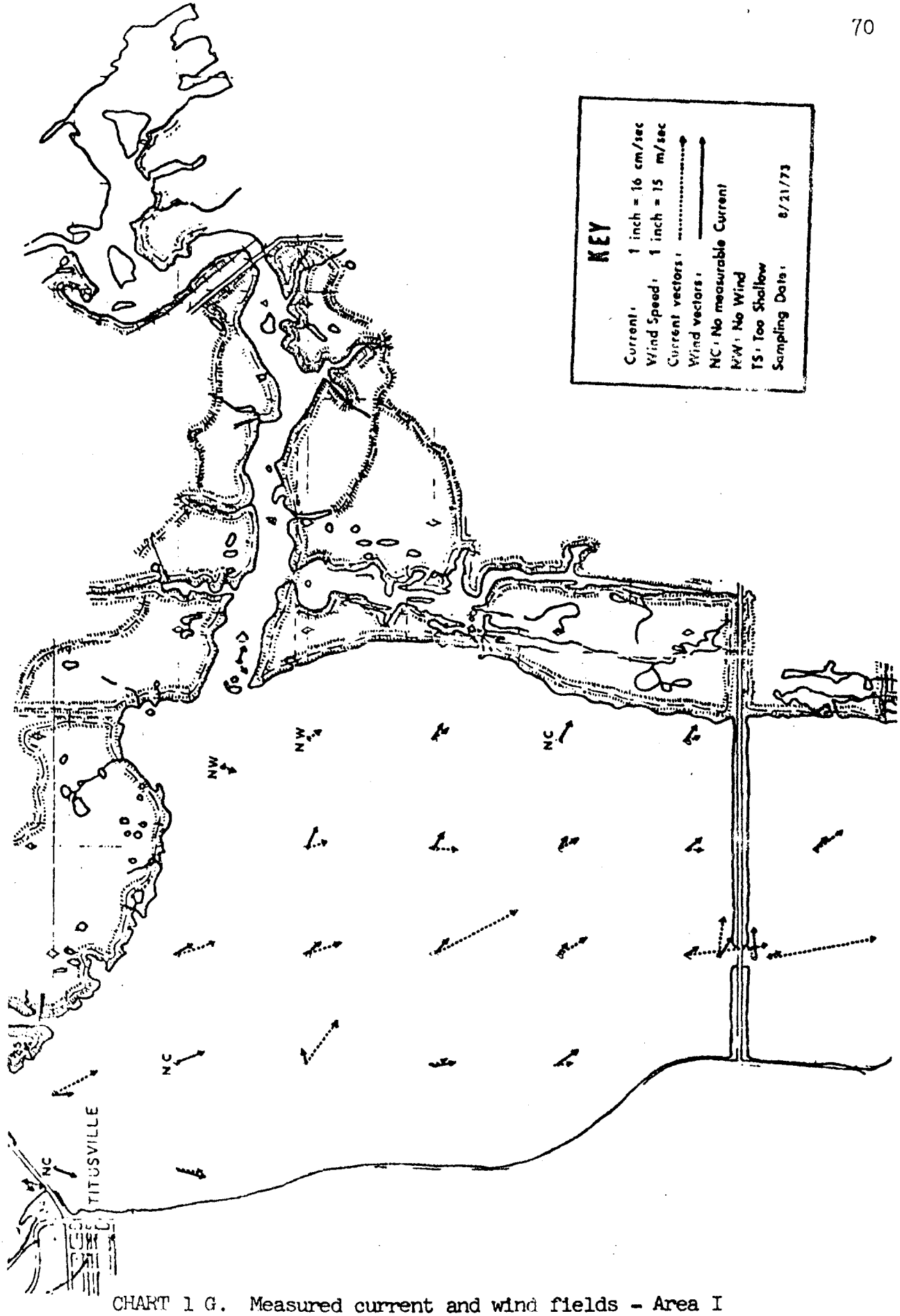


CHART 1 G. Measured current and wind fields - Area I

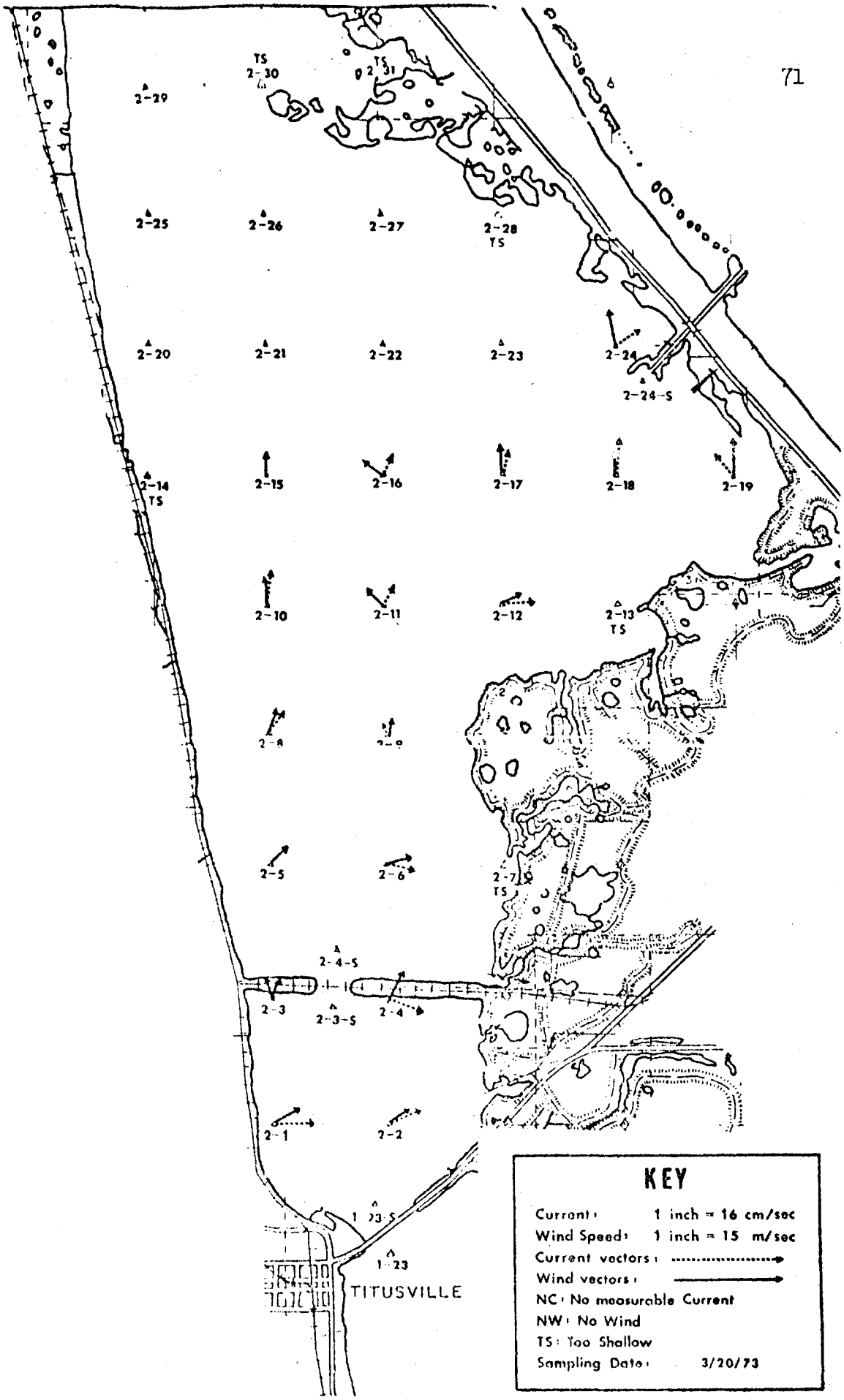
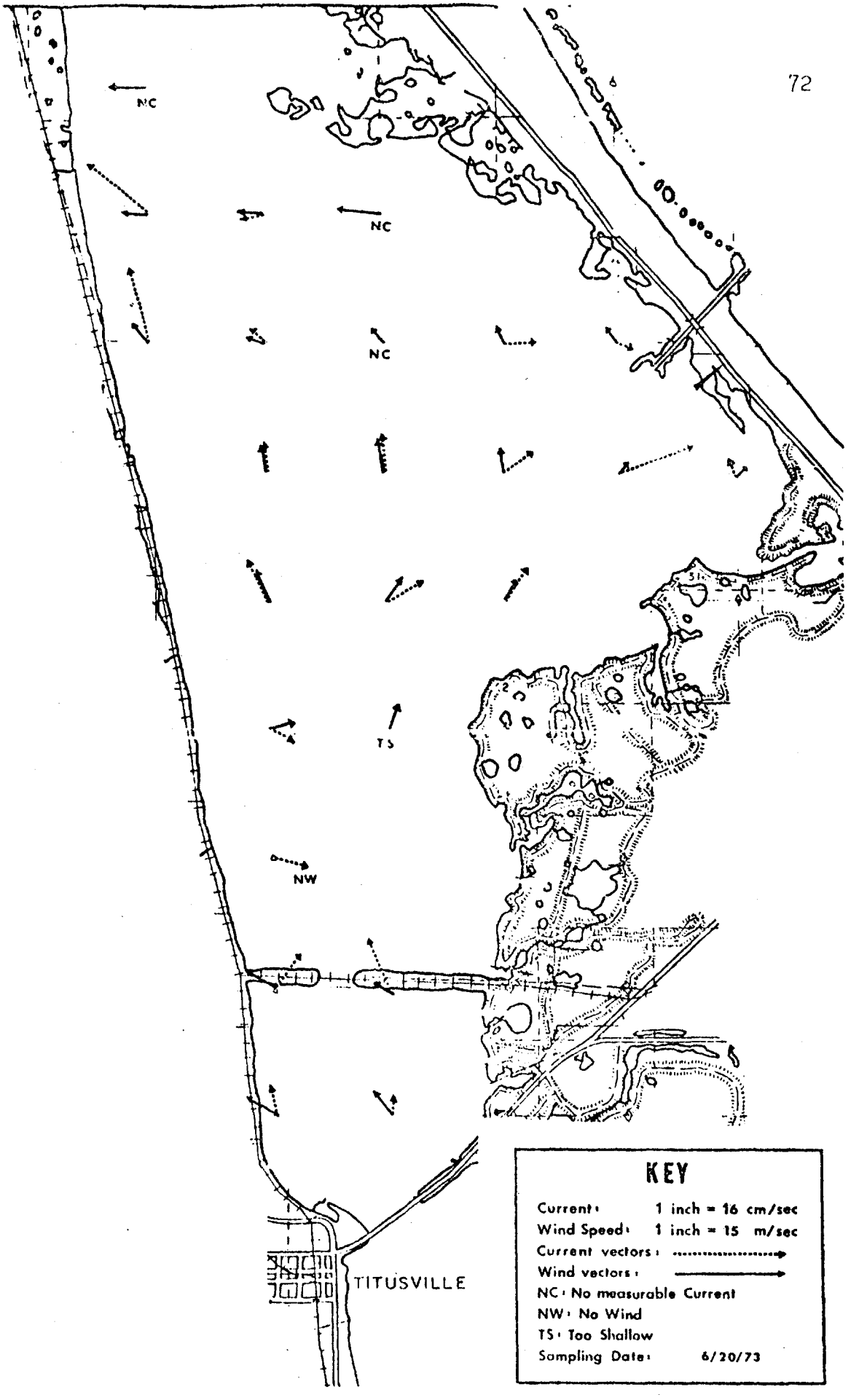


CHART 1 H. Measured current and wind fields - Area II



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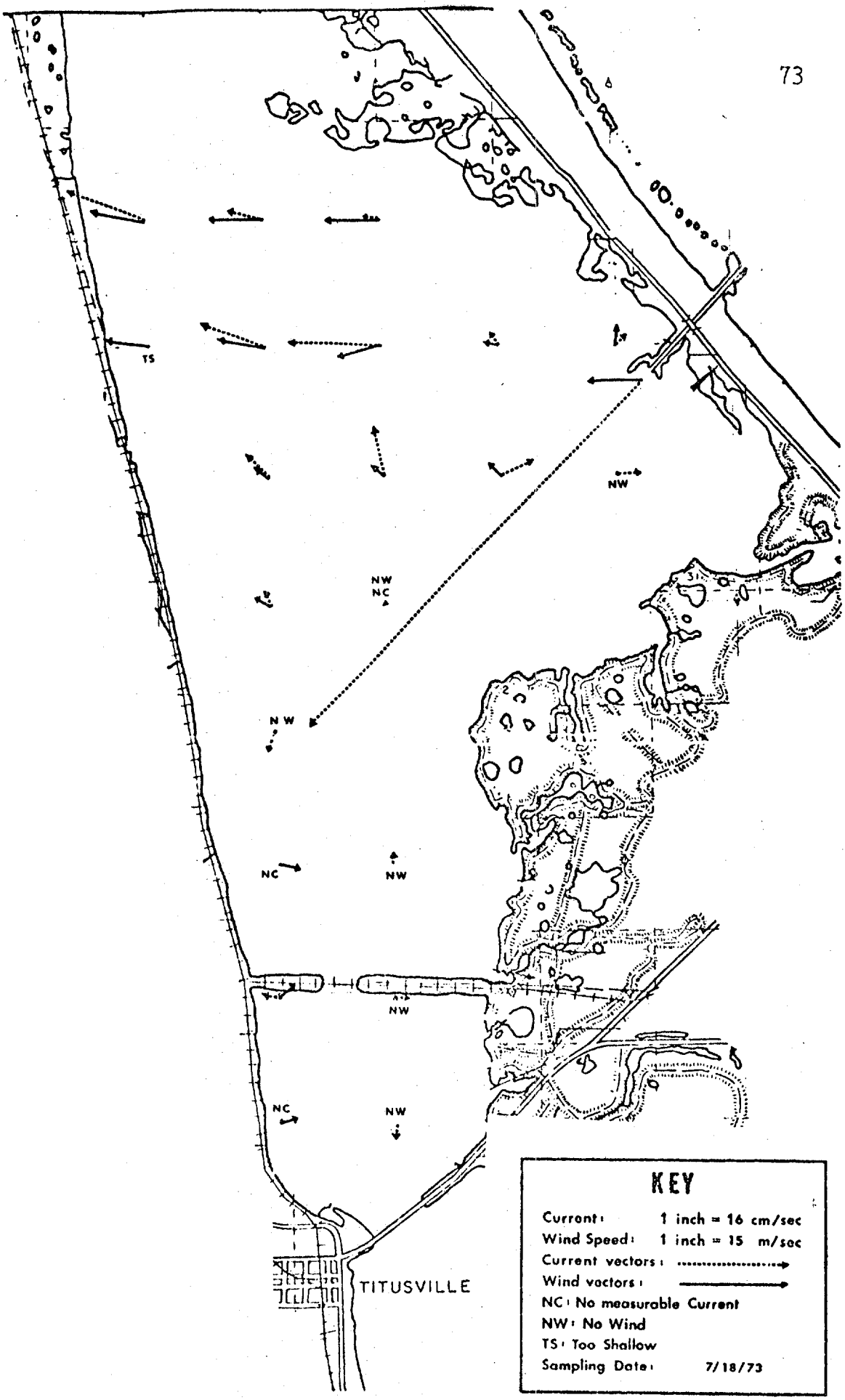

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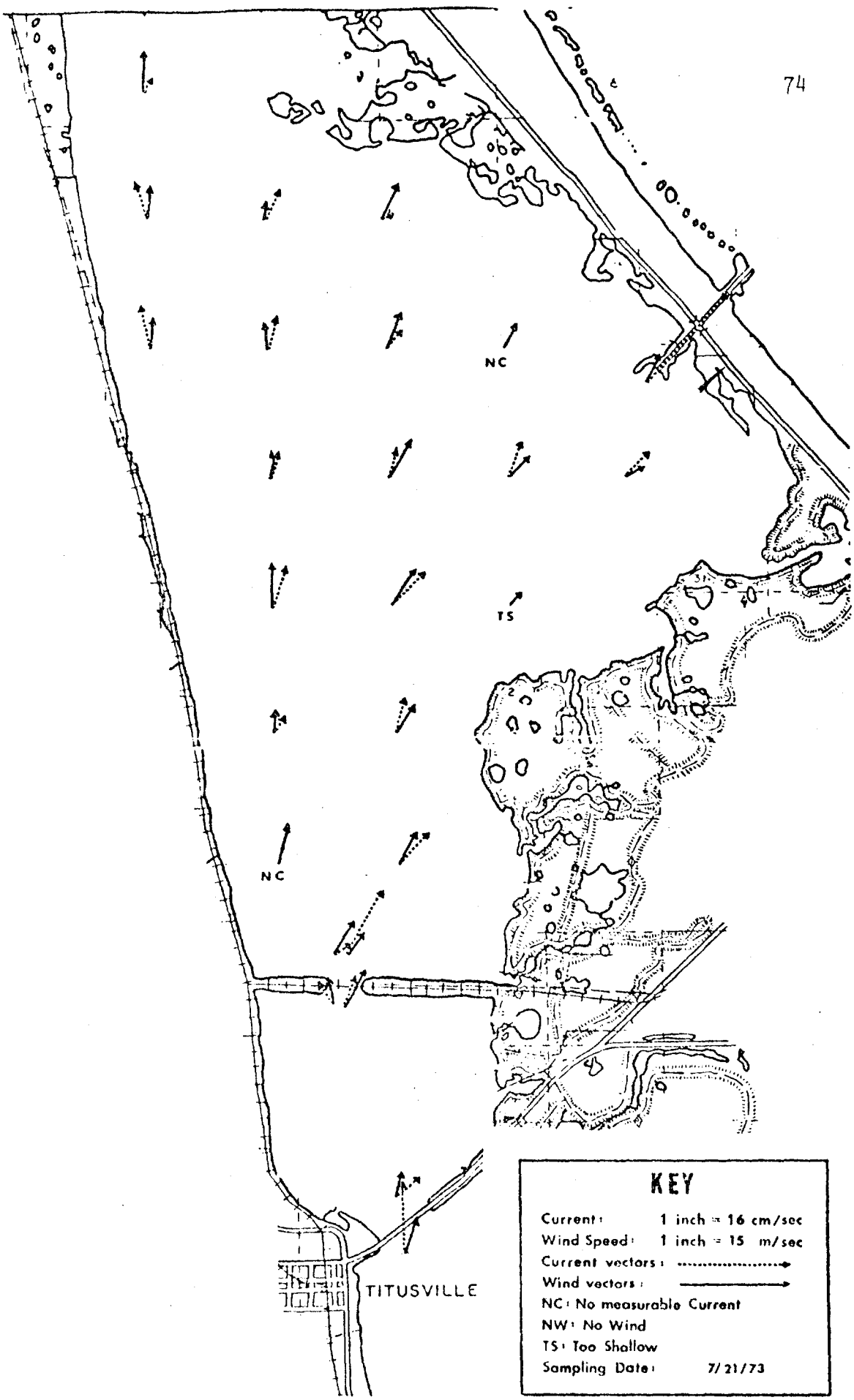
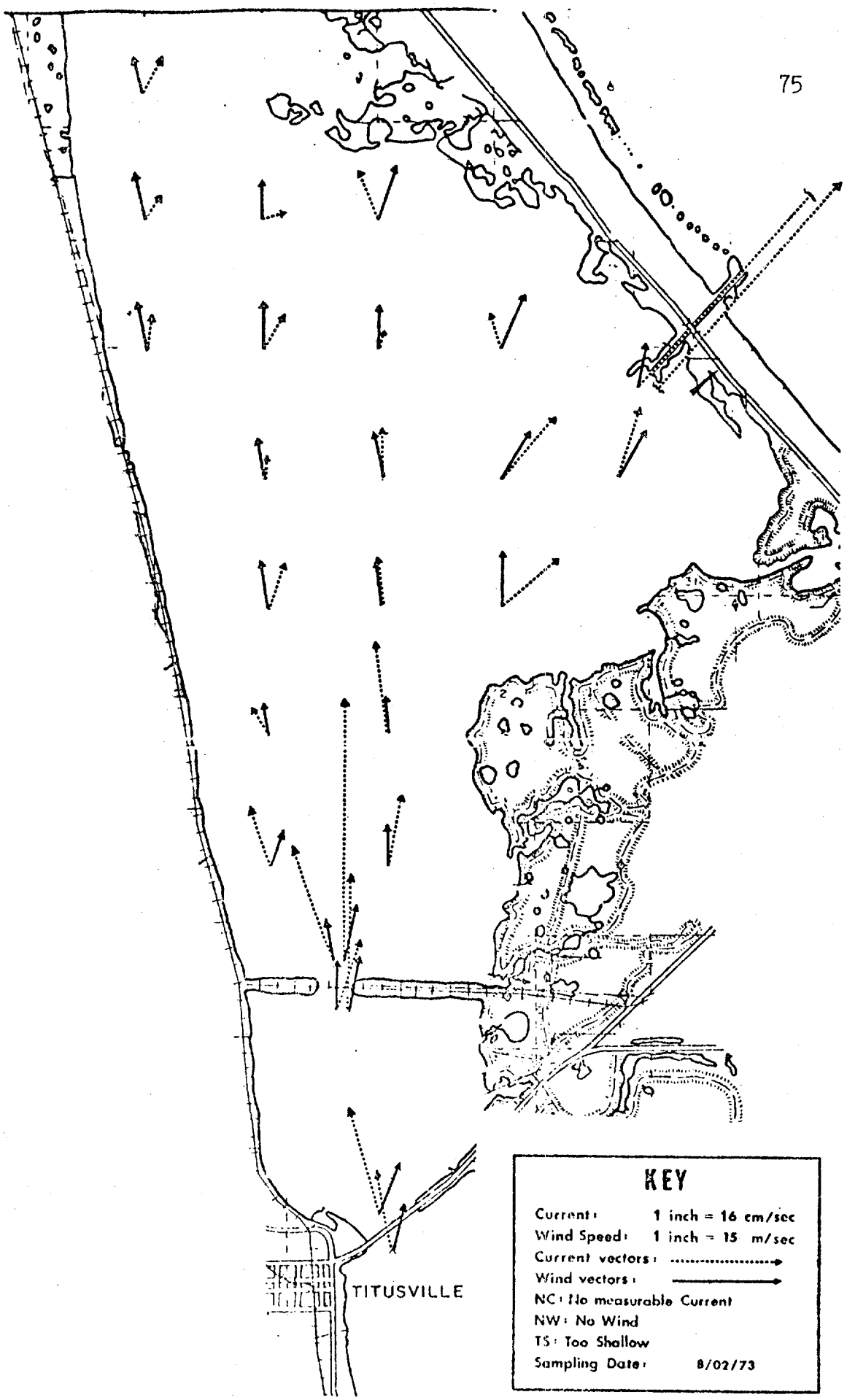


FIGURE K. Measured current and wind fields - Area II



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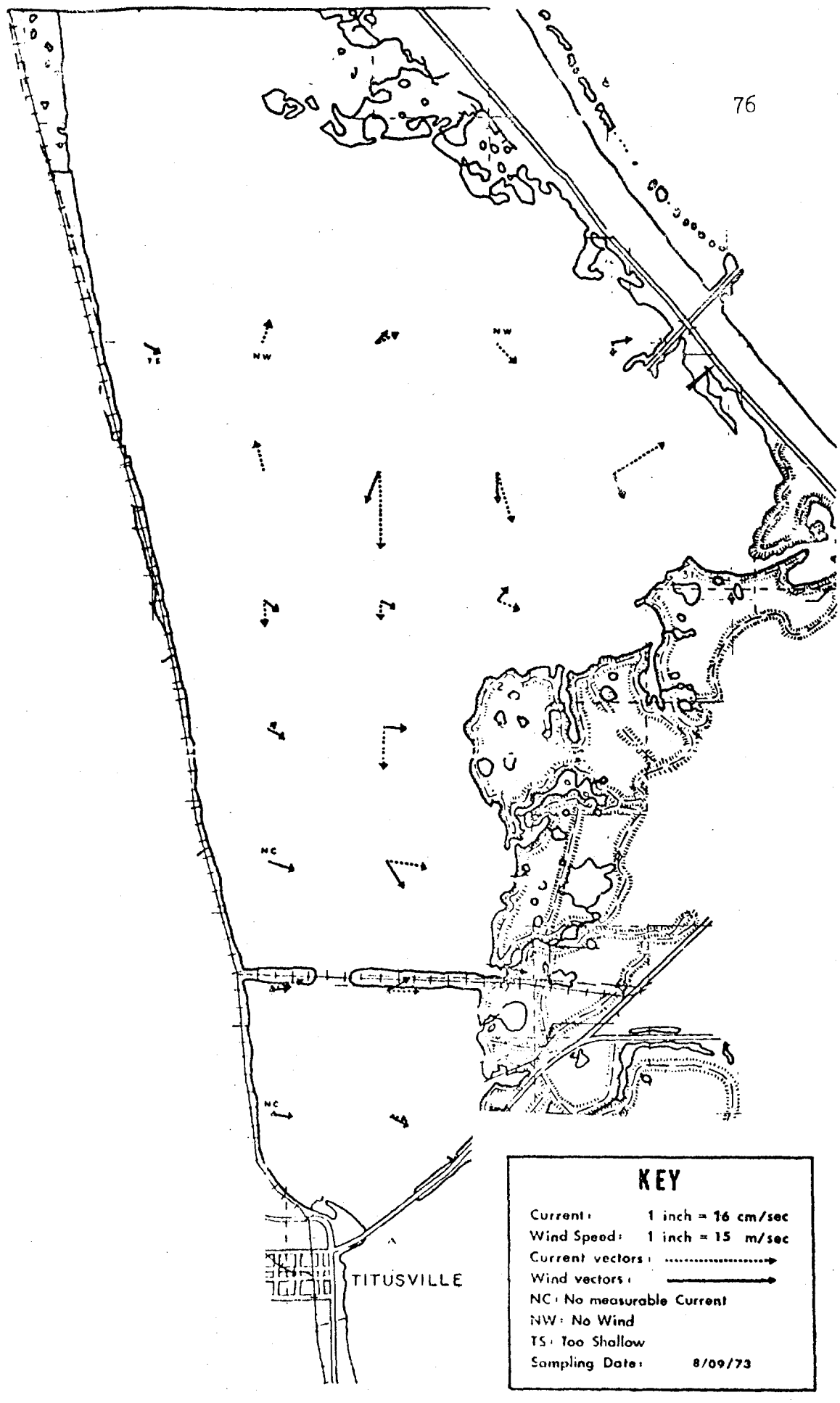


CHART 1 M. Measured current and wind fields - Area II

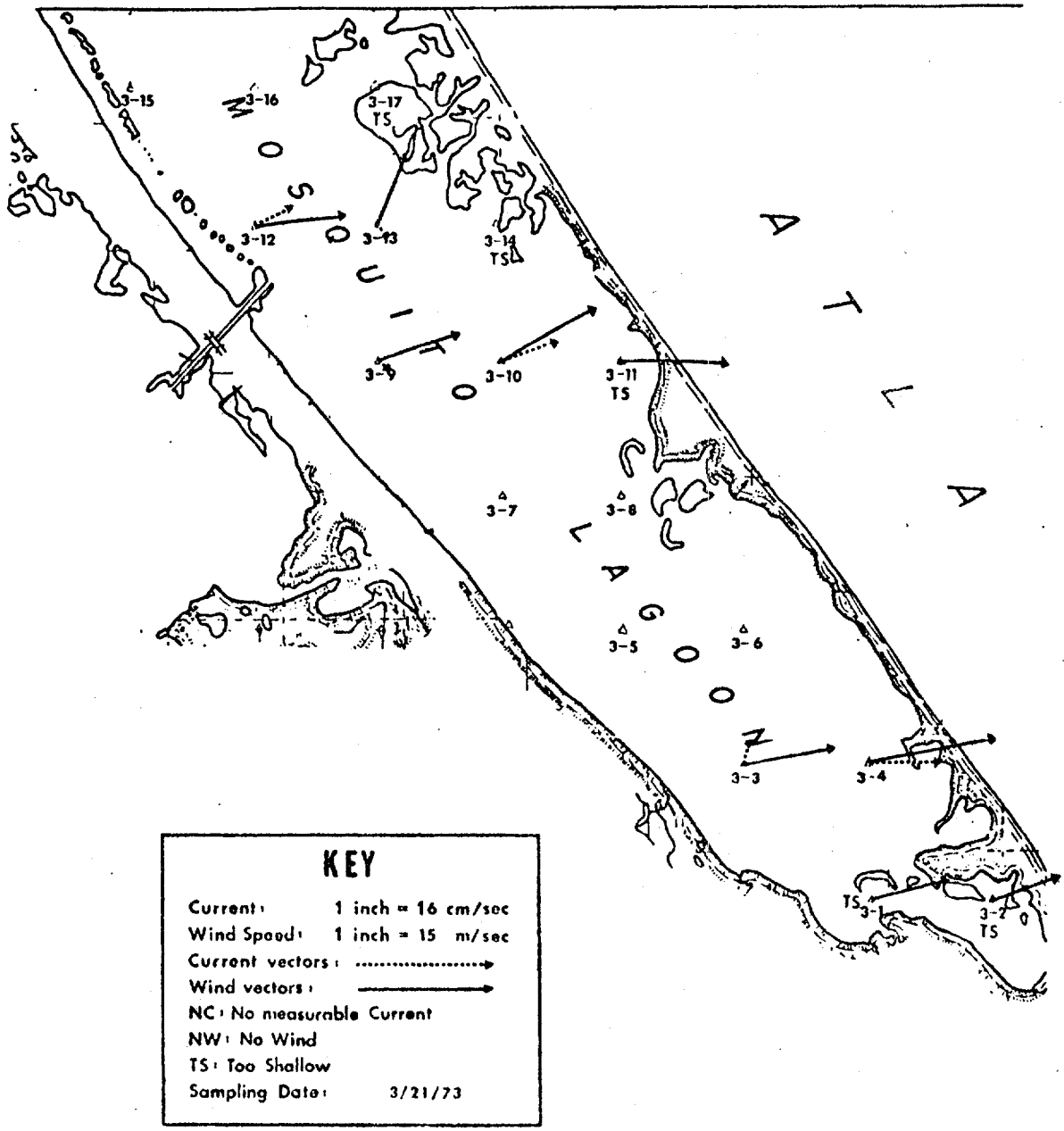


CHART 1 N. Measured currents and wind fields - Area III

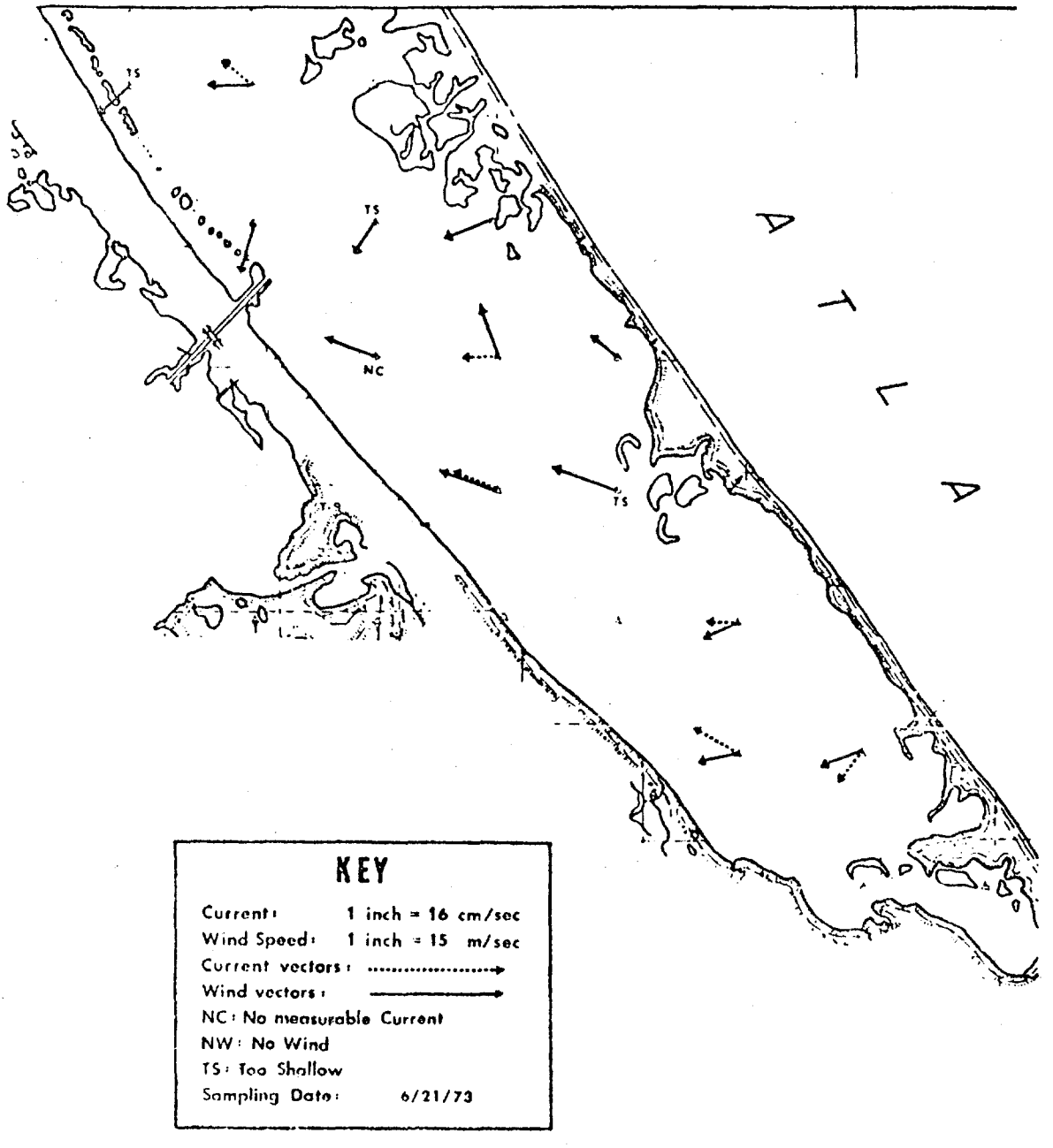


CHART 1 O. Measured current and wind fields - Area III

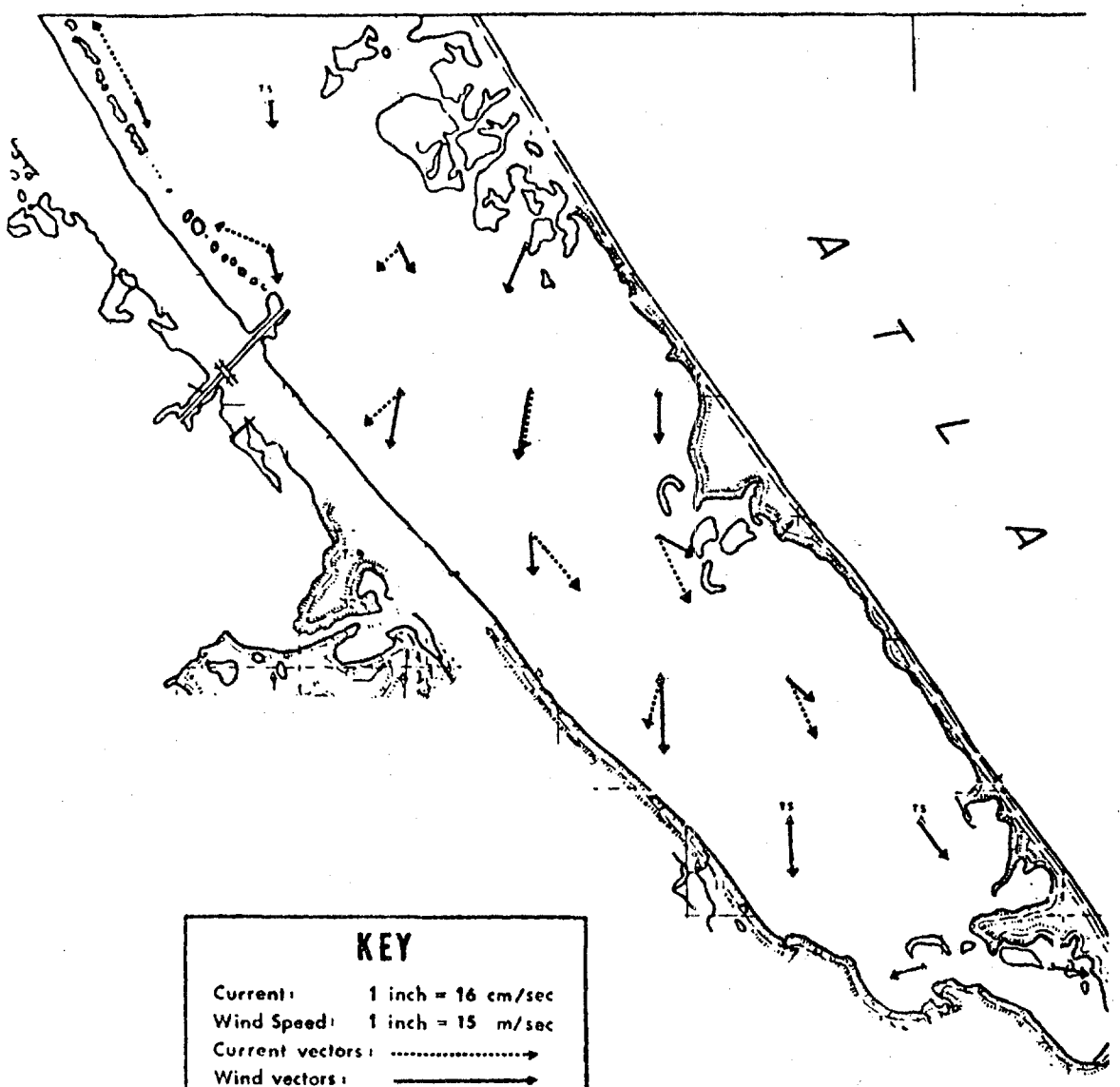
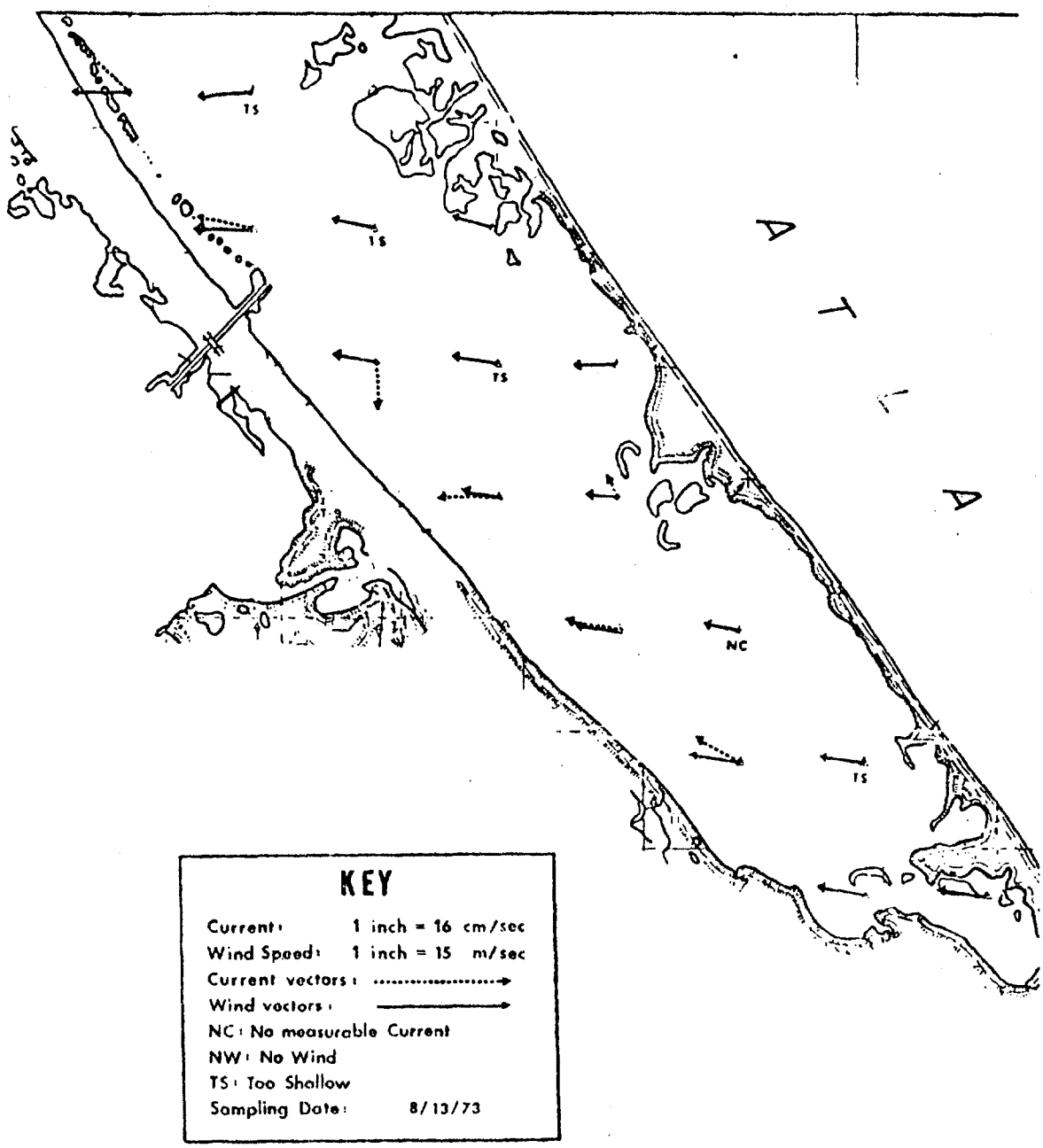


CHART 1 P. Measured current and wind fields - Area III



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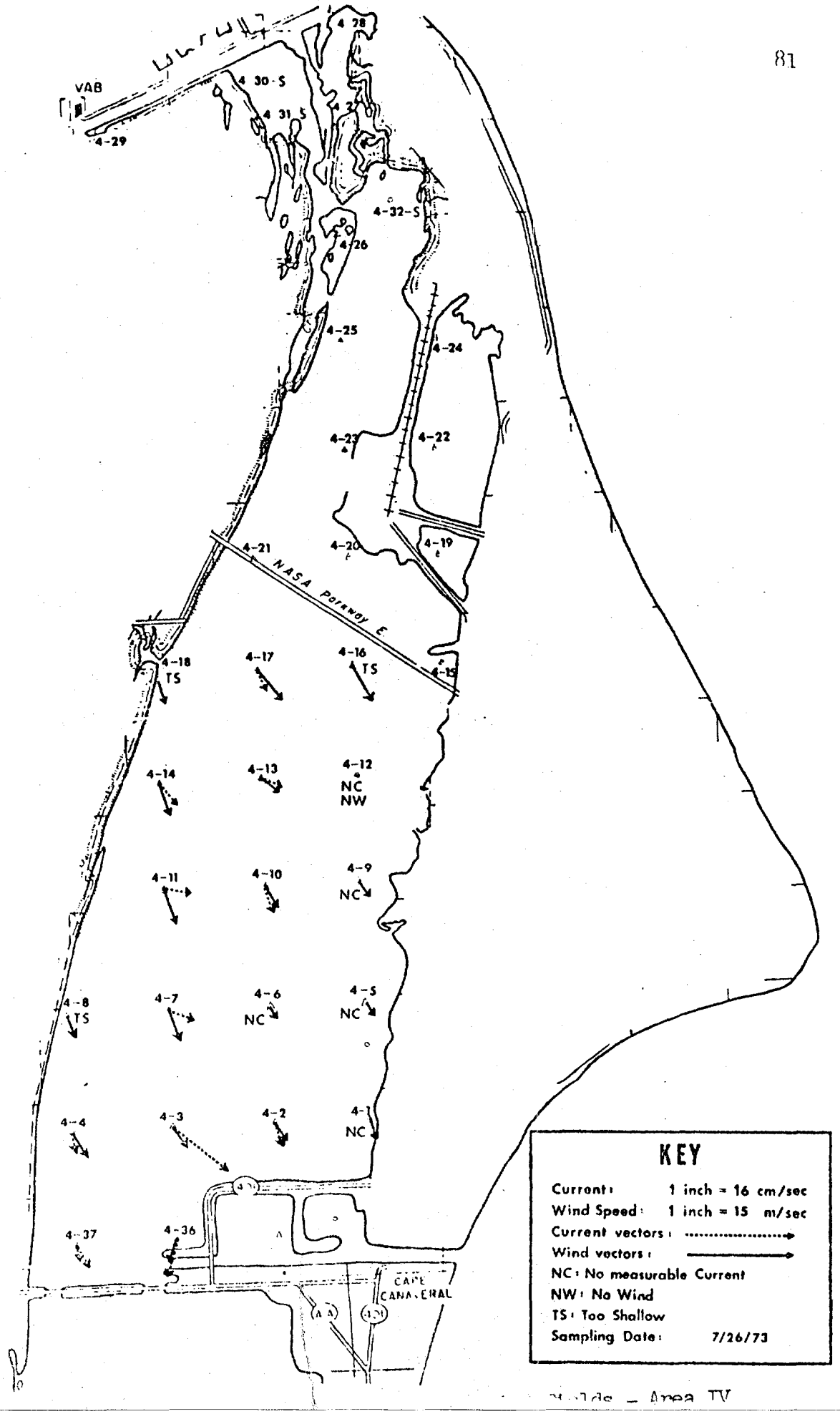


Fields - Area IV

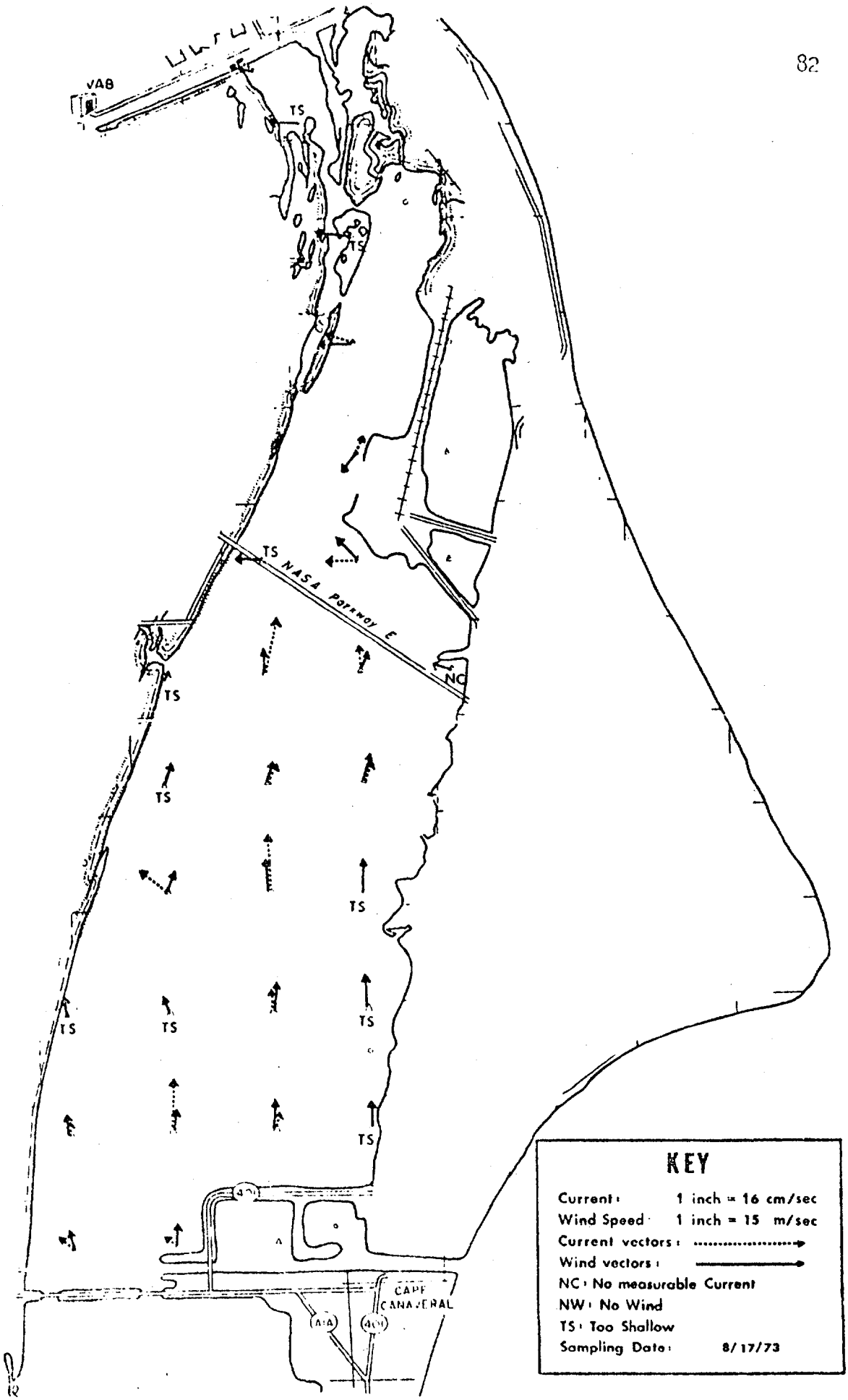


CHART 1 S. Measured current and wind fields- Area IV

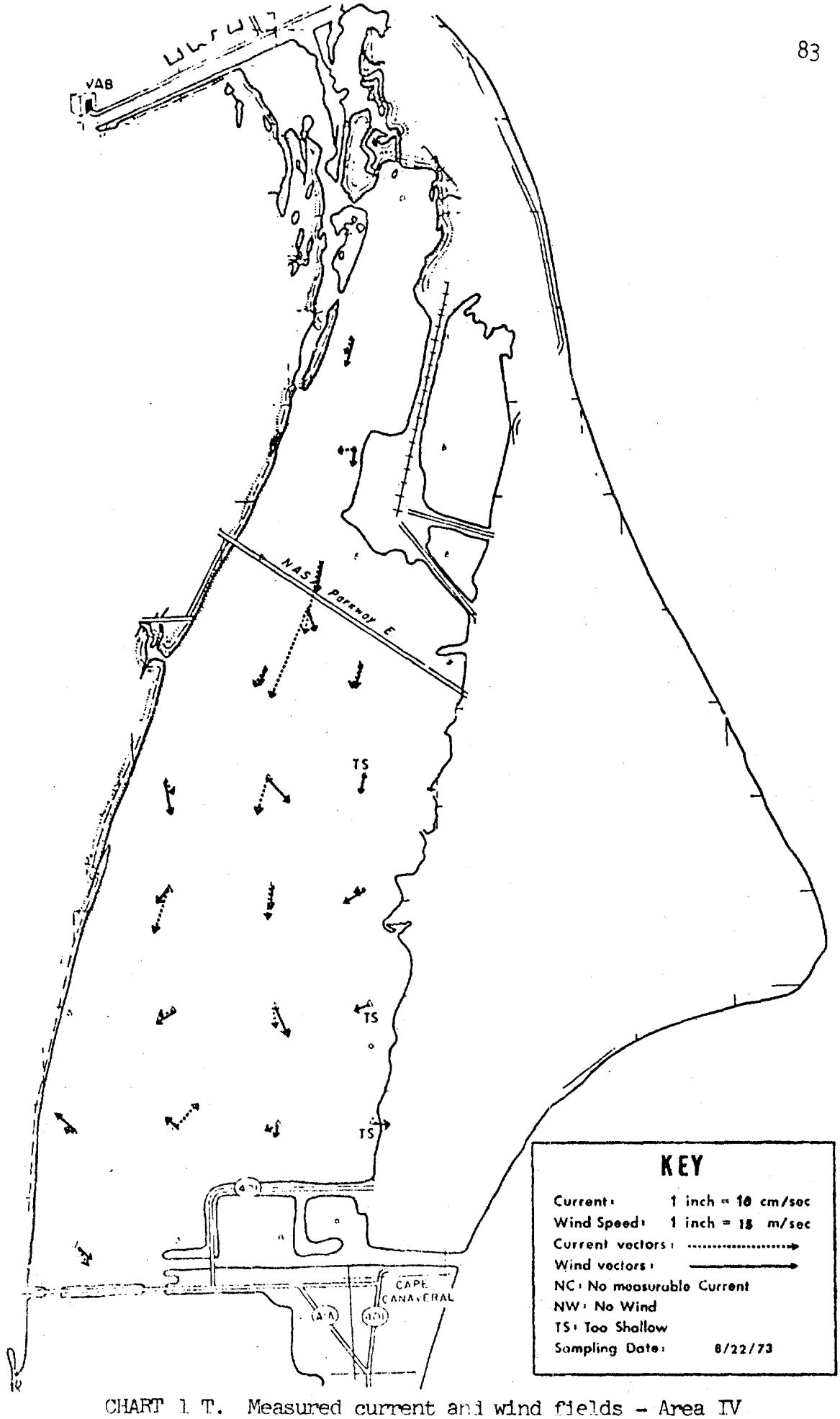


CHART 1 T. Measured current and wind fields - Area IV

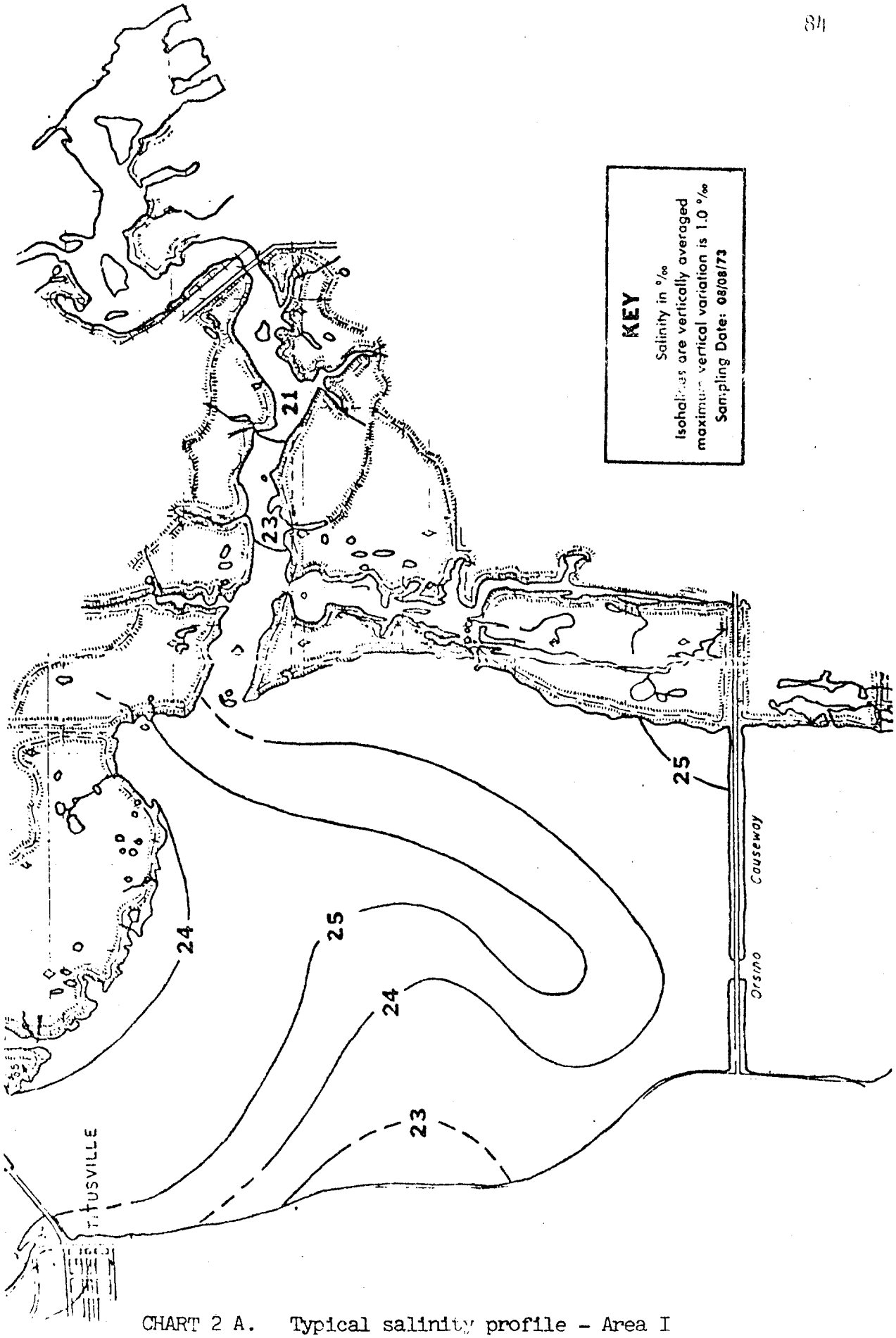


CHART 2 A. Typical salinity profile - Area I

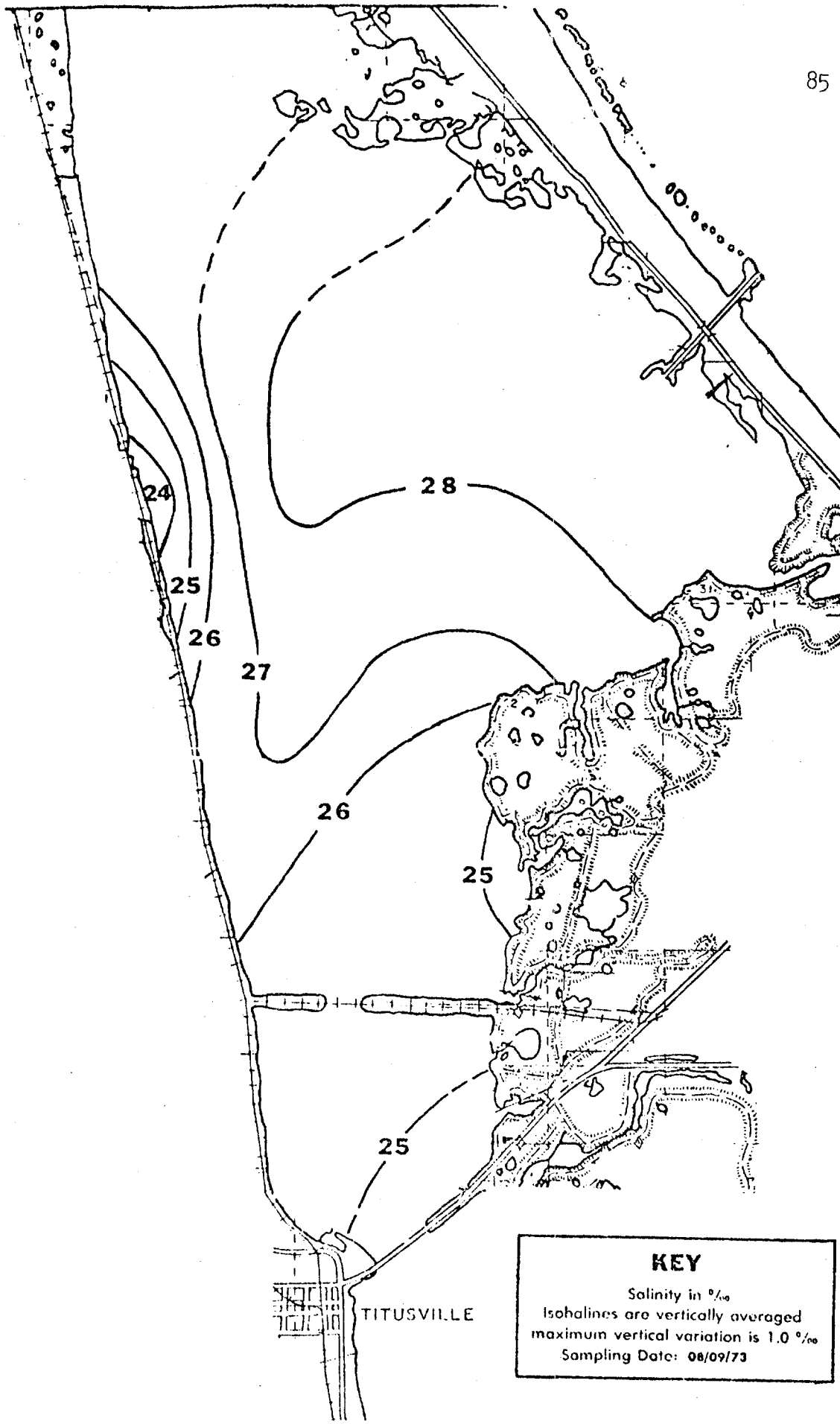
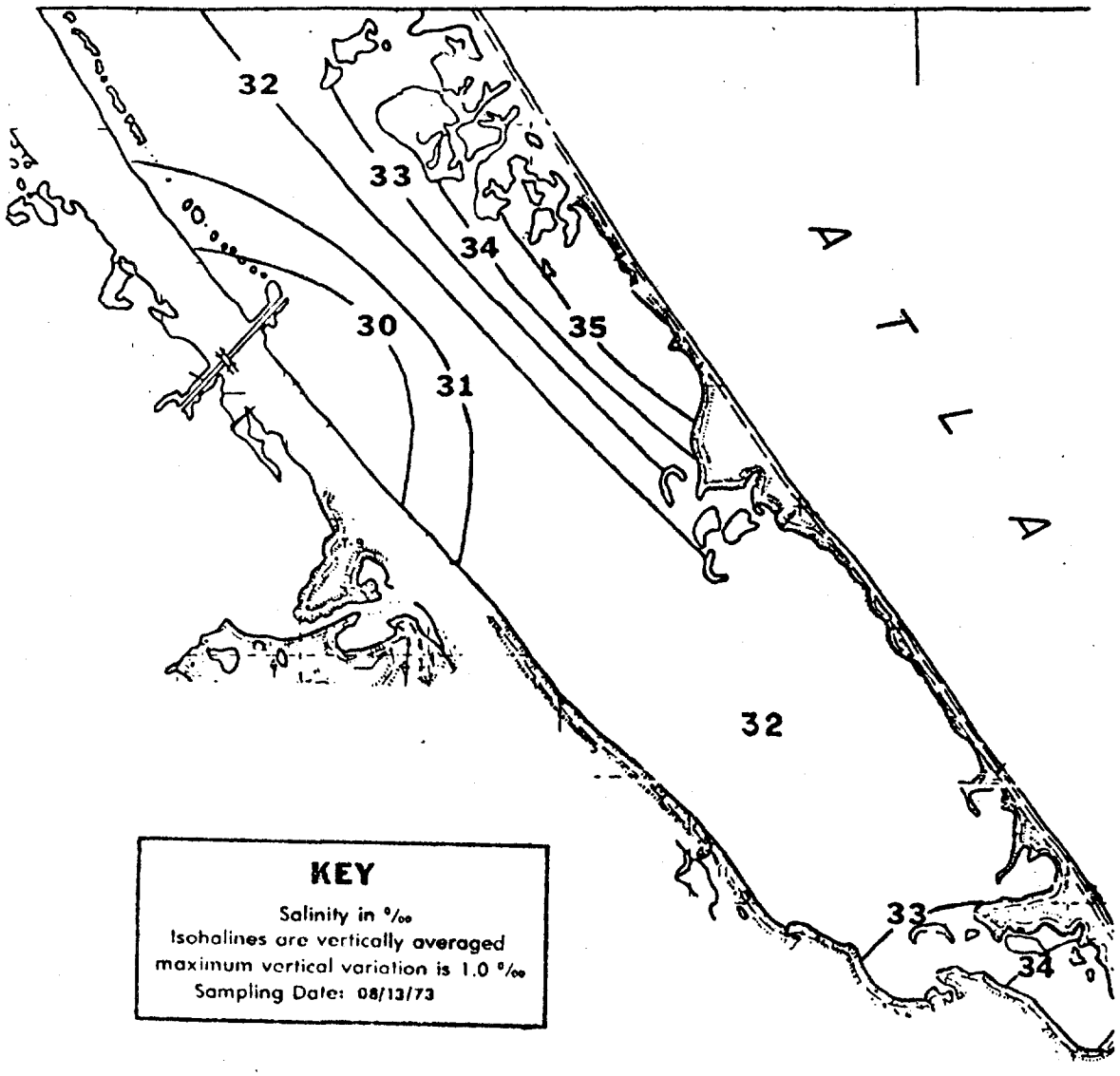


CHART 2 B. Typical salinity profile - Area II



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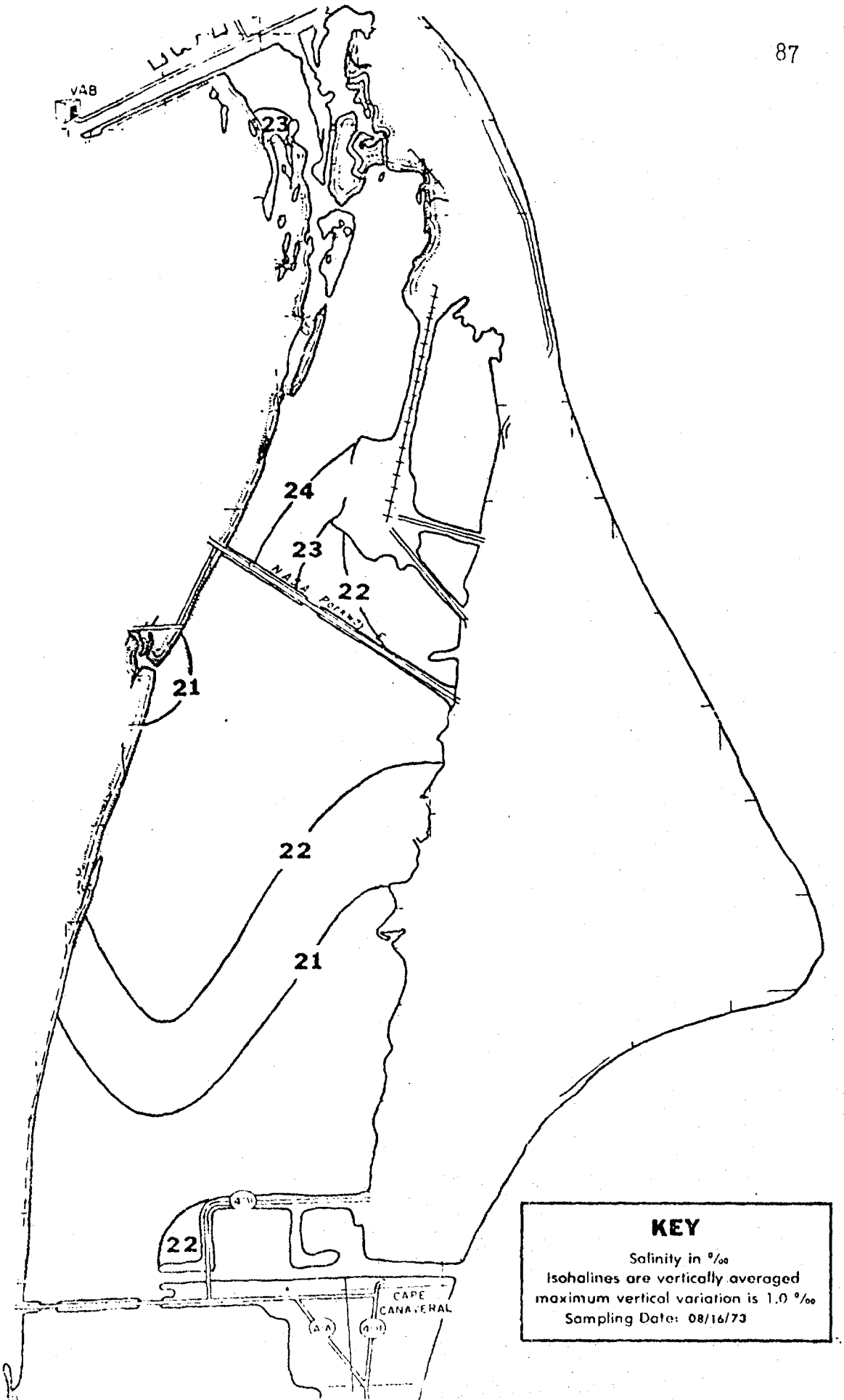


CHART 2 D. Typical salinity profile - Area IV

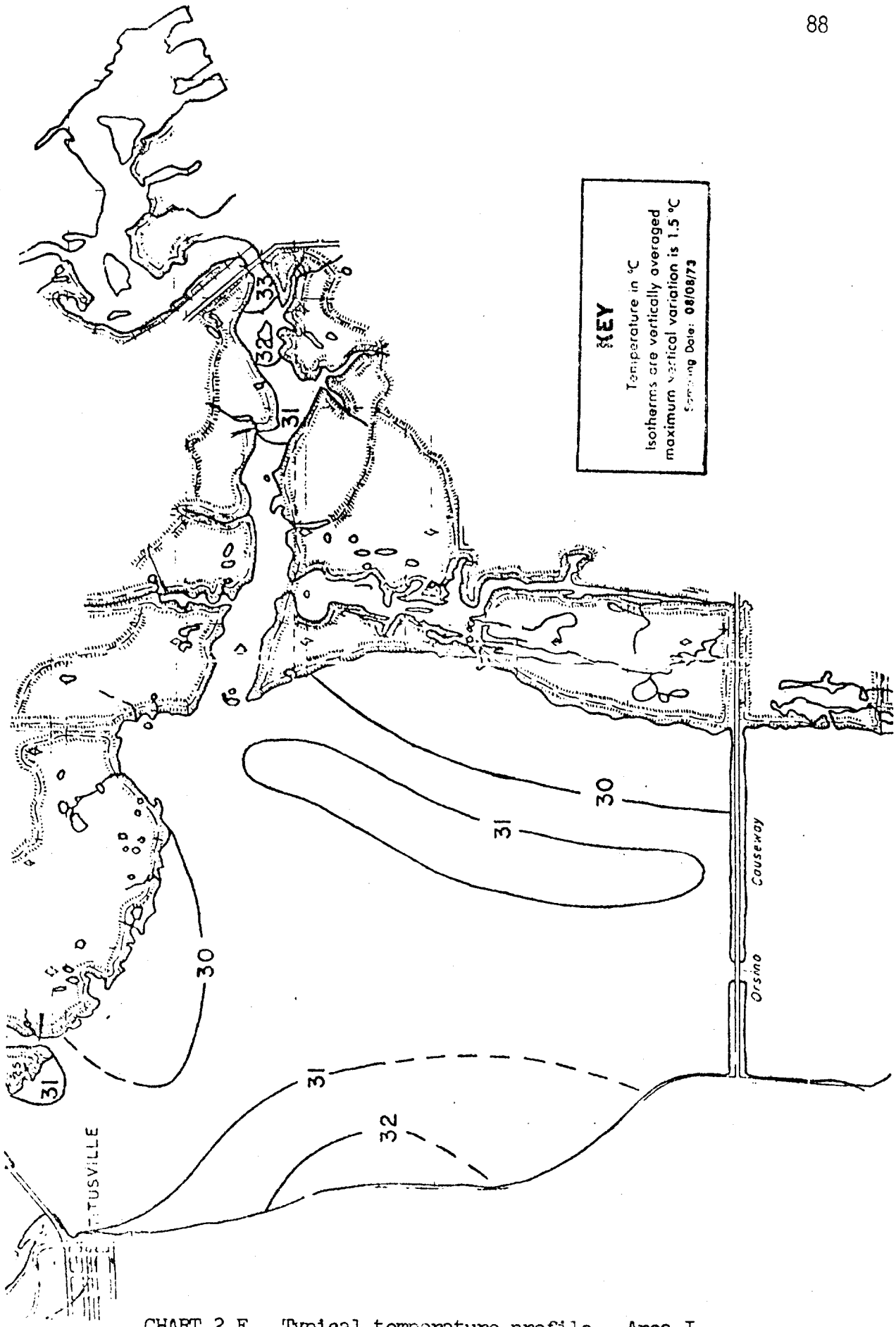


CHART 2 E. Typical temperature profile - Area I

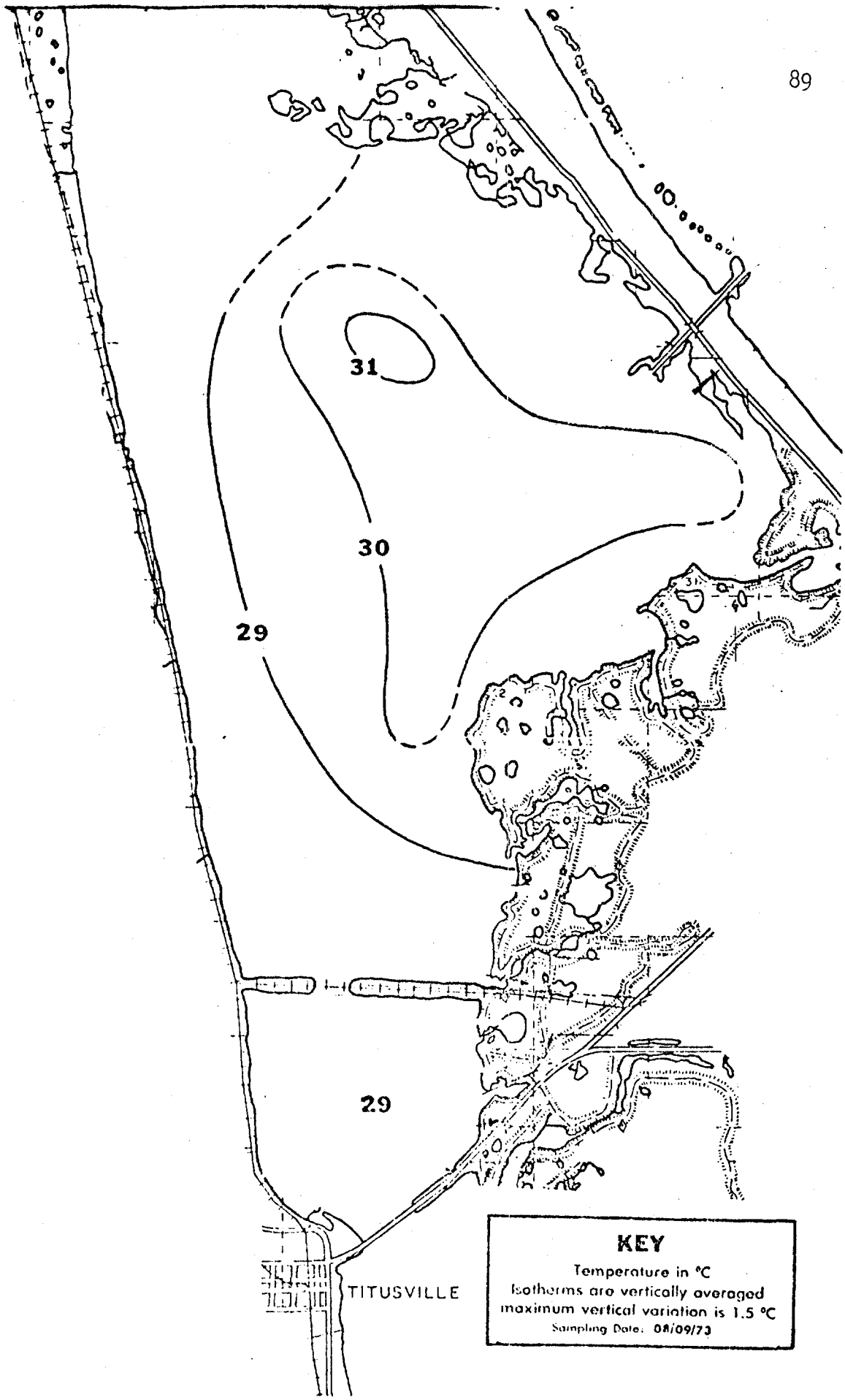
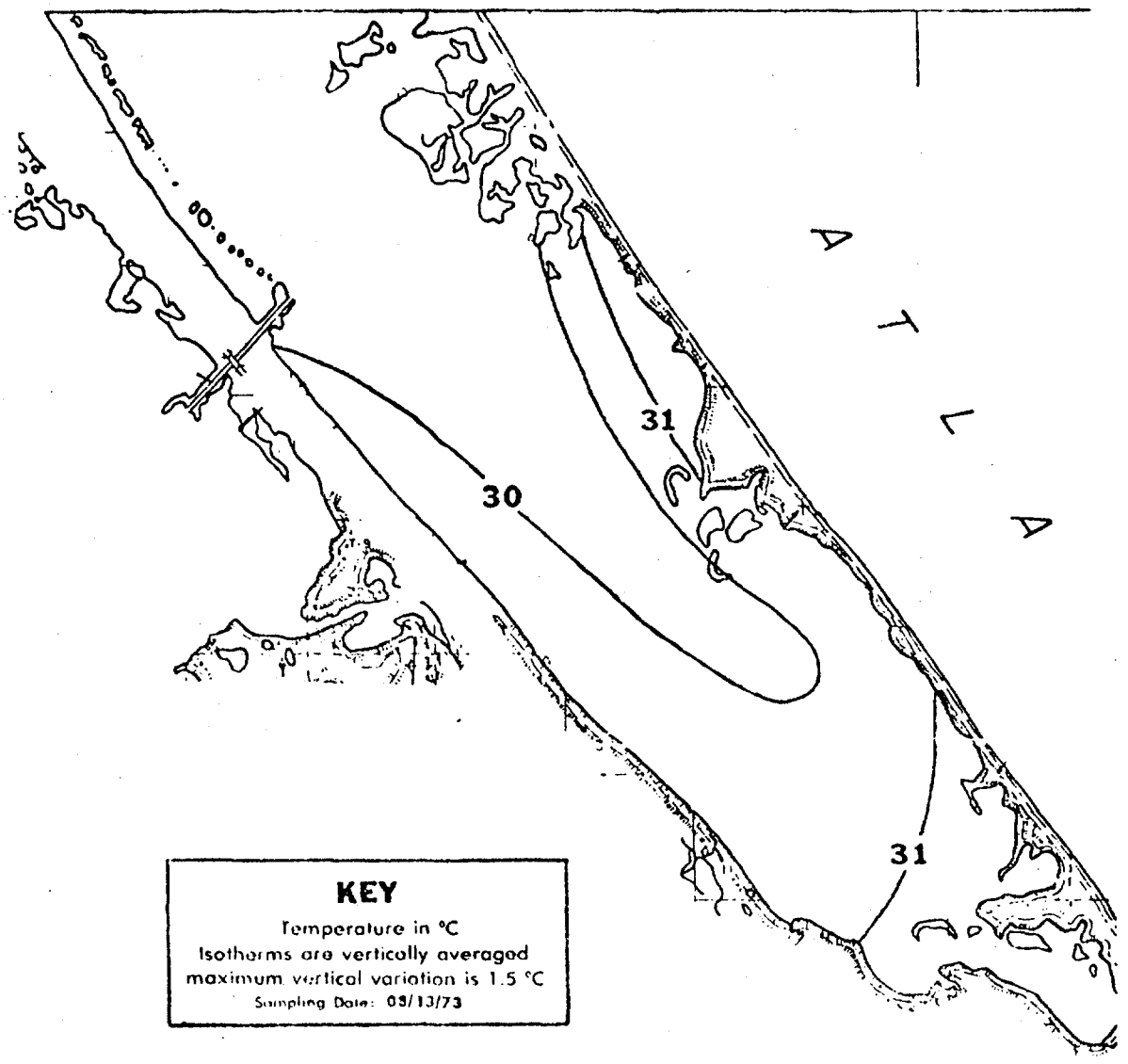


CHART 2 F. Typical temperature profile - Area II



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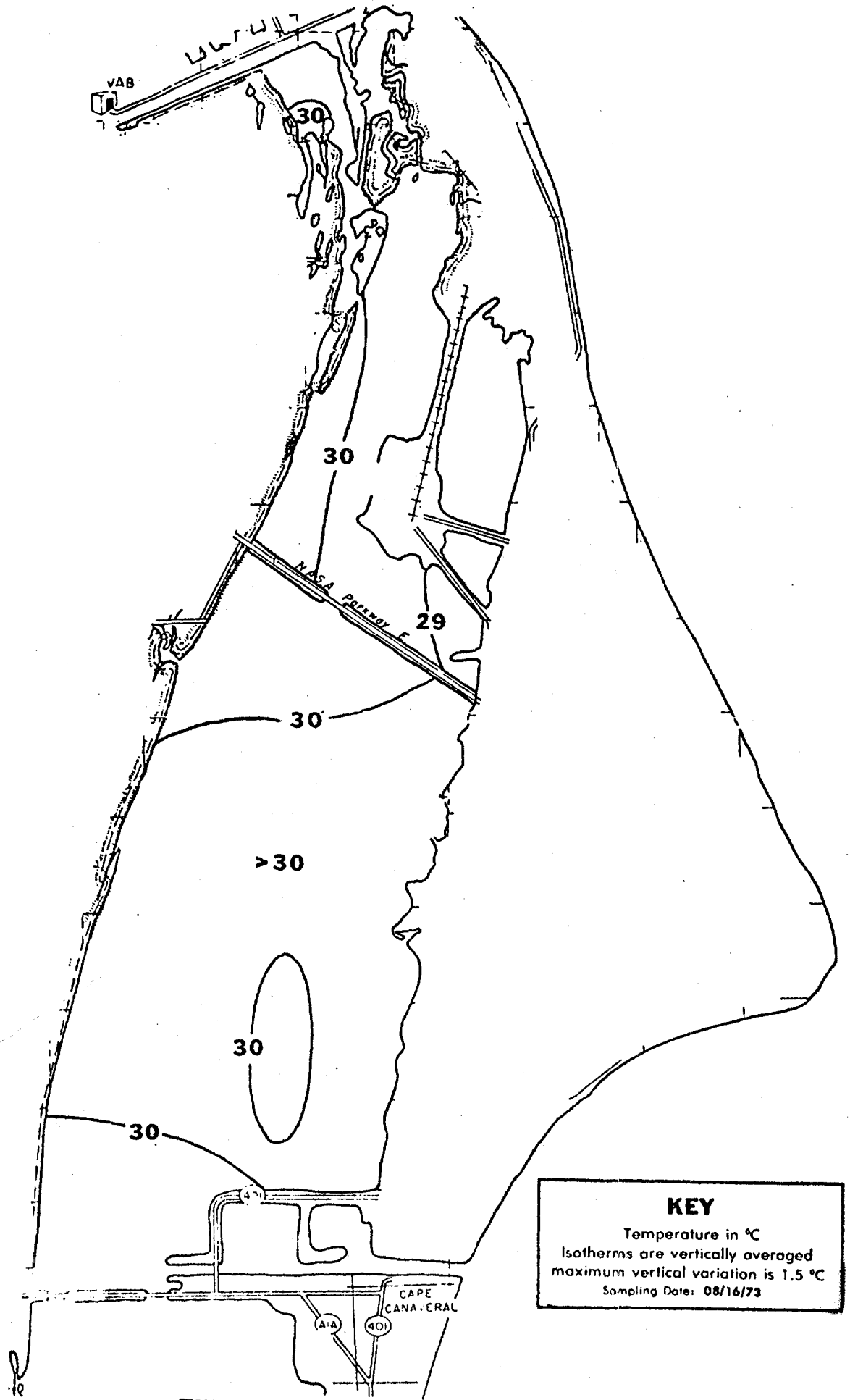

CHART 2 H. Typical temperature profile - Area IV

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Section V, Article 15

A Study of the Transport of Water Through the Haulover Canal

David Richard Browne

A STUDY OF THE TRANSPORT OF WATER THROUGH THE HAULOVER CANAL

by

David Richard Browne

B.S., Physical Sciences

University of Maryland, 1970

Submitted to the Graduate Faculty

in partial fulfillment of

the requirements for the degree of

Master of Science

in

Physical Oceanography

Florida Institute of Technology

1974

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CONTENTS

ABSTRACT

Haulover Canal is a prismatic channel connecting two large bodies of water, the Indian River and the Mosquito Lagoon. The Manning equation for uniform flow is found to be satisfactory in describing the relation between the transport through the canal and the slope of the water surface. The correlation between the suspected driving force, the prevailing winds, and the currents in the canal is established. Also a wind direction causing the maximum transport through the canal is found.

INTRODUCTION

This study is basically one of hydraulics, and to be more specific, one of open channel flow. Much of the literature reviewed has established theoretically and experimentally the same basic equations for both uniform and nonuniform flow in open channels. This has been done to such an extent that open channel flow has been made text book material.

Haulover Canal connects two large bodies of water. The water level of each, as a function of the wind field, undergoes slow changes affecting a flow in the canal in either direction. The rate of change of the water elevations at each end of the canal is believed to be so slow that the flow in the canal may be considered to be steady at any instant. This consideration is evident in the equations of motion developed for the flow through the Haulover Canal.

It will be discussed whether the equation of motion for varied flow or that of uniform flow (or gradually-varied flow) best describes the water transport through the canal as a function of the water level differences for the time period observed. When the flow is uniform, the boundary friction is in balance with the head loss; and therefore, controls the depth-velocity relation for a given flow rate. When the flow is nonuniform, it may be further classified as gradually-varied or rapidly-varied flow. In gradually-varied flow, the local time derivative of the velocity and the advective terms are of such small magnitude that the water surface slope changes slowly; and, therefore, boundary friction very nearly balances the head loss. In rapidly-varied flow, the momentum and inertial forces become more dominant in the role of establishing the water transport in a channel (Daily and Harleman, 1966).

A correlation between the wind field and the water surface slopes and resulting currents will be established. The preferred direction of the wind is practically defined as the direction from where the wind field approaches causing the maximum water surface slope in, and the consequent maximum current through the Haulover Canal; wind magnitude being held constant. The preferred direction of the wind causing this maximum piling of water at the mouths of Haulover Canal was found for the surface and average currents running through the canal and the water level differences between the canal ends. Correlating coefficients were also computed for the above three parameters with the east-west and north-south components of the wind.

LOCATION AND DESCRIPTION OF HAULOVER CANAL

Haulover Canal is part of the Merritt Island Wildlife Refuge in Brevard County, Florida. The canal is located east, across the Indian River, from Titusville on the mainland and is approximately 12 km north of the Vehicle Assembly Building at Kennedy Space Center. The canal connects the Indian River and the Mosquito Lagoon.

Haulover Canal is a prismatic channel (one that is uniform in cross-section and bed slope) running in the 045° and 225° directions. It was designed and excavated by the Army Corps of Engineers. The canal has a trapezoidal cross-section with side slopes of 1 on 1.5. The canal was designed to have a depth of 4.27 m but the average of actual readings indicate an actual depth of 4.53m. There is no bottom slope in the canal and the canal bed is considered parallel with the horizontal datum. The length of Haulover Canal is approximately 2.054 km. From these dimensions the cross-sectional area "A" is calculated to be 203.37m^2, the wetted perimeter "P" is calculated to be 54.43 m, and the hydraulic radius "R", which is the cross-sectional area divided by the wetted perimeter, is calculated to be 3.74 m.

As will be seen later, the hydraulic radius will be an important dimension in considering the flow through the canal.

Figure 1a

HAULOVER CANAL AND SURROUNDING AREA

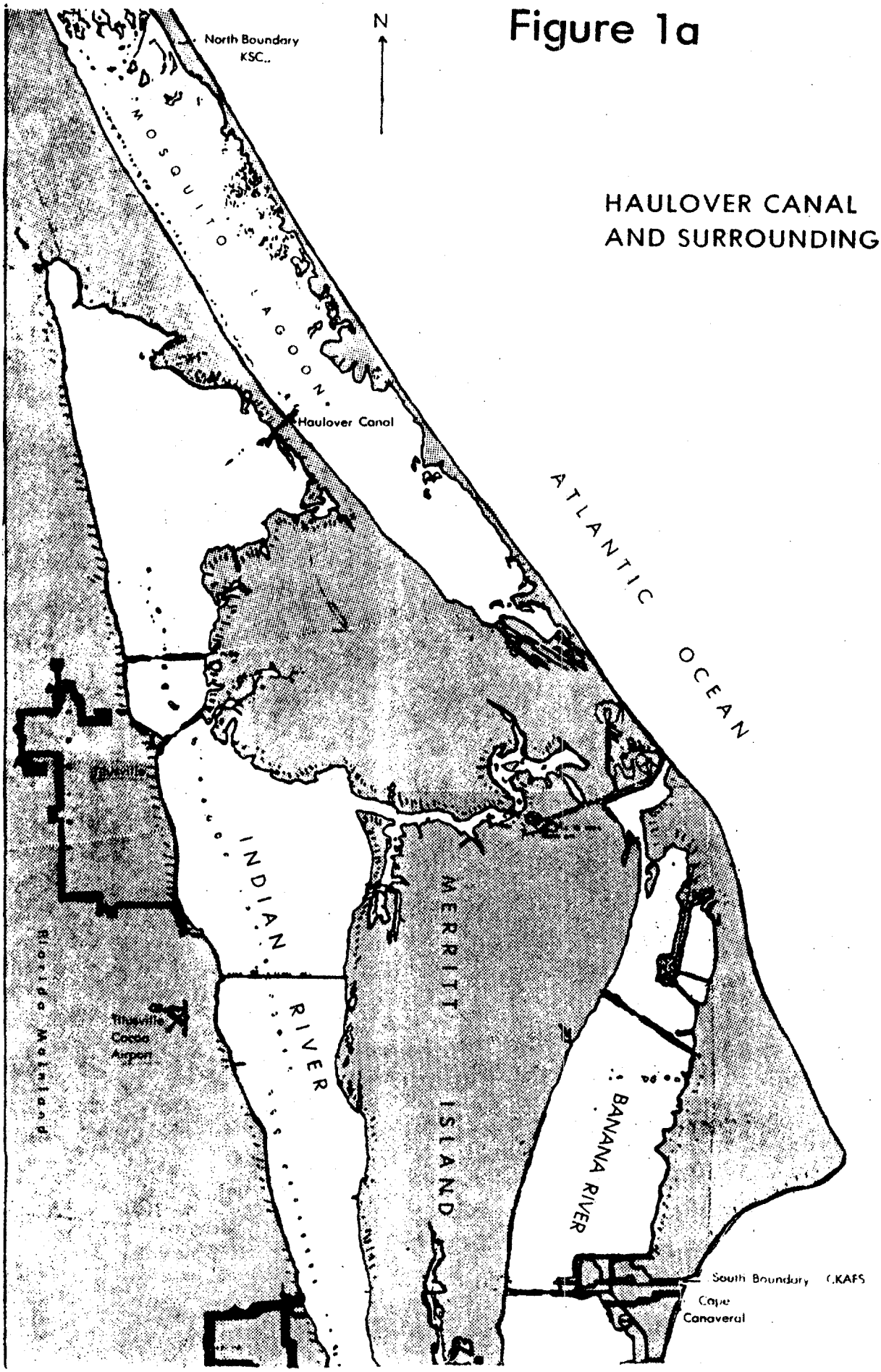
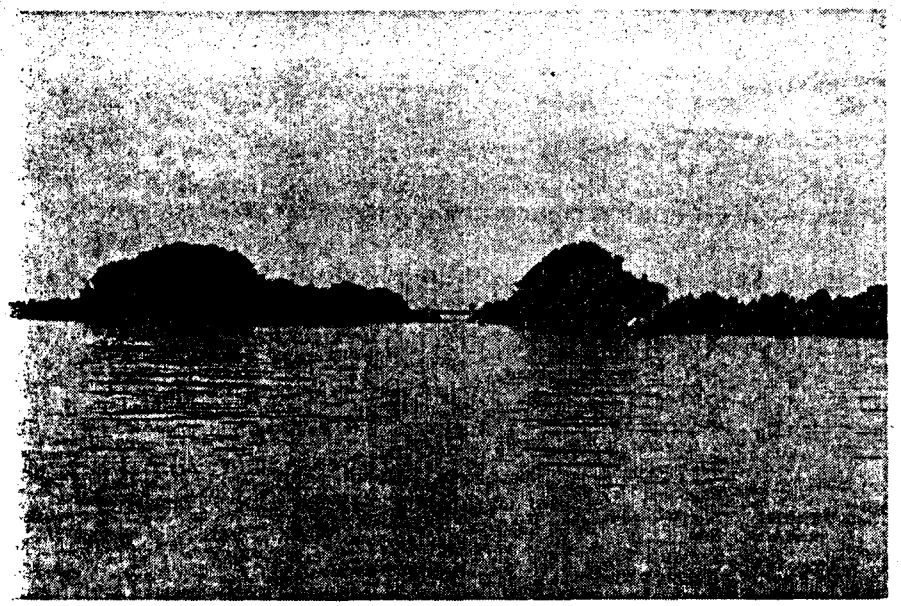
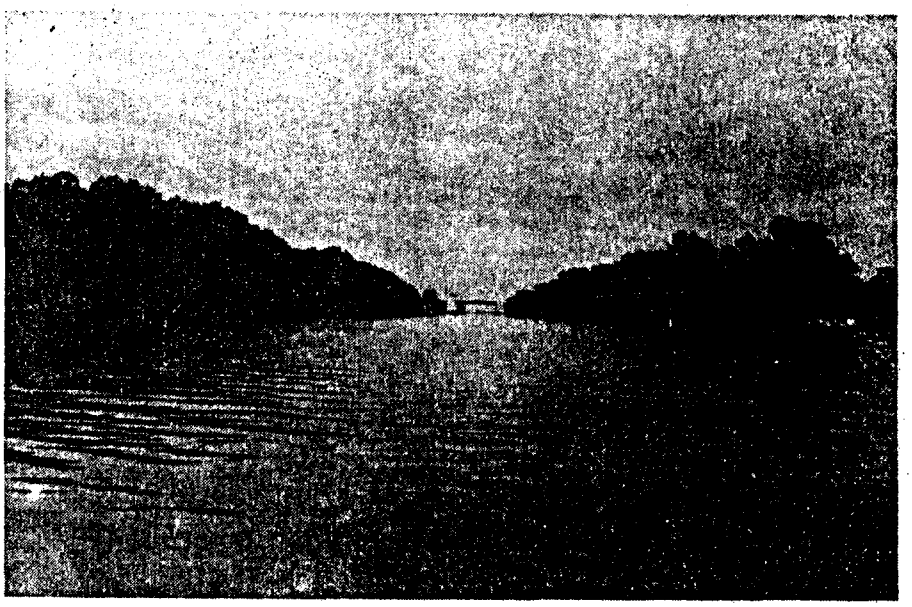


Figure 1b



NORTH-EAST MOUTH OF HAULOVER CANAL



SOUTH-WEST MOUTH OF HAULOVER CANAL

THEORETICAL DISCUSSION

This discussion will concern itself with those subjects pertaining to open-channel flow that apply, or may apply, in particular to the canal being studied. Basic energy principles will be used in our discussion of open-channel flow. Momentum concepts are used when there are severe and unknown energy losses rendering useless any flow description based on energy principles. There were no flows of this type observed at Haulover Canal.

Basic definitions will be introduced, the velocity distribution examined, and the energy equation, deduced from the general equation of motion, will be used to describe different states of flow. Finally, resistance equations describing uniform and non-uniform flow will be developed, and their applicability to the particular situation at Haulover Canal discussed.

A. Definitions

"Steady flow" is flow where the velocity field does not change with time and as a consequence, the depth of flow in an open channel is constant during the time interval considered. The depth of flow, by definition, extends from the water surface to the bottom of the channel. "Unsteady flow" is a flow where discharge or depth of flow does change with time. Of course, in some cases this is dependent on the reference frame of the observer. An observer watching a disturbance, such as a surge wave in its early stages, from the bank would call the flow unsteady; whereas an observer traveling with the wave front sees no change in flow velocity or depth, either upstream or downstream of the front. This is assuming, of course, that those conditions existed before the disturbance was generated.

"Uniform flow" in an open channel is strictly defined as a flow where the velocity is the same in both magnitude and direction throughout the channel. Hydraulicians use a less restrictive definition of uniform flow. This definition allows the velocity of flow to be independent of the width and depth of the channel but not in the direction of the flow, ie. the length of the channel. (Henderson, 1966). Therefore, identical velocity profiles as a function of depth and width exist from channel section to channel section in this relaxed definition of uniform flow. This is in keeping with the definition found in another major textbook (Chow, 1959), that in uniform flow the depth of flow does not change from one channel section to another. The connection between these two definitions can be seen by looking at the specific energy equation discussed later in this section. It follows then, that "varied" flow, the depth of flow and mean velocity may change from point-to-point.

Chow (Chow, 1959) summarizes the types of flow in an outline, and for clarity it is reproduced here:

A. STEADY FLOW

1. Uniform flow
2. Varied flow

   a. Gradually varied flow
   b. Rapidly varied flow

B. UNSTEADY FLOW

1. Unsteady uniform flow
2. Unsteady varied flow

   a. Gradually varied unsteady flow
   b. Rapidly varied unsteady flow

It is noted that the unsteady uniform flow is a rare occurrence, and when one refers to "unsteady flow" he usually means "unsteady varied flow."

The state of flow is governed by the relative magnitude of the inertial forces in comparison to the forces of viscosity. A flow is said to be "laminar" if the viscous forces dominate and the water particles move in definite streamlines. In "turbulent" flow, the inertial forces dominate and the water particles, although moving "forward," are moving in unfixed erratic paths. The effect of the viscous and inertial forces are compared by the use of the "Reynold's number" defined as

$$R = \frac{VL}{\nu}$$

V = velocity of flow

L = characteristic length, which is equal to the hydraulic radius, "R", of the channel.

ν = the kinematic viscosity of water

Note: The hydraulic radius is the cross-sectional area of the channel divided by its wetted perimeter.

Experimental evidence has shown that the flow in open channels changes from laminar to turbulent at the critical Reynold's number of 500 (Chow, 1959).

Gravity also affects the state of flow, and this effect is represented by the Froude number. This dimensionless number is the ratio of the inertial forces to the gravity forces. It is defined as

$$F = \frac{V}{\sqrt{gL}}$$

V = mean velocity of flow.

g = acceleration of gravity.

L = characteristic length which is the "hydraulic depth" D.

The hydraulic depth is the cross-sectional area of the canal section divided by the width of the free surface.

When $F = 1$ or $V = \sqrt{gD}$, we have a balancing of the inertial force to that of gravity, and the flow is said to be in a "critical" state. When $F<1$, or $V<\sqrt{gD}$, the flow is "subcritical." Gravity dominates over inertial forces in this case and the flow is described as tranquil or streaming. When $F>1$, or $V>\sqrt{gD}$, the flow is "supercritical." In this state, the inertial forces are dominant and the flow is described as shooting or torrential.

Four regimes of flow are possible from the effects of viscosity and gravity. They are: 1) subcritical-laminar, 2) supercritical-laminar, 3) supercritical-turbulent, and 4) subcritical-turbulent. The first two regimes are not usually observed in open-channel flow and are not considered in engineering problems (Chow, 1959).

The analysis carried on later in this work will determine the usual flow regime and type observed in the Haulover Canal.

B. Basic Velocity Distribution

The velocity profile either as a function of depth or across a channel section is not uniform due to the viscous drag effects near the channel boundaries. If the non-uniformity in the velocity profiles along the channel cross-section is great enough, the true velocity head is generally greater than that calculated by using the mean velocity. Coriolis (Coriolis, 1836) proposed a velocity-distribution coefficient to correct this discrepancy in the velocity head.

Coriolis' coefficient or energy coefficient α is defined by

$$\alpha = \frac{\left(\frac{V^2}{2g}\right)_m}{\frac{V_m^2}{2g}}$$

Where V_m = mean velocity

As found in the literature α ranges from a value of 1.00 to a value of 2.00.

The severity of departure of the cross-sectional velocity distribution from that of a uniform profile in an open channel is determined by a number of factors. Aside from the fact that α has a much higher value for laminar flow than for turbulent flow which is found in nature, the degree of uniformity in the channel cross-section is the most dominate factor. Experiments have shown that the value of α is close to unity for prismatic channels of uniform cross-section and fairly straight alignment. Therefore, for a channel with these characteristics, α is assumed to be unity due to the uncertainties involved in flow computations (Henderson, 1966).

The fact that a channel is "wide open" also affects the velocity distribution. Experiments have shown that the velocity distribution in the central region of a "wide

open" rectangular canal whose width is greater than 5-to-10 times the depth (depending on the surface roughness), will be the same as the velocity distribution that would be found in a rectangular channel of infinite width. That is to say that the side walls of a canal with the above width-to-depth ratio have almost no affect on the velocity distribution in the central region of the canal section. Therefore, for a wide open channel, as defined, the velocity distribution may be thought of as two-dimensional for experimental and analytical purposes (Chow, 1959).

In "wide-open" channels, the vertical velocity profile is of more importance to consider than the velocity profile with the width of the channel in establishing the mean velocity. General conclusions concerned with the vertical velocity profile found by many investigators and summed up by King (King, 1954) are stated here: 1) The maximum velocity occurs somewhere between the free surface in the case of a shallow stream down to approximately 0.25 of the depth in the case of a deep channel, 2) The mean velocity of the flow in the vertical is ordinarily between 0.55 and 0.65 of the depth of flow. Measurements at 0.6 of the depth usually gives the mean velocity with about 5 percent accuracy, 3) The mean of measurements at 0.2 and 0.8 of the depth of flow gives the average current velocity to within 2 percent, 4) The mean velocity of the flow approaches an upper limit of 95 percent of the surface velocity of flow in a deep open channel; whereas, in a shallow stream the mean velocity of flow approaches a lower limit of 80 percent of the surface velocity.

A mathematical description of the velocity profile with depth of a wide open channel is deferred to the next section where the boundary layer development is discussed first.

C. Boundary Layer Development and Velocity Distribution of Turbulent Flow

In order to discuss later the effects of boundary roughness on open channel flow, the basic concepts of boundary layer development must first be presented. The discussion which follows will be of a qualitative nature.

The flow entering the channel is assumed to be laminar and uniform, and the depth of flow is large enough to be considered constant on entering the channel. (Figure 2). The flow above line abc is uniform, while the velocity of the flow below varies with the distance to the boundary. The latter region of flow is the "boundary layer." As can be seen, the boundary layer thickness δ increases until point b is reached where we have a turbulent boundary region and a laminar boundary layer developing out of a purely laminar flow. δ, now defined as the vertical distance from the boundary to the point of flow where the velocity $v_o = 0.99v_{max}$, (Bauer, 1954) increases at a faster rate until the turbulent boundary region is fully developed (i.e., reaches the flow surface). The velocity profile in the turbulent layer is logarithmic as developed by Prandtl and Von Karman (O'Brien, 1937).

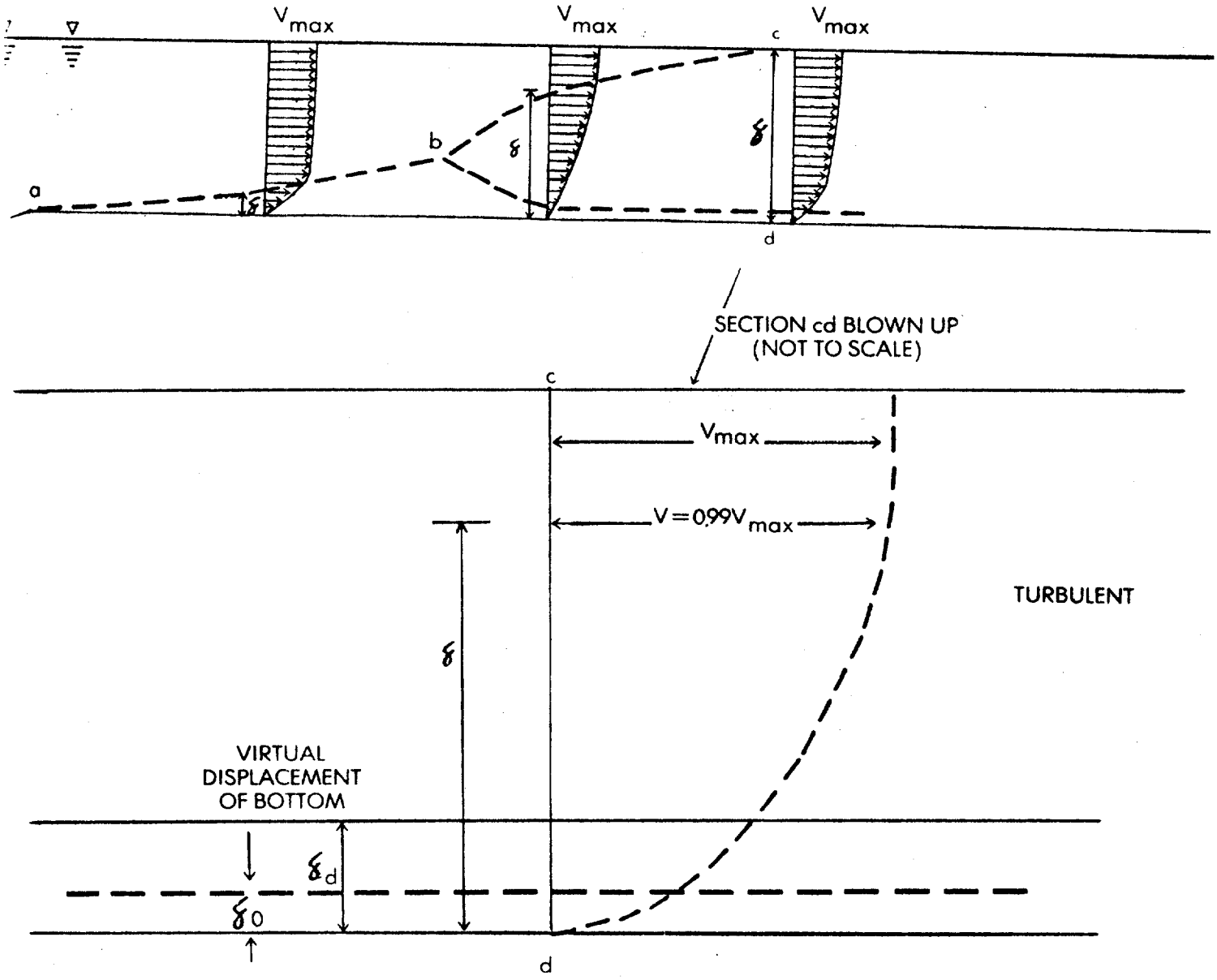
At a distance δ_d above the channel bottom lies the bottom of the turbulent boundary region and the top edge of the transitional layer. This point is called the "virtual bottom" of the channel which is in effect a ficticious vertical displacement of the channel bottom caused by the boundary layer. It is defined as

$$\delta_d \qquad \int_0^{\delta} \left(1 - \frac{v}{v_o}\right) dy \cong (0.100)\,\delta \text{ to } (0.125)\,\delta$$

where v is the flow velocity at a distance y from the channel bottom (Delleur, 1957; Bauer, 1954).

Figure 2

DEVELOPMENT OF BOUNDARY LAYER IN AN OPEN CHANNEL
(NOT TO SCALE)



In reducing the depth of flow from y to y- δ_d we get the effective cross-sectional area for the turbulent flow. If the average current velocity is obtained from the average of current measurements at different depths, a truer value of the total transport is obtained by using the effective cross-sectional area rather than a geometrical one. Due to the particular method used in this work of measuring the average velocity, the free-instrument method, the effect of the laminar flow near the bottom is inherent in the measured value of the average velocity. Therefore, in this case, the geometrical cross-sectional area is used in the calculation of the total transport in the Haulover canal.

Within this δ_d lies the laminar boundary layer of thickness δ_o , and it is the effect of the bottom surface on this laminar sublayer that determines how the surface roughness will affect the total flow regime.

If the laminar sublayer completely submerges the roughness elements we have what is called a "smooth channel," and the roughness elements have no effect on the turbulent boundary layer. If the effective height of the roughness elements is of sufficient magnitude to disturb the laminar sublayer, they will also effect the total flow in the channel. We then, appropriately enough, call the channel a "rough channel."

It has been determined from ponar grab samples taken from the bottom of the Haulover Canal that the canal bottom and side walls are completely covered with small shells. From this and the fact that the Manning coefficient computed from the current data is relatively low, we see that the Haulover Canal is best described by the former classification.

If the flow is uniform the velocity distribution will be fully developed at cd and will have that definite pattern thereafter.

As said before, the velocity profile with depth in a wide open channel is logarithmic in the turbulent region. First consideration in deriving the expression

defining the profile is Prandtl's shearing stress (Prandtl, 1952) at any point in the turbulent flow moving over a solid surface:

$$\tau = \rho L^2 \left|\frac{\partial v}{\partial y}\right| \frac{\partial v}{\partial y}$$

where

ρ = mass density

L = mixing length which is proportional to the depth of flow y.

Prandtl assumed the shear stress to be constant in the region close to the boundary and equal to τ_o where τ_o is the average value of the tractive force per unit wetted area of the boundary. τ_o is called the unit tractive force and is defined by

$$\tau_o = \frac{WALS}{PL} = WRS$$

where W=ρ =unit weight of fluid

P =wetted perimeter of the channel

A =cross-section area of the channel

R =hydraulic radius of the channel

S =slope of the channel bed surface

We see that the expression for Prandtl's shearing stress may be rearranged to show that

$$dv = \frac{1}{\kappa}\sqrt{\frac{\tau_o}{\rho}}\,\frac{dy}{y}$$

where κ is the Von Karman constant of proportionality between L and y and is approximately equal to 0.40. We then see that

$$\int_{\delta_o}^{y} dv = 2.5\sqrt{\frac{\tau_o}{\rho}} \int_{\delta_o}^{y} \frac{dy}{y} = 2.5\sqrt{gRS}\,\ln\frac{y}{y_o}$$

where, upon integration,

$$v = 2.5\sqrt{gRS}\ \ln\frac{y}{y'}$$

y' is a constant of integration, which, as found by Nikuradse, depends on the "friction velocity" gRS, and the kinematic viscosity ν for channels which are hydraulically smooth. In this case

$$y' = \frac{m\nu}{\sqrt{gRS}} \quad m = \frac{1}{9} \quad \text{for smooth surfaces.}$$

For rough channel beds y depends solely on the roughness height k (grain size of surface soils) introduced by Nikuradse (R.W. Powell, 1950; Chow, 1959).

$$y' = m\ k \text{ where } m = \frac{1}{30}$$

The expression just found for the vertical velocity profile in the turbulent region is the Prandtl - von Karman universal velocity distribution law. We will refer to this expression in a later discussion on boundary resistance.

D. Equations of Flow

As previously defined a flow is uniform if the velocity distribution across the channel section and with depth is unaltered over the whole canal length. The velocity profiles with respect to these two coordinates are established as soon as the turbulent flow region is fully developed. A consequence of this definition is the the flow possesses a constant mean velocity throughout the canal. Strictly speaking, uniform also requires that the slopes of channel bottom, water surface, and energy line (dH/dx) are all equal.

As indicated earlier, unsteady uniform flow is nonexistent in nature. Flow in natural streams and waterways rarely conforms to the strict conditions of steady uniform flow (Posey and Woodward, 1969). However, uniform flow is frequently assumed by engineers in their flow computations for natural streams. The results are only approximate, but are considered to be a satisfactory solution to most practical problems (Chow, 1959).

A basic equation of the flow in a channel balanced by friction will now be developed. In most books on hydraulics, figures used for defining the variables used in their equations depict the sloping water surface parallel to the sloping channel bottom. This just is not the case at Haulover Canal where wind, and not the bottom slope, is the driving force. The canal bed is horizontal (Army Corps of Engineers) with a typical water surface slope comparable to a flow depth difference of a few inches over a canal length of well over a mile. The range of slopes that are characteristic to Haulover Canal are considered very mild by most investigators in this field. This coupled with the fact that the energy head line is considered to be parallel to the water surface, as expected from continuity, means the flow is not too far from uniform and is at most, a gradually varied flow.

Therefore, the slope of the water surface will be used in place of the channel bed slope in the following conventional arguments used to develop the resistance equation. The channel bed will be the horizontal datum plane.

Now, referring to Figure 4, we know that the pressure distribution is hydrostatic, and therefore the pressure difference on a streamline between the upstream and the downstream face of the element is $-\rho g \Delta y$, where Δy is the rise of the water surface in the downstream direction. Therefore, the downstream component of the force due to this pressure gradient is $-\rho g A \Delta y$ for small $\frac{\Delta y}{y}$.

Two basic assumptions, the first made by Chezy in 1769, are inherent in the resistance term. Chezy stated "..that the force resisting the flow per unit area of the stream bed is proportional to the square of the velocity." The other assumption is that in uniform flow the force causing the flow is equal to the total force of resistance (Chow, 1959; Posey, 1969). Using Posey's solution we use the proportionality factor N where N is a measure of the boundary roughness and turbulence (Posey, 1969; Henderson, 1966; Chow, 1959). Therefore, the force of resistance is represented by

$$N v^2 P \Delta x$$

where P is the wetted perimeter and $P\Delta x$ is the surface contact of the fluid element with the canal bottom. We, therefore, have $-\rho g A \Delta y - N v^2 P \Delta = 0$ since there is no acceleration in uniform flow. Solving for the square of the velocity we have

$$v^2 = \frac{\rho g}{N} \frac{A}{p} \left(-\frac{\Delta y}{\Delta x}\right)$$

We denote the water surface slope, $-\frac{\Delta y}{\Delta x}$, by "S," $\frac{\rho g}{N}$ by "C^2" which is the square of the well known Chezy's C, and $\frac{A}{P}$ by "R," which is the hydraulic radius. We then have for the flow velocity

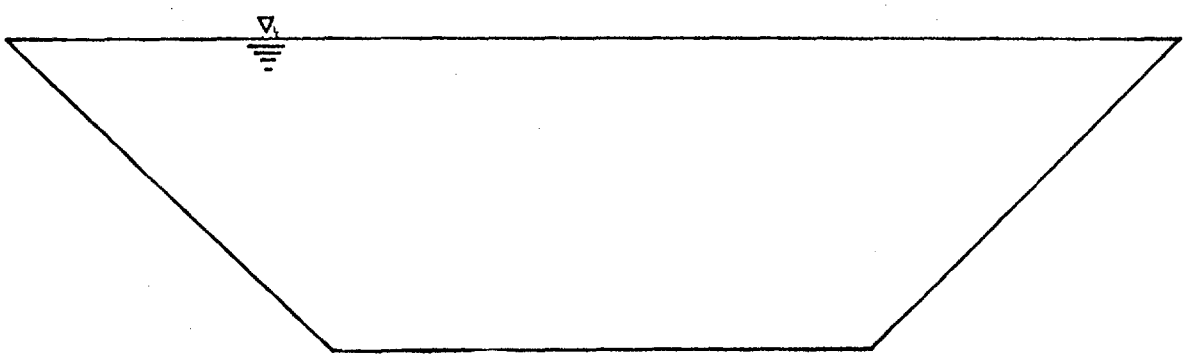
$$v = C\sqrt{RS}$$

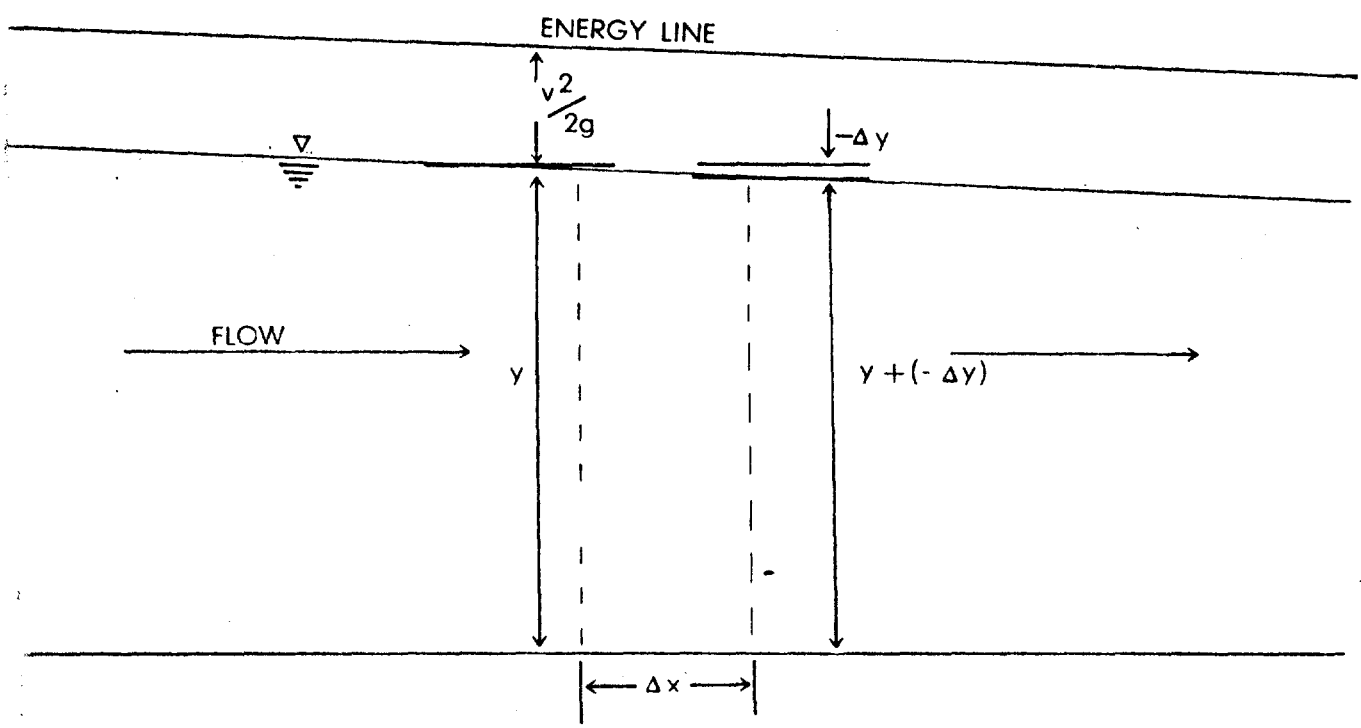
Attempts at a more explicit expression for Chezy's C will be discussed later.

Figure 3

DERIVATION OF RESISTANCE EQUATION

A) CROSS SECTION NOT TO SCALE WITH HAULOVER CANAL





B) WATER SURFACE SLOPE IS EXAGGERATED IN LONGITUDINAL PROFILE

The general case of non-uniform flow with a possible change in velocity down-stream will be looked at now. In this case we clearly have an accelerating flow and the sum of the flow and resistance forces no longer equal zero. The piling of water due to wind over the Mosquito Lagoon and the Indian River is considered to cause the rate of change of water levels to be slow enough so that the flow at any instant is steady. For this reason, the flow will be treated as non-uniform steady flow and, therefore, there will be no local term in the expression for the acceleration. The acceleration will consist solely of the advective term and we have

$$-\rho g A \Delta y - N v^2 P \Delta x = \rho A \Delta x \, v \frac{dv}{dx}$$

$$\Rightarrow N v^2 P \Delta x = -\rho g A \Delta y - \rho A \Delta x \, v \frac{dv}{dx}$$

$$\Rightarrow v^2 = -\frac{\rho g}{NP\Delta x} \left(A\Delta y + A\Delta x \frac{v}{g} \frac{dv}{dx} \right)$$

or

$$v^2 = -\frac{\rho g}{N} R \left(\frac{dy}{dx} + \frac{v}{g} \frac{dv}{dx} \right)$$

$$= -C^2 R \frac{d}{dx} \left(y + \frac{v^2}{2g} \right) \quad \text{where we again let } C^2 = \frac{\rho g}{N}$$

$$= C^2 R S_H$$

$$S_H = -\frac{dH}{dx} = -\frac{d}{dx}\left(y + \frac{v^2}{2g} \right) = \text{slope of the energy line.}$$

Where $y + \frac{v^2}{2g}$ is the specific energy head of the flow through the channel. In uniform flow the slope of the energy line is equal to the slope of the water surface, and following strict requirements, is also equal to the bed slope. However, in flow that is non-uniform the change in the velocity head over the length of the channel $\frac{d}{dx}\left(\frac{v^2}{2g}\right)$, which is our advective term in our equation of motion, is no longer zero and we may express the equation above as

$$v^2 = C^2 R\left(-\frac{dy}{dx} - \frac{d}{dx}\left(\frac{v^2}{2g}\right)\right)$$

again denoting $-\frac{dy}{dx}$ by S and dividing by C^2R we have

$$\frac{v^2}{C^2R} = S - \frac{d}{dx}\left(\frac{v^2}{2g}\right)$$

or

$$S = \frac{v^2}{C^2R} + \frac{d}{dx}\left(\frac{v^2}{2g}\right)$$

which is the classical form of the equation of varied flow. (Bakhmeteff, 1932; Ming Lee, 1952). Here we simply have the uniform flow equation with the added term allowing for the change in velocity downstream. In gradually-varied flow, this term is usually negligible and the uniform flow formula may be used with good accuracy to determine the energy slope. General considerations of continuity would tell us that this is the case at Haulover Canal. This assumption will be shown to be correct by the actual data taken at the canal.

There have been many formulas derived for the determination of Chezy's C appearing in the equations just discussed. The most important are Ganguillet and Kutter's formula in 1869, the Bazin formula in 1897 (Chow, 1959), and the Powell formula in 1950 (Powell, 1959; Chow, 1959). These formulas are more complicated, give results that are, at times, less consistent, or have not been verified in many instances as has the Manning formula. The Manning equation for Chezy's C is the universally accepted equation throughout the Western World. (Posey, 1941; Chow, 1955; Henderson, 1966; King, 1948). The formula that was "wrongly attributed" to Manning in 1891 (Henderson, 1966) is expressed as

$$v = \frac{1}{n} R^{2/3} S^{1/2}$$

where we see that

$$C = \frac{R^{1/6}}{n}$$

where n is the Manning's coefficient of roughness. Manning's n has the units sec $m^{1/3}$ In converting n to units of sec $ft^{-1/3}$ for use with lengths in units of feet the number 1.486 appears in the numerator of the above expression for c. Evidently the literature has found it convenient to leave this conversion factor in the expression of c rather than have seperate tables of n values for each system of units. Due to the imprecision of n the value of 1.49 is more appropriate for the conversion from the metric to the English system.

Determination of the Manning roughness coefficient is one of the greater difficulties in applying Manning's formula to determine the flow through a canal. Various approaches are possible. One is to give weight to all the factors that may affect the friction coefficient. Essentially they are: 1) size and shape of the grains of the material, 2) amount of vegetation, 3) channel cross-sectional irregularity, 4) channel alignment, 5) obstructions, 6) results of silting and scouring. W.L. Cowan introduced a procedure that includes these factors for estimating n. (Cowan, 1956). He set

$$n = (n_0 + n_1 + n_2 + n_3 + n_4)\, m_5$$

where n_0 is a basic value for a straight, uniform, smooth, channel. n_1 through n_4 takes on correction values representing the degree to which each of the factors just mentioned could affect the flow. m_5 is a correction for the meandering of the channel. Although according to the literature, Cowan was correct to attach significance to factors other than just the type material lining the channel wall, his values representing the degree of severity of each factor is consistently high for channels of large hydraulic radius. These values were obtained from experiments with canals ranging in sizes around that of drainage ditches. The lowest possible Manning coefficient attainable using Cowan's values is 0.020 sec $m^{-1/3}$ and there are channels on record with coefficients as low as 0.012 sec $m^{-1/3}$.

Many engineers turn to descriptive tables (King, 1954; Chow, 1959) giving coefficient values for channels classified according to soil types and other major considerations.

Analytical procedures based on the theoretical velocity distribution and on velocity measurements or surface roughness height data have been used. Boyer and others verified the concept of using the logarithmic distribution equation, such as discussed by M.P. O'Brien (M.P. O'Brien, 1937), H. Rouse (Boyer, 1954), and W.B. Langbein (Langbein, 1940), and the Manning equation to solve for the Manning coefficient n as a function of the ratio of the velocities at two-tenths and eight-tenths the depth.

For smooth channels we use the value of $\frac{\nu}{9\sqrt{gRS}}$, obtained from Nikuradse's data for smooth pipes (Chow, 1959), for the constant y' in the universal-velocity-distribution equation. We have

$$v = 2.5\sqrt{gRS}\ \ln\ \frac{9\,y\sqrt{gRS}}{\nu}$$

or

$$v = 5.75\ \sqrt{gRS}\ \log\ \frac{9y\ \sqrt{gRS}}{\nu}$$

The velocity at 0.2y below the surface is

$$v_{0.2} = 5.75\sqrt{gRS}\ \log\ \frac{7.2\,y\ \sqrt{gRS}}{\nu}$$

The velocity at 0.8y below the surface is

$$v_{0.8} = 5.75\ \sqrt{gRS}\ \log\ \frac{1.8\,y\ \sqrt{gRS}}{\nu}$$

Again, "y" is the depth of flow from the channel bottom to the surface. "ν" is the kinematic viscosity of the fluid. Upon eliminating $\sqrt{gRS}$ from these two last expressions and solving for $\log \frac{y\sqrt{gRS}}{\nu}$ we get

$$\log \frac{y\sqrt{gRS}}{\nu} = \frac{0.255\,r - 0.857}{1-r} \qquad \text{where } r = {}^{v_{0.2}}\!/_{v_{0.8}}$$

Substituting this expression for $\log \frac{y\sqrt{gRS}}{\nu}$ in Keulegan's theoretical uniform-flow equation for smooth channels (Keulegan, 1938)

$$V = \sqrt{gRS}\,(3.25 + 5.75 \log \frac{R\sqrt{gRS}}{\nu})$$

and assuming that y = R, the hydraulic radius, we get

$$\frac{V}{\sqrt{gRS}} = \frac{1.78r + 1.68}{(r-1)}$$

From Manning's equation for the velocity v we see that

$$\frac{R^{2/3} S^{1/2}}{n\sqrt{gRS}} = \frac{R^{1/6}}{n^{1/2} g^{1/2}} = \frac{1.78\,r + 1.68}{(r-1)}$$

Solving for the Manning coefficient "n" we finally have

$$n = \frac{R^{1/6}(r-1)}{5.57r + 5.26} \quad \text{sec } m^{-1/3}$$

This equation gives the Manning coefficient for wide open smooth channels where the unit of length is the meter.

For rough channels we use the value of mk for y in the same equation for the vertical velocity distribution used for smooth channels. Nikuradse arrived at the value of 1/30 for m from his data on rough pipes. Using this value we have

$$v = 2.5\sqrt{gRS}\,\ln \frac{30y}{k}$$

which describes the velocity distribution in the turbulent region of flow for wide open

rough channels. "y" is the depth of flow from the channel bottom to the surface and "k" is the roughness height of the bottom. Following the same procedure as for smooth channels and using Keulegan's theoretical uniform flow equation for rough channels (Keulegan, 1938)

$$v = \sqrt{gRS}\,(6.25 + 5.75\ \log\frac{R}{k})$$

We get the same equation for Manning's n, that is

$$n = \frac{R^{1/6}\ (r\text{-}1)}{5.57r + 5.26}\quad \text{sec } m^{-1/3}$$

A reasonable estimate of n can be obtained by this method if velocity measurements are made at the levels mentioned.

Another analytical method which has been more thoroughly investigated is expressing Manning's n in terms of the roughness height k (usually the grain size coarser than 65 percent of the surface sediments). (Boyer, 1954; Chow, 1959). This method is unfavorable in that Manning's n, as discussed earlier, is affected by more factors than just surface roughness. Also, if one is working with a smooth canal surface, which is the case at Haulover Canal with its flat shell layer, the roughness height is small enough to be completely covered by the laminar sublayer and, therefore, has very negligible effect on the turbulent layer.

So far, the best method to date in determining Manning's coefficient is experience and consulting the tables in hydraulics handbooks. If one lacks experience, he may consult the pictures of various canals with Manning's coefficient values displayed in Chow's text. (Chow, 1959).

This investigator will proceed with Boyer's method of determining n by velocity ratios, look over the various tables, and get an estimate of the coefficient by looking at the data trends in this work.

INSTRUMENTATION AND PROCEDURE

A. Instrumentation

Current velocity, wind velocity, and the water levels at both ends of the canal were the parameters measured. Surface current velocity was measured by an aluminum current cross 4 inches in width and a span of 1 yard. The cross itself was suspended by a 1.5-foot line with an orange painted chlorox bottle as a float (Figure 5). A stopwatch was used for time and the range was determined by a range finder with a maximum range of 100 feet with an acceptable error of 5 percent at a range of 40 feet or less.

Average current velocity with respect to depth was measured by the "free-instrument method."(Richardson, 1968). The "free-instrument" in this case was a jar rigged to hold a release mechanism made up of two paper clips. These clips were fashioned in such a way as to support a fishing weight which is released on contact with the bottom of the canal (Figure 6). The jar was made buoyant enough for the jar cap itself to be in the same plane as the water surface when filled to a certain level. When the fishing weight was attached to the release mechanism lever arm, the jar would sink to the bottom where, on contact, the weight would slip off allowing the jar to become buoyant again. The jar would then rise and break the water surface where it would be spotted. During the jar's downward and upward travel, it is deflected horizontally by the current running through the canal. The velocity of the current is different at different depths, and what is sought is the average velocity with respect to depth. The average velocity, as is proven in appendix A, equals the total horizontal deflection from the point of release to the point of surfacing over the total time taken

Figure 4

SURFACE CURRENT CROSS

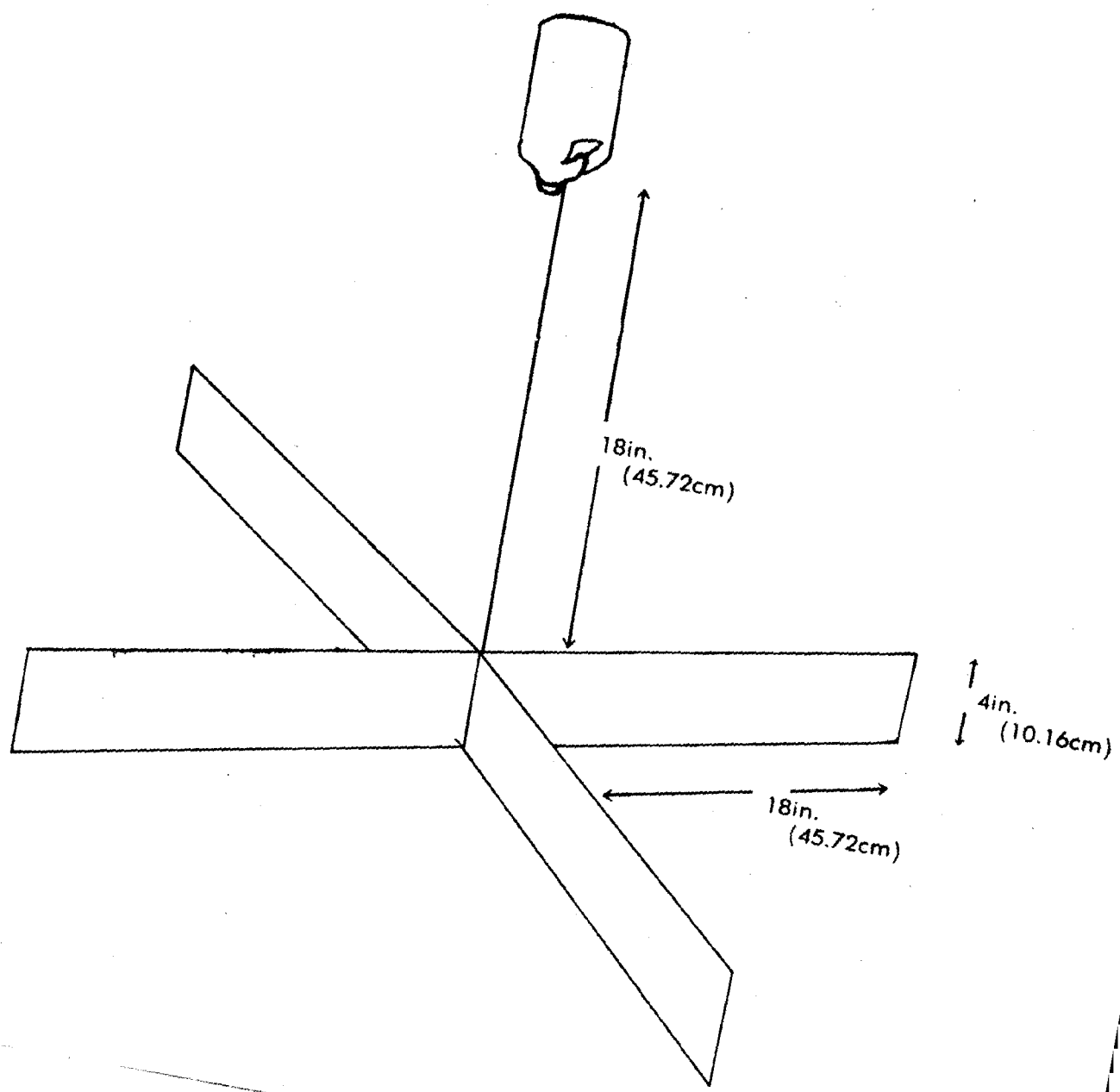
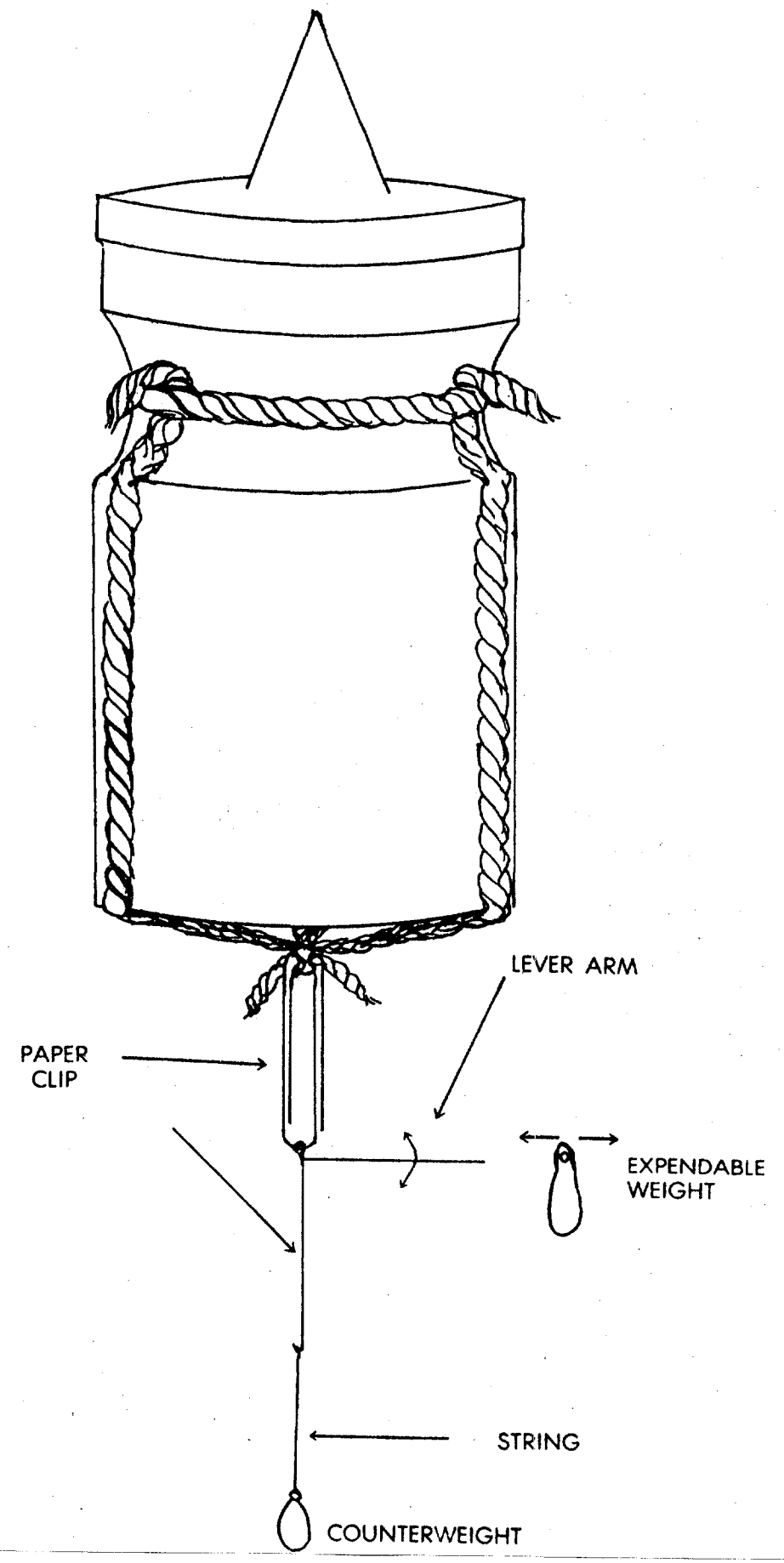


Figure 5

FREE INSTRUMENT JAR



for the jar to traverse between these same two points.

A current cross set at an 11.5-foot depth was also used to indicate any kind of uniformity of the velocity at that depth to that of the surface. The 11.5-foot current cross was also used when the current was too swift to allow the use of the jar, since the jar surfaced out of range of the range finder. In this case, the velocities of both crosses were compared for the degree of uniformity (Chow, 1959).

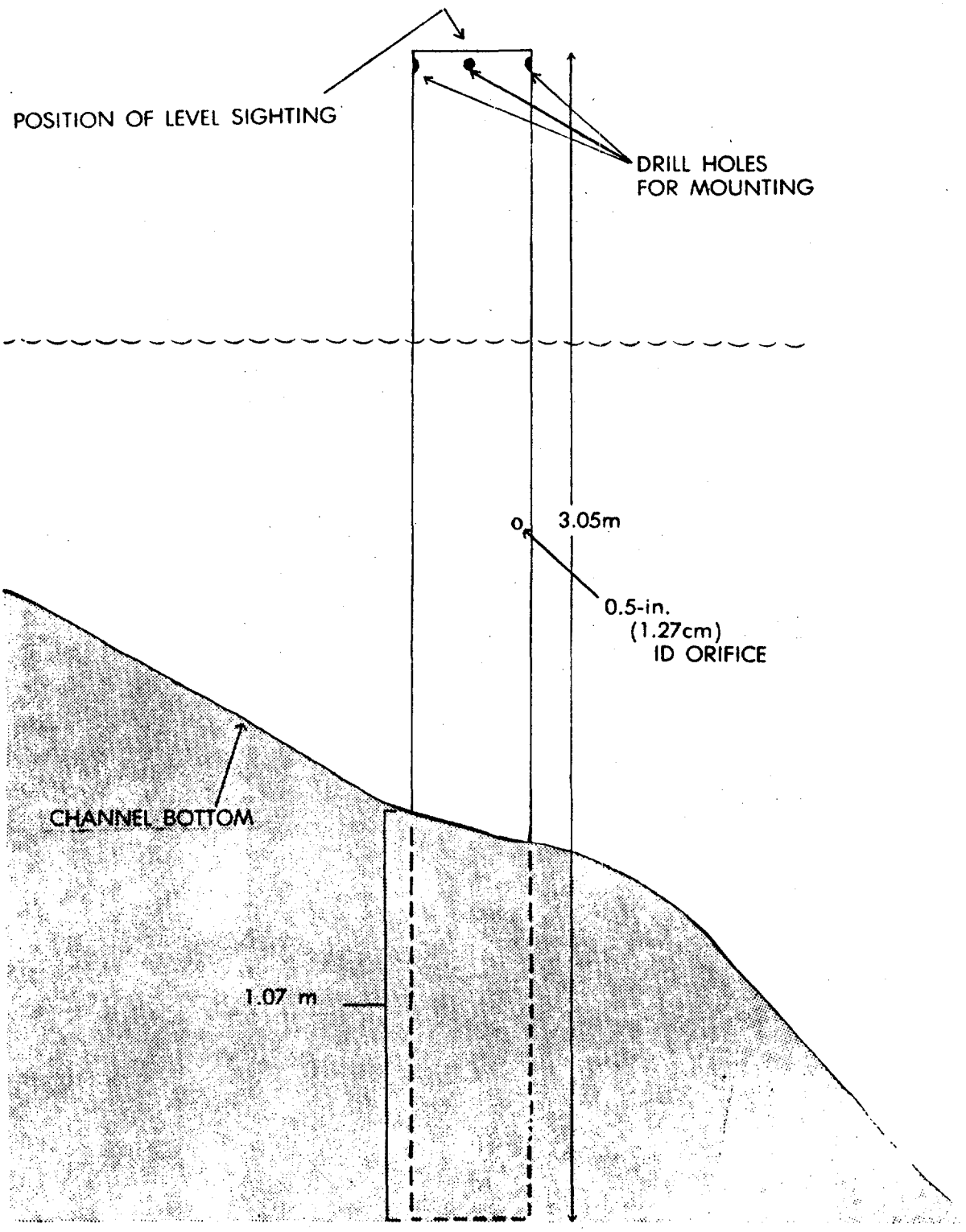
Wind velocity measurements were recorded by the weather service at Kennedy Space Center. The tower where the data were collected is approximately eight miles from the Haulover Canal. Wind velocities at 3.66 and 16.46 meters were measured at this particular tower. Local winds play a negligible effect on the currents through an open channel. (Chow, 1958). The driving mechanism of the currents is considered to be the change in water levels due to the wind piling of water on the Mosquito Lagoon and the Indian River (U.S. Department of Commerce). Thus, wind data from the source already mentioned is considered sufficient.

Water levels at both ends of the canal were recorded both electronically and visually by two stilling well tide gauges with electronic readouts on recorders positioned on the nearby bank. Since no power source was near the area, recorders with windup chart drives were necessary. The gauges were positioned approximately 6 meters from the banks, and 1790 ± 4 meters from each other along the length of the canal.

As shown in Figure 7, the stilling well itself is a 10-foot (3.05m) long, 6.0-inch (15.24cm) ID PVC pipe with a 0.5-inch (1.27cm) diameter hole drilled in the side of the pipe half way down its length. This pipe was jetted and hammered 1.07m into the side wall of the canal. The water line at the time was 1.22m above the bottom.

The rest of the gauge is portable. It is made up of a 6.0-inch (15.24cm) ID PVC

Figure 6a


POSITION OF LEVEL SIGHTING
DRILL HOLES
FOR MOUNTING
3.05m
0.5-in.
(1.27cm)
ID ORIFICE
CHANNEL BOTTOM
1.07 m

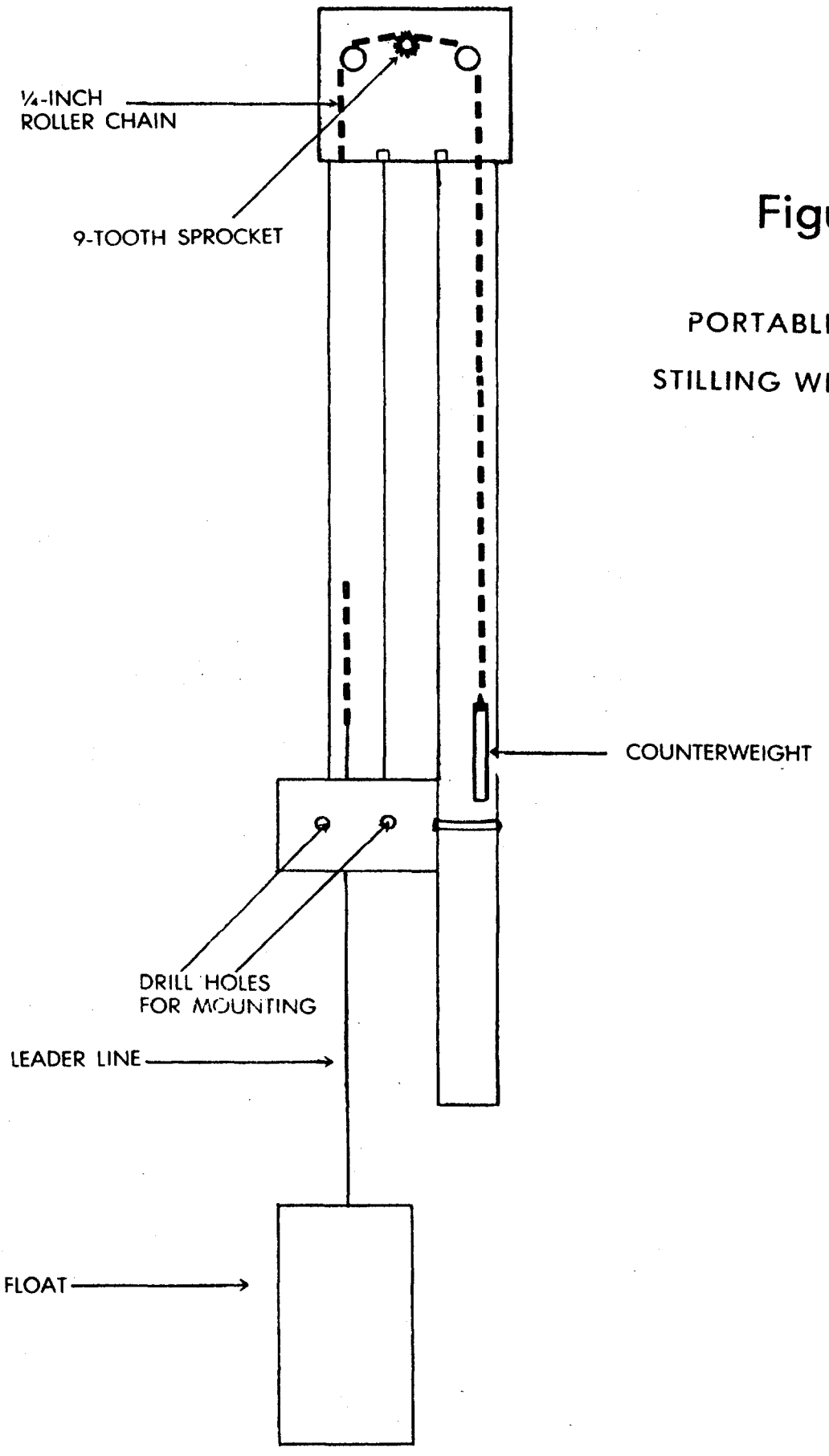


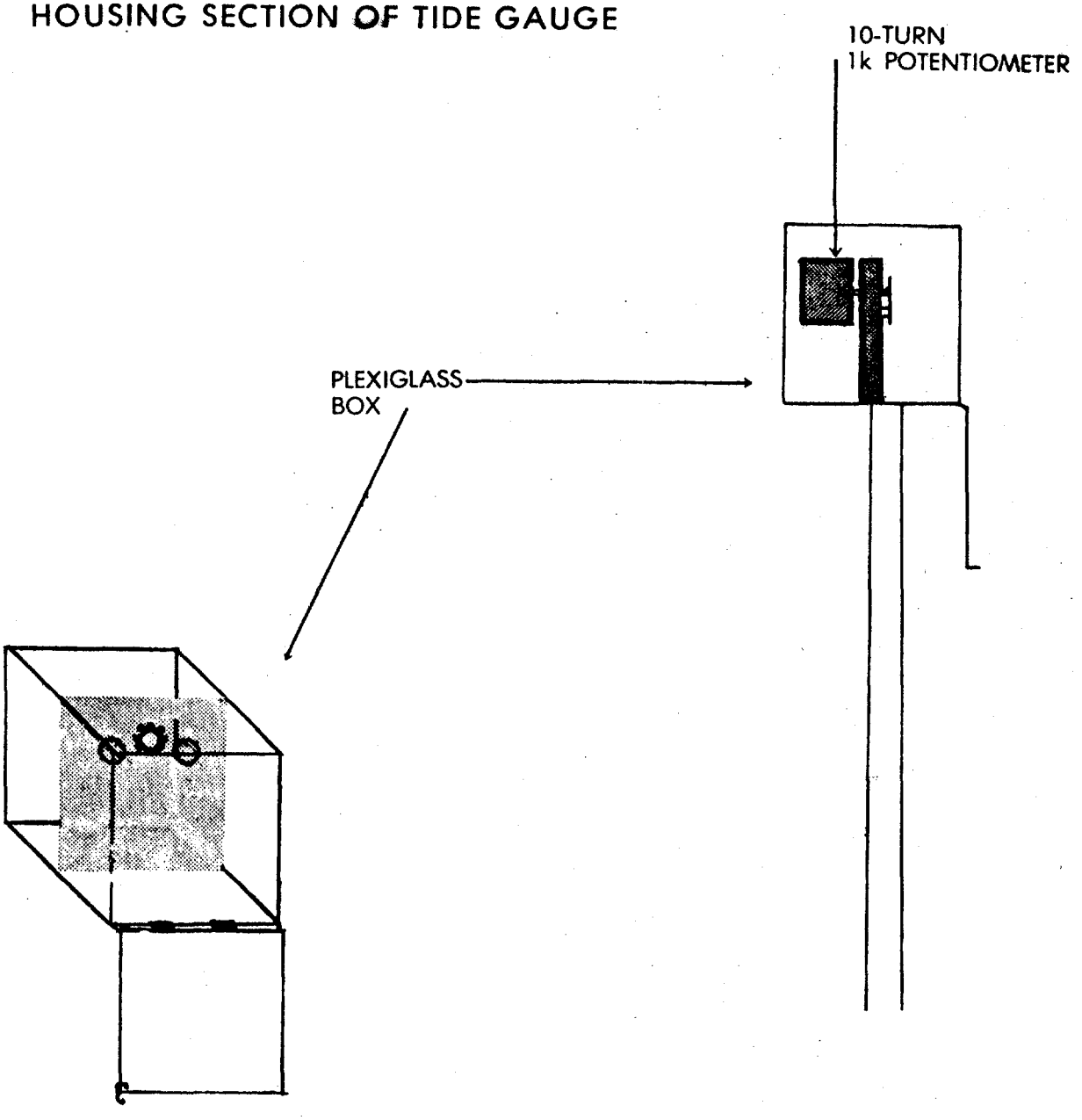
Figure 6b

PORTABLE SECTION OF

STILLING WELL TIDE GAUGE

Figure 6c

HOUSING SECTION OF TIDE GAUGE



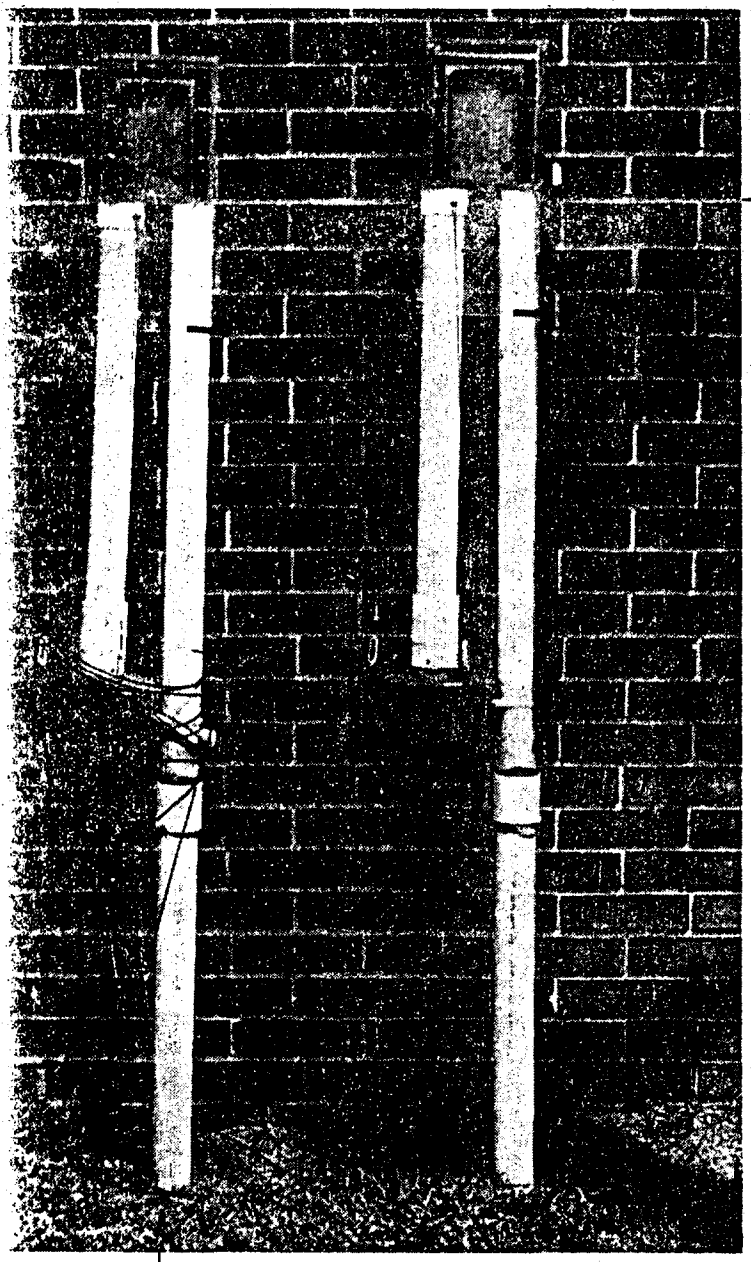
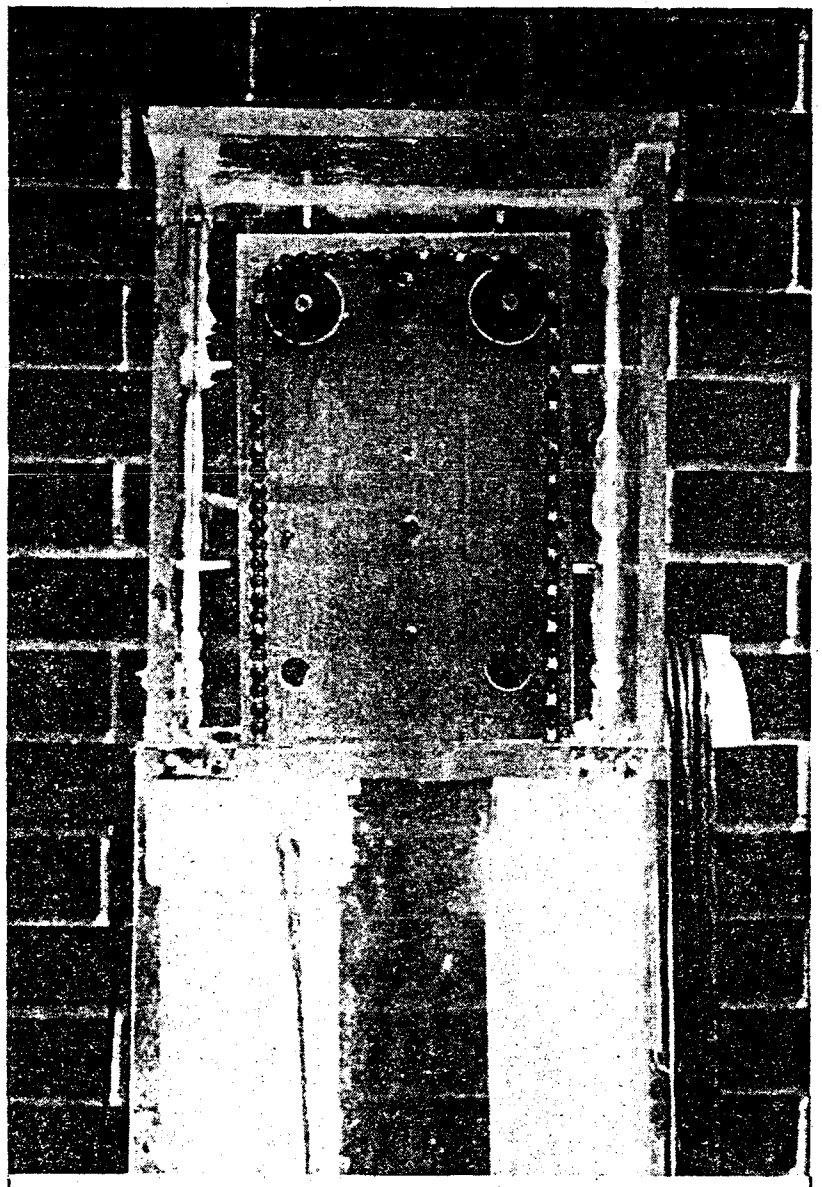


Figure 7a

PORTABLE SECTIONS OF STILLING WELL TIDE GAUGES



FRONT VIEW OF HOUSING OF
STILLING WELL TIDE GAUGE

Figure 7b

SIDE VIEW OF HOUSING OF
STILLING WELL TIDE GAUGE

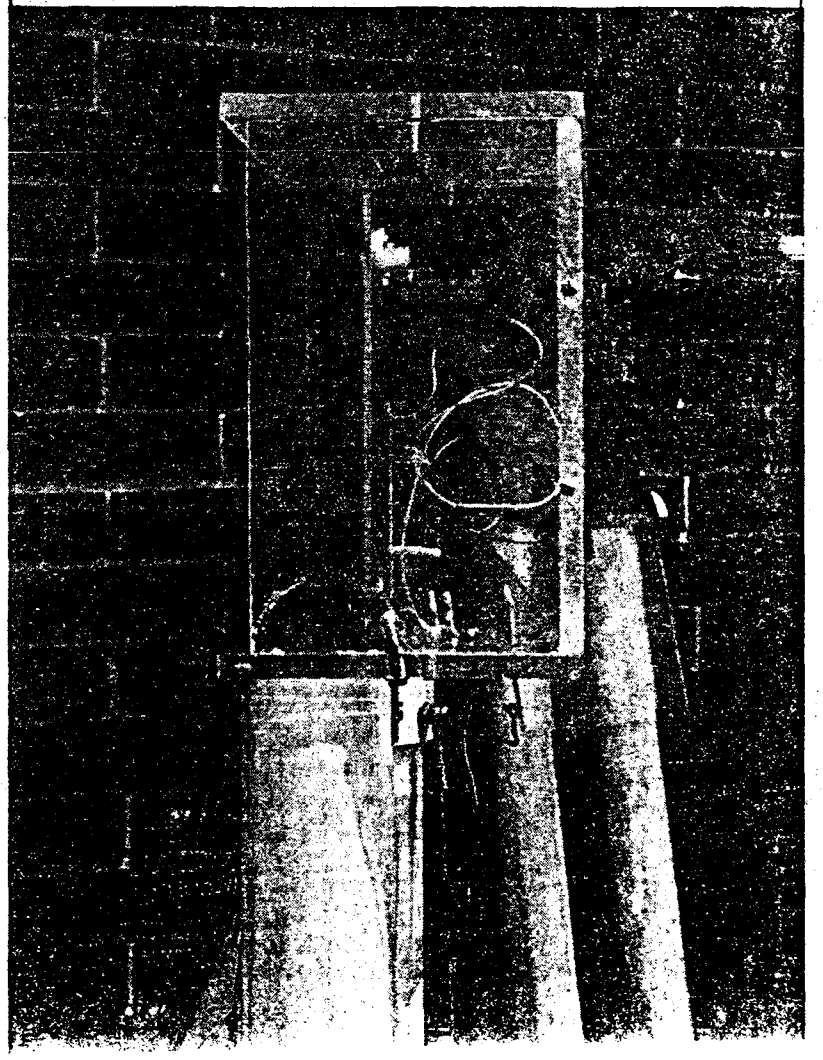
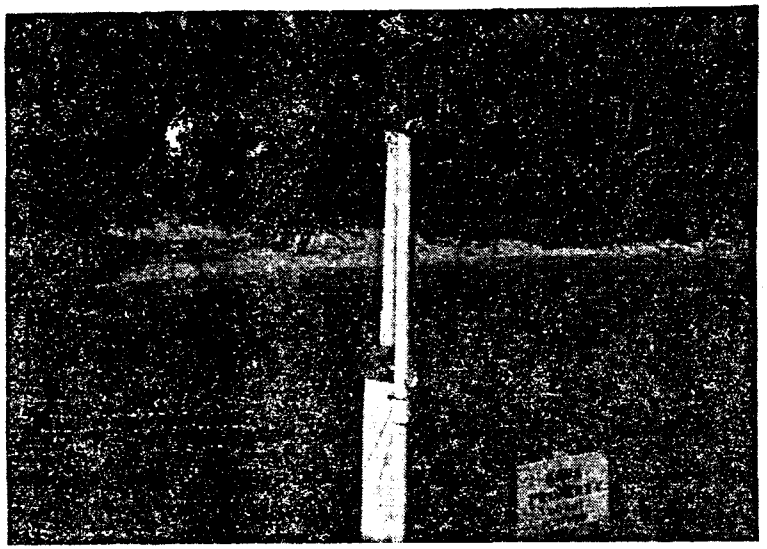
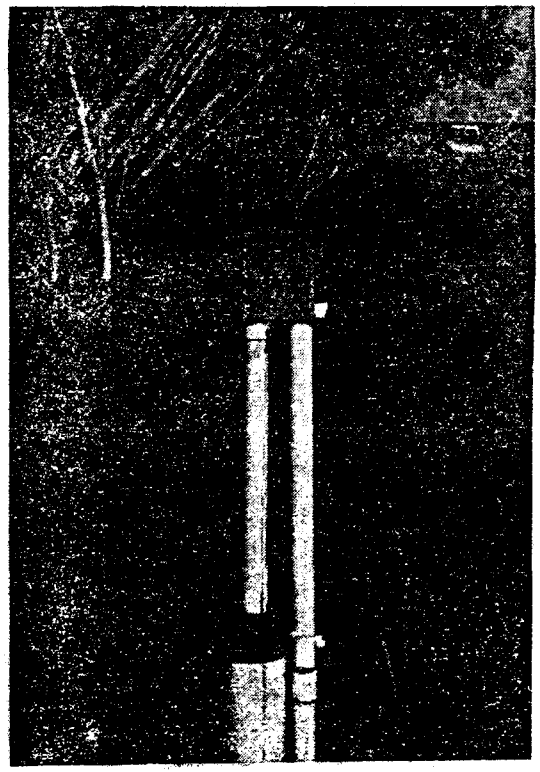


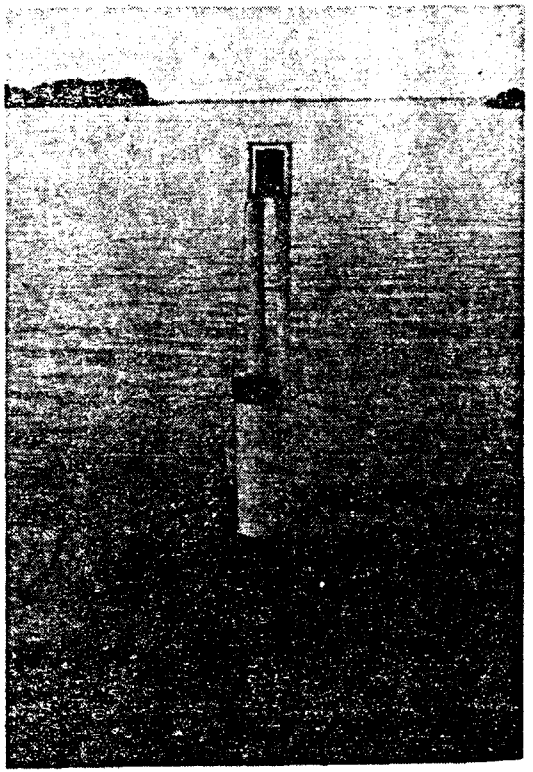
Figure 7c

STILLING WELL TIDE GAUGES ON LOCATION



NORTH-EAST END OF THE CANAL





SOUTH-WEST END OF THE CANAL

pressure cap supporting a 2.0-foot (0.61cm) length of 2.0-inch (5.08cm) ID PVC pipe, in turn supporting a plexiglass box. This box houses a 10-turn 1K potentiometer with a 9 tooth sprocket on its axis. The sprocket has and effective diameter of 0.719-inches (1.826cm), which means that each turn of a tooth amounts to 0.251-inches (0.637cm). These dimensions make possible a recordable range of 22.58-inches (57.35cm), which is almost twice the expected range.

A float 4.75-inches (12.07cm) in diameter floats inside the stilling well. The top of the float was connected to a 0.25-inch roller chain by a leader line and two ball bearing swivels. The color-coded roller chain (for visual water level measurements) was mounted on the sprocket and two roller guides. The chain then led back down in another 2.0-inch (5.08cm) ID PVC pipe about 3-feet (0.9m) long where, at the end of the chain, a 1.0-pound (453.59gm) lead counterweight was attached.

A chain and sprocket was used instead of a fan belt and wheel combination in order to eliminate undetectable error due to the possible slipping of the belt on the wheel during readings.

The threshold of the potentiometer or in other words, the amount of torque required to turn the pots' axles is 44.70 gm-cm and 34.39 gm-cm. This means, taking into account the cross-sectional area of the float, a water-level change of 0.32cm at the north-east end, and 0.42cm at the south-west end is required to get a change in reading. The torque was found by allowing grains of sand to fall in a small aluminum cup dangling from a 1.0-inch (2.54cm) torque arm fastened to the 10-turn pot axle. After the axle turned under the increasing torque, the aluminum cup containing the sand was weighed to a hundredth of a gram. The highest readings for both pots were used in computing the water level change required to turn the pot axles.

A dumpy level and surveyor's rod were used to determine the relative heights of the stilling wells to each other and to the U.S. Coast and Geodetic Survey bench mark which is 4.68-feet (1.43m) above the mean water level. Because the surveying parties

were inexperienced and trees lining the canal banks to the water line made sightings difficult, four level measurements were made of each stilling well. The average of each set of four measurements was taken as the actual height above mean water level of the respective stilling wells. The height of the top edge of the south-west stilling well was found to be 87.0cm, and that of the north-east stilling well to be 86.8cm. A standard deviation of 6mm was observed in each set of four measurements taken, and a height difference (relative to the bench mark already mentioned) between the stilling wells was found to be less than 0.2cm as shown in appendix B.

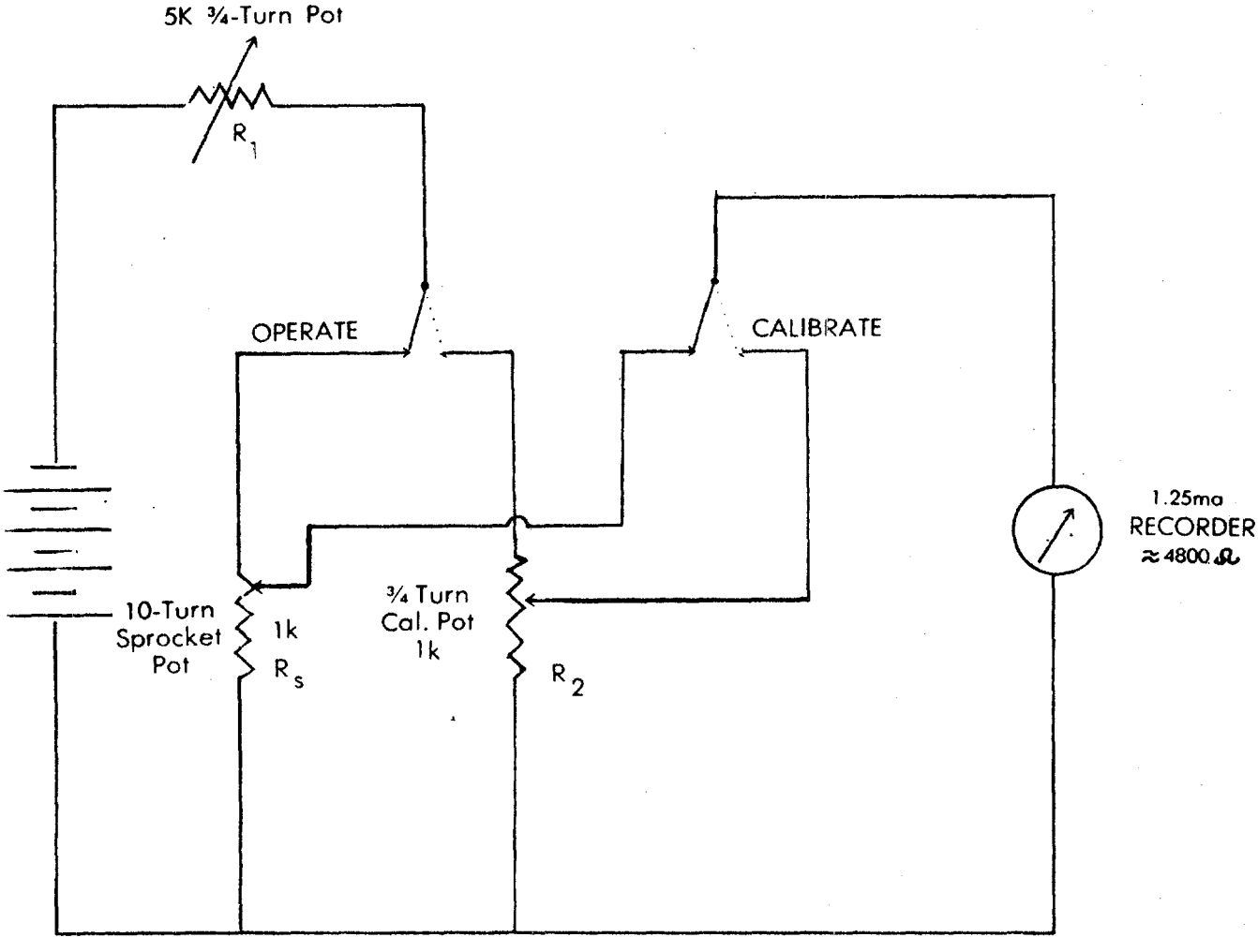
The length of the leader line used to connect the chain with the float was such that when the water line was a mean water level the reading at the sprocket and chain connection would read "0". The dimensions of the portable sections of the gauges, the measured height of the stilling well, the height of the unsubmerged part of the float and the length of the chain were used in determining the proper length of the leader line.

The readout was accomplished by a recorder with a windup chart drive. The recorder scale is 11.43cm, and the actual water level range is 57.35cm. So, the ratio of actual water level change to recorder increment is 5:1. Each recorder was driven by a 6 V car battery.

A schematic diagram of the circuit used for the recording tide gauges is shown in Figure 8. (Tempel, 1972). After connecting the battery, the recorder is initially calibrated by first setting the DPDT switch on "operate," thus including the 10-turn 1K pot (sprocket pot) in the circuitry. The sprocket pot is turned the full 10 turns for a maximum reading on the recorder. The recorder needle is set to a full-scale reading by adjusting R_1. Once the full-scale adjustment is accomplished, the sprocket pot is turned back five turns and the position of the recorder needle noted. The DPDT switch is set to the calibrate position and R_2 (calibration pot) adjusted so that the recorder

Figure 8

TIDE GAUGE CIRCUITRY



needle is brought back to the 5-turn or middle position. The calibration circuitry is designed to indicate a voltage dropoff of the 6 V batteries.

In interpreting the readings taken, a calibration curve and visual recordings at specified times were used. In this way, accurate water level measurements were retrieved. A fairly consistent 20-minute lag was observed for small-level changes of 0.32cm to 0.64cm between the turn of the sprocket and the position change of the recorder needle. This was possibly due to friction between the needle and the recorder paper and the mechanical response of the meter movement to small changes in signal strength. A discussion of the response of the tide gauges to water level changes outside the gauge stilling wells is deferred to Appendix C.

B. PROCEDURE

The day was started by first transporting the recorders, batteries, and gauges to the stilling wells already secured in the ground. The recorders and batteries were set up on the banks of the canal.

The gauge, battery, and recorder were then connected and the recorder was adjusted for accurate zero and full-scale readings. The portable section of the tide gauge was then secured to the stilling well. When this procedure was carried out at both ends of the canal, and the first level readings were recorded visually, current measurements were ready to be taken. Current measurements were taken at six different locations along the canal. All canal sections have the same geometrical shape and dimensions, except for the area close to the canal bridge (U.S. Army Corps of Engineers, 1953). After anchoring the boat, time and sites of the measurements were recorded. The surface cross was released and time was started on the stopwatch. The range finder was preset at 40.0-feet (12.19m), and when the two images of the orange chlorox bottle merged into one, time was stopped. A range of 40.0-feet (12.19m) and the time it took the surface current cross to reach that distance were then recorded. Next, the jar was released with the fishing weight attached. Time was taken from the time of release to the time of surfacing. The range finder was then fixed on the jar upon its surfacing, and the range and elapsed time were recorded. After the jar and current cross were picked up, the boat was anchored to the next site.

Whenever the end of the canal was reached (the final current measurement site) a visual measurement of the water level was taken at the end and then at the "upstream" end before beginning the next set of current measurements. This was done to compare with the continous recordings being taken and also to be used in the event

that one or both the recorders broke down. At the end of the day, final visual water level measurements were taken, the portable sections of the tide gauges were secured, and the recorders and batteries were removed from the banks, all to be stowed for the next day.

The reason for setting up and securing the equipment measuring water level changes each day was fear of possible vandalism. This process grew a bit tiresome. It was decided that the gauges and equipment would be left out overnight so all that was required each morning was to re-adjust and wind up the recorders. The recorders and batteries were protected from moisture by resting them on a plywood board and covering them with plastic trash can liners. Some desiccant was also placed inside the recorder.

Since wind measurements were being taken 24 hours a day, the recorders were left on overnight so that water level measurements could be correlated with them.

DISCUSSION OF EXPERIMENTAL RESULTS

It will now be seen how well the Manning equation for uniform flow, our suspected relation between water transport through the canal and the water surface slope, conforms to the actual data taken at Haulover Canal. Using the method of linear regression a line of best fit for the data may be found, from which, the best value of the Manning roughness coefficient may be taken.

Evidence of good correlation between the wind field and the three measured parameters at the canal: the surface current, the average current, and the water surface slope along the length of the canal is presented. The preferred wind direction for each of the above mentioned parameters, while not strictly conforming to the definition given in the introduction to this work, is found for water transport to the Indian River and the Mosquito Lagoon.

Uniformity of Vertical Profile

The vertical velocity gradient was found to be small. The surface current, the current measured at eight tenths the depth and the measured average velocity were all very nearly the same. The average ratio of the surface current to the current at eight-tenths the depth is 1.150 $\pm$ 0.001, and the average ratio of the surface current to the average velocity is 1.007 $\pm$ 0.001. These averages were obtained from 290 sets of measured values, and therefore, as a general rule, the average current in the canal can be fairly well approximated from the surface current.

Uniformity of Flow

As stated previously, the Manning equation for flow in an open channel has much support in the literature. The degree of uniformity in the flow has to be established to see whether Manning's equation for uniform flow in an open channel

$$S = \frac{v^2 n^2}{R^{4/3}}$$

is appropriate or whether the data exhibits an apprciable non-uniformity and is more accurately described by the varied-flow equation

$$S = \frac{v^2 n^2}{R^{4/3}} + \frac{d}{dx}\left(\frac{v^2}{2g}\right)$$

The additional term, as defined before, is the change of the velocity head with the length of the channel. Measurements of the velocity at both ends of the canal at close time intervals and at equal water surface slopes, indicate an average change in the velocity, $\overline{\Delta v} = +1.81\%$, or an average change in the velocity squared, $\overline{\Delta v} = +6.38\%$ over a distance of 1.790 km.These average percentages are well within the range of error inherent in the range finder used in current measurement. Therefore, one may think that any variation of flow from uniformity would be too small to measure and drop any further discussion of a possible varied-flow in the channel. These average percentages, however, represent only a few measured variations with high standard deviation. Therefore, we should investigate a little further to see to what degree of varied flow we could expect in Haulover Canal.

From our energy equation we know that the flow velocity is inversely proportional to the depth of flow.

$$v=k/y$$

where y is the depth of flow and k is a constant of proportionality. Substituting this expression for the velocity we have, for the change in the velocity head

$$\frac{d}{dx}\left(\frac{v^2}{2g}\right) = -\frac{1}{g}\frac{k^2}{y^3}\frac{dy}{dx} = -\frac{v^2}{gy}\frac{dy}{dx}$$

Equating the change in the velocity head to the change in the water surface slope we have

$$-\frac{v^2}{gy}\frac{dy}{dx} = \Delta S$$

or, since $-\frac{dy}{dx} = S$

$$\frac{v^2}{gy} = \frac{\Delta S}{S}$$

What we have here is the fractional variation of the water surface slope equal to the square of the froude number. For a flow depth y=4.5m and a flow velocity v=1 m/sec we have a 2.3% change in the water surface slope. This effects even a smaller percentage variation in the flow velocity. From this we see that the expected variation from uniform flow is indeed small compared to the inaccuracies of the method of current measurement. Therefore, it seems reasonable to assume that Manning's equation of uniform flow gives a good representation of the flow in the Haulover Canal for the range of velocities measured.

Correlation of

Water Surface Slope

with

Surface and Average Current

and

the Determination of the Manning Coefficient

In Figures 9 & 10 there is a definite positive correlation of both the average and surface currents with the water level differences. A strong linear relation is evident between the average and surface currents and the water surface slope taken to the one-half power (Figures 11 & 12)

To show the degree of correlation of the surface and average current with $S^{1/2}$ we compute their correlation coefficients. A simple definition of the correlation coefficient "r", measuring the degree of correlation between two parameters x and y is

$$r = \frac{n \sum xy - \sum x \sum y}{\sqrt{(n \sum x^2 - (\sum x)^2)(n \sum y^2 - (\sum y))^2}}$$

where n is the number of sets of data of x and y. The value of r lies in the range of (-1,1). A high positive correlation implying a direct relation is represented by values of r close to 1. No correlation at all is represented by value of r close to 0 and a high negative correlation, implying an inverse relation is represented by values of r close to -1. The correlation coefficient showing the degree of correlation between the square root of the water surface slope and the average current was calculated to be + 0.922, implying a strong positive correlation. A correlation coefficient of + 0.929 indicates a strong positive correlation also exists between the surface current and the water surface slope, as would be expected.

Figure 9

MANNING UNIFORM FLOW EQUATION RELATING THE SURFACE VELOCITY TO THE WATER LEVEL DIFFERENCE BETWEEN THE ENDS OF HAULOVER CANAL

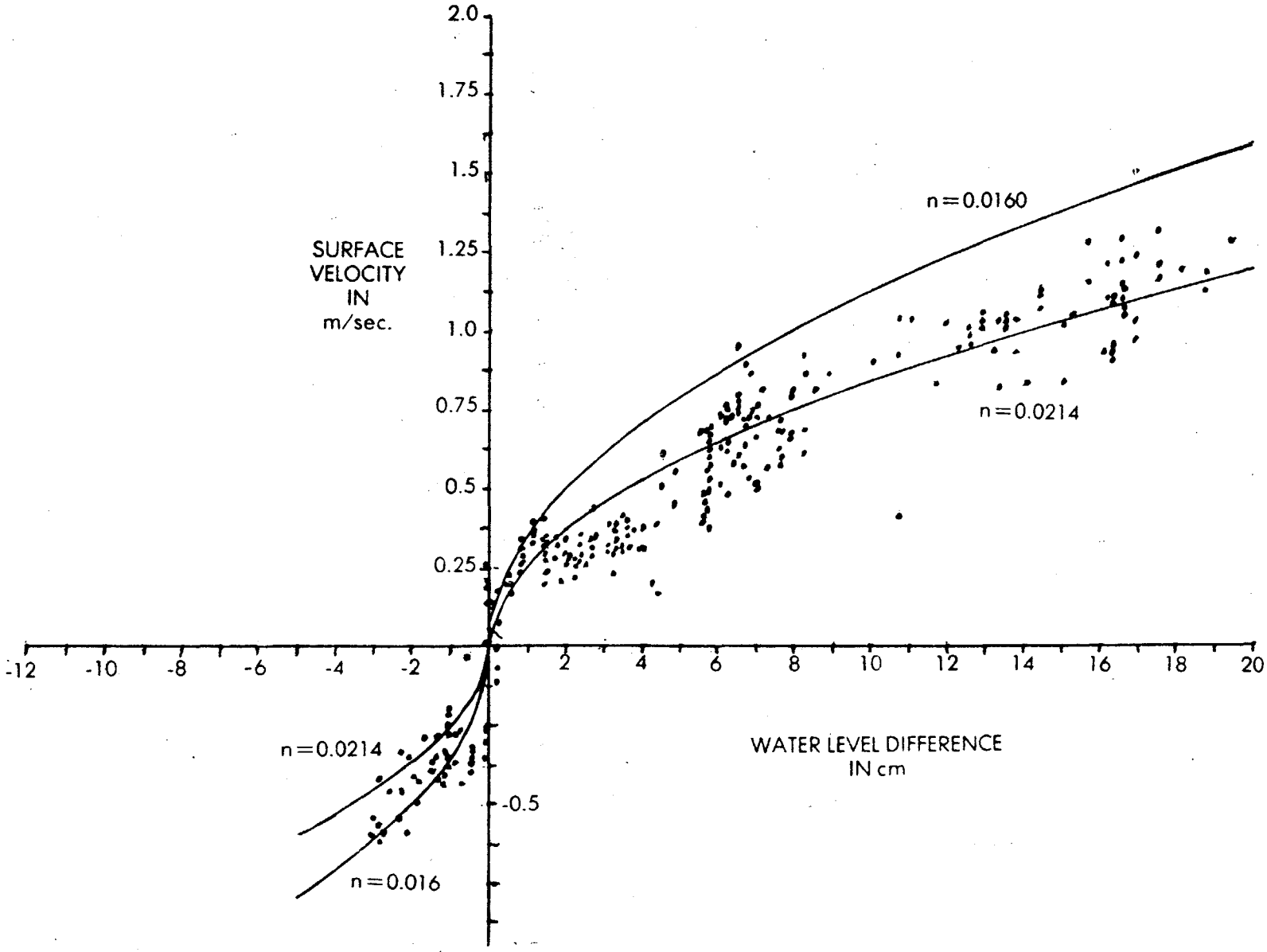


Figure 10

MANNING UNIFORM FLOW EQUATION RELATING THE AVERAGE VELOCITY TO THE WATER LEVEL DIFFERENCE BETWEEN THE ENDS OF HAULOVER CANAL

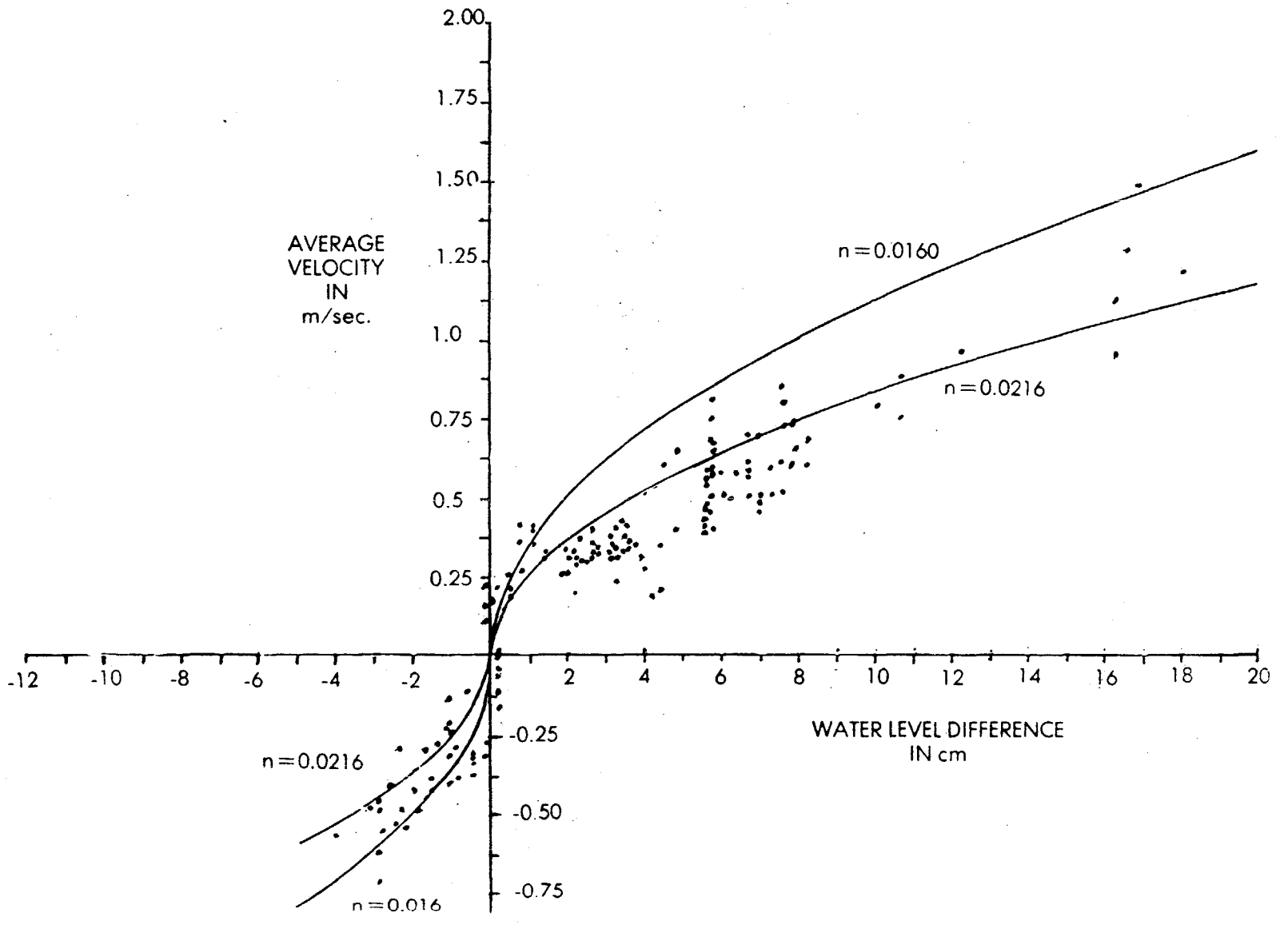


Figure 11

MANNING UNIFORM FLOW EQUATION RELATING THE SURFACE VELOCITY TO THE WATER SURFACE SLOPE

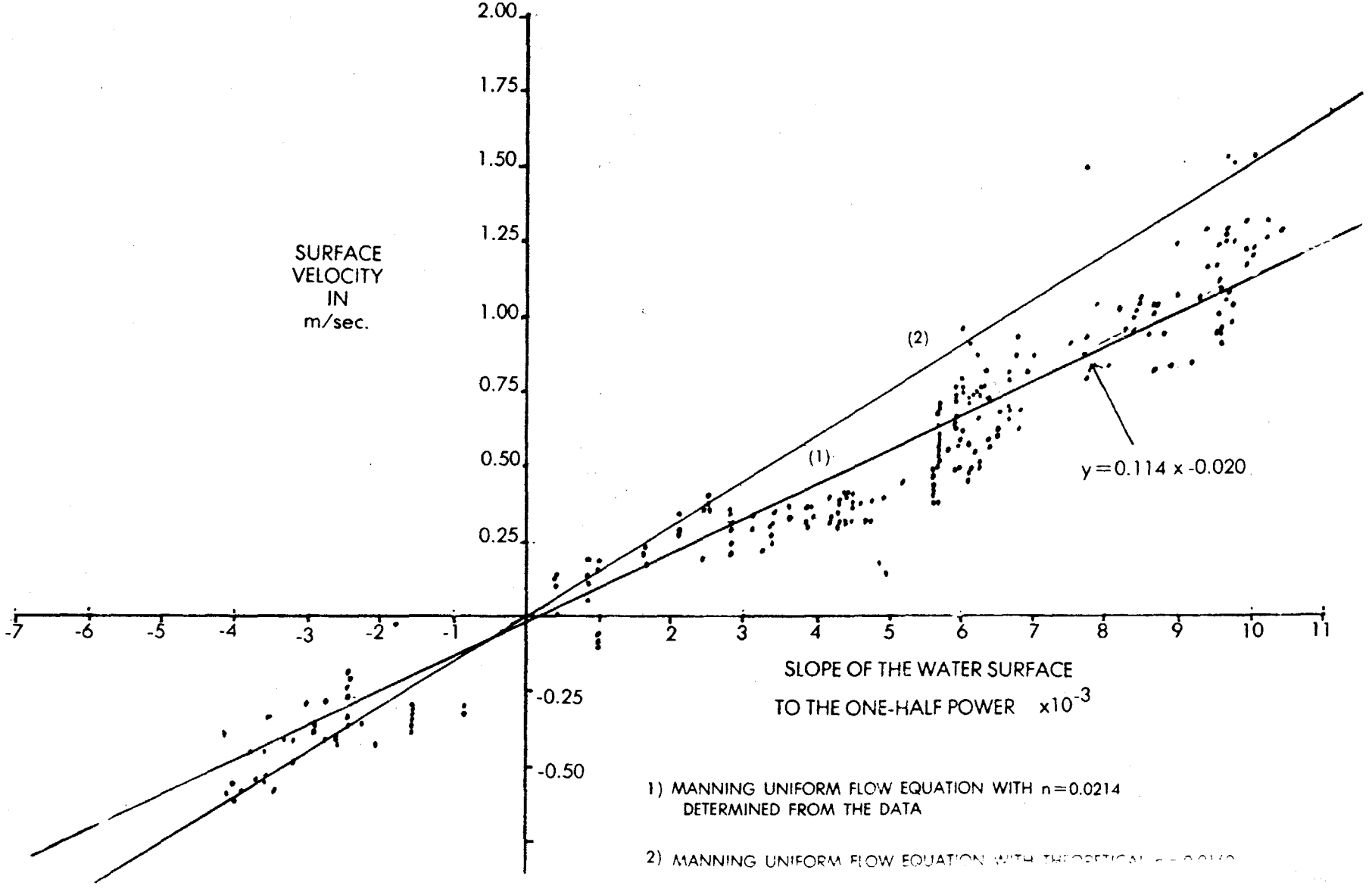
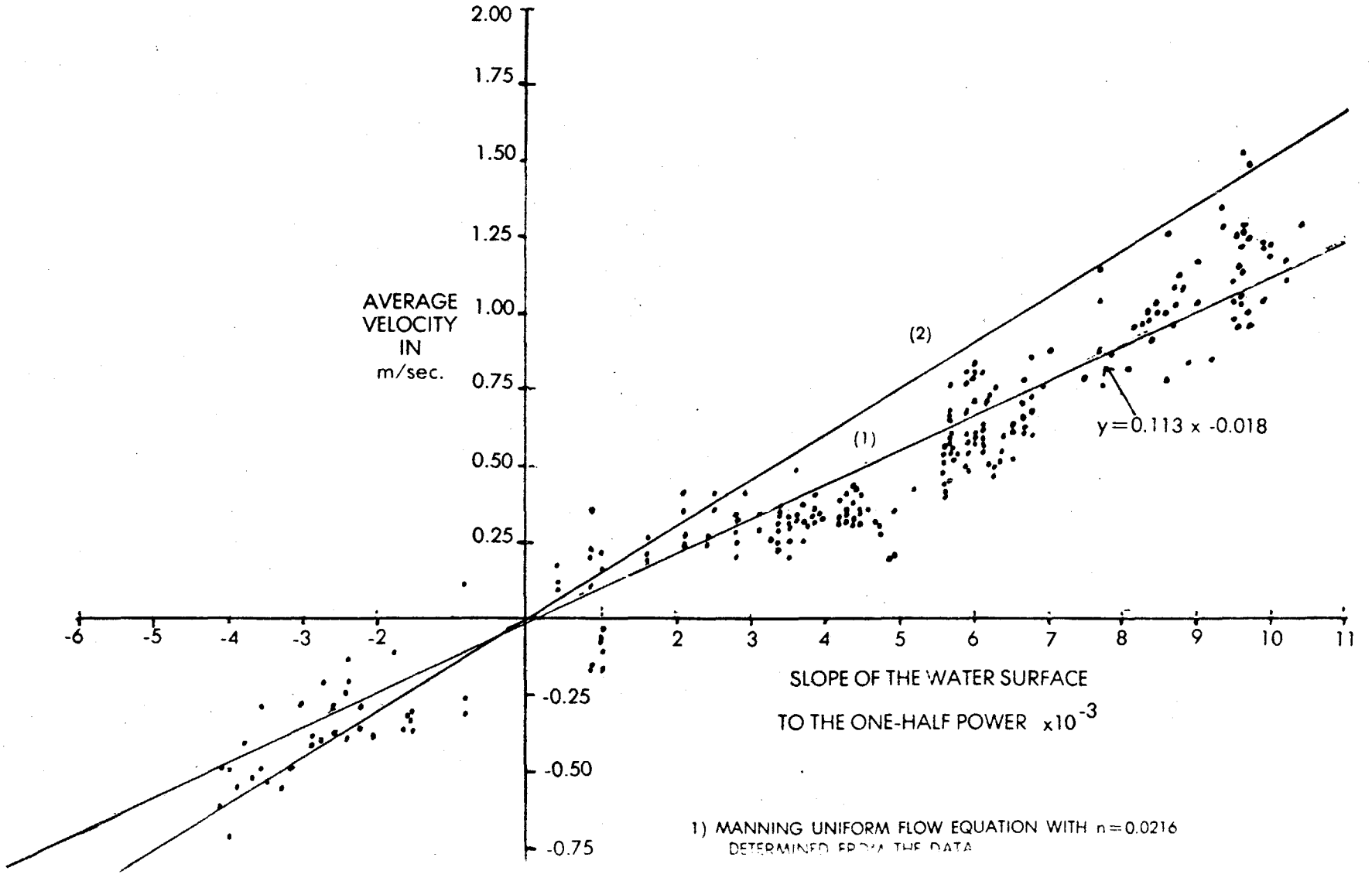


Figure 12

MANNING UNIFORM FLOW EQUATION RELATING THE AVERAGE VELOCITY TO THE WATER SURFACE SLOPE



The method of least squares was used to determine a line of best fit for data points on the plots of current vs. the square root of the water surface slope. These lines give the most probable value of the current for a particular value of the water surface slope. From this line and the Manning uniform flow equation, the best value of the Manning roughness coefficient was determined. Particular values of the current velocity and the square root of the slope were introduced in the Manning equation

$$n = \frac{R^{2/3} S^{1/2}}{v}$$

where the hydraulic radius "R" is 3.74 m. The values of 0.0216 sec $m^{-1/3}$ and 0.0214 sec $m^{-1/3}$ were determined for n for the average current and surface current, respectively, through the canal. These values for n compare favorably with those found in the Manning tables. The n value that one extensive table gives (Chow, 1959) for a straight, excavated, and uniform channel that is clean after weathering is 0.022 sec $m^{-1/3}$. Rounding off the last digit of our n value for the average current we see that we get the same value.

Substituting the values of n and R we get the following relations between current velocities and the water surface slope:

Surface Velocity $= V_s = 112.6\ S^{1/2}$ m/sec

Average Velocity $= V_a = 111.5\ S^{1/2}$ m/sec

The Manning coefficient was also determined by theoretical means using the average value of the ratios of the measured current at two-tenths the depth to the measured current at eight-tenths the depth. The relation between the Manning coefficient and this average ratio is

$$n = \frac{R^{1/6}\ (r-1)}{5.57r + 5.26} \quad \text{sec } m^{-1/3}$$

as derived for smooth channels in a previous section with "R" calculated to be 3.74m and the average ratio found to be 1.15 we get

$$n = 0.0160. \text{ sec } m^{-1/3}$$

This method of determining n has yet to be completely verified experimentally by others investigating this subject. It is not clear how promising this last method is in determining an accurate value of the Manning coefficient for a particular channel. We see that by subtracting 1 from the ratio of the velocities we make the value of n extremely sensitive to inaccuracies in flow measurement. This fact alone may make this method of computing n impractical for engineering purposes.

Plots of the Manning uniform flow equation with the theoretical value of n are also in Figures 9-12 for a vivid comparison with the line plots representing the value of n established by the data.

Correlation of the Prevailing Wind with the Transport Through the Haulover Canal and with the Water Surface Slope

There may be some question as to whether the wind is the only significant driving force for the transport through Haulover Canal. The question of any tidal action in the area has already been resolved from a report from the Tides Branch of NOAA, U.S. Dept. of Commerce, stating there are no measurable tides to a 100th of a foot in the area. No periodic fluctuation was noticed in this investigator's own data. One may also question whether any appreciable current may be established due to a typical salinity gradient between the ends of the canal. For a salinity gradient of a much as 10°/$_{oo}$ we have the equivalent water level difference of 3.2cm. From salinity measurements in both the Indian River and the Mosquito Lagoon, the usual salinity difference between the two in the proximity of the Haulover Canal is approximately 2°/$_{oo}$. The equivalent water level difference for a salinity gradient of this magnitude is 0.61cm. With water level differences ranging from 1.0cm where we have little or no current to 21.0cm where we have a water transport at the rate of 1.5m/sec it is obvious that any salinity gradient that may exist between the two ends of the canal has little to do with the transport through the same. The only driving force that could be of significance is the prevailing wind.

The preferred direction of the wind, as stated in the introduction to this work, is the direction from which the wind field approaches causing the maximum transport through the canal; wind magnitude being held constant. The preferred direction of the wind field found for the transport in both directions through

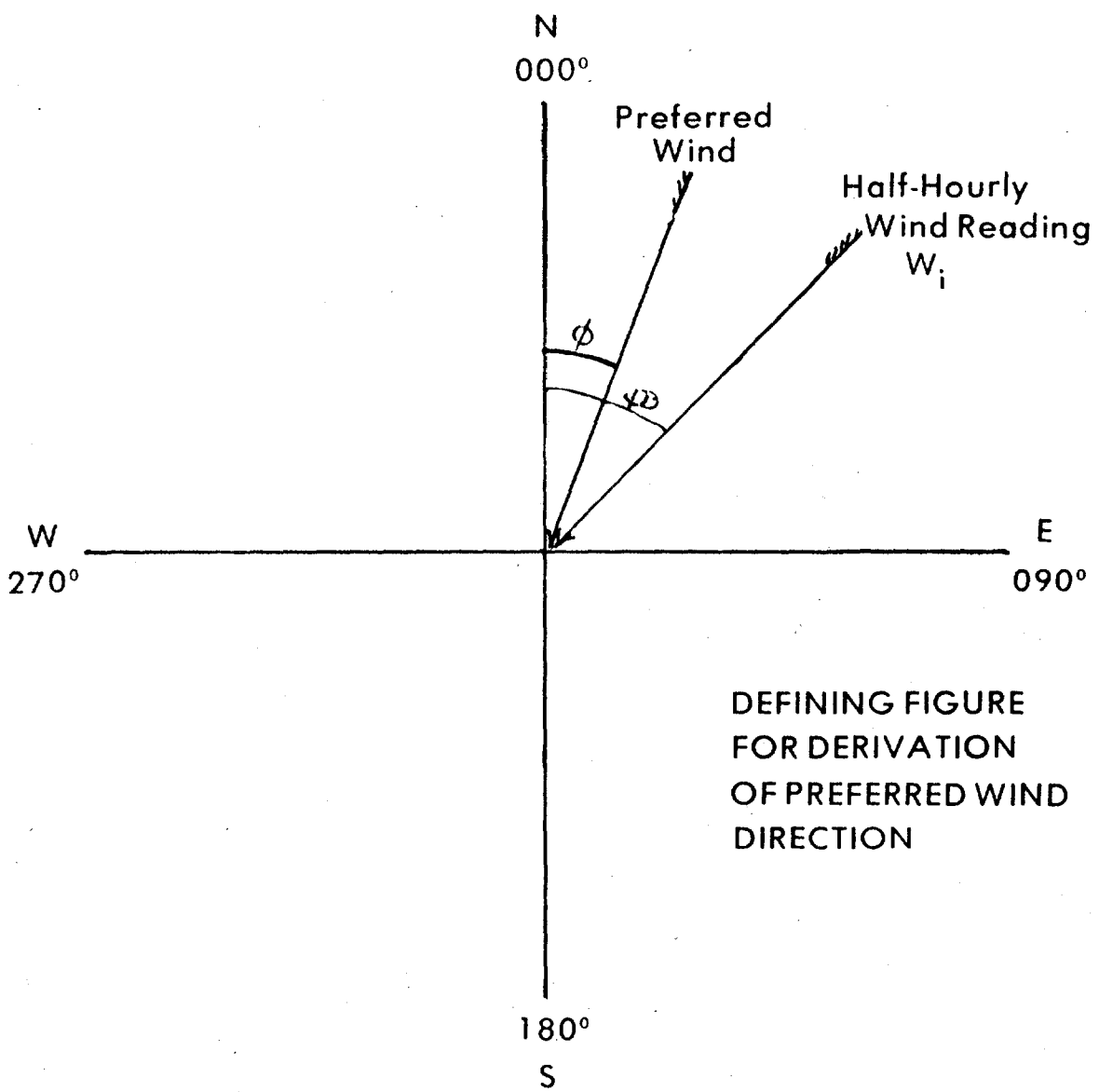
the Haulover Canal does not conform to this definition. Due to the degree of variation in wind magnitudes it was impossible to determine this preferred direction from 290 sets of measured values. Rather, the preferred directions found for the measured parameters at the canal represent a combination of two wind factors causing a particular flow in the canal. One is the direction from which the strongest winds came causing a greater current through the canal. The other is the wind direction causing the maximum water surface slope in the Haulover Canal. This wind direction is largely dependent on the orientation of the canal, and the orientation and shape of the Indian River and the Mosquito Lagoon. The latter specifies the wind direction that allows the wind to act over the greatest fetch (distance over water). The depth and variation thereof is considered to be of minimal influence in establishing the preferred wind direction due to the fact that the depth in both bodies of water is, for all practical purposes, uniform.

The problem is to find the wind direction giving the maximum response in water level difference at the canal ends or current magnitude through the canal. Looking at Figure 13, we define "Θ" as the direction of a particular wind vector. "$\varnothing$" is the preferred direction of the wind which is our unknown. The degree of correlation of the winds projected on the preferred wind direction with either the surface current, average current, or the water level difference between the ends of the canal is found by using the correlation coefficient. The latter three parameters are those that were measured at the same half hour interval as the particular wind reading. The projected wind on the preferred wind direction $\varnothing$, for a particular wind reading, is

$$W\varnothing_i = W_i \cos(\varnothing - \Theta)_i$$

The correlation coefficient for $W\varnothing_i$ and the surface current (sc_i) is

Figure 13



DEFINING FIGURE
FOR DERIVATION
OF PREFERRED WIND
DIRECTION

$$r = \frac{n\sum_{i=1}^{n} sc_i\, w_i\, \cos(\phi-\theta)_i \;-\; \sum_{i=1}^{n} W_i\, \cos(\phi-\theta)_i \sum_{i=1}^{n} sc_i}{\sqrt{\left[n\sum_{i=1}^{n}(W_i\cos(\phi-\theta)_i)^2 - (\sum_{i=1}^{n} W_i\cos(\phi-\theta)_i)^2\right]\left[n\sum_{i=1}^{n} sc_i^2 - (\sum_{i=1}^{n} sc_i)^2\right]}}$$

When the value of the preferred wind direction for the surface current, ϕ_{sc_i}, is substituted for ϕ, the value of r is a maximum. To find this value of ϕ_{sc} we first maximize the correlation coefficient by taking the partial derivitive of r with respect to ϕ and equate the result to zero:

$$\frac{\partial r}{\partial \phi} = 0$$

The complexity of the resulting expression is such that the method of iteration must be used to find the value of ϕ that satisfies the above relation. Since we know that the surface current closely approximates the average current and both are directly related to the water surface slope, it would be reasonable to assume that

$$\phi_{sc} \approx \phi_{ac} \approx \phi_d$$

Preferred wind directions for the three parameters mentioned are calculated for each of the two possible directions of the current through the canal. Correlation coefficients measuring the degree of correlation of the surface current, average current and the water surface slope with the east-west and north-south components of the wind, $W_{ew_i} = W_i \sin\theta_i$ and $W_{ns_i} = W_i \cos\theta_i$ respectively, for each direction of flow were also computed. This was done simply for a comparison with the values of r found for the

same parameters measured at the canal and the winds projected on the preferred wind directions.

The values of the preferred wind direction are as follows

	For water transport in the direction of	
	225° (Indian River)	045° (Mosquito Lagoon)
$\emptyset_{sc}$ =	357.5°	227.8°
$\emptyset_{ac}$	357.1°	225.5°
$\emptyset_{d}$ =	356.6°	217.7°

As one can see, the values of the preferred wind directions for the surface current, the average current and the water level difference are in close proximity to each other for each of the two flow directions. This was suspected due to their direct relationship with each other. The small differences in the values of $\emptyset$ computed for the three canal parameters are most likely due to error in measurement of these parameters.

The preferred wind directions computed for current flow toward the south-west and emptying into the Indian River is supported by 236 sets of readings. The computed values of $\emptyset_{sc}$, $\emptyset_{ac}$, and $\emptyset_{d}$ for current flow in the north-easterly direction, (emptying in the Mosquito Lagoon) are supported by only 49 sets of data and therefore the results should be looked upon as very approximate.

Figure 14 shows these preferred wind directions relative to the orientation of the two large bodies of water and the Haulover Canal. From looking at this figure it is evident that these values of the preferred wind direction are close to what intuition would tell us. The fact that fetch plays a role in determining the preferred wind direction for transport through the canal is evident.

The computed values of the correlation coefficients for the transport in each direction is now presented.

Values of "r" Computed for Transport in the South-west Direction

	Surface Current	Average Current	Water Level Difference
W_{ew}	-0.231	-0.262	-0.244
W_{ns}	0.797	0.787	0.810
$W_{\emptyset}$	0.798	0.790	0.811

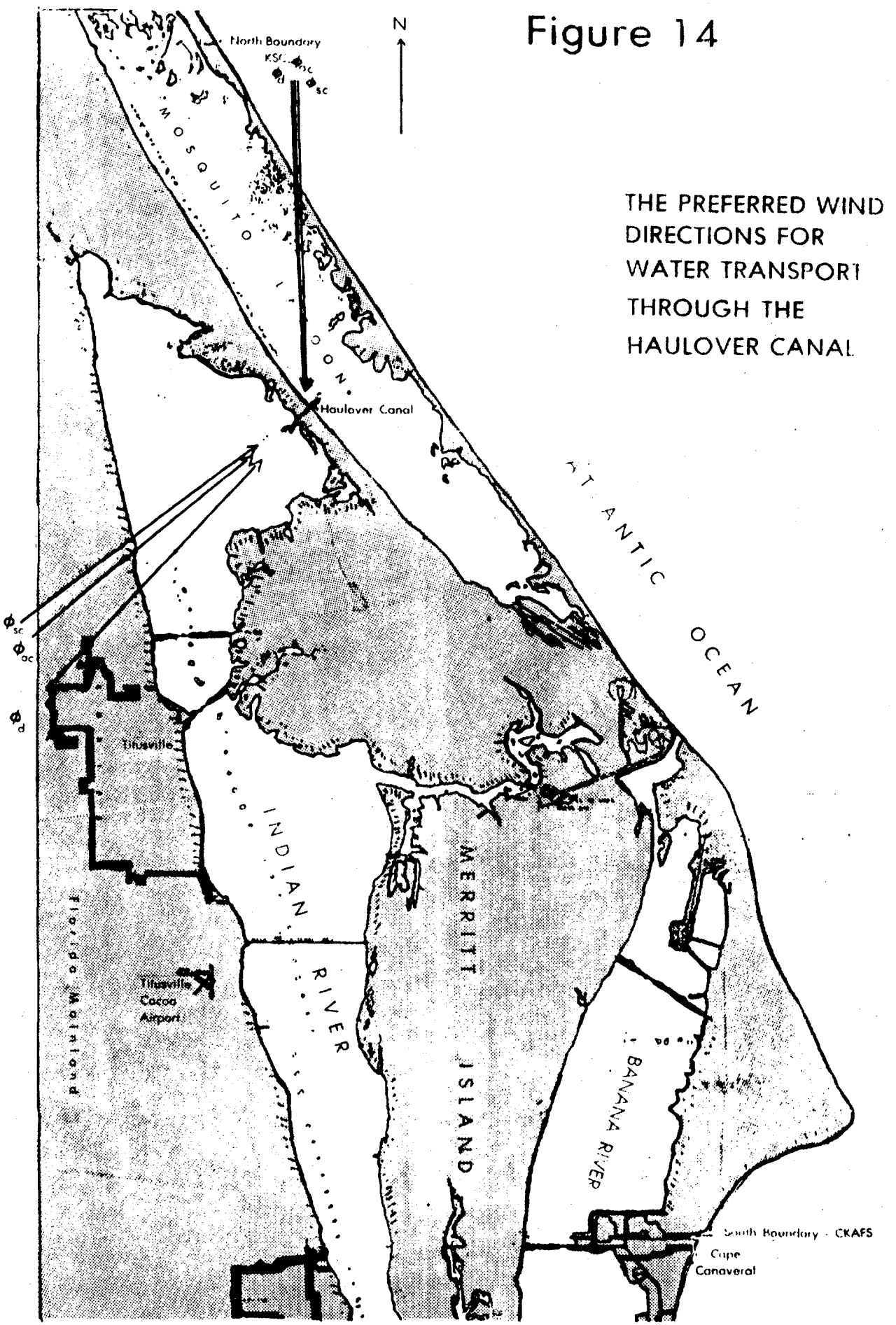
Values of "r" Computed for Transport in the North-east Direction

	Surface Current	Average Current	Water Level Difference
W_{ew}	0.716	0.707	0.640
W_{ns}	0.314	0.348	0.724
$W_{\emptyset}$	0.678	0.683	0.851

For water transport to the Indian River we see a strong positive correlation of the surface and average current, and the water level differences with the north-south component of the wind, as one would expect. Looking at the data in particular, we know that this north-south component of the wind is actually only the north component of the wind. There is, of course, a slightly higher positive correlation for the winds projected on the preferred directions correlated with the same parameters.

The computed values of the correlation coefficient for water transport towards the north-east, indicate a good positive correlation of the western component of the

Figure 14



THE PREFERRED WIND DIRECTIONS FOR WATER TRANSPORT THROUGH THE HAULOVER CANAL

wind with the current velocities and water level differences as one would expect. However one also expects from our value of the preferred wind direction, that there would also be equally good correlation between the south component of the wind and all the measured parameters at the canal. It is found that this is the case for the water level differences but not for surface or average current. As said before, the values of $\varnothing$ and r were taken from only 49 sets of data for transport towards the north-east, and therefore, we cannot count on their precision too heavily.

CONCLUSION

The transport through the Haulover Canal is related to the slope of the water surface by the Manning equation for uniform flow. The Manning coefficient used in this equation is approximately 0.022 sec $m^{-1/3}$.

The evidence points to the fact that the prevailing winds are the driving force for the transport through the canal. The preferred wind direction for the transport of water from the Mosquito Lagoon to the Indian River was found to be approximately 357°. For the water transport from the Indian River to the Mosquito Lagoon the the computed preferred wind direction was found to be in the proximity of 224°.

It is hoped that the results and conclusions of this work will be an incentive for further investigation with instrumentation sophisticated enough to allow for more accurate measurements and a much longer period of observation.

APPENDIX A

DERIVATION OF THE FREE – INSTRUMENT METHOD OF DETERMINING AVERAGE CURRENT VELOCITY

Average velocity with depth $= \frac{1}{H}\int_{o}^{H} V_x\,(z)dz = \overline{V}_x$

$$R_{x_1} = \int_{o}^{H} V_x(z)dt$$

Introducing the fall velocity $\bar{V} = \frac{dz}{dt}$ as constant.

$$R_{x_1} = \int_{o}^{H} V_x(z)dt = \int_{o}^{H} \frac{V_x}{V}\,dz = \frac{H\overline{V}_x}{V_1}$$

In like manner, $R_{x_2} = \frac{H\overline{V}_x}{V_2}$

Since $t_1V_1 = H$ and $t_2V_2 = H$

$$R_{x_1} = \frac{\overline{V}_xH}{V_1} = \frac{t_1\overline{V}_xH}{H} = t_1\overline{V}_x \text{ and } R_{x_2} = \frac{\overline{V}_xH}{V} = \frac{t_2\overline{V}_xH}{H} = t_2\overline{V}_x$$

Therefore, we see that

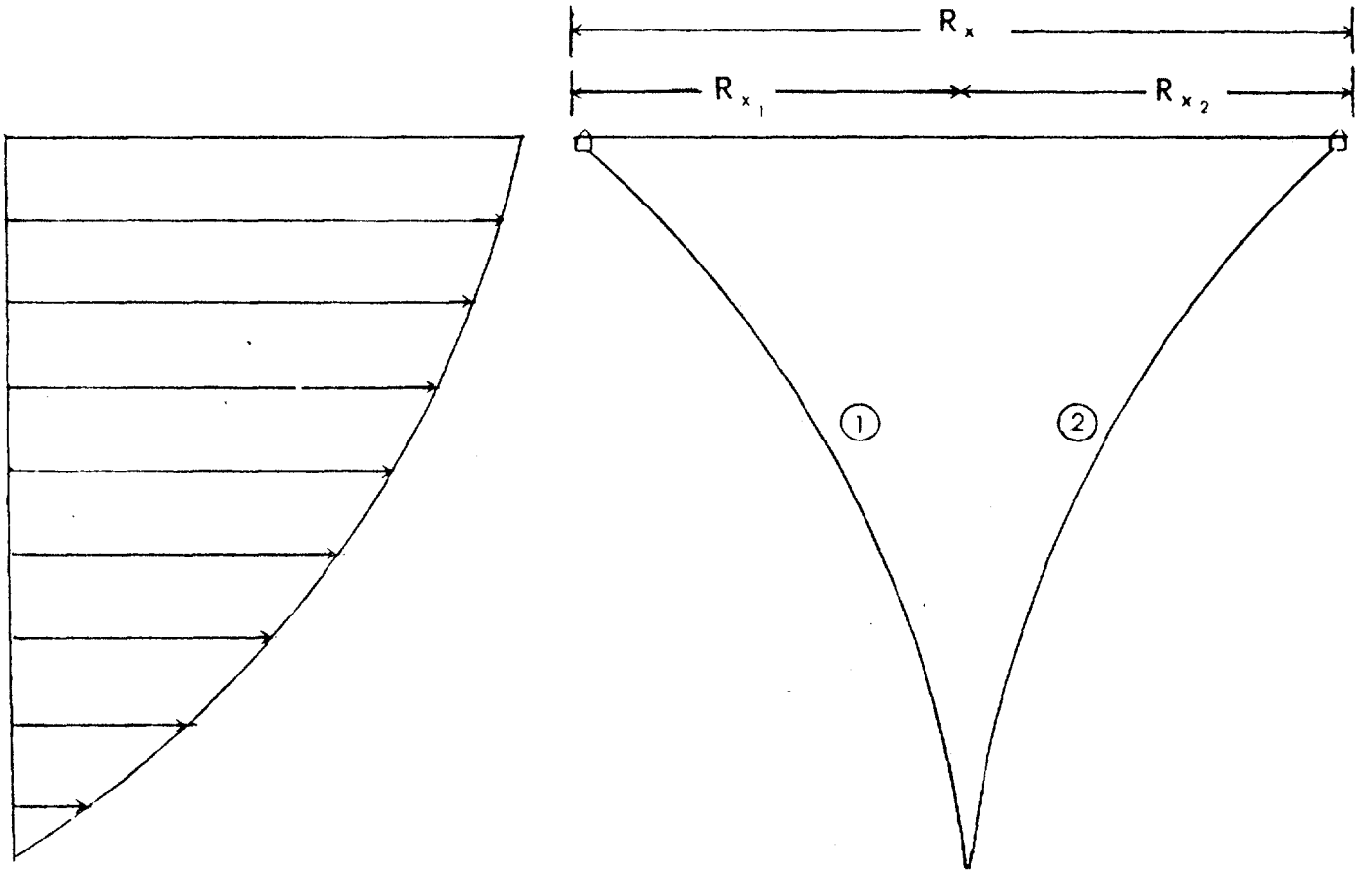
$$R_x = (R_{x_1} + R_{x_2}) = (t_1 + t_2)\,\overline{V}_x = t\,\overline{V}_x \quad \text{implying,}$$

$$\overline{V}_x = \frac{R_x}{t}$$

The average velocity with depth is equal to the total horizontal range over the total time. (Richardson, 1969).

Figure 15

DEFINING FIGURE FOR DERIVATION IN APPENDIX A



APPENDIX B

DETERMINATION OF THE RELATIVE HEIGHT DIFFERENCE OF THE STILLING WELLS

Surveying Data: (Top of stilling wells in cm below bench mark no. 2, 1972, U.S. Coast and Geodetic Survey).

Date	S.W. Stilling Well	N. E. Stilling Well
Sept. 22, 1973	-57.0 cm	-57.3 cm
Sept. 29, 1973	-56.0 cm	-54.7 cm
Oct. 1, 1973	-54.2 cm	-56.3
Oct. 3, 1973	-55.4 cm	-55.0

Average reading of the southwest stilling well is

$\frac{-222.6}{4}$ = -55.65 cm below the bench mark.

Average reading of the northeast stilling well is

$\frac{-223.3}{4}$ = -55.83 cm below the bench mark.

Southwest Standard Deviation (σ_{sw}):

u_{sw} = -55.65 cm

$x_i - u_{sw}$	$(x_i - u_{sw})^2$
1.35	1.82
0.35	0.12
-1.45	2.10
-0.25	0.06
	4.11

$$\sigma_{\overline{sw}} = \sqrt{\frac{\sum_{i=1}^{n} (x_i - u)^2}{n(n-1)}} = \sqrt{\frac{4.11}{12}} = 0.59 \text{ cm}$$

Northeast Standard Deviation ($\sigma_{\overline{ne}}$):

$u_{ne} = -55.83$ cm

$(x_i - u_{ne})$	$(x_i - u_{ne})^2$
1.48	2.18
-1.13	1.27
0.48	0.23
-0.83	0.68
	4.36

$$\sigma_{\overline{ne}} = \sqrt{\frac{\sum_{i=1}^{n} (x_i - u_{ne})^2}{n(n-1)}} = \sqrt{\frac{4.3475}{12}} = 0.60 \text{ cm}$$

The difference in elevation below the bench mark between the two stilling wells found by averaging the four readings for each stilling well and subtracting is

$$u_{ne} - u_{sw} = 0.18 \text{ cm} \pm 0.60 \text{ cm}$$

Elevation of the stilling wells above mean water level:

Bench mark no. 2, 1972, U.S. Coast and Geodetic Survey is 142.65 cm above mean water level.

Height of the northeast tide gauge is

142.65 cm -55.83 cm = 86.82 cm

Height of the southwest tide gauge is

142.65 cm -55.65 cm = 87.00 cm

As seen above, the height difference between the two stilling wells is 0.18 cm.

APPENDIX C

FREQUENCY RESPONSE OF THE STILLING WELL WATER LEVEL GAUGES

The main idea behind the stilling well water level gauge is to measure the long period water level changes due to the tide or wind piling over a large water area without loss of amplitude while damping out short period or high frequency wind-waves or waves due to local disturbances. This free exchange of water with a wave damping effect was accomplished by drilling a 0.5-inch (1.27cm) ID hole at mid-length of each of the 6-inch (15.24cm) ID pipes to be used as stilling wells. After the stilling wells were jetted into the canal side wall, the drilled orifice for each were 65.5cm below the mean water level.

The orifice coefficient of discharge denoted by "c", is defined as the ratio of the actual discharge through the orifice to the ideal discharge. The value of c for the orifices of the stilling wells used in this work will first be determined before we begin the actual analysis of the gauge response to water level fluctuations of the open water.

The value of c was determined by first observing the time necessary for the water level inside the stilling well to fall to within a mm of the water level outside the well for a specific head, h_1, above the outside water level. To observe this, the 0.5-inch (1.27cm) diameter orifice was plugged with a cork. The orifice was 77.14cm below the external water level at the time these observations were taken. Water was then poured inside the well to a level of 71.74cm above the water level outside. Time was taken from the time the cork was removed from the orifice to the time the water level

inside the stilling well reached the water level of the open water. This procedure was repeated 11 times with each measurement coming within the second of the average time of 89 seconds. This experimental value of t=89 seconds will determine our orifice velocity coefficient.

At the instant when the head is h above the mean water level, $Q = ca\sqrt{2gh}$ cm^3/sec where a = area of the orifice.

In the time interval dt, a volume of dV will be discharged where

$$dV = Qdt = ca\sqrt{2gh}\ dt$$

In the same time interval dt, the head will drop dh cm and, therefore, the same volume discharged can be represented by

$$dV = A\,dh\ cm^3$$

where A = stilling well cross-sectional area. Equating these two expressions for the change in volume, we have

$$-A\,dh = ca\sqrt{2gh}\ dt$$

The negative sign is used since we have a decreasing head with increasing time. We now see that we can represent this time interval dt as

$$dt = \frac{-Ah^{-1/2}\,dh}{ca\sqrt{2g}}$$

or

$$t = \int_{t_1}^{t_2} dt = \frac{-A}{ca\sqrt{2g}} \int_{h_1}^{h_2=0} h^{-1/2}\,dh$$

Integrating, we find

$$t = t - t_1 = \frac{2Ah_1^{1/2}}{ca\sqrt{2g}}$$

With the known experimental value of t, we can use the expression just derived to find the orifice velocity coefficient.

$$c = \frac{2Ah_1^{1/2}}{ta\sqrt{2g}} = 0.62$$

where

$h_1 = 71.74\text{cm}$

$t = 89\text{sec}$

$a = 1.27\text{cm}^2$

$A = 182.41\text{cm}^2$

This value falls within the small range of values cited in King's tables of orifice coefficients (King, 1949), for water discharging into air for the same orifice diameter and head, h . He cites his values to be about the same as that of a submerged orifice.

With the value of c established we may now proceed with a discussion of the frequency response of the water level gauges. The following analysis is based on Keulegan's study of basins connected to the open sea, (Keulegan, 1951), with modifications made by Cross (Cross, 1967), for stilling well tide gauges.

The diameter of the stilling well, is 6.0-inches (15.24cm). The diameter of the orifice connecting the well to the sea is 0.5-inches (1.27cm). Continuity requires that any flow through this orifice results in a specific change of the level in the well. If a is the cross-sectional area of the orifice, A is the cross-sectional area of the well, H_1 is the water surface elevation inside the well and V is the flow velocity through the orifice, we have

$$aV = A\,\frac{dH_1}{dt} \qquad (1)$$

or

$$\frac{dH_1}{dt} = \frac{a}{A}V \qquad (1a)$$

Since the flow through the orifice is due to a difference between the inside and outside hydrostatic pressure, the velocity through the orifice may be expressed as

$$V = c\,\sqrt{2g\,(H_2 - H_1)} \qquad (2)$$

for flow into the well, and

$$V = -c\sqrt{2g\,(H_1 - H_2)} \qquad (3)$$

for flow out of the well. H_2 is the water surface elevation of the sea. Substituting these expressions for the flow velocity into the expression for the time rate of change of the water level elevation inside the well, we have

$$\frac{dH_1}{dt} = \frac{a}{A}\, c\sqrt{2g(H_2 - H_1)} \qquad (4)$$

for flow into the well, and

$$\frac{dH_1}{dt} = -\frac{a}{A}\, c\sqrt{2g(H_1 - H_2)} \qquad (5)$$

for the flow out of the well. If H_0 is the amplitude of the sea level fluctuation we have the following dimensionless variables

$$h_1 = H_1/H_0 \qquad (6a)$$

$$h_2 = H_2/H_0 \qquad (6b)$$

If we also introduce the following transformation,

$$t/T = \Theta/2\pi \qquad (7)$$

Where T is the period of the sea level fluctuation, we finally obtain

$$\frac{dh_1}{d\Theta} = K\sqrt{h_2 - h_1} \qquad h_2 > h_1 \qquad (8)$$

and

$$\frac{dh_1}{d\Theta} = -K\sqrt{h_1 - h_2} \qquad h_2 < h_1 \qquad (9)$$

where

$$K = \frac{T}{2\pi H_0}\,\frac{a}{A}\, c\sqrt{2gH_0} \qquad (10)$$

K is called the coefficient of repletion.

In finding an expression for h_1 we begin by assuming that the water surface elevation of the sea fluctuates sinusoidally. The displacements of the water surfaces in the sea and in the basin are given on a common axis of the dimensionless time parameter Θ(Figure 16). The origin of time is taken at the moment h_1 and h_2 are equal. The moment thereafter h_2 begins to gain over h_1. Then $h_2=0$ when $t=\tau$. The fluctuation of the surface of the sea is therefore given by

$$h_2 = \sin(\Theta - \tau) \qquad 0<\Theta<2\pi \qquad (11)$$

Since it is assumed that $h_2 > h_1$, for a time $T/2$ and vice versa, Keulegan determines h separately for the first range, $0<\Theta<\pi$, and the second range, $\pi<\Theta<2\pi$. Also, instead of determining h_1 directly, the difference $h_1 - h_2$ is more conveniently found. Thus for the first range we have

$$z = h_2 - h_1 \qquad h_2 > h_1 \qquad 0<\Theta<\pi \qquad (12)$$

$$h_2 = \sin(\Theta - \pi)$$

$$\frac{dz}{d\Theta} = -K\sqrt{z} + dh_2 \qquad (13)$$

$$z = 0, \ \Theta = 0 \text{ and } \pi$$

Introducing our expression for h_2 into equation 13

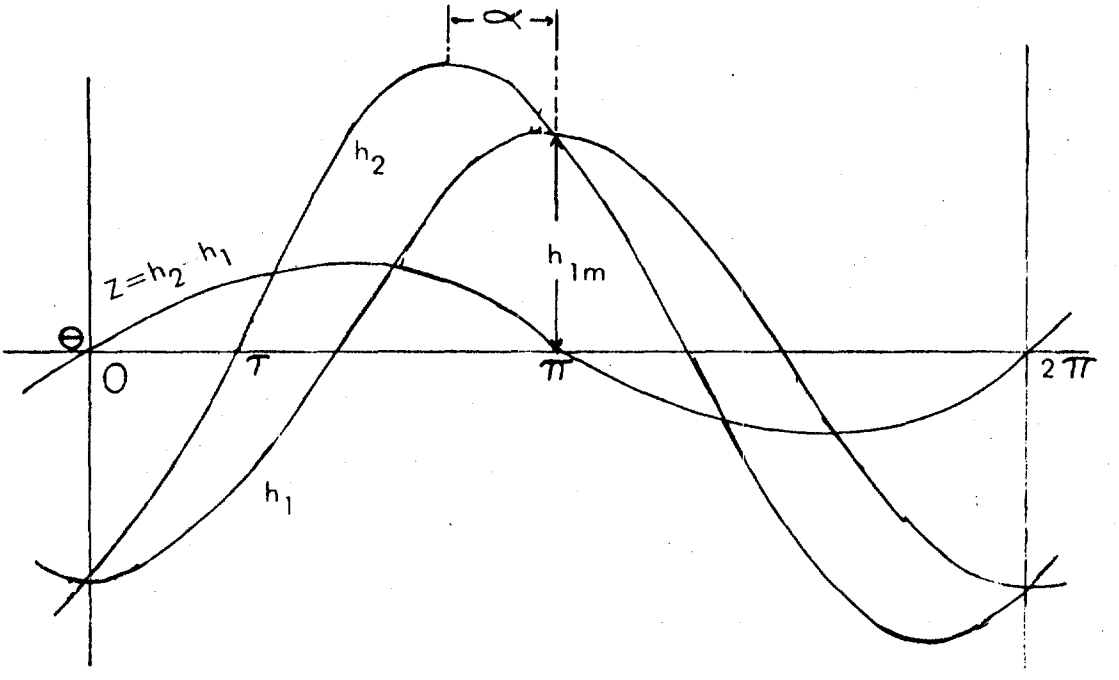
$$\frac{dz}{d\Theta} = -K\sqrt{z} + \cos\Theta \cos\tau + \sin\Theta \sin\tau \qquad (14)$$

For the sake of brevity there will be no further discussion of the determination of h_1, for the second range. Keulegan shows that the curve of h_1 for the second range is merely the curve of h_1 for the first range displaced along the axis of Θ by an amount π. He, therefore, deems it sufficient to determine for the first range only.

For a detailed solution the reader is referred to Keulegan (Keulegan, 1951). Only the major steps in his paper will be mentioned in what follows.

Figure 16

SURFACE FLUCTUATIONS OF THE SEA AND IN THE STILLING WELL



Since we are dealing with periodic changes, a series of circular functions is selected as a possible solution to equation 13 or 14, Keulegan chooses

$$z = \sum_{n=1} An \sin n\Theta + \sum_{n=1} Bn[\cos n\Theta - \cos(n+z)\Theta] \qquad (15)$$

$$n=1, 3, 5, \ldots\ldots\ldots\ldots, 2m+1$$

where we see that z vanishes when $\Theta=0$ and π .

In equation 1 there is the term $\sqrt{z}$ and it is found necessary to make use of the fourier expansion of $\sqrt{\sin\Theta}$. The $\sqrt{\sin\Theta}$ is single valued, finite, and continuous between the limits $\Theta=0$ and $\Theta=\pi$ and can therefore be developed into the series

$$\sqrt{\sin\Theta} = a_1 \sin\Theta + a_2 \sin 2\Theta + a_3 \sin 3\Theta \qquad (16)$$

where the coefficients have the values

$$a_m = \frac{2}{\pi}\int_0^{\pi} \sqrt{\sin\Theta} \sin m\Theta \, d\Theta \qquad (17)$$

Keulegan writes the following series for $\sqrt{\sin\Theta}$ in conforming with the above rule and his particular solution for;

$$\sqrt{\sin\Theta} = N_1 \sin\Theta + N_3 \sin 3\Theta + N_5 \sin 5\Theta \qquad (18)$$

where

$$N_m = \frac{2}{\pi}\int_0^{\pi} \sqrt{\sin\Theta} \sin m\Theta \, d\Theta$$

The values of the n's are found numerically by replacing the process of integration by the process of summation. For example

$$N_1 = \frac{2}{\pi} \sum \sqrt{\sin\Theta} \sin\Theta \, \Delta\Theta \qquad 0 \leq \Theta \leq \pi \qquad (19)$$

The summations were made by letting the interval $\Delta\Theta=0.03491$ radians. Since high accuracy was not needed the first two terms in the series were considered a good approximation of $\sqrt{\sin\Theta}$. The solution for

$$\frac{dz}{d\Theta} = -K\sqrt{z} + \cos\Theta \cos\tau + \sin\Theta \sin\tau$$

was taken to be

$$z = a_1 \sin\Theta + a_1 b_3 (\cos\Theta - \cos 3\Theta) + a_1 a_3 \sin 3\Theta \qquad (20)$$

The unknown quantities are the coefficients a_1, a_3, b_3, and the phase angle τ.

The square root of z, with small terms neglected, and the expression obtained by differentiating z with respect to Θ are both substituted in equation 14. From the result, Keulegan is able to obtain four separate expressions relating the four unknowns mentioned with each other and with N, and K whose values can be computed independently. With four equations and four unknowns it was found that a_1, a_3, b_3, and τ all depend individually on the coefficient of repletion K.

In recalling that

$$h_1 = z + h_2$$

and substituting the expressions found for a_1, a_3, and b_3 in equation 20 and that found for τ in equation 11; we see that the water level fluctuation in the stilling well can be expressed soley as a function of time for a particular value of K. We have

$$h_1 = a_1 \sin\Theta + a_1 b_3 (\cos\Theta - \cos 3\Theta) + a_1 a_3 \sin 3\Theta + \sin(\Theta - \tau) \qquad (21)$$

for

$$0 < \Theta < 2\pi$$

The maximum and minimum displacements of the water level in the stilling well was found to correspond to the zeroes of z ($\Theta = 0, \pi$) since $\frac{dh_1}{d\Theta}$ was found to vanish at these points (Figure 16). Now remembering a dimensionless quantity we see that h_{1m} gives the ratio of the range of the fluctuation inside the stilling well to the range of the fluctuation of the sea. Since at $\Theta = \pi$, $h_{1m} = h_2$ and at $\Theta = \pi$, $h_2 = \sin\tau$, the ratio of the range of the water level fluctuation in the well to that of the water level fluctuation of the sea is

$$h_{1m} = \sin\tau \qquad (22)$$

The values of h_{1m} as a function of K, that were presented by Keulegan (Keulegan, 1951), are given in the following table.

THE RESPONSE,

$$R = H_{1m}/H_0 = \sin\tau,$$

OF THE STILLING WELL TIDE GAUGE

AS A FUNCTION OF THE COEFFICIENT

OF REPLETION, K

K	$\sin\tau$	K	$\sin\tau$
0.1	0.1158	4.0	0.9999
0.2	0.2293	5.0	0.9999
0.3	0.3387	6.0	1.0000
0.4	0.4414	7.0	1.0000
0.5	0.5359	8.0	1.0000
0.6	0.6209	9.0	1.0000
0.7	0.6955	10.0	1.0000
0.8	0.7592	20.	1.0000
0.9	0.8165	30.	1.0000
1.0	0.8555	40.	1.0000
1.2	0.9168	50.	1.0000
1.4	0.9536	60.	1.0000
1.5	0.9745	70.	1.0000
1.8	0.9861	80.	1.0000
2.0	0.9926	90.	1.0000
3.0	0.9996	100.	1.0000

In Figure 17 we have plots of h_{1m} as a function of the wave period, T for the stilling wells used at Haulover Canal. Each line plot was for a specific value of h_0. Recalling the expression for K, we see that the coefficient of repletion and the wave period are directly related. We get the specific relation between K, T and h_0 for the stilling wells used at Haulover Canal by substituting in the expression for K the values of the cross-sectional area of the stilling well, the orifice, and the value of our particular orifice coefficient. We see that

$$K=0.0055\frac{T}{H_o^{1/2}} \qquad (23)$$

For sea level fluctuations with an amplitude of 0.91m and for periods of over 13 minutes we have a 100% representation of that amplitude in the stilling wells used at Haulover Canal. At the amplitudes which were in the range of those measured at Haulover Canal, H_0=0.30m and H_0=0.15m, we have periods of 7 and 5 minutes, respectively, that are necessary for 100% representation in the stilling wells. It is certain that the time necessary for the prevailing winds to pile water at the canal to 15cm above the previous level is much greater than 5 minutes. Therefore, we can see that the water level inside the stilling well, at any instant is an accurate representation of the water level outside the well, resulting from wind piling. As Figure 17 shows, waves of high frequency are damped out, which is, of course, the purpose of the stilling well.

The lag denoted as α, between the maximum displacement of the water level of the sea and the water level in the stilling well is also of importance in looking at the total pictures of the response of our gauges. Our expression for h_2:

$$h_2=\sin(\Theta-\tau)$$

tells us that h_2 is a maximum when $\Theta-\tau=\pi/2$. The maximum displacement in the well occurs when $\Theta=\pi$. Therefore, the lag is

$$\alpha=\pi/2-\tau \qquad (24)$$

Figure 17

RESPONSE OF THE TIDE GAUGE AS A FUNCTION OF WAVE PERIOD

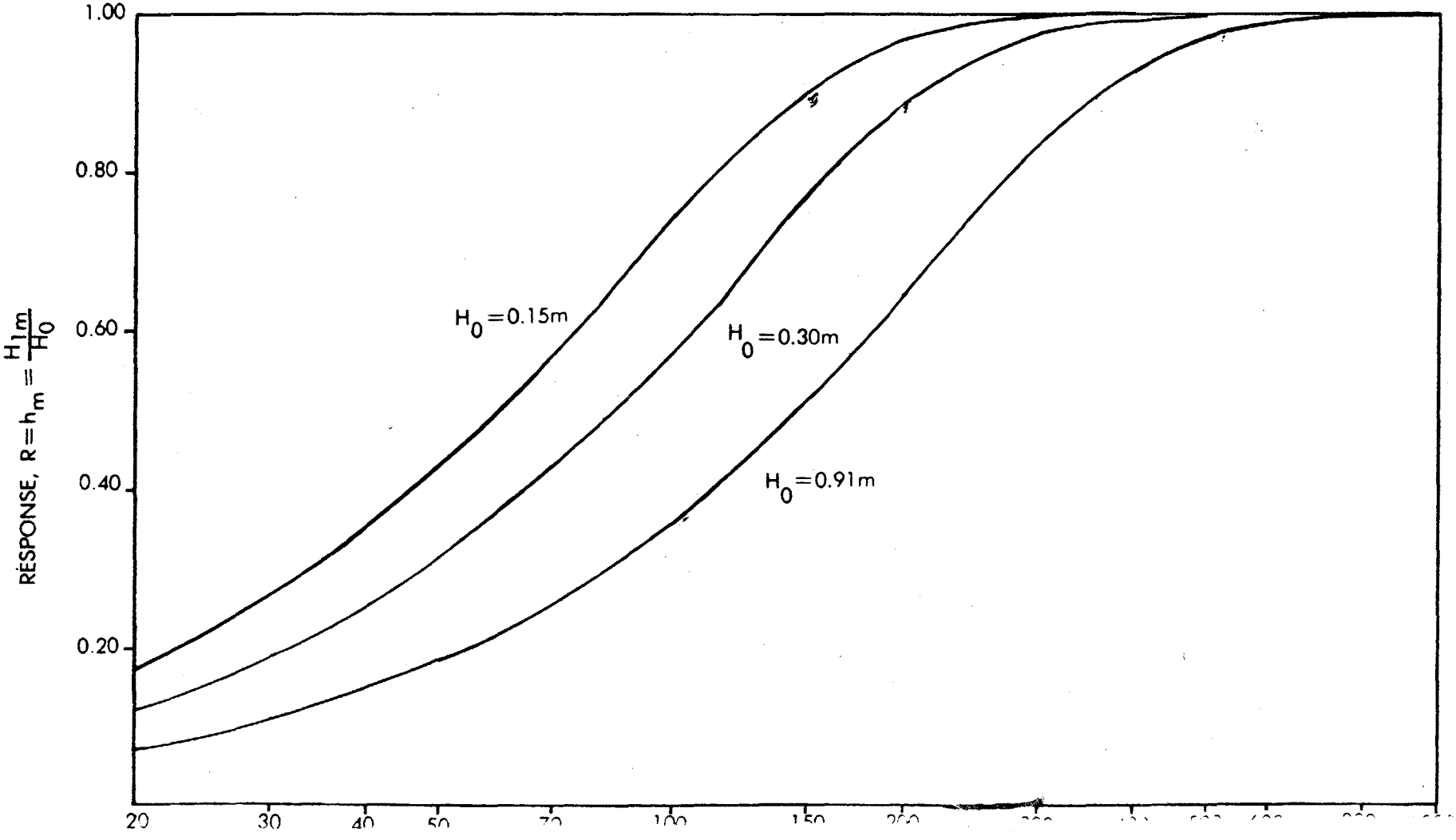
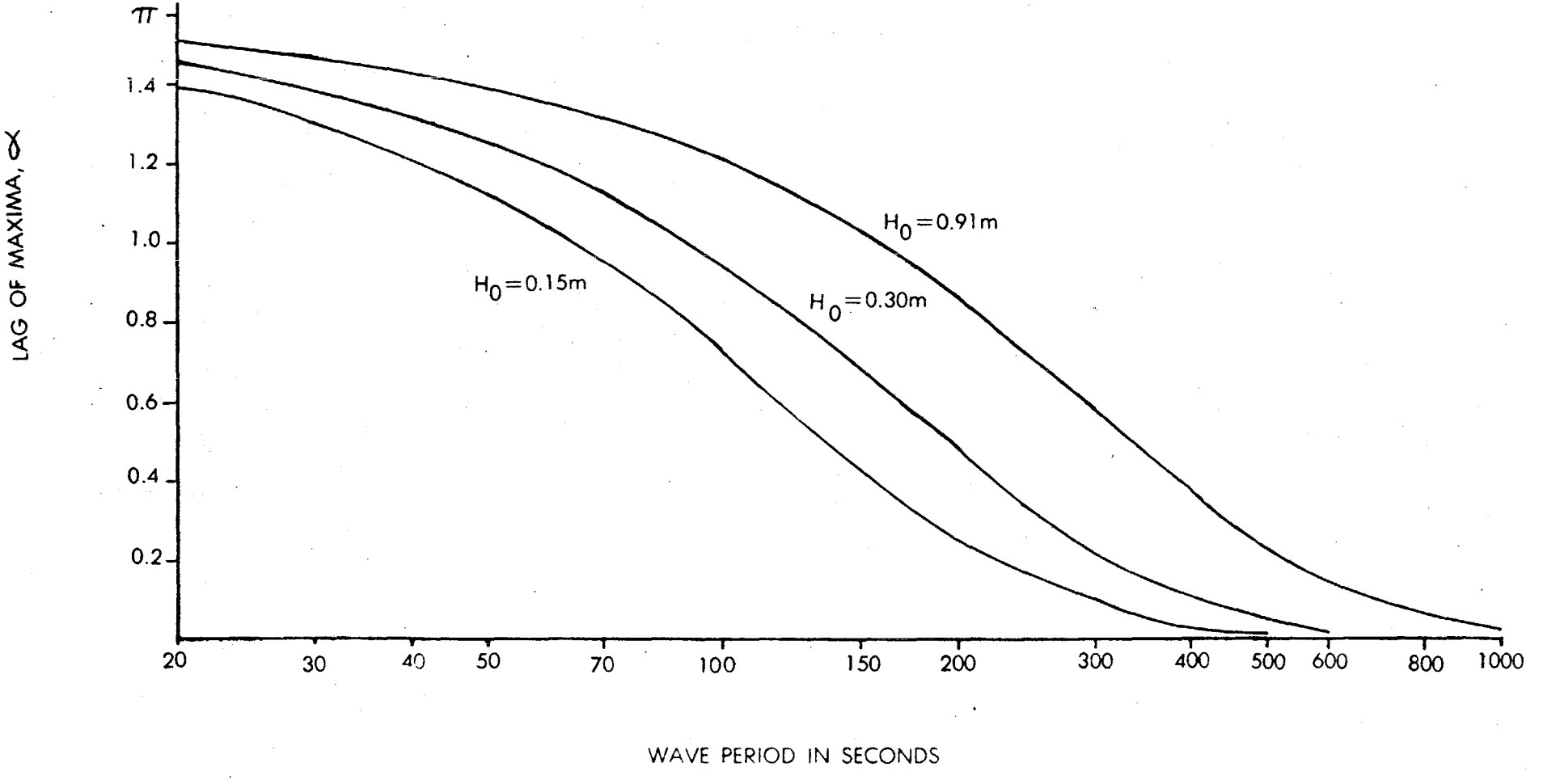


Figure 18

LAG OF THE TIDE GAUGE RESPONSE AS A FUNCTION WAVE PERIOD



The values of α are obtained from substituting the values of $\tau = \sin^{-1} h_{1m}$ in the above equation. Again making use of the direct relationship between K and the wave period T, lines representing the lag of the maxima as a function of wave period were plotted for the three specific values of h_0 used in Figure 17. We see that there is no appreciable lag between the maximum amplitudes inside and outside of the well for external amplitudes of 0.15m, 0.30m, and 0.91m with the respective periods of 8, 10, and 16 minutes.

We see from both Figure 17 and Figure 18 that the stilling well tide gauges used in this work show good response to water level changes induced by wind piling while filtering out undesirable high frequency waves.

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Section V, Article 16

Statistical Study of the Total Surface Area and Total Volume of the Lagoonal System of the East Florida Coast (Mosquito Lagoon and Indian River) from $28^{\circ}52'N$ to $27^{\circ}10'N$

Bernard Cohenour

Statistical Study
of
Total Surface Area and Total Volume
of
the Lagoonal System of East Florida Coast
(Mosquito Lagoon and Indian River)
from $28^{O}52'$ N to $27^{O}10'$ N

Bernard Cohenour
Spring 1974
Florida Institute of Technology

Definition of Numerical Classification
of the Lagoonal System

I. $28^{o}52'$ N - $28^{o}40'$ N (Mosquito Lagoon)
II. $28^{o}48'$ N - $28^{o}39'$ N (Railroad Bridge)
III. Railroad Bridge - Titusville Causeway (SR 402)
IV. Titusville Causeway - Addison Pt. Bridge (SR 405
V. Addison Pt. - Canaveral Barge Canal Causeway
VI. Canaveral Barge Canal - Cocoa Causeway (SR 520)
VII. Cocoa Causeway - Pineda Causeway
VIII. Pineda Causeway - Eau Gallie Causeway (SR 518)
IX. Eau Gallie Causeway - Melbourne Causeway (SR 516)
X. Melbourne Causeway - Cape Malabar
XI. Cape Malabar - Grant Farm
XII. Grant Farm - Sebastian Inlet
XIII. Sebastian Inlet - Vero Beach Canal Causeway
XIV. Vero Beach - Fort Pierce Inlet
XV. Fort Pierce Inlet - Bascule Bridge ($27^{o}15'$N)
XVI. Bascule Bridge - Baker Pt. (AIA)
XVII. Baker Pt. - St. Lucie Inlet ($27^{o}10'$ N)

Conversions

1 sq. ft. = 0.0929 m^2

1 ft. = 0.3048 m

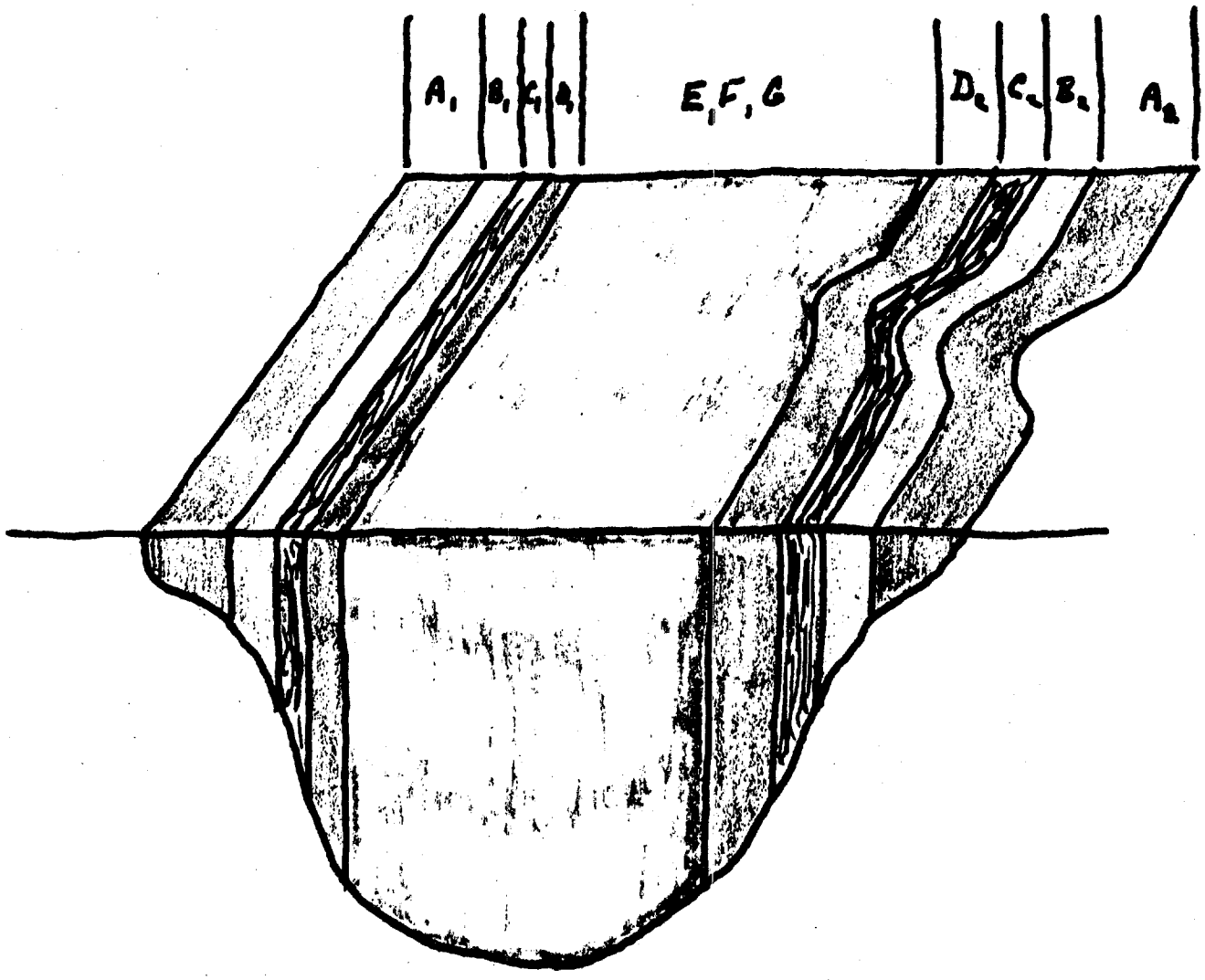
Alphabetical Classification of Depths

	feet		
A	0-2	0- .6096	0-0.6
B	2-4	.6096-1.2192	.6-1.2
C	4-6	1.2192-1.8288	1.2-1.8
D	6-8	1.8288-2.4384	1.8-2.4
E	8-10	2.4384-3.0480	2.4-3.0
F	10-12	3.0480-3.6576	3.0-3.6
G	12-14	3.6576-4.2672	3.6-4.3

Charts Used:

1. Nautical Chart #843-SC (1973)
2. Nautical Chart #845-SC (1971)

U.S. Department of Commerce, N.O.A.A.
National Ocean Survey



CROSS SECTION OF THE LAGOONAL SYSTEM

THREE DIMENSIONAL REFERENCE OF SURFACE AREA AND VOLUME MEASUREMENTS

$A_1 + A_2$ + Areas around Island at 0-2 ft = A_1
$B_1 + B_2$ + Areas around Island at 2-4 ft = B_1 etc.

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Project: _____ Date of Sampling: _____

Location: _____ Specific Area: _____

Site	Depth	MEASUREMENTS Area $ft^2 \times 10^6$	Area $m^2 \times 10^6$	Vol gal $\times 10^9$	Vol 1×10^9	Partial % Area	Partial % Vol	Total % Area	Total % Vol
I	A	567.5	52.7	4.2	16.1	51.0	19.1	8.1	2.0
	B	180.7	16.8	4.1	15.3	16.2	18.1	2.6	1.9
	C	339.9	31.6	12.7	48.1	30.6	57.0	4.9	6.1
	D	24.2	2.2	1.3	4.8	2.2	5.7	.3	.6
		1112.3	103.3	22.3	84.3	100.0	99.9	15.9	10.7
II	A	305.6	28.4	2.3	8.6	32.3	9.8	4.4	1.1
	B	226.5	21.0	5.1	19.2	24.0	22.0	3.2	2.4
	C	396.1	36.8	14.8	56.1	41.9	64.2	5.7	7.1
	D	17.5	1.6	.9	3.5	1.8	4.0	.2	.4
		945.7	87.8	23.1	87.4	100.0	100.0	13.5	11.0
III	A	25.2	2.3	.2	.7	24.2	5.8	.4	.1
	B	21.5	2.0	.5	1.8	20.8	14.9	.3	.2
	C	31.1	2.9	1.2	4.4	30.0	36.4	.4	.6
	D	26.3	2.4	2.4	5.2	25.0	43.0	.4	.6
		104.1	9.6	3.3	12.1	100.0	100.0	1.5	1.5
IV	A	80.0	7.4	.6	2.3	13.3	2.6	1.1	.3
	B	69.3	6.4	1.6	5.9	11.5	6.6	1.0	.7
	C	165.6	15.4	6.2	23.4	27.5	26.4	2.4	3.0
	D	282.0	26.2	14.8	55.9	46.8	63.0	4.0	7.0
	E	5.1	.5	.3	1.3	.9	1.5	.1	.2
		602.0	55.9	23.5	88.8	100.0	100.1	8.6	11.2

Project: _____ Date of Sampling: _____

Location: _____ Specific Area: _____

Site	Depth	MEASUREMENTS Area $ft^2 \times 10^6$	Area $m^2 \times 10^6$	Vol gal $\times 10^9$	Vol 1×10^9	Partial % Area	Partial % Vol	Total % Area	Total % Vol
V	A	107.3	10.0	.8	3.0	17.6	4.1	1.5	.4
	B	138.5	12.9	3.1	11.8	22.6	16.2	2.0	1.5
	C	146.5	13.6	5.5	20.7	23.9	28.4	2.1	2.6
	D	184.8	17.2	9.7	36.6	30.2	50.1	2.6	4.6
	E	34.6	3.2	.2	.9	5.6	1.2	.5	.1
		611.7	56.9	19.3	73.0	99.9	100.0	8.7	9.2
VI	A	24.6	2.3	.2	.7	20.4	4.1	.4	.1
	B	21.8	2.0	.5	1.8	18.0	10.6	.3	.2
	C	22.6	2.1	.8	3.2	18.8	18.8	.3	.4
	D	37.8	3.5	2.0	7.5	31.3	44.1	.5	.9
	E	8.2	.8	.6	2.1	6.8	12.3	.1	.3
	F	5.5	.5	.4	1.7	4.6	10.0	.1	.2
		120.5	11.2	4.5	17.0	99.9	99.9	1.7	2.1
VII	A	32.9	3.1	.2	.9	10.4	1.4	.5	.1
	B	28.5	2.6	.6	2.4	9.0	3.7	.4	.3
	C	48.0	4.4	1.8	6.8	15.2	10.5	.7	.9
	D	54.4	5.0	2.8	10.8	17.2	16.6	.8	1.4
	E	88.4	8.2	5.9	22.5	28.0	36.4	1.3	2.8
	F	29.6	2.7	2.4	9.2	9.3	14.1	.4	1.2
	G	33.7	3.1	3.3	12.4	12.9	19.1	.5	1.6
		315.5	29.1	17.0	65.0	100.0	100.0	4.6	8.3

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Project: _____ Date of Sampling: _____

Location: _____ Specific Area: _____

Site	Depth	MEASUREMENTS Area $ft^2 \times 10^6$	Area $m^2 \times 10^6$	Vol gal $\times 10^9$	Vol $l \times 10^9$	Partial % Area	Partial % Vol	Total % Area	Total % Vol
VIII	A	5.8	.5	.04	.2	2.8	.4	.1	.02
	B	15.4	1.4	.3	1.3	7.3	2.4	.2	.2
	C	19.2	1.8	.7	2.7	9.0	5.0	.3	.3
	D	24.0	2.2	1.2	4.8	11.4	8.9	.3	.6
	E	24.2	2.2	1.7	6.3	11.5	11.7	.3	.8
	F	116.5	10.8	9.6	36.3	55.2	67.5	1.7	4.6
	G	5.9	.6	.6	2.2	2.8	4.1	.1	.3
		211.0	19.5	14.1	53.8	100.0	100.0	3.0	6.8
IX	A	19.8	1.8	.1	.6	11.2	1.8	.3	.1
	B	32.0	3.0	.7	2.7	18.2	8.3	.5	.3
	C	28.4	2.6	1.1	4.0	16.0	12.3	.4	.5
	D	27.8	2.6	1.4	5.5	15.8	17.0	.4	.7
	E	29.9	2.8	2.0	7.6	16.9	23.4	.4	1.0
	F	38.5	3.6	3.2	12.0	21.8	37.0	.6	1.5
		176.4	16.4	8.5	32.4	99.9	99.8	2.6	4.1
X	A	25.8	2.4	.2	.7	11.8	1.9	.4	.1
	B	35.3	3.3	.8	3.0	16.1	8.0	.5	.4
	C	40.7	3.8	1.5	5.8	21.5	15.5	.7	.7
	D	40.6	3.8	2.1	8.1	18.5	21.6	.6	1.0
	E	52.7	4.9	3.5	13.4	24.0	35.7	.8	1.7
	F	17.8	1.6	1.5	6.5	8.0	17.3	.2	.8
		212.9	19.8	9.6	37.5	99.9	100.0	3.2	4.7

Project:_____ Date of Sampling:_____

Location:_____ Specific Area:_____

Site	Depth	MEASUREMENTS Area $ft^2 \times 10^6$	Area $m^2 \times 10^6$	Vol gal $\times 10^9$	Vol 1×10^9	Partial % Area	Partial % Vol	Total % Area	Total % Vol
XI	A	73.7	6.8	.5	2.1	21.5	5.1	1.0	.3
	B	107.8	10.0	2.4	9.2	31.4	22.5	1.5	1.2
	C	71.2	6.6	2.7	10.1	20.8	24.7	1.0	1.3
	D	66.3	6.2	3.5	13.1	19.3	32.0	1.0	1.6
	E	16.7	1.6	1.1	4.2	4.9	10.3	.2	.5
	F	7.2	.7	.6	2.2	2.1	5.4	.1	.3
		342.9	31.9	10.8	40.9	100.0	100.0	4.8	5.2
XII	A	62.0	5.8	.5	1.8	23.0	6.8	.9	.2
	B	84.0	7.8	1.9	7.1	31.1	26.7	1.2	.9
	C	119.6	11.1	4.5	16.9	44.3	63.5	1.7	2.1
	D	4.2	.4	.3	.8	1.6	3.0	.1	.1
		269.8	25.1	7.2	26.6	100.0	100.0	3.9	3.3
XIII	A	114.1	10.6	.8	3.2	24.3	13.5	1.6	.4
	B	225.7	21.0	.5	1.9	48.0	8.0	3.2	.2
	C	128.7	12.0	4.8	18.2	27.3	76.8	1.8	2.3
	D	1.9	.2	.1	.4	.4	1.7	.02	.05
		470.4	43.8	6.2	23.7	100.0	100.0	6.6	2.9
XIV	A	204.8	19.0	1.5	5.8	43.5	15.7	2.9	.7
	B	143.6	13.3	3.2	12.2	30.5	33.0	2.1	1.5
	C	91.1	8.5	3.4	12.9	19.4	34.9	1.3	1.6
	D	30.8	2.9	1.6	6.1	6.6	16.5	.4	.8
		470.3	43.7	9.7	37.0	100.0	100.1	6.7	4.6

Project: _____ Date of Sampling: _____

Location: _____ Specific Area: _____

Site	Depth	MEASUREMENTS Area $ft^2 \times 10^6$	Area $m^2 \times 10^6$	Vol gal. $\times 10^9$	Vol 1×10^9	Partial % Area	Partial % Vol	Total % Area	Total % Vol
XV	A	125.4	11.6	.9	3.6	17.0	4.2	1.8	.4
	B	171.9	16.0	3.8	14.6	23.4	16.9	2.5	1.8
	C	331.6	30.8	12.4	46.9	45.0	54.3	4.8	5.9
	D	107.1	10.0	5.6	21.2	14.5	24.6	1.5	2.7
		736.0	68.4	22.7	86.3	99.9	100.0	10.6	10.8
XVI	A	23.4	2.2	.2	.7	15.8	4.1	.3	.1
	B	37.6	3.5	.8	3.2	25.7	18.7	.5	.4
	C	68.4	6.4	2.6	9.7	46.4	56.7	1.0	1.2
	D	17.8	1.6	.9	3.5	12.0	20.5	.2	.4
		147.2	13.7	4.5	17.1	99.9	100.0	2.0	2.1
XVII	A	37.7	3.5	.3	1.1	31.3	11.7	.5	.1
	B	61.8	5.7	1.4	5.2	51.2	55.3	.9	.7
	C	18.6	1.7	.7	2.6	15.5	27.7	.3	.3
	D	2.3	.2	.1	.5	1.9	5.3	.03	.1
		120.4	11.1	2.5	9.4	99.9	100.0	1.7	1.2

Project: _____ Date of Sampling: _____

Location: _____ Specific Area: _____

Site	Depth	MEASUREMENTS Area $ft^2 \times 10^6$	Area $m^2 \times 10^6$	Vol gal $\times 10^9$	Vol 1×10^0		Total % Area	Vol						
I		1112.3	103.3	22.3	84.3		15.9	10.7						
II		945.7	87.8	23.1	87.4		13.5	11.0						
III		104.1	9.6	3.3	12.1		1.5	1.5						
IV		602.0	55.9	23.5	88.5		8.6	11.2						
V		611.7	56.9	19.3	73.0		8.7	9.2						
VI		120.5	11.2	4.5	17.0		1.7	2.1						
VII		315.5	29.1	17.0	65.0		4.6	8.3						
VIII		211.0	19.5	14.1	53.8		3.0	6.8						
IX		176.4	16.4	8.5	32.4		2.6	4.1						
X		212.09	19.8	9.6	37.5		3.2	4.7						
XI		342.9	31.9	10.8	40.9		4.8	5.2						
XII		269.9	25.1	7.2	26.6		3.9	3.3						
XIII		470.4	43.8	6.2	23.7		6.7	2.9						
XIV		470.3	43.7	9.7	37.0		6.7	4.3						
XV		736.0	68.4	22.7	26.3		10.6	10.8						
XVI		147.2	13.7	4.5	17.1		2.0	2.1						
XVII		120.4	11.1	2.5	9.4		1.7	1.2						
		6969.1	647.2	208.8	792.3		99.7	99.4						

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Project: _____ Date of Sampling: _____

Location: _____ Specific Area: _____

Site	Depth	Total % Area - Depth A	B	C	D	E	F	G		Total % Each Site				
I		8.1	2.6	4.9	.3					15.9				
II		4.4	3.2	5.7	.2					13.5				
III		.4	.3	.4	.4					1.5				
IV		1.1	1.0	2.4	4.0	.1				8.6				
V		1.5	2.0	2.1	2.6	.5				8.7				
VI		.4	.3	.3	.5	.1	.1			8.7				
VII		.5	.4	.7	.8	1.3	.4	.5		4.6				
VIII		.1	.2	.3	.3	.3	1.7	.1		3.0				
IX		.3	.5	.4	.4	.4	.6			2.6				
X		.4	.5	.7	.6	.8	.2			3.2				
XI		1.0	1.5	1.0	1.0	.2	.1			4.8				
XII		.9	1.2	1.7	.1					3.9				
XIII		1.6	3.2	1.8	.02					6.7				
XIV		2.9	2.1	1.3	.4					6.7				
XV		1.8	2.5	4.8	1.5					10.6				
XVI		.3	.5	1.0	.2					2.0				
XVII		.5	.9	.3	.03					1.7				
		26.2	22.9	29.8	13.3	3.7	3.1	.6		99.7				

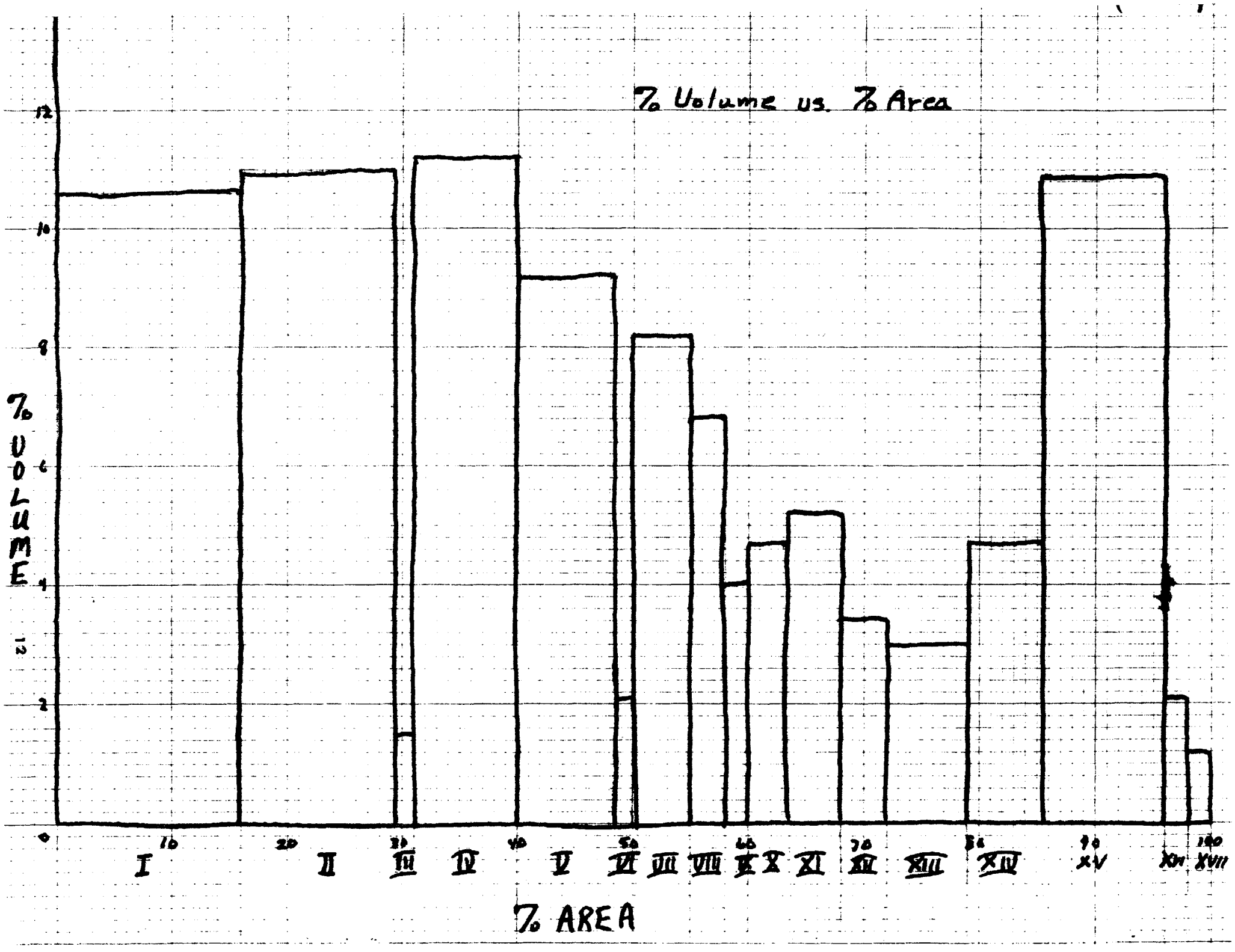
Project: _____ Date of Sampling: _____

Location: _____ Specific Area: _____

Total % Vol - Depth

Site	Depth	A	B	C	D	E	F	G		Total % Each Site				
I		2.0	1.9	6.1	.6					10.7				
II		1.1	2.4	7.1	.4					11.0				
III		.1	.2	.6	.6					1.5				
IV		.3	.7	3.0	7.0	.2				11.2				
V		.4	1.5	2.6	4.6	.1				9.2				
VI		.1	.2	.4	.9	.3	.2			2.1				
VII		.1	.3	.9	1.4	2.8	1.2	1.6		8.3				
VIII		.02	.2	.3	.6	.8	4.6	.3		6.8				
IX		.1	.3	.5	.7	1.0	1.5			4.1				
X		.1	.4	.7	1.0	1.7	.8			4.7				
XI		.3	1.2	1.3	1.6	.5	.3			5.2				
XII		.2	.9	2.1	.1					3.3				
XIII		.4	.2	2.3	.05					2.9				
XIV		.7	1.5	1.6	.8					4.3				
XV		.4	1.8	5.9	2.7					10.8				
XVI		.1	.4	1.2	.4					2.1				
XVII		.1	.7	.3	.1					1.2				
		6.5	14.8	36.9	23.5	7.4	8.6	1.9		99.4				
									99.6					

11


% Volume vs. % Area
% VOLUME
% AREA
0
2
4
6
8
10
12
10
20
30
40
50
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70
80
90
100
I
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VIII
IX
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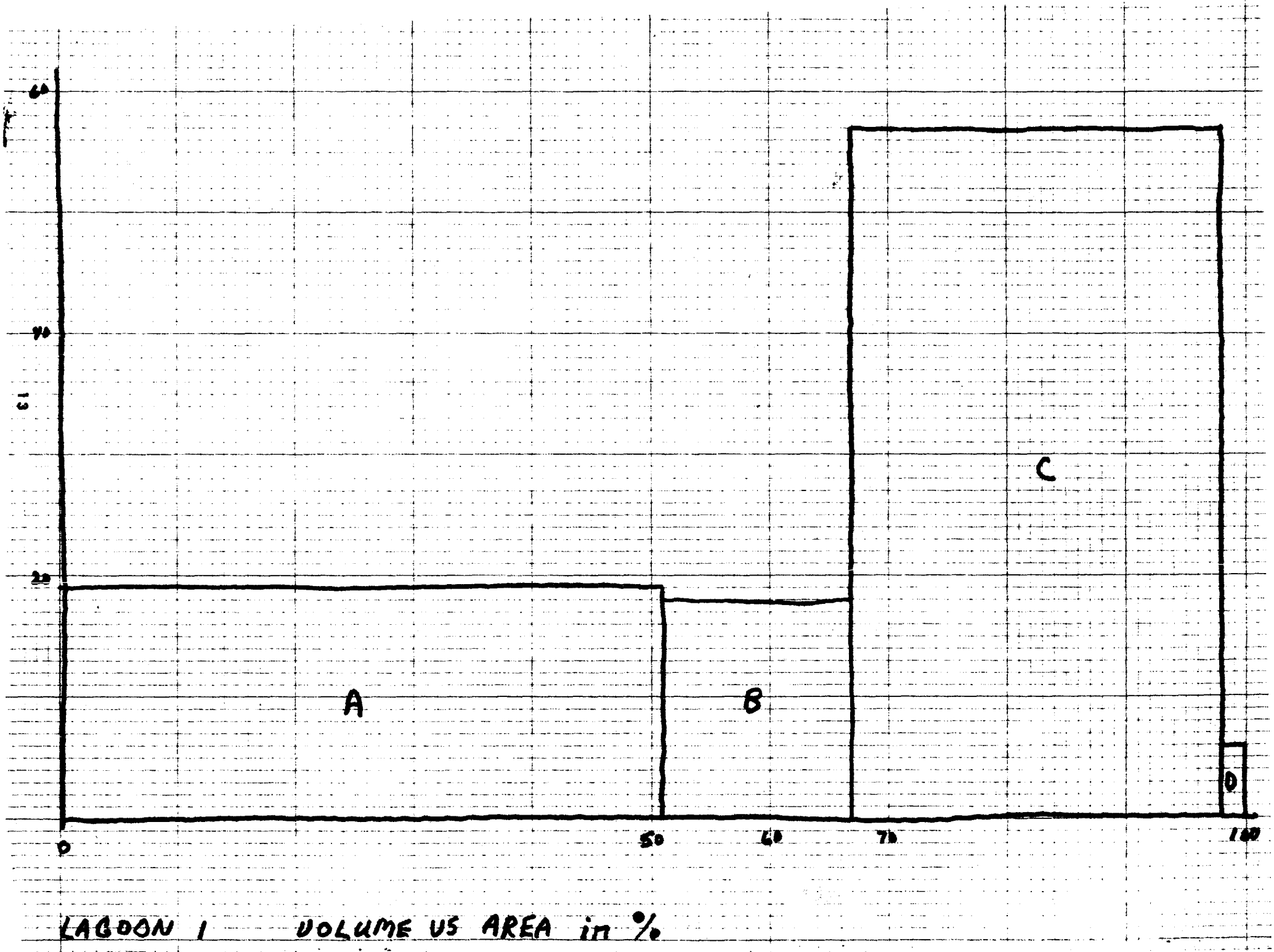
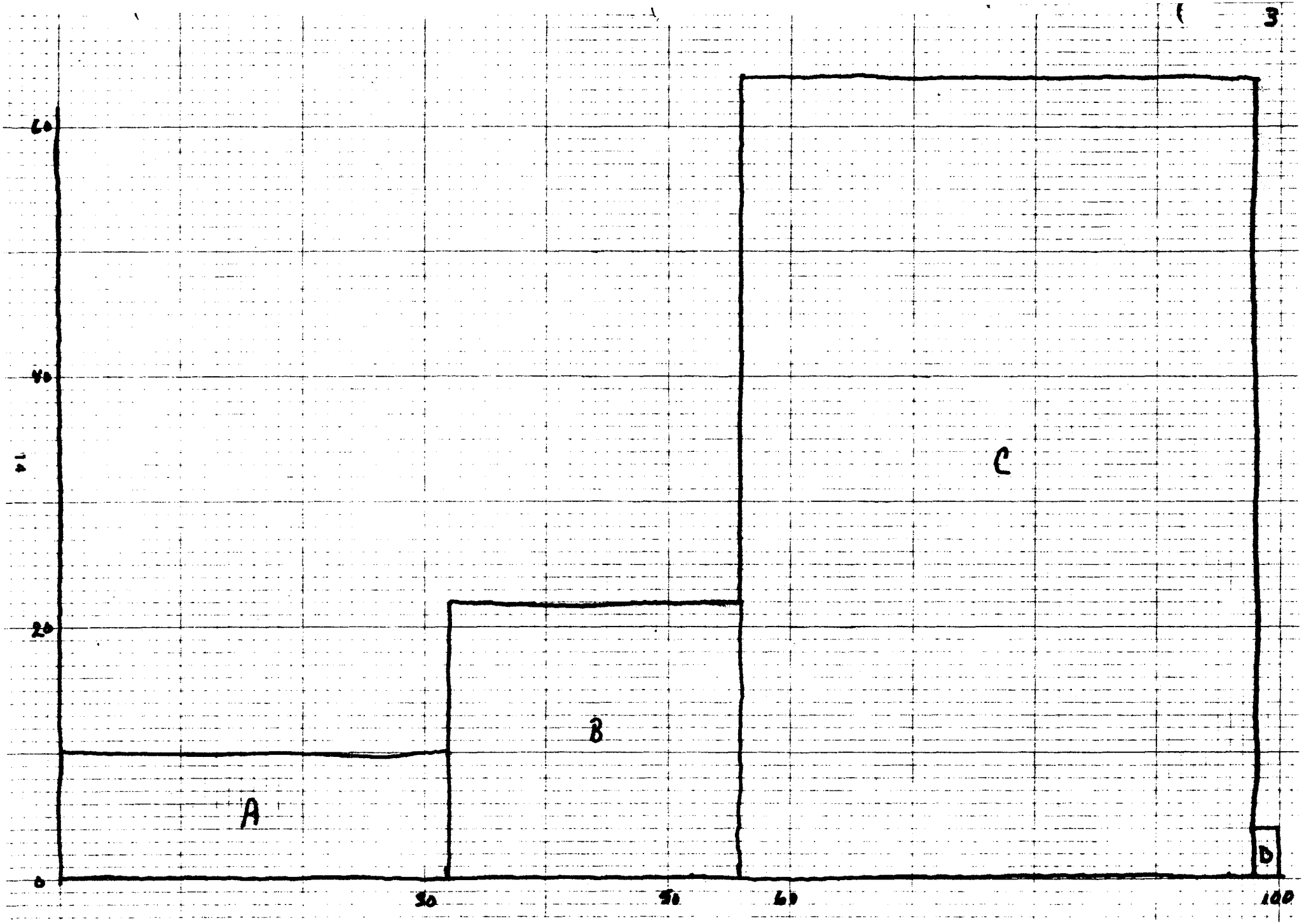
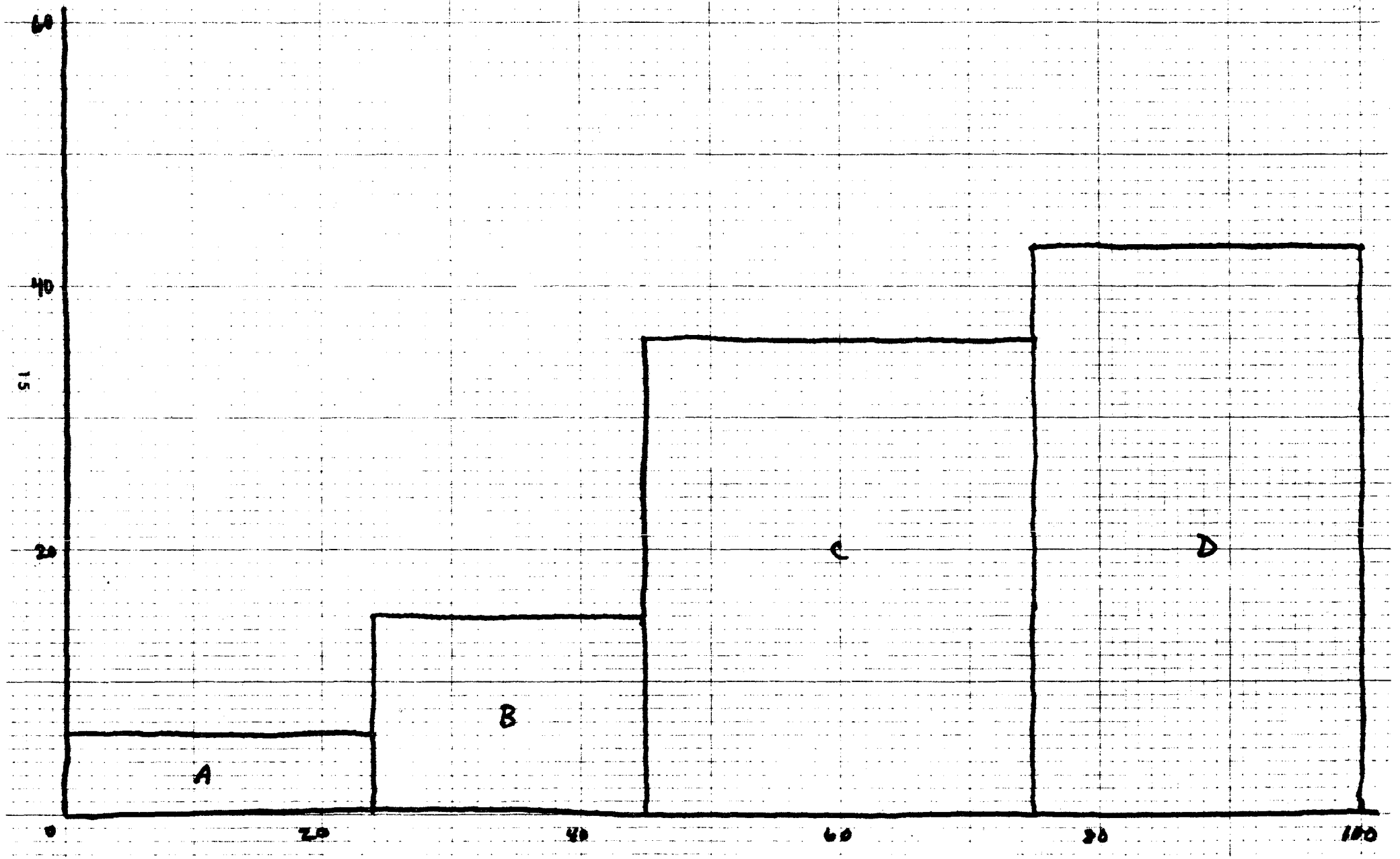
XI
XII
XIII
XIV
XV
XVI
XVII



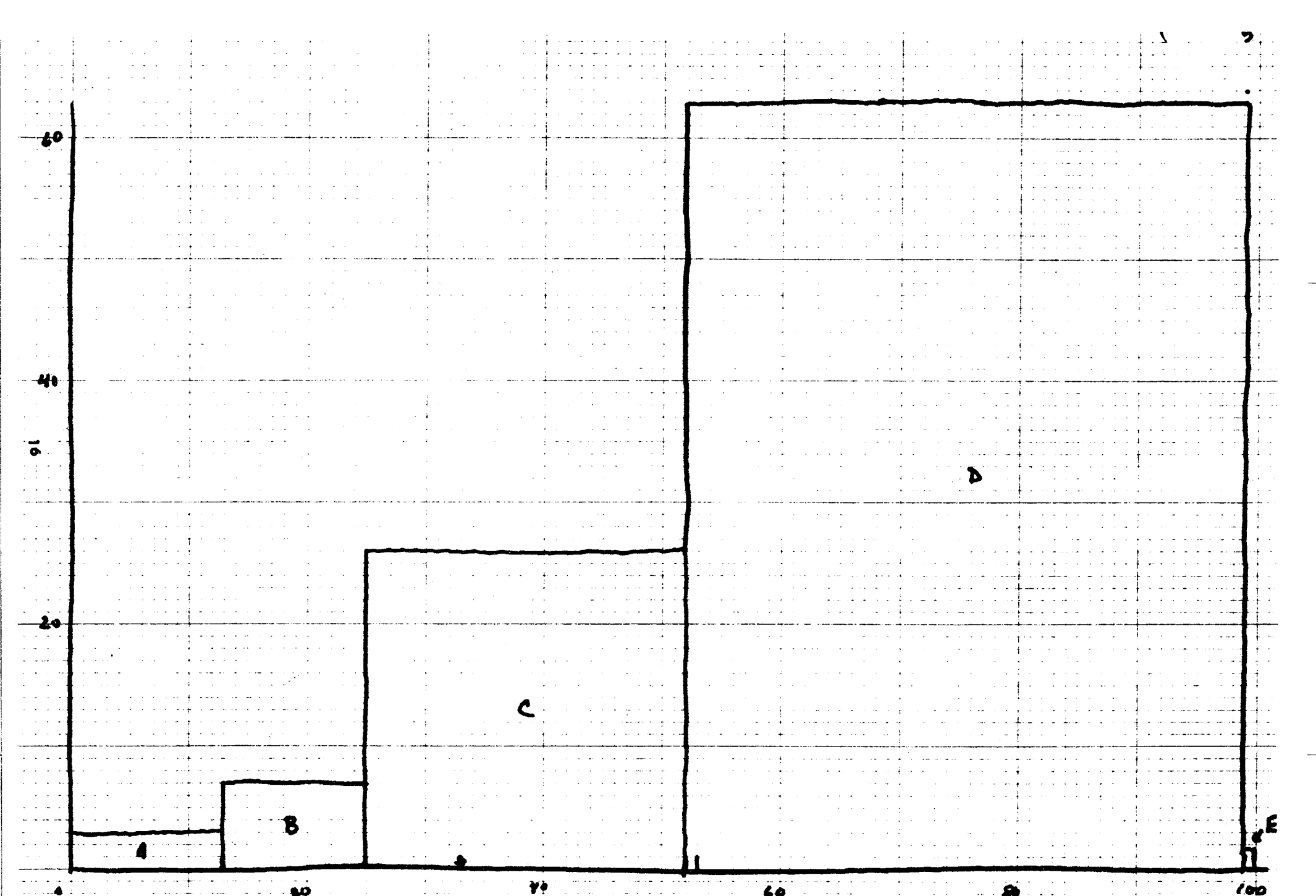
LAGOON 1 VOLUME VS AREA in %



JACKSON T... VOLUME VS. AREA ... 01



LAGOON III VOLUME VS AREA in %



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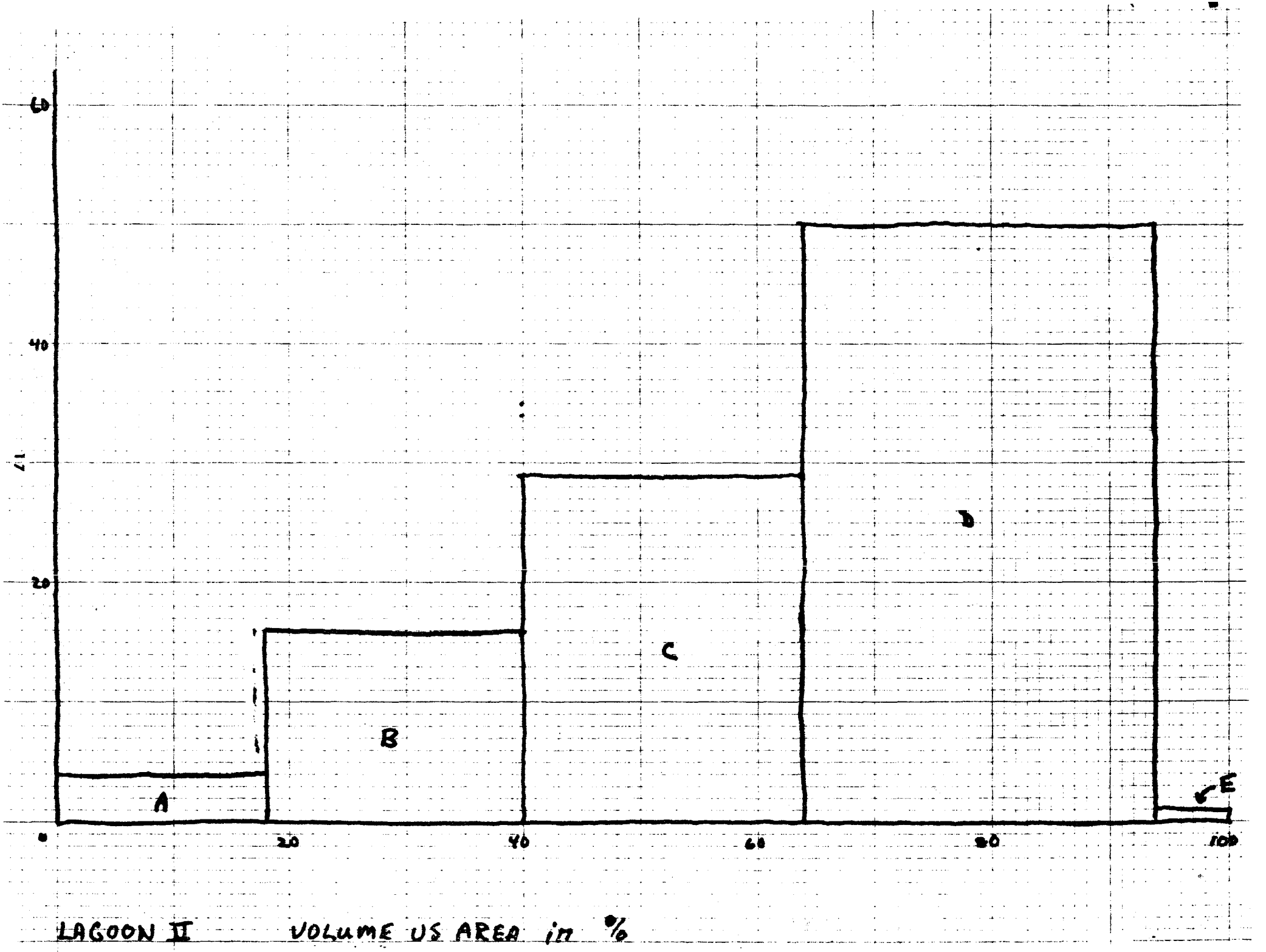
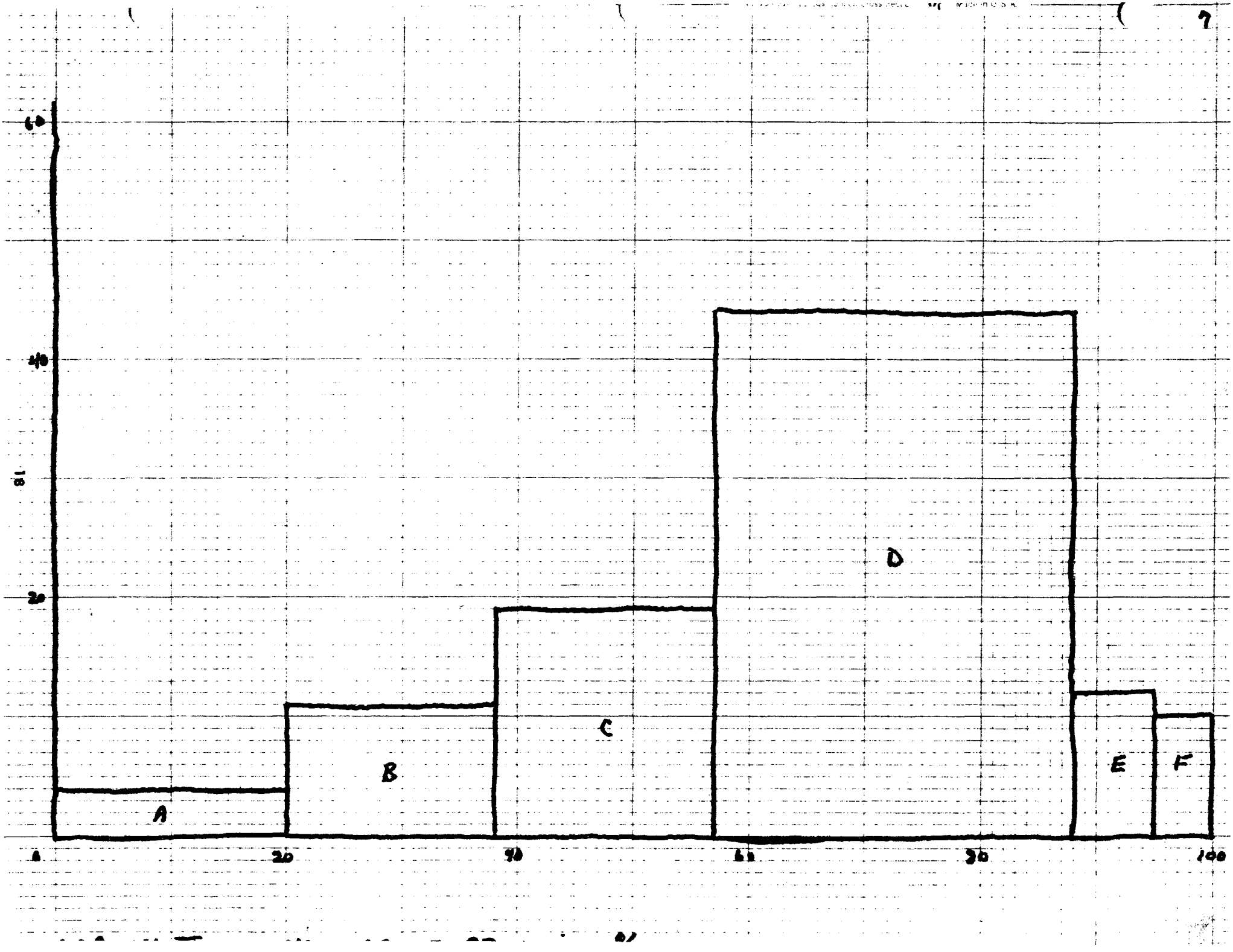


LAGOON II VOLUME US AREA in %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A
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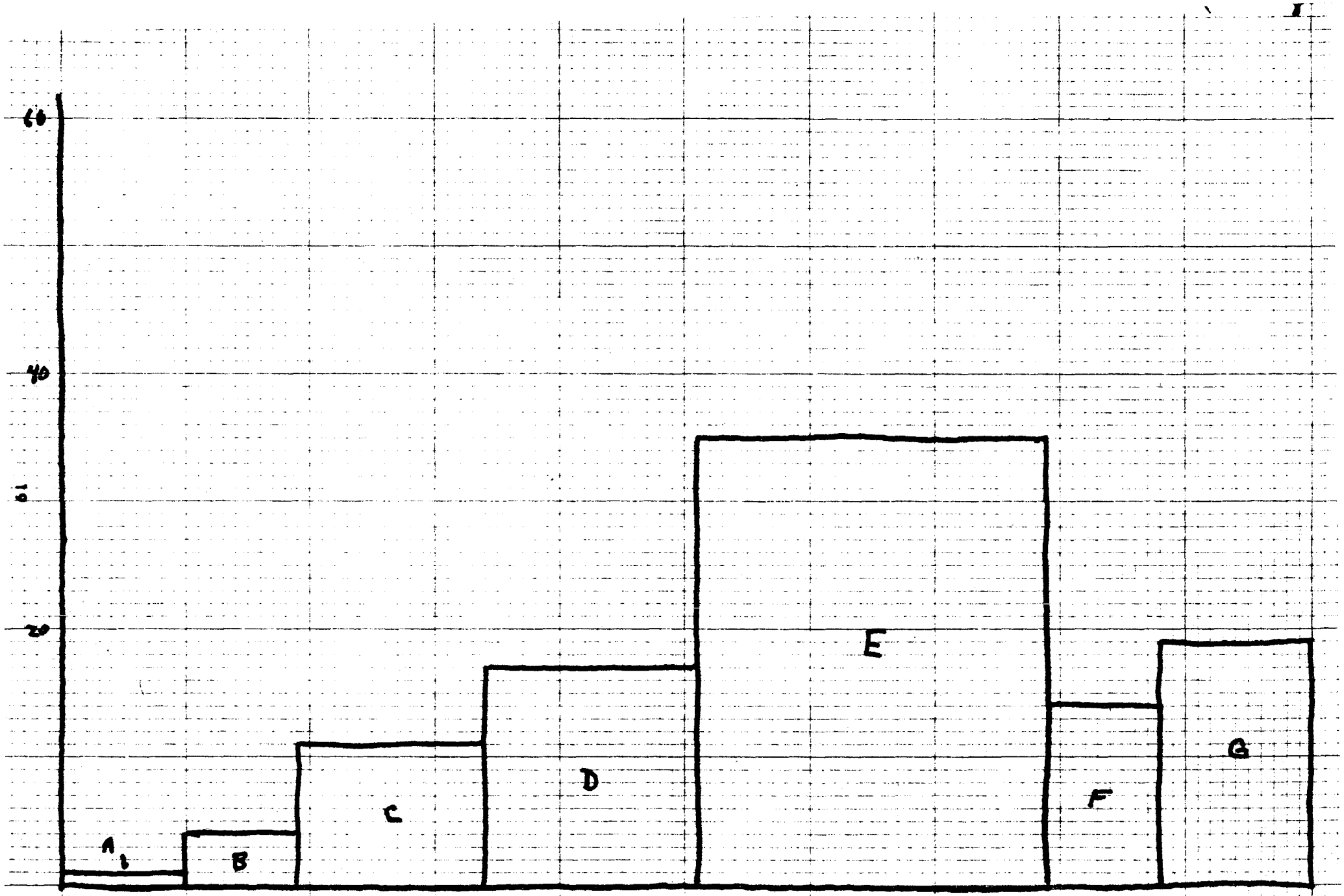
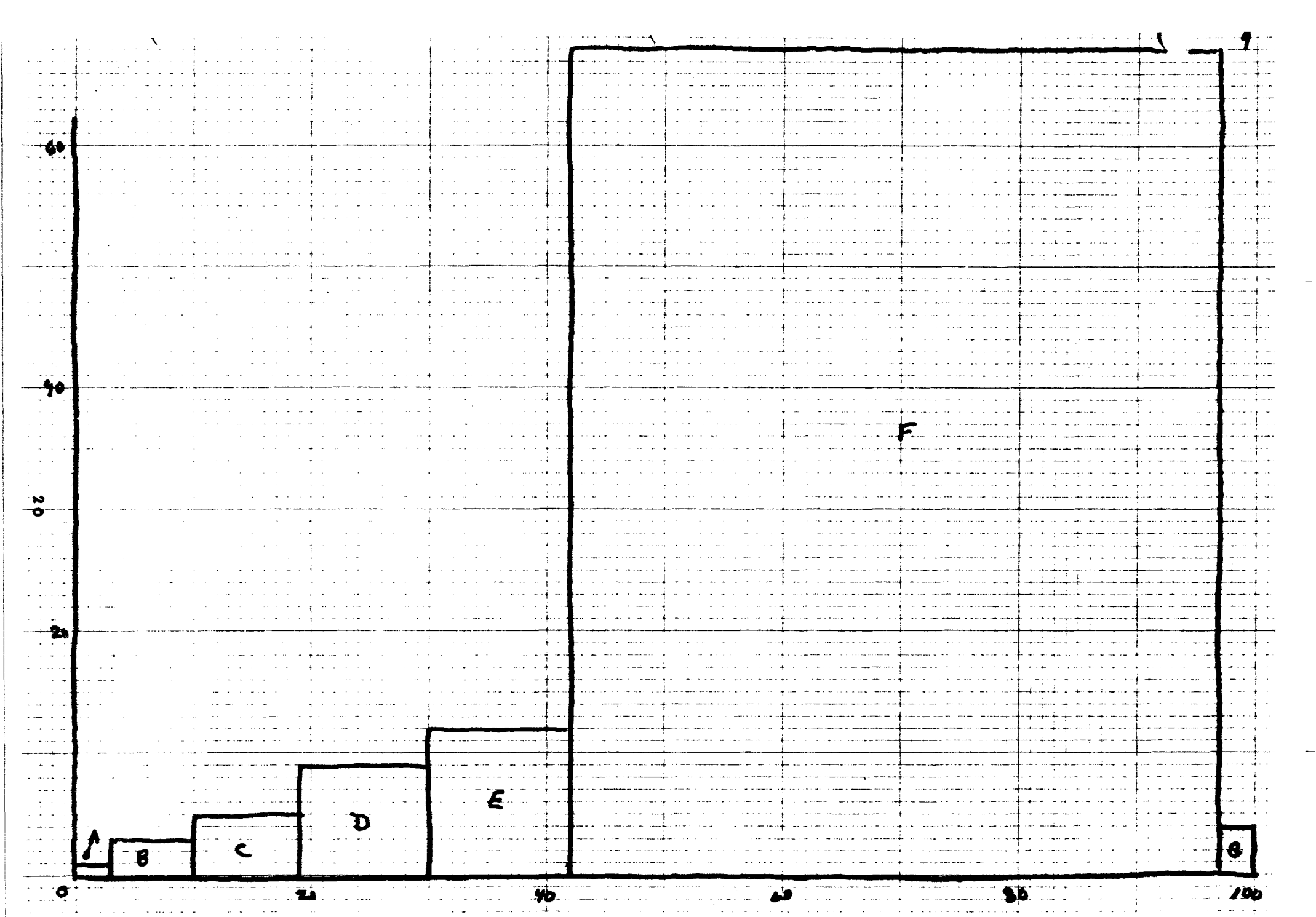
C
D
E
F
20
90
50
100



LAGOON III VOLUME VS AREA in %


60
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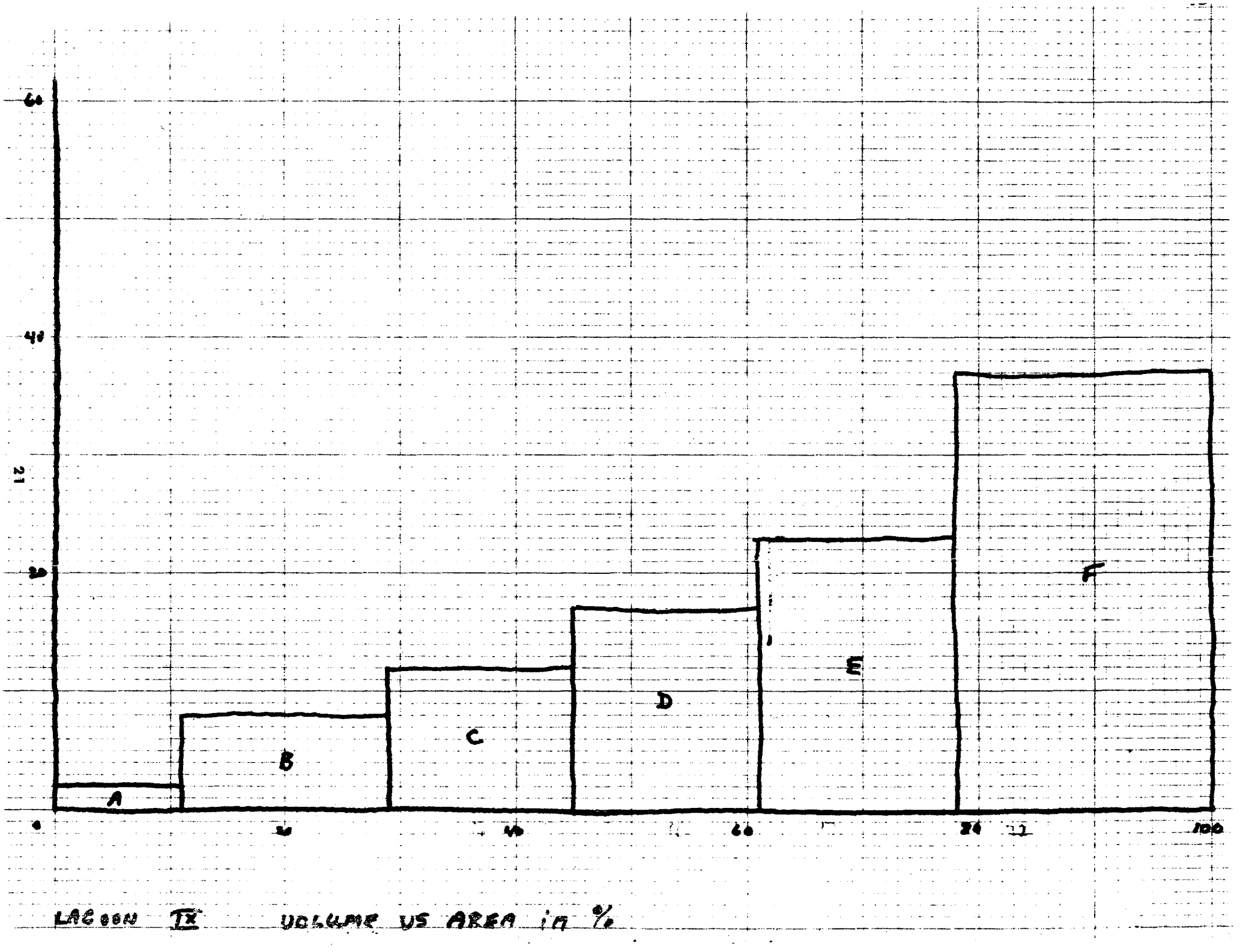
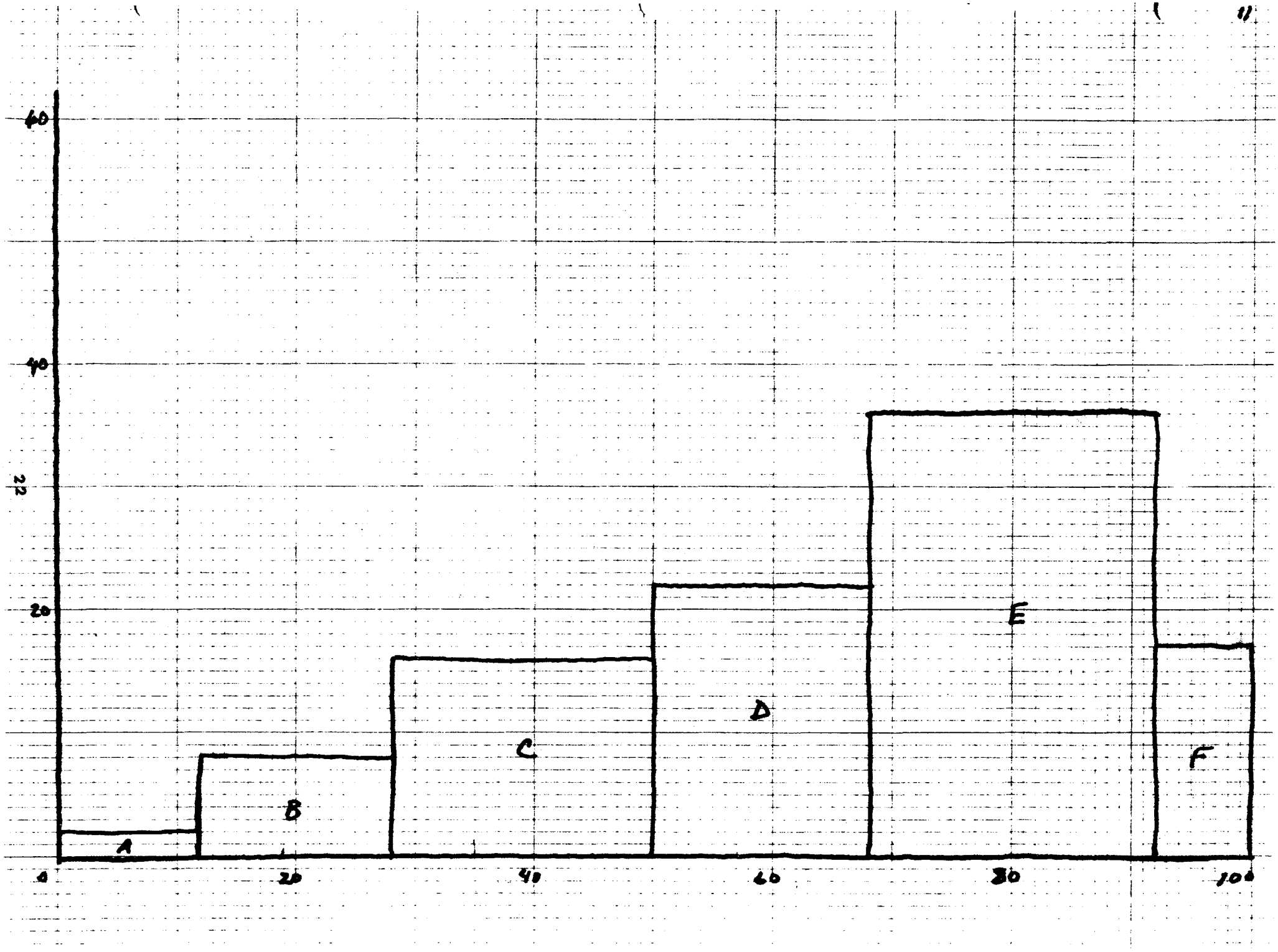
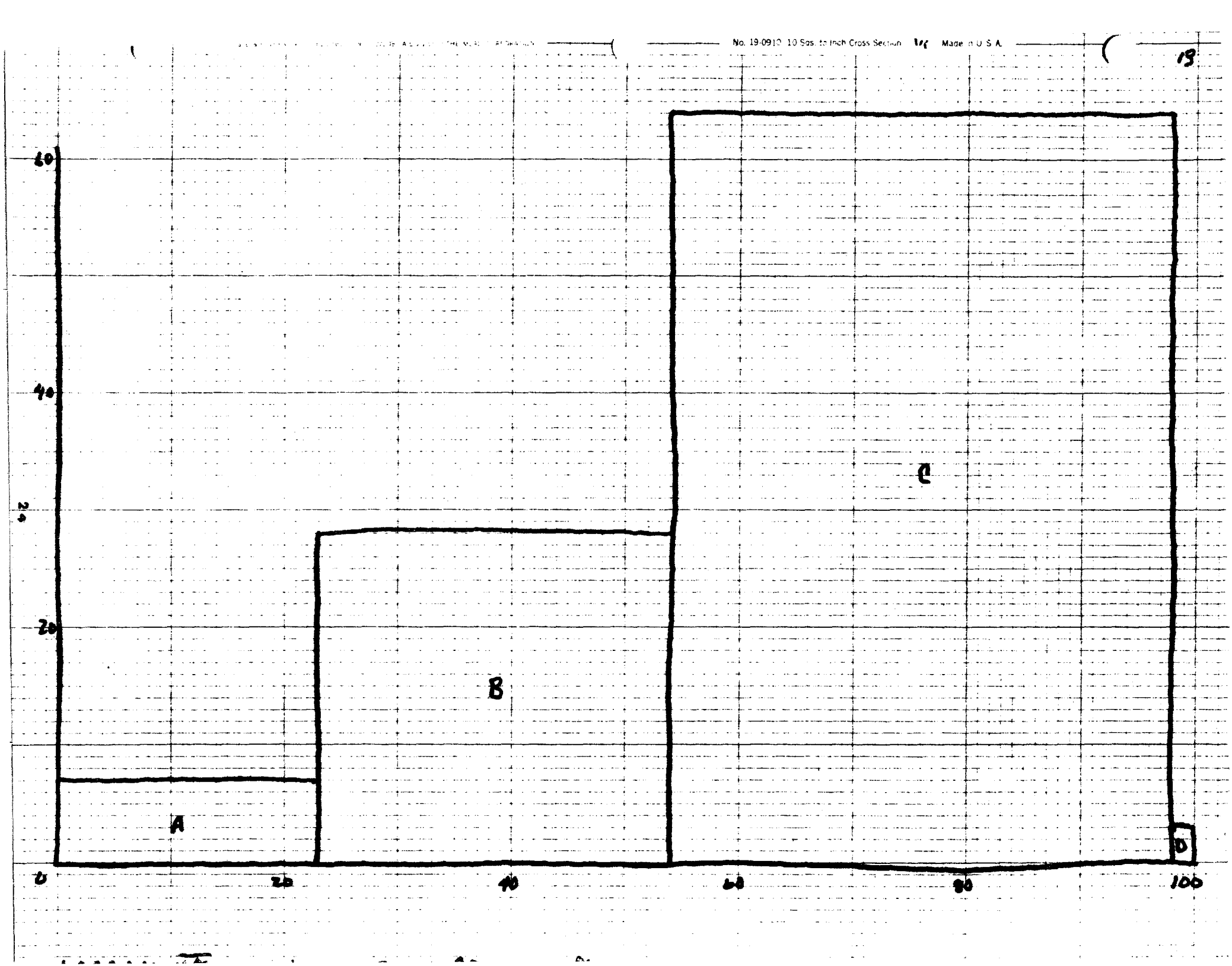


LAGOON IX VOLUME VS AREA in %


60
40
22
20
A
B
C
D
E
F
0
20
40
60
80
100

LAGOON XI VOLUME VS AREA in %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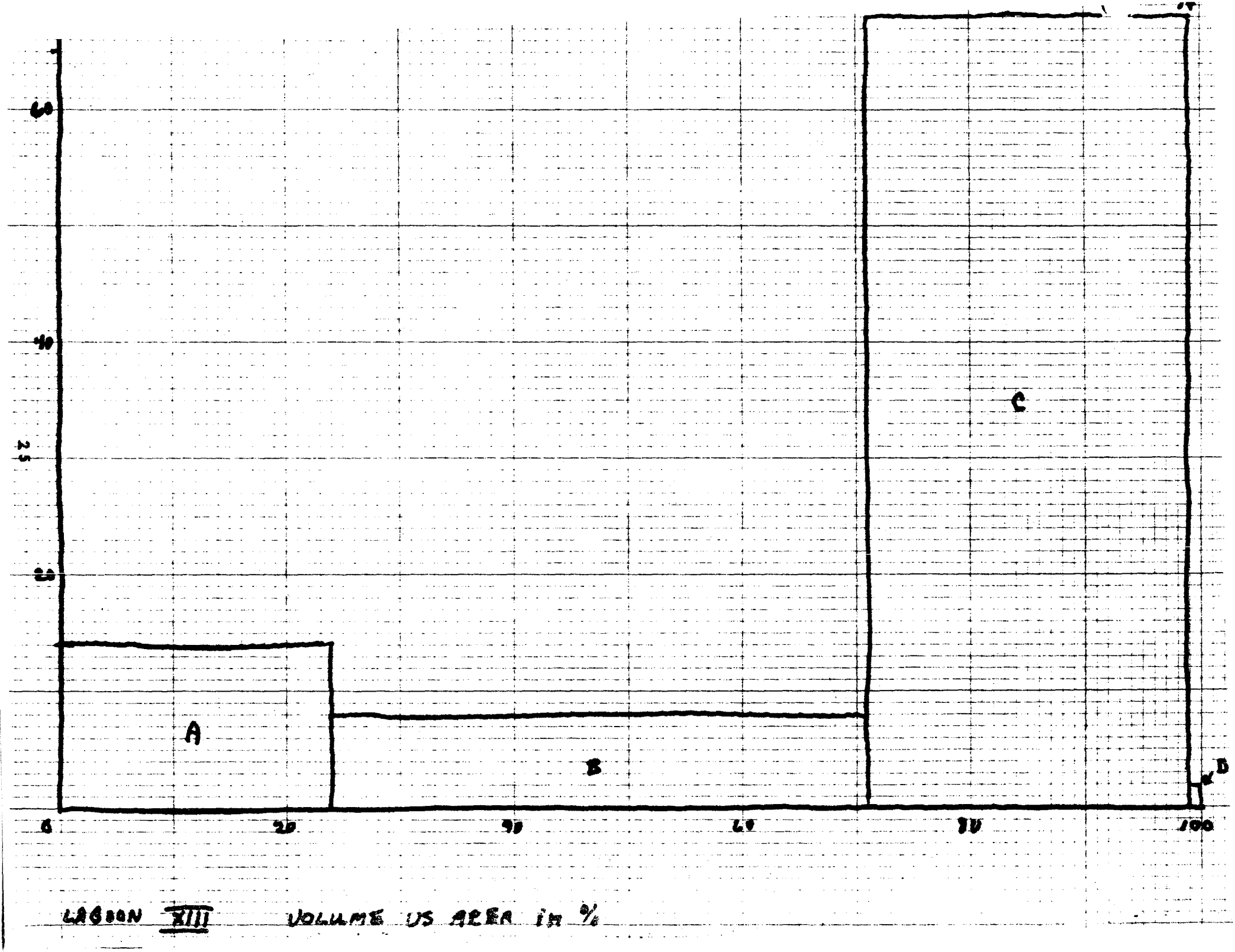
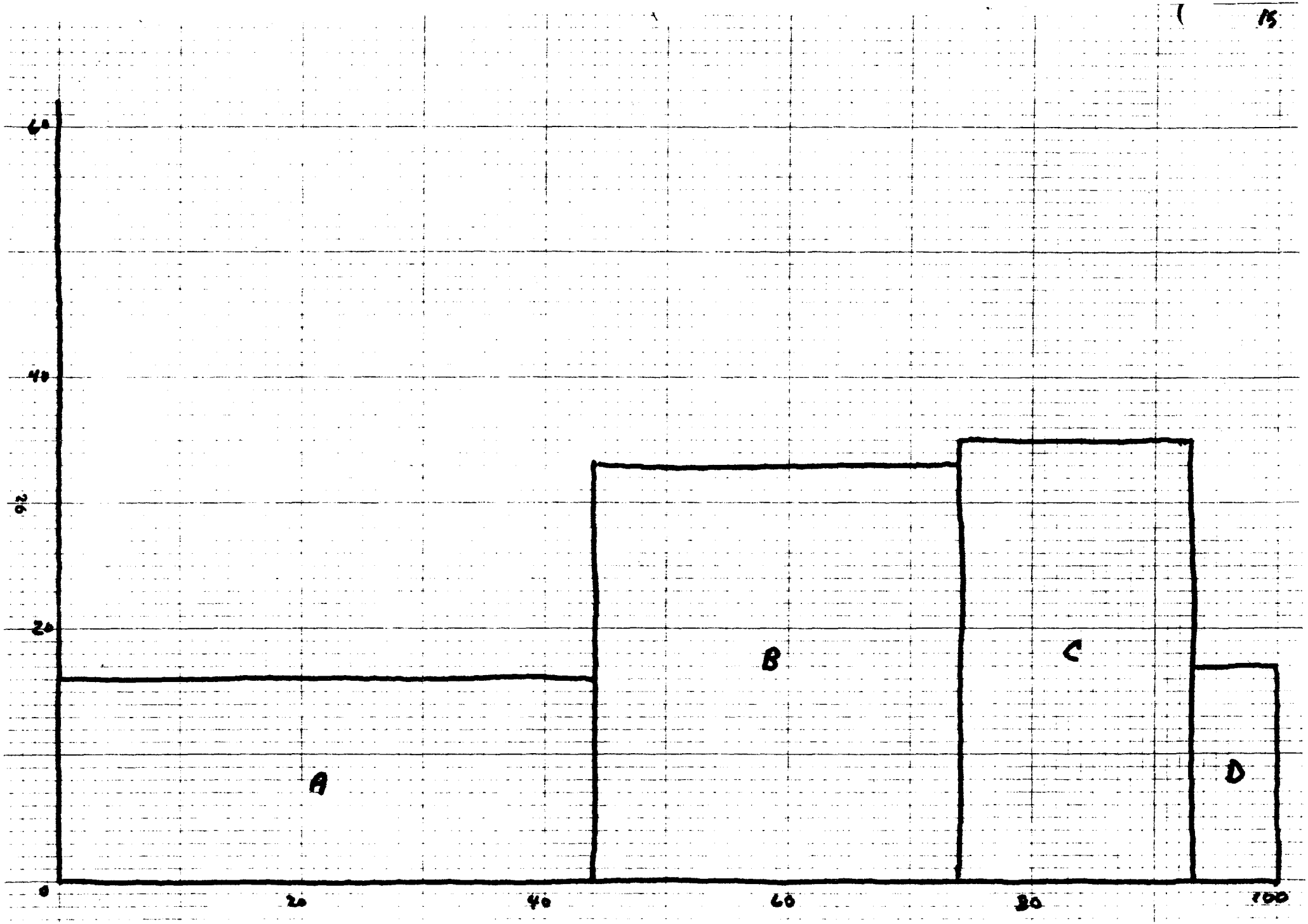
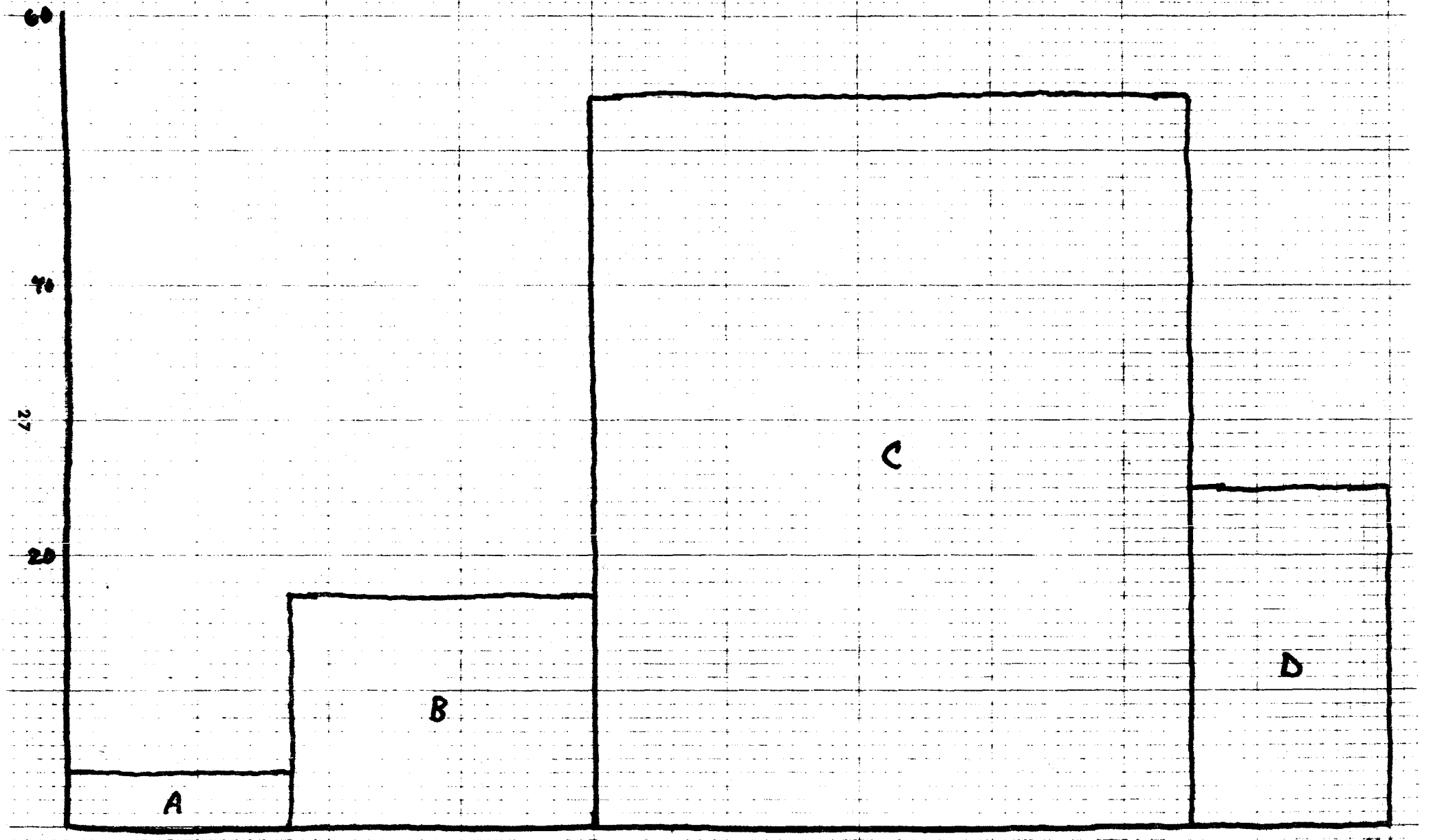
80
100
A
B
C
D



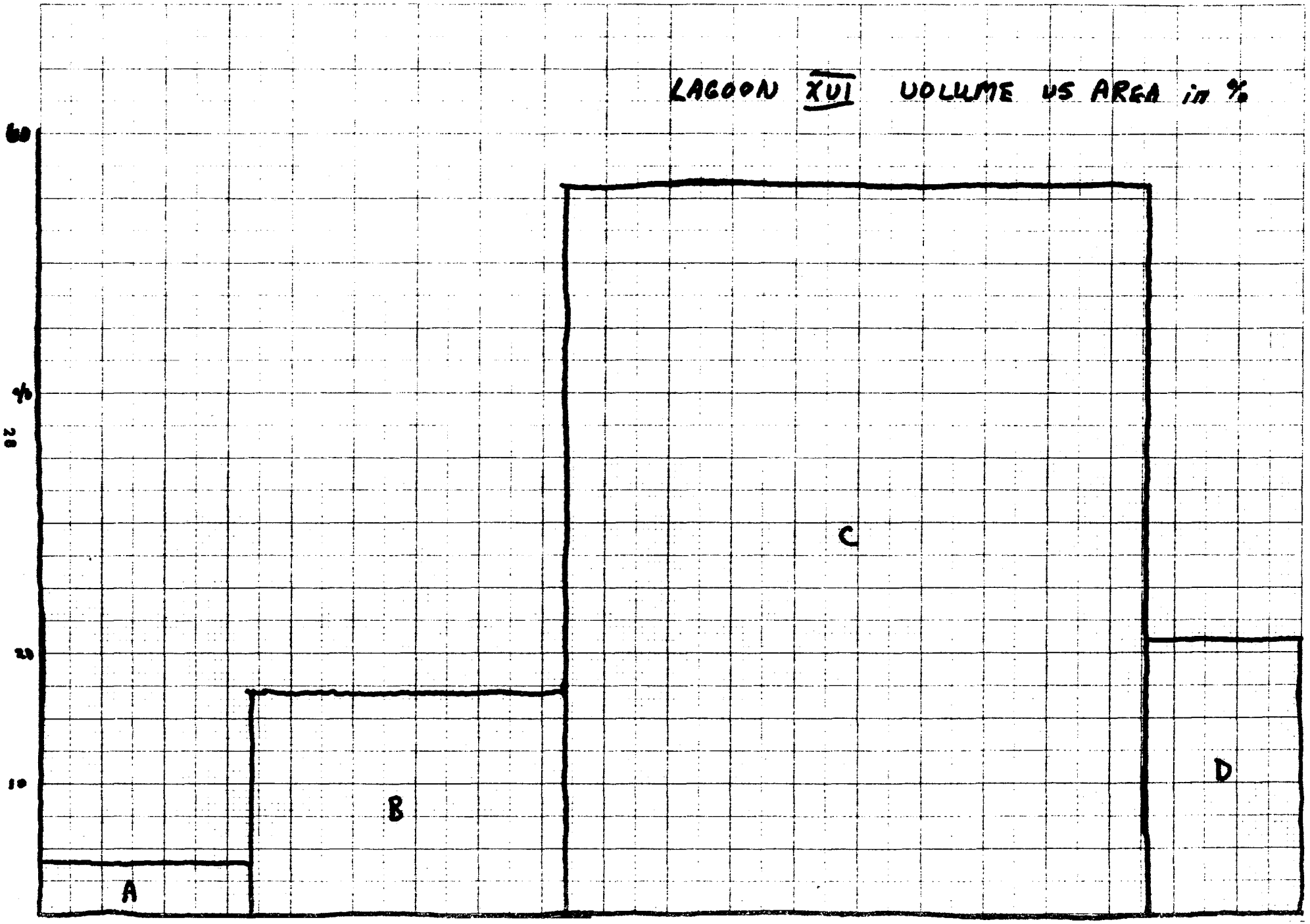
LAGOON XIII VOLUME VS AREA in %

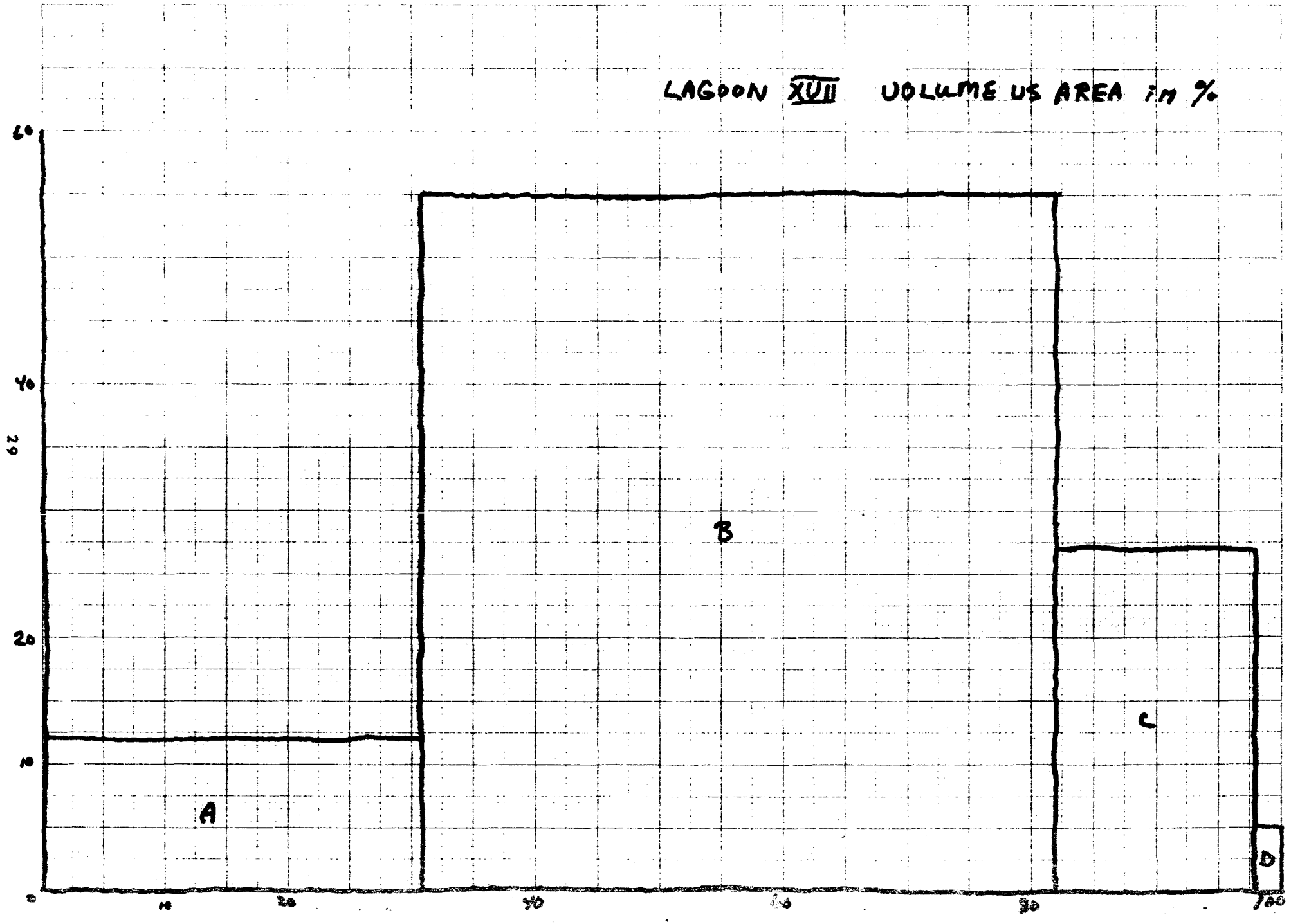


LAGOON XIV VOLUME VS AREA in %



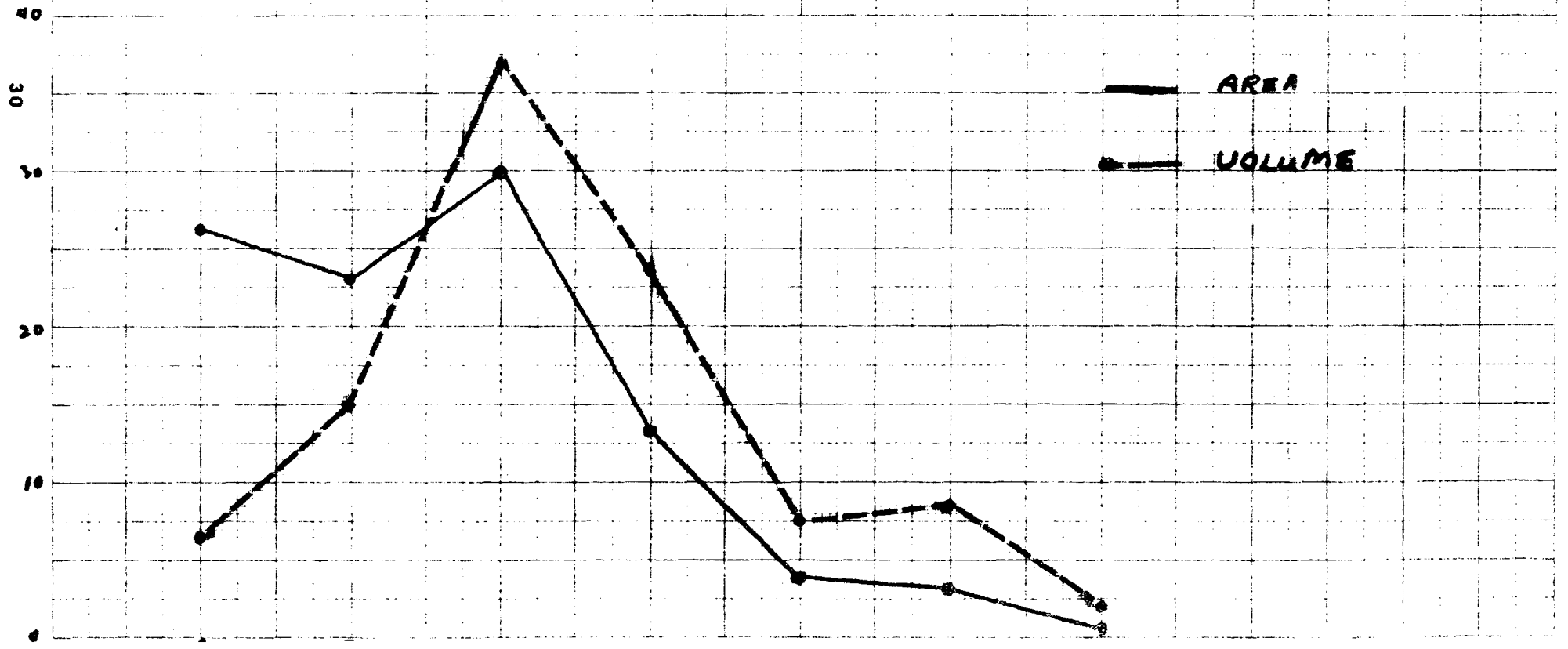
LAGOON XV VOLUME VS AREA in %


LAGOON XVI VOLUME VS AREA in %
60
40
20
10
A
B
C
D


LAGOON XVII VOLUME VS AREA IN %
60
40
20
0
20
40
60
80
100
A
B
C
D

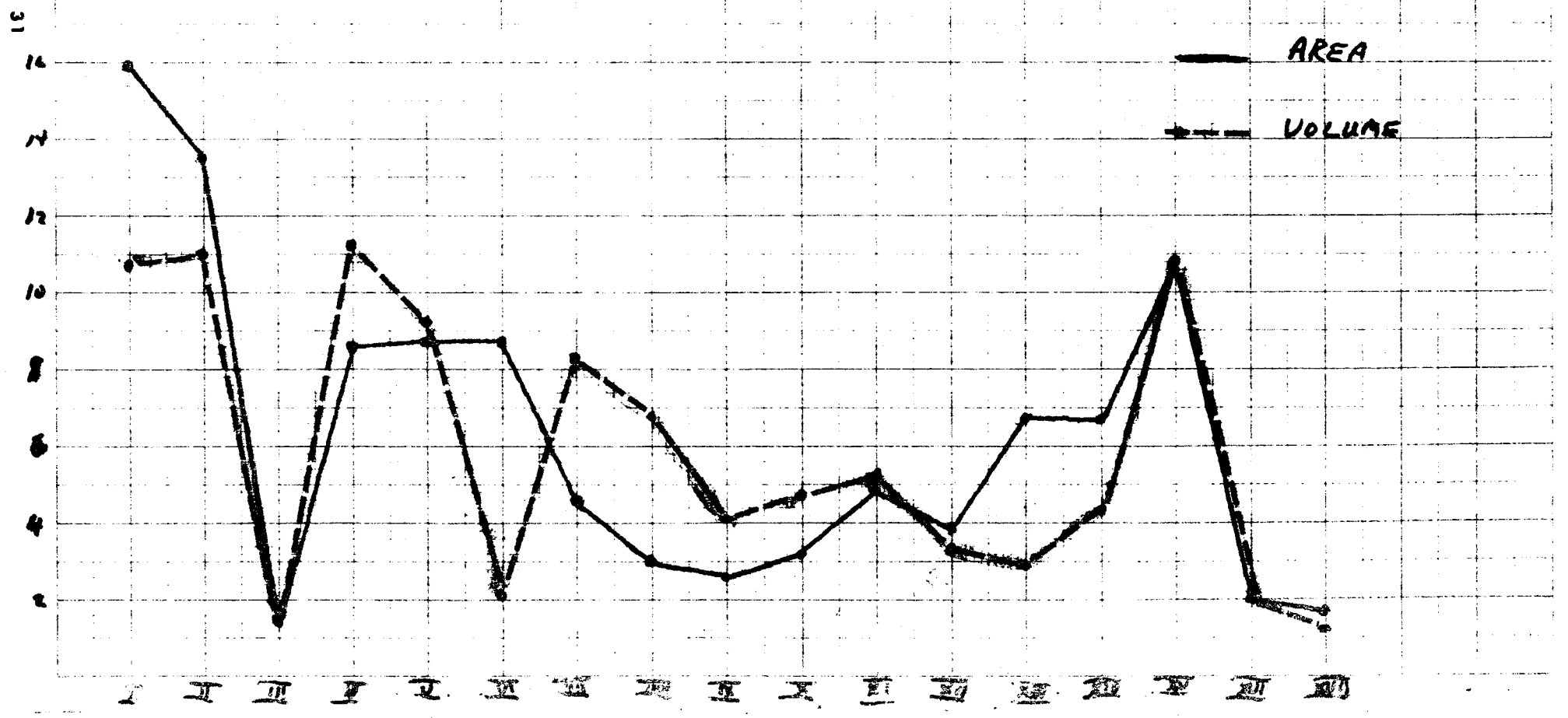
COMPARISON OF AREA TO VOLUME

TO EACH DEPTH LEVEL



COMPARISON OF AREA TO VOLUME

TO EACH INDIVIDUAL LAGOON, in %



Section V, Article 17

Wind-Induced Flow for a Shallow Water Basin

Ronald W. Nenart

SPECIAL TOPICS

0-5104

Wind-Induced Flow for a Shallow Water Basin

Ronald W. Nenart

CONTENTS

Wind-Induced Flow for a Shallow Water Basin

Ronald W. Nenart

ABSTRACT

A linearized model of wind-driven transport is considered for a basin of shallow depth. The concept of time constants, the period for the equilibrium surface to be established (steady state), are introduced into the time-dependant modeling equations. The effect of rotation, friction, stratification, and topography are investigated for a shallow basin.

I. Introduction

In the past considerable attention has been given to wind-driven circulation in the oceans. Many of these papers have become the foundations of wind-driven theory and are designated as the classical papers of oceanography.

Recently there has been an additional undertaking to investigate wind-driven lake circulation.

Birchfield(1967),Rao and Murty(1970) have developed steady state linearized models for a homogeneous fluid. A limitation of this time-independent theory is that it will only predict the average velocity of flow.

Inviscid time-dependent theory was largely developed by Csanady(1967,1968,1972). Within these models the response of a fluid to an applied wind stress is the sum of internal and external inertial gravity waves and a quasistatic response.

Friction and time-dependent models of circulation have been solved by numerical methods such as those formulated by Paskausky(1971) and Simons(1971,1972).

The present paper is devoted to a study of wind-induced flow in a shallow water basin. The relevant scale factors to determine the effect of rotation,topography,friction,and stratification for this basin model will be investigated within this paper. For a model basin of typical horizontal and vertical lengths,2km by 17km and 10m respectively,rotation and stratification are neglected.

II. Flow Parameters

1. Rotation

To determine the relative importance of rotation the relevant scale factor has to be established. The scale factor will then give an indication of the importance of rotation in the theoretical and actual systems.

Consider first the frictionless case and the corresponding modes of oscillation.

Ball(1965),"First-class modes depend for their existence on gravitational restoring forces resulting from the deformation of the free surface,whereas the second-class modes merely require a gradient of potential vorticity within the liquid".

Lamb(1932),"Types of circulatory motion which are of infinite period in the case of no rotation,may be converted by the slightest degree of rotation into oscillatory modes (second-class modes) of periods comparable with that of the rotation".

The relevant scale factor to determine the effect of Coriolis accelerations are the modes of the second-class, not the first-class modes(seiche).

For a rotating basin the low frequency(longitudinal) mode is decreased and particles exhibit anticlockwise rotation in the nothern hemisphere. This type of motion has been observed in Lake Erie by Platzman and Rao(1963). Similarly the high frequency(transverse) mode is increased and particles acquire clockwise motion. These conclusions by Ball(1965) are in agreement with earlier work by Rayleigh(1903),Jeffreys(1925), and Goldstein(1929). The existence of a negative amphidromic point for the high frequency mode is in disagreement with Taylor's(1920) hypothesis of the existence of only positive amphidromic points.

Csanady(1973),has proposed that the Coriolis acceleration is negligible in comparison with the local acceleration if the basin width is small compared to the radius of deformation, $(gh)^{1/2}/f$. Here,g is gravity,h the basin depth,and f the Coriolis parameter. Rossby(1936) introduced the radius of deformation in the investigation of his wake-stream theory. See the appendix for a mathematical derivation. Utilizing this formulation one may conclude that the Coriolis acceleration is indeed small for the particular shallow water basin model under study.

Simons(1973) has criticized Csanady(1973) in his method of determining the effect of the Coriolis parameter. Alternatively Simons(1973) and Bennett(1973) arrive at similar results in their investigation of the influence of the Coriolis force. These results only apply if the Coriolis force is negligible in determing the flow pattern. As stated by Csanady(1973) this cannot be rigorously proved. The physical meaning of comparing basin width and radius of deformation to determine the importance of the Coriolis force is admittedly an unresolved point of present day modeling. The width of a basin may plausibly limit the development of transverse motion. Exactly how this is manifested into an understanding of the influence of the Coriolis force is not physically understood.

Blanton(1974),has observed that within the frictional boundary layer rectilinear currents predominate and outside this region rotary motion is increased. Friction appears to be a significant parameter in impairing the existence of rotational motion.

Csanady(1973),has illustrated that frictional(decay) and rotational(period) time scales are comparable for the Great Lakes. "The rotation of the quasi-steady flow pattern may be

observable . . . it is unlikely that such rotation could be followed for a prolonged period."

Rotation of the second-class type stated by Ball(1965) and Lamb(1932) for these prescribed geometric conditions is not likely to be found as a result of frictional influences.

In conclusion,the neglect of the earths rotation is a workable approximation but it cannot be rigorously substantiated.

2. Topography

Of particular interest when considering topography is the Taylor-Proudman constraint;transport is directed along contours of constant depth in accordance with observations. The Taylor-Proudman restraint may be a useful concept in the modeling of streamline patterns of circulation.

The effect of a variable depth basin and how this may be formulated in the equations of motion and continuity was investigated by Csanady(1973). In a nonrotating basin of constant depth the forced response is a "set up",a constant nonzero slope balancing the wind stress. In this case transport is equal to zero,for a constant depth. For a basin of variable depth the "set up" is accompanied by an additional forced flow pattern. Csanady(1973) then states that this consideration yields the transport as a function of time,for a variable depth basin. This conjecture by Csanady(1973) of an additional forced flow pattern and a time-dependent transport for a time-independent elevation distribution does satisfy the governing equations but the physical meaning of this model is not clearly understood.

In addition to bottom topography, the surface configuration must also be considered in the general formulation of the model. To apply wind stress on a level surface one must assume the rigid lid approximation. Ball(1965), claimed that surface gravity waves may be neglected if "e" is small.

$$e = L^2 f^2 / gh$$

Here, g is gravity, h the basin depth, L the basin width, and f is the Coriolis parameter. This ratio is the square of the ratio of the fundamental seiche period to the inertial period. The dimensionless number "e" has also been used by Csanady(1965), and is presented on page 4 of this paper.

3. Stratification

Stratification is a vertically sensitive parameter and may be related to the vertical flux of momentum. The central problem in every wind driven model of circulation is the turbulent exchange of momentum in the vertical direction.

The distribution of the current flow is dependent on the stratification which restricts the vertical motion and the effective influence of wind stress(see Bennett 1974).

Of particular importance is the influence of wind mixing in a shallow basin. How effective is the penetration of a turbulent layer into a stratified fluid? Kato and Phillips(1969) from experimental results have proposed a method to determine the depth of mixing.

The rate of increase with time of the surface mixed layer under the influence of wind is

$$D(t) = u_*(15T^*/N_o^2)^{1/3},$$

here T^* is the duration of the wind, N_o the buoyancy frequency, u_* the frictional velocity, and D the depth of the mixed layer. For the values $T^* = 10^5$ sec., $N_o = 2.7 \cdot 10^{-2}$ sec.$^{-1}$, and $u_* = 1$cm/sec., the depth of the homogeneous layer is 12.5m.

A further consideration of stratification is the physical process of diffusion. Since we are also dealing with a dynamical system it will be useful to investigate also the dependence of shear on relative diffusion. The following references give an historical development of the influence of shear on relative diffusion. For a more inclusive investigation see Kullenberg(1972).

Taylor(1954) introduced the idea of shear-diffusion in his investigation of flow through a pipe.

$$k_x = 10u_* a$$

Here, k_x is the longitudinal diffusion coefficient, u_* the frictional velocity, and a the radius of the pipe.

Nikikov(1958) concluded that the shear effect dominates the horizontal diffusion after an initial period.

Elder(1959) claimed that dispersion is determined by the combined action of lateral diffusion and advection of the mean flow. Elder defined the effective longitudinal diffusion as

$$k_x = 5.9u_* h \ ,$$

where u_* is the frictional velocity, and h the depth of the channel.

Deacon(1962) considered diffusion for the case of wind driven lake circulation and formulated the following equations.

$$T = .0012\rho_a u^2$$

$$u_* = (T/\rho_w)^{1/2}$$

$$k_x = 5.9h\left((.0012\rho_a u^2)/\rho_w \right)^{1/2}$$

$$k_z = mu_* z$$

The expressions are defined as before with the addition of ρ_a and ρ_w which are respectively the density of air and water. Also u is the wind velocity, T the wind stress, and k_z is the vertical diffusion.

Deacon has experimentally found typical values of vertical and horizontal diffusion, $k_x = 3000 cm^2/sec.$ and $k_z = .1$ to $1.5\ cm^2/sec$ Spatial dispersion for a given time scale are 60m for horizontal diffusion and 1.5m for vertical diffusion.

Bowden(1965) has concluded that dispersion is inversely proportional to the vertical diffusion.

The apparent horizontal diffusion is interpreted by Kullenberg(1972) as an effect of the combined action of vertical diffusion and advection due to the mean flow. Small scales affect the diffusion, large scales affect the advection. For small diffusion times the small scale determines the dispersion at the initial time, the large scale merely advects the whole spot. For large diffusion times, the large scale components of the motion are important for dispersion.

Blanton and Murthy(1974) have observed that high shear values usually do not coincide with high winds, but are usually related to the inability of the nearshore currents to adjust to a slowly varying wind regime. Simple momentum arguments suggest that the time for adjustment decreases as water depth nearshore decreases.

For a shallow water basin the time scales of diffusion may be considerably reduced yielding the large scale advection properties of flow. From considerations of the development of dispersion relationships it appears that relative diffusion is less effective than meandering as a means of dispersion.

In addition to meandering the process of wind mixing is also a dominant condition to determine stratification. For a given time scale and a shallow water basin of weak stratification the approximation of a homogeneous fluid may be a valid assumption.

In summary a basin of shallow depth has a relatively small adjustment time scale to a transient wind field. The time scale is decreased under these conditions allowing the effect of meandering and wind mixing to intensify the mixing process.

4. Friction

Frictional effects appear to become predominant in the model of a shallow water basin. The Ekman number as an indicator of frictional influence suggests that the flow pattern may not have an outer region that is inviscid(see Jacobs,1974). For a basin of typical horizontal and vertical length scales of 2 km. and 10 m. respectively what is implied when defining a frictional layer in terms of an Ekman number? This question becomes significant when considering previous analysis of the influence of friction on rotation.

The rate of transport is reduced by bottom friction. The friction term may be defined in terms of a drag coefficient,a constant that is a reciprocal of the time scale in which a given transport pattern would be reduced. This model will utilize this concept and define the rate of decay of transport in terms of linear friction.

Csanady(1973) has proposed that the effect of friction reduces the magnitude but does not alter the general flow pattern. Simons(1974),in his modeling of analytical and numerical theory,has similarly concluded that friction has only a quantitative influence on circulation.

Model theory that has considered friction,Paskausky(1974), and Simons(1971,1972),has normally been solved by numerical techniques. These formulations are not of simple form and may not be checked against field observations easily for they lack physical representation of the dynamics of the problem.

III. Formulation of the problem

Time-dependent transport is dependent upon the pressure and wind stress terms of the general Navier Stokes equation. The following model utilizes the concept of a transport "decay constant" as was proposed by Csanady(1973). In addition the time constant for the equilibrium slope("set up") to be established is represented in the equation of motion. This model does not yield an explicit solution for the transport but attempts to give an insight into the growth and decay of the equilibrium surface.

For a linear model assuming the hydrostatic approximation and neglecting the Coriolis acceleration and stratification the depth integrated equations of motion and continuity are

$$\partial U/\partial t = -gh\ \partial h^*/\partial x + T_x/\rho \quad , \tag{1}$$

$$\partial V/\partial t = -gh\ \partial h^*/\partial y + T_y/\rho \quad , \tag{2}$$

$$\partial U/\partial x + \partial V/\partial y = -\partial h^*/\partial t \quad , \tag{3}$$

where U and V are transport components(x and y respectively), T_x and T_y are wind stress components, g is gravity, ρ is density, h is water depth and h^* is elevation from equilibrium.

1. Initial Period

During the initial period a constant wind stress acts on a still basin producing a time dependent transport. The equations of motion and continuity for the initial period are

$$k_1 U = -gh\ \partial h^*/\partial x + T_x/\rho \tag{1.1}$$

$$(2.1) \qquad k_1 V = -gh\,\partial h^*/\partial y + T_y/\rho \quad ,$$

$$(3.1) \qquad \partial U/\partial x + \partial V/\partial y = -\partial h^*/\partial t \quad , \quad 0 \le t < 1/k_1 \, ,$$

where k_1 is the reciprocal of the time scale to attain the equilibrium slope.

2. Later Period

After some initial period the transport will be reduced by bottom friction. During this later period of the model, linear friction is introduced into the governing equations such that

$$(4) \qquad F_x = k_2 U \quad ,$$

$$(5) \qquad F_y = k_2 V \quad ,$$

where F_x and F_y are the x and y components of friction, and k_2 is the reciprocal of the time scale for the equilibrium slope to vanish. The governing equations for this later period are

$$(1.2) \qquad 0 = -gh\,\partial h^*/\partial x + T_x/\rho - F_x \quad ,$$

$$(2.2) \qquad 0 = -gh\,\partial h^*/\partial x + T_y/\rho - F_y \quad ,$$

or,

$$(1.3) \qquad k_2 U = -gh\,\partial h^*/\partial x + T_x/\rho \quad ,$$

$$(2.3) \qquad k_2 V = -gh\,\partial h^*/\partial y + T_y/\rho \quad ,$$

$$(3.3) \qquad \partial U/\partial x + \partial V/\partial y = -\partial h^*/\partial t \quad , \quad 1/k_1 \le t < 1/k_2 .$$

3. Intermediate Period

When both the initial time dependent and frictional transports are important in determining the flow pattern the equations of motion and continuity are

$$(1.4) \qquad (\partial/\partial t + k_2)U = -gh\,\partial h^*/\partial x + \tau_x/\rho \quad ,$$

$$(2.4) \qquad (\partial/\partial t + k_2)V = -gh\,\partial h^*/\partial y + \tau_y/\rho \quad ,$$

or,

$$(1.5) \qquad k_1 U + k_2 U = -gh\,\partial h^*/\partial x + \tau_x/\rho \quad ,$$

$$(2.5) \qquad k_1 V + k_2 V = -gh\,\partial h^*/\partial y + \tau_y/\rho \quad ,$$

$$(3.5) \qquad \partial U/\partial x + \partial V/\partial y = -\partial h^*/\partial t \quad ,$$

for, $0 < t' \leq t \leq t'' < 1/k_2$.

4. Determination of Time Scales

From geometrical considerations of a basin of length L, the transport is defined as

$$U = (uh)t = 1/4\ h^*L \quad . \tag{6}$$

The slope of the surface is

$$B = h^*/(L/2) \quad . \tag{7}$$

In addition to the above form the slope may be expressed as an Ekman slope:

$$B = 3/2\ T/\rho gh \quad . \tag{8}$$

Combining these three equations yields

$$k_1 = 16u\rho gh^2/3TL^2 \quad , \tag{9}$$

where k_1 is the reciprocal of the time scale for the equilibrium slope to be established. For a basin 17km in length and with a constant wind stress of 2gm/cm-sec^2, the period to attain a steady state slope is 10^3 seconds.

Friction will tend to bring the surface level back to the original condition of zero slope. An approximate order of magnitude for this period may be found by assuming

$$k_2 = 16u\rho gh^2/3T_bL^2 \quad , \tag{10}$$

$$T_b = C_d u^2 \text{ (bottom stress)}, \tag{11}$$

where k_2 is the reciprocal of the time scale for the equilibrium slope to be zero. For the values, z=200cm, $C_d = 2 \cdot 10^{-3}$ (bottom drag coefficient), u=10cm/sec, the time for this current to decay is approximately 10^4 seconds.

5. General Solution

The x-component of the linearized equation of motion is

$$ku = -g\,\partial h/\partial x + A/\,\partial^2 u/\partial z^2 \quad , \tag{1.6}$$

where A is the constant eddy viscosity coefficient,and k is the reciprocal of the time scale to reach an equilibrium surface.

For the transient period the surface slope is a function of time:

$$-g\,\partial h(x,t)/\partial x = H(x)\,M(t) \quad . \tag{1.7}$$

Assume the velocity has a solution of the form,

$$u = M(t)\,F(z) \quad . \tag{1.8}$$

Upon substitution of the solution form into the general equation(1.6) yields,

$$kF(z) = H + A/\rho\,\partial^2 F(z)/\partial z^2 \quad . \tag{1.9}$$

At the surface,z = 0,thus

$$F(0) = 0 \quad \text{and} \quad \partial^2 F(0)/\partial z^2 = 0 \quad . \tag{1.10}$$

Solving equation (1.9) by use of the Laplace transform yields,

$$L(\,kF(z) = H + A/\rho\,\partial^2 F(z)/\partial z^2\,) \quad , \tag{1.11}$$

$$= (\,kF(s) = H/s + A/\rho\,(s^2 F(s))\,) \quad , \tag{1.12}$$

(1.13) $$F(s) = -(H/s)/(A/\rho\ s^2 - k) \quad ,$$

(1.14) $$F(z) = L^{-1}(f(s)g(s)) = \int_0^z f(u)g(z-u)\ du \quad ,$$

(1.15) $$f(z) = L^{-1}(-H/s) = -H$$

(1.16) $$g(z) = L^{-1}(1/(A/\rho\ s^2 - k)) \quad ,$$

(1.17) $$= 1/k\ (\rho k/A)^{1/2}\ L^{-1}((\rho k/A)^{1/2}/(s^2 - \rho k/A)) \ ,$$

(1.18) $$g(z) = 1/k\ (\rho k/A)^{1/2}\ \sinh((\rho k/A)^{1/2}\ z) \ ,$$

(1.19) $$F(z) = \int_0^z -H/k\ (\rho k/A)^{1/2}\ \sinh((\rho k/A)^{1/2}\ (z-u))\ du,$$

(1.20) $$F(z) = -H/k\ (1 - \cosh((\rho k/A)^{1/2}\ z) \quad .$$

The velocity is defined as, $u = F(z)\ M(t)$, thus

(1.21) $$u = -H(M(t)/k)(1 - \cosh((\rho k/A)^{1/2}\ z) \quad .$$

By definition H is of the form,

(1.22) $$H = (-g\ \partial h/\partial x)/M(t) \quad ,$$

and the derived solution is of the form,

(1.23) $$u = (H/k)\ M(t) \ .$$

Consider an inspectional analysis form of the general governing equation(1.6):

(1.24) $$(ku)k'u' = -(g\ h/x)g'\ \partial h'/\partial x' +$$

$$+ (Au/\rho D^2)\ A'/\rho'\ \partial^2 u'/\partial z'^2$$

From a general comparison of terms of equation (1.24), the general form of velocity(u) and the depth(D), the following relationships may be formulated:

$$u = (gh)/(xk) \quad , \tag{1.25}$$

or,

$$u = (\rho g h D^2)/(xA) \quad , \tag{1.26}$$

where,

$$D = (A/\rho k)^{1/2} \quad . \tag{1.27}$$

The velocity form represented by equation (1.25) concurs with equation (1.8) and the general derived form of velocity expressed by equation (1.23).

IV Summary and Conclusion

The effect of rotation, stratification, friction and topography on the general flow pattern have been investigated for a shallow water basin. In conclusion, the influence of rotation and stratification are neglected in the analytical model of wind-induced flow.

The Coriolis parameter is omitted since the local acceleration is considerably larger in magnitude than the Coriolis acceleration. The influence of rotation may induce second-class modes of oscillation, however frictional forces will probably dissipate these rotational modes.

Wind mixing and meandering are the predominant factors to determine the extent of stratification. From geometrical considerations the time-scale of diffusion is reduced letting the larger scale effects of advection dominate the diffusion process. With the effect of advective mixing and the vertical penetration of wind stress the approximation of a homogeneous fluid may be a valid assumption for an initialy weakly stratified shallow fluid.

The concept of introducing time constants into the equations of motion yields an understanding of the establishment and decay of the wind-induced sloping surface. Time constants are defined as the period to attain an equilibrium balance between the pressure and frictional forces of the general Navier Stokes equation. When the above forces are in balance the transport for this steady state condition is zero. Friction is incorporated into the transient state pattern in terms of a negative transport function. The combined transport function defined by time constants is an attempt to give a general insight into the balance of forces for a wind generated flow.

This model,being two-dimensional and linear,does not admit a complete understanding of the general phenomenon of circulation. The concept of a constant eddy viscosity may be an over simplification of the problem. The eddy viscosity should be a function of depth for motion is generated at the surface by wind and inhibited at the rigid bottom. Other inherent limitations of the model are the assumptions not to consider advective terms and horizontal diffusion,both of which may become significant in the proximity of the boundaries.

Of special interest in the dynamics of shallow water flow is the condition of a basin composed of a narrow channel with shallow outer regions. From momentum principles a reduction of water level may alter the flow pattern of circulation. Precipitation formulated into the continuity equation may also be an important consideration when investigating a shallow water basin.

APPENDIX

Formulation of the model equations of motion and continuity for a homogeneous,linear,and frictionless fluid are

$$\partial u/\partial t = -1/\rho\ \partial P/\partial x$$

at t=0,apply wind stress,T_x

$$\partial u/\partial t = -1/\rho\ \partial P/\partial x + 1/\rho\ \partial T_x/\partial z$$

assume the hydrostatic appoximation,

$$\partial u/\partial t = -g\ \partial h/\partial x + 1/\rho\ \partial T_x/\partial z$$

integrate over depth,

$$\int \partial u/\partial t\ dz = -g \int \partial h/\partial x\ dz + 1/\rho \int \partial T_x/\partial z\ dz$$

using Leibniz's rule and neglecting nonlinear terms and defining transport as,

$$U = \int u\ dz$$

yields,

$$(1) \qquad \partial U/\partial t = -gh\ \partial n^*/\partial x + T_x/\rho$$

where T_x is the x-component of wind stress,h the depth and n^* the elevation from equilibrium.

Continuity for a homogeneous fluid is:

$$\partial \rho/\partial t + \rho(\partial u/\partial x + \partial v/\partial y) = 0$$

integrating over depth and defining transport as,

$$U = \int u\ dz$$

$$V = \int v\ dz$$

apply Leibniz's rule and neglecting nonlinear terms yields,

$$(3) \qquad -\partial n^*/\partial t = \partial U/\partial x + \partial V/\partial y$$

Appendix continued.

Effect of Coriolis force:An approximate comparison of the Coriolis acceleration and local acceleration in terms of the radius of deformation,Csanady(1973).

The depth integrated linearized equations of motion and continuity with the hydrostatic approximation are:

(1) $$\partial U/\partial t = -gh\ \partial h^*/\partial x + T_x/\rho$$

(2) $$\partial V/\partial t = -gh\ \partial h^*/\partial y + T_y/\rho$$

(3) $$\partial U/\partial x + \partial V/\partial y = -\partial h^*/\partial t$$

introducing the Coriolis parameter and considering a long basin,

(1.1) $$\partial U/\partial t - fV = -gh\ \partial h^*/\partial x + T_x/\rho$$

(2.1) $$fU = -gh\ \partial h^*/\partial y$$

(3.1) $$\partial^2 V/\partial y^2 = -\partial^2 h^*/\partial t \partial y$$

(3.2) $$V = \iint \partial/\partial t(\partial h^*/\partial y)\ dydy$$

(3.3) $$V = \iint \partial/\partial t(fU/gh)\ dydy$$

(3.4) $$fV/(\partial U/\partial t) = f^2y^2/\ gh$$

if y,the basin width is small compared to the radius of deformation, $(gh)^{1/2}/f$,the Coriolis acceleration may be neglected in comparison with the local acceleration.

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