

# CHARACTERISTICS OF TOTAL SUSPENDED MATTER AND ASSOCIATED HYDROCARBON

## CONCENTRATIONS ADJACENT TO THE CHESAPEAKE BAY ENTRANCE

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### INTRODUCTION

#### Purpose

The Department of Oceanography, Old Dominion University, participated in three series of experiments within the NOAA/NASA Superflux study. The initial oceanographic objective of the experiments was to characterize the quality of Chesapeake Bay outwelling onto the contiguous continental shelf. The long-term objective of the experiments was to assess the impact of the natural and anthropogenic effluents of the Bay on the living resources of the continental shelf. Hydrocarbons and suspended particulates have natural and anthropogenic sources; however, concentrations of these substances are a major concern in water quality assessment. An extensive survey of hydrocarbon and suspended solid concentration was designed for the lower Bay and contiguous shelf. Superflux missions were conducted in March, June, and October, 1980, to evaluate (1) a high runoff period associated with a spring phytoplankton bloom, (2) a low runoff period without a phytoplankton bloom, and (3) a low runoff period corresponding with a fall phytoplankton bloom. While all missions have been completed only the results from the June 1980 experiment are presented in this report.

In support of the oceanographic objectives of Superflux, there were also some remote sensing objectives. The overall remote sensing objective was to determine the feasibility of using a variety of remote sensors to generate a synoptic data set of various water quality parameters. This required carefully coordinating experimental design between remote sensing overflights and oceanographic measurements.

The purpose of this study was to determine concentrations of hydrocarbons and associated suspended particulates at stations in and adjacent to the entrance to the Chesapeake Bay and to determine if hydrocarbon concentrations could be estimated from remotely sensed concentrations of suspended matter. Sampling was accomplished from the R/V Linwood Holton and the NOAA ships George B. Kelez and Delaware II. Four remote sensing instruments flown during the Superflux II mission had potential value for sensing turbidity variations generated by changes in suspended solid concentration; they are passive sensors (Multichannel Ocean Color Scanner, MOCS; Test Bed Airborne Multispectral Scanner, TBAMS), and active laser systems (Airborne Lidar Oceanographic Probing Experiment, ALOPE and Airborne Oceanographic Lidar, AOL). The airborne oceanographic laser induces emission spectra from Raman backscatter. The water Raman backscattered signal essentially defined the volume of water fluorescent by the laser pulse.

Thus, as the concentration of suspended solids is increased, fewer water molecules are accessed.

The passive sensors scanned the water surface from elevations ranging from 3 to 7.5 km, whereas the laser sensors were flown in a profiling mode at 152 m. Passive and active remote sensing data were acquired in conjunction with sea truth data collection.

#### Experimental Design and Techniques

Ninety-two samples were collected from Superflux II mission station locations (fig. 1). These stations were primarily located above the continental shelf south of the entrance to the Chesapeake Bay. Only two stations were located in the Bay entrance and no stations were located in continental shelf water north of the Bay. To supplement these data, the ODU-BAPLEX program collected a data set at six stations across the Chesapeake Bay entrance. Samples were analyzed for hydrocarbon concentration, total suspended matter, total organic and inorganic matter, and particulate size frequency distribution following techniques described by Wade and Oertel (ref. 1), Gingerich and Oertel (ref. 2), and Byrnes and Oertel (ref. 3). Data were collected during an 11-day period between the 17th of June and the 27th of June, 1980. Four samples were collected at evenly spaced depths of the water column at each station. Temperature and salinity measurements were also made at each station in order to illustrate thermohaline gradients that are useful in determining Chesapeake Bay outwelling patterns.

#### OBSERVATIONS AND DISCUSSION OF RESULTS

The relatively long duration (8 days) over which the majority of the Superflux II samples were collected limited the interpretation of process events. During the 8-day period, it was obvious that some amount of variability in the data could be explained by the natural dispersion of water by tides and coastal currents. The comparison of data among stations of a specific transect (all taken on the same day) are more reliable than comparisons between adjacent transects (taken one or more days apart).

Analysis of total hydrocarbon concentration by gas chromatography provided data in values of micrograms hydrocarbon per liter ( $\mu\text{g}/\ell$ ) of water. However, laboratory studies (ref. 4) have illustrated that greater than 90 percent of hydrocarbon material in seawater samples is generally associated with suspended particulate matter. Thus, hydrocarbon concentrations are expressed as micrograms hydrocarbon per milligrams of total suspended sediment ( $\mu\text{g}/\text{mg}$ ).

The areal distribution of hydrocarbon concentrations ( $\mu\text{g}/\text{mg}$ ) illustrated relatively high surface concentrations in the Bay entrance (6 to 7  $\mu\text{g}/\text{mg}$ ). Two areas of relatively high surface concentrations extend seaward from the Bay entrance (fig. 2c). One area was contiguous with the shore of Virginia Beach and extended approximately 10 n. mi. south of Cape Henry. The second and

more prominent high concentration extended seaward from just north of Cape Henry along an azimuth of  $150^{\circ}$  (true) for approximately 15 n. mi. The axis of the second area of high concentration was approximately 7.5 n. mi. offshore and parallel to Virginia Beach. An areal plot of the total suspended matter illustrated that the nearshore high in hydrocarbon concentration corresponded with the position of a high concentration of total suspended matter, whereas the offshore increase in hydrocarbon concentration was not associated with an increase in total weight of suspended matter concentration (fig. 2a). In a "gross" sense, low-salinity water can be used as a tracer of the outwelling from Chesapeake Bay (fig. 2b). In an attempt to associate hydrocarbon and suspended matter concentrated with the outwelling of the Chesapeake Bay, the surveys of the distribution of low salinity water ( $<29$  o/oo) were compared with hydrocarbon and total suspended matter concentration. The axis of the low salinity water was almost exactly between the two areas of relatively high hydrocarbon concentration. It is tempting to suggest that the effluent from the Chesapeake Bay is depleted in hydrocarbons, however, it is more appropriate to speculate on the mechanics of boundary conditions that may have caused the two anomalously high concentrations in those areas.

Vertical sections of data for transect lines B, C, and D illustrate that the concentration of hydrocarbons and suspended solids increased with depth in the nearshore zone but was apparently a surface phenomenon in the offshore area (figs. 3 and 4). Increases in concentration with depth may result from two different processes. The first and most plausible explanation is that re-suspension of fine grains from the seabed was the major source of suspended matter in the water column. After particulates with associated hydrocarbons were elevated into the water column, they were apparently transported southward in a hyperpycnal flow of higher salinity (28 to 32 percent) bottom water adjacent to Virginia Beach. The second explanation for the anomalously high nearshore concentration of hydrocarbons and particles is that the anomaly was associated with a hypopycnal (surface) flow and that the particulate fraction had partially settled through the water column. This would account for the increase in concentration of suspended particulates (by weight) with depth. There is no doubt that both of these processes have, in part, contributed to the distribution of hydrocarbon and suspended solid concentrations in the nearshore area.

At transect B, it is extremely difficult to distinguish between the nearshore and offshore hydrocarbon anomalies. However, it is apparent from profiles of the particulate data that the axis of the inner area was between standard stations 69 and 802 (fig. 5). The axis of the offshore anomaly was apparently located just seaward of standard stations 802, 806, and 810 at transects B, C, and D, respectively. This places the axis of the offshore anomaly along the vertical and areal boundary of the prominent low salinity outwellings of the Chesapeake Bay. Studies of other water mass boundary conditions in the Bay entrance have illustrated an increase in the concentration of buoyant materials (including hydrocarbons) at frontal interfaces.

In an attempt to correlate hydrocarbon concentration with total suspended solids, a correlation coefficient for all data was calculated. The correlation

coefficient of 0.2 illustrated that a very poor correlation existed for all data. This was anticipated since there was a diversity of sources and processes that had different influences on the concentration and dilution of hydrocarbons and suspended particles. The correlations between hydrocarbon and suspended particulate concentrations showed an increased correlation of 0.59.

While the offshore hydrocarbon anomaly was very well defined, that area was very poorly correlated with the weight concentration of suspended particulate matter. Two potential reasons for this poor correlation relate to sources and processes influencing the total concentration. The easiest explanation for the low correlation coefficient is that there were two independent and different sources of suspended solids and hydrocarbons for this zone. The second possibility is that the sorting characteristics of particles comprising the suspended solids of the nearshore and offshore anomalies were independently altered with time, and therefore the adsorption rates of hydrocarbons were variable. Microscopic analysis of filters illustrated that the particulate fraction was composed of approximately 25 types of particles, and that different proportions of these particles were present in the nearshore and offshore zones. While specific studies of surface area characteristics have not been completed, a wide variety of particle shapes was observed by microscopic inspection.

In general, particles with irregular shapes provided more surface area and sites for hydrocarbon adsorption than the more regular spherical particles. On a per-weight basis the smaller particles provide greater surface areas than larger particles. Thus a water sample having a relatively low concentration (mg/l) because it is primarily composed of very fine-grained particles may have more surface area for hydrocarbon adsorption than a sample having a relatively high concentration (mg/l) but composed of a fewer number of large particles. The offshore hydrocarbon anomaly had a relatively low weight concentration of suspended matter but had a relatively large surface area availability for hydrocarbon adsorption since the particles were very fine grained (table 1). This relationship was well illustrated in sample 71-6, where the volume percentage in the smaller mode (12.7 to 16.0  $\mu\text{m}$ ) was one-third of the volume present in the larger mode (80.6 to 101.6  $\mu\text{m}$  mode); however, the smaller size mode had approximately twice the available surface area of the larger mode (fig. 5). Since larger and heavier particles settle more rapidly than smaller ones, the settlement of larger particles should have been more complete in the offshore zone than in the nearshore zone. Therefore, reduction in the relative weight concentration of suspended matter may have resulted in only a minor reduction in surface area available for adsorption of pollutants. A simpler explanation would be that the offshore area had a finer-grained source to begin with. Table 1 illustrates variations in the characteristics of particulate matter at four distinct areas: the Bay entrance, the nearshore hydrocarbon anomaly, the offshore hydrocarbon anomaly, and shelf water. In an attempt to determine the relative surface area available, the volume-percents of fine and coarse-grained particles were determined for the four areas described above. It was apparent from these data that samples with a high percentage (greater than 75 percent) of material less than 32  $\mu\text{m}$  in diameter also had high concentrations of hydrocarbons. Samples with a low percentage

of the less than 32  $\mu\text{m}$  material had no measurable hydrocarbons. Samples comprised of a moderate volume percent (25 to 50 percent) of small grains (less than 32  $\mu\text{m}$ ) had traces of hydrocarbons (1.8 to 2.5 micrograins per liter).

The weight concentration (mg/l) of particles, the volume percent of large particles, and the absence or presence of quartz grains in the 70 to 120  $\mu\text{m}$  size range provided additional data on the source of suspended particulates and hydrocarbons. The presence of suspended quartz grains in the 70 to 120  $\mu\text{m}$  size range required a very close proximity to the source of the inorganic fraction, otherwise the large grains would have settled to the bottom. Raman data (ref. 5) for the Bay entrance illustrated a turbidity maximum across the Bay entrance with no apparent up-Bay or down-Bay source. The presence of relatively large quartz grains at the Bay entrance and along Virginia Beach (BAPLEX stations 1-s and 2-s, and Superflux II stations 69-s and 805-s) illustrated that high turbidity was apparently produced by local resuspension. At the offshore hydrocarbon anomaly, large quartz grains were not found in the water. While the volume percent of coarse and small particles was approximately equal, the fine fraction had greater than twice the surface area as the coarse, apparently planktonic fraction. On a weight basis the larger particles (both organic and inorganic) had the more significant influence on the total suspended matter (TSM) concentration, whereas the smaller inorganic particles (because of increased number and surface area) apparently had a greater influence on the relative amount of hydrocarbons that adsorbed to the suspended particles measured on a weight basis.

It is apparent from the above discussion that further attempts to correlate hydrocarbons with suspended particulates should consider relative surface area and grain shape characteristics.

#### CONCLUSIONS

While there was generally good correlation between anomalies of high hydrocarbon and suspended matter concentration, no linear correlation between concentrations could be established. Failure to determine a linear correlation was apparently due to the fact that the concentration of suspended matter was determined on a weight basis and adsorption characteristics of hydrocarbons are apparently dependent on a variety of other characteristics of suspended matter, including shape, surface, area, etc.

High concentrations of total suspended matter were associated with the shoals in the Bay entrance and its margins. Variations in concentrations of total suspended matter were generally produced by changes in the inorganic concentrations since organic concentrations remained relatively constant. Adjacent to Virginia Beach, local resuspension of bottom sediment was suspected because of the presence of suspended quartz particles in the 70 to 120  $\mu\text{m}$  size range. The nearshore area of high suspended solid concentration and relatively high hydrocarbon concentration was landward of the inner boundary of the low salinity outwelling from Chesapeake Bay.

High concentrations of hydrocarbons were also measured along the seaward boundary of the low salinity outwelling from Chesapeake Bay. A combination of frontal boundary mechanics and particle surface area availability may have influenced the formation of this offshore hydrocarbon anomaly.

#### REFERENCES

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TABLE 1.- CHARACTERISTICS OF SUSPENDED PARTICULATE MATERIAL AT THE  
BAY ENTRANCE, NEARSHORE, OFFSHORE, AND INNER SHELF

Location	Sample no.	Date	Percent <32 $\mu\text{m}$ particles	Percent 50-80 $\mu\text{m}$ particles	Presence of 70-120 $\mu\text{m}$ quartz	Weight hydrocarbon $\mu\text{g}/\ell$
Bay entrance	1-S	6-24	80.0	10.5	yes	18.0
	2-S	6-24	80.0	9.3	yes	14.0
Nearshore anomaly	69-S	6-18	N.D.	N.D.	yes	4.2
	805-S	6-19	N.D.	N.D.	yes	5.1
	71-6	6-21	24.0	24.3	no	2.5
Offshore anomaly	806-S	6-19	N.D.	N.D.	no	2.7
	810-S	6-20	N.D.	N.D.	no	10.0
	812-S	6-21	45.0	24.1	no	1.8
Shelf	811-S	6-21	9.4	34.4	no	0.0
	813-S	6-21	8.6	41.5	no	0.0

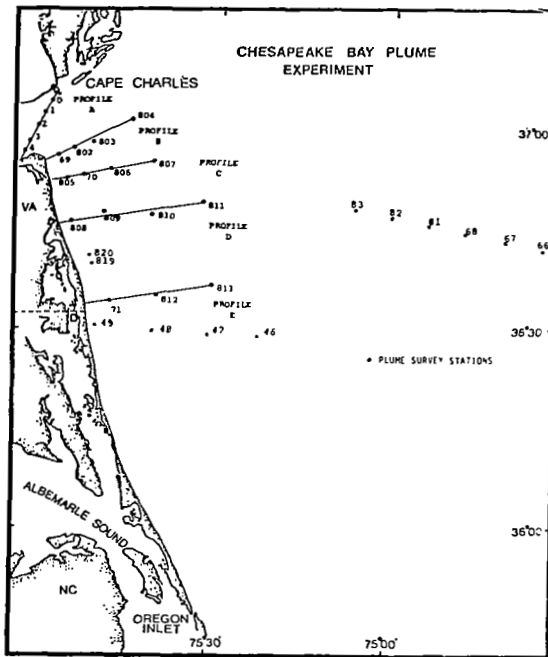


Figure 1.- Map showing station location for water samples.

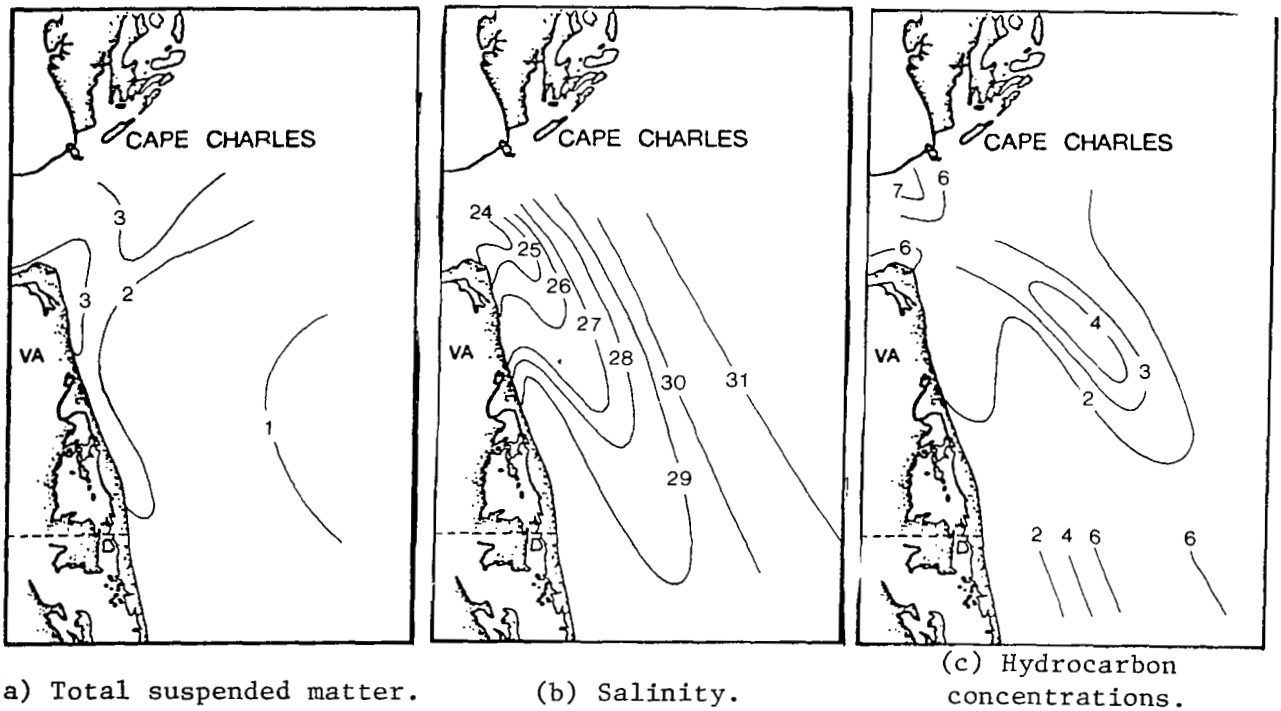
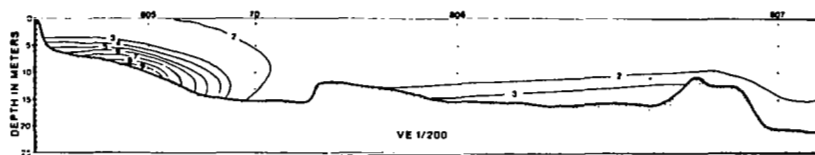
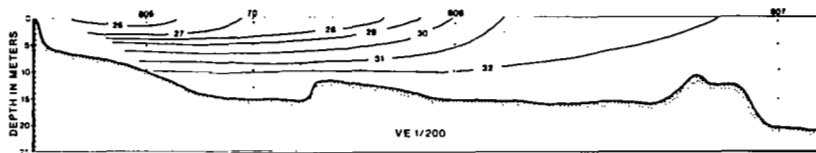


Figure 2.- Map illustrating concentration of total suspended matter (mg/l), salinity (‰), and hydrocarbon µg/mg) in surface water adjacent to the Chesapeake Bay entrance.

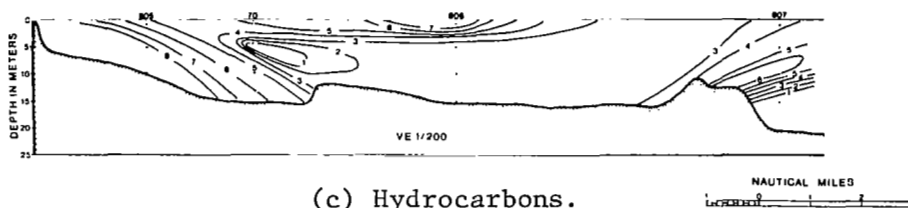




(a) Total suspended matter.

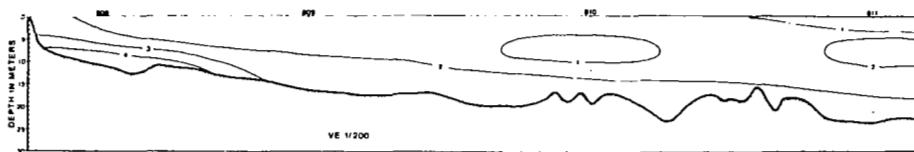


(b) Salinity.

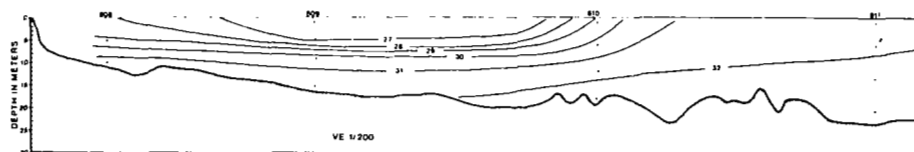


(c) Hydrocarbons.

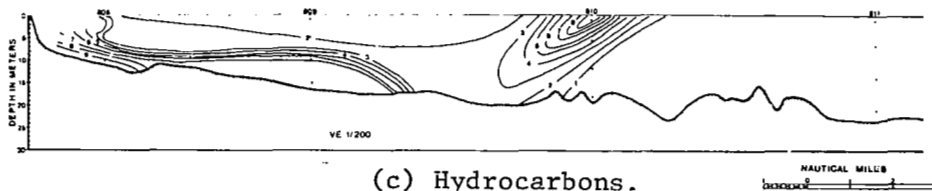
Figure 3.- Profile of transect C illustrating total suspended matter concentration (mg/l), salinity (‰), and hydrocarbon concentration (μg/l).



(a) Total suspended matter.



(b) Salinity.



(c) Hydrocarbons.

Figure 4.- Profile of transect D illustrating total suspended matter concentration (mg/l), salinity (‰), and hydrocarbon concentration (μg/l).

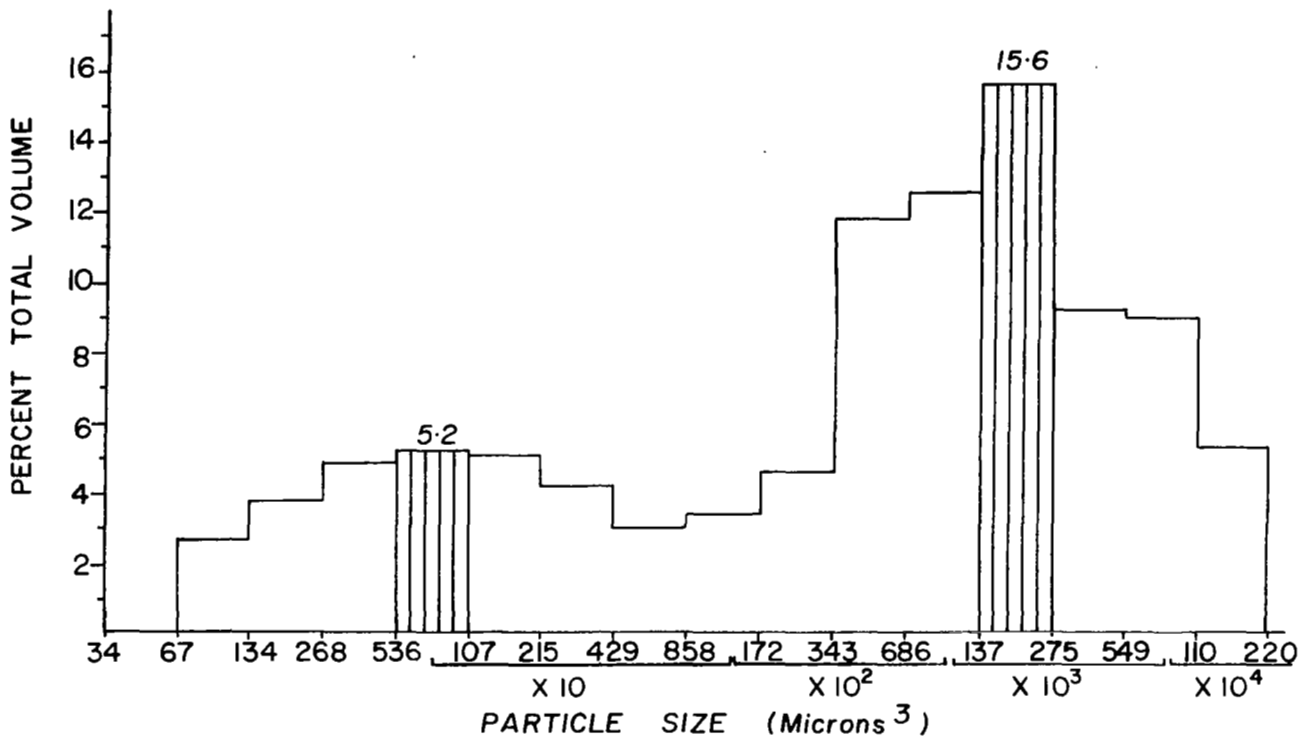


Figure 5.- Histogram of size frequency distribution of particles for sample 71-6.