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DEPARTMENT OF PHYSICS
SCHOOL OF SCIENCES AND HEALTH PROFESSIONS
OLD DOMINION UNIVERSITY
NORFOLK, VIRGINIA

AMBIENT AMMONIA MEASUREMENTS USING LASER PHOTO-ACOUSTIC SPECTROSCOPY

By

Melville Dannehl Aldridge, III
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and

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Principal Investigator: Gary E. Copeland

Final Report
For the period ending June 19, 1981

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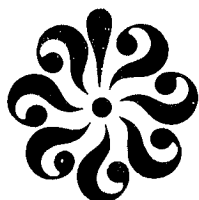
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Melville Dannehl Aldridge, III[1], Gary E. Copeland[2],
and Charles N. Harward[3]

ABSTRACT

Measurements of gaseous atmospheric ammonia from September 1980 to mid-March 1981 were obtained with an experimental system employing laser photo-acoustic spectroscopic techniques. Ammonia concentrations reached minimal levels (approximately 0.1 ppb) in early winter, followed by a sudden late winter increase. A direct relationship between ambient ammonia levels and air temperature was inferred from the data (linear correlation coefficient $r=0.53$). Ammonia concentrations were determined to be directly related to the absolute humidity of the air ($r=0.72$); a weaker relationship between ammonia concentrations and relative humidity was discovered ($r=0.37$). The data also indicated that ammonia levels were generally higher within continental air masses than those of maritime origin. Soil parameters such as pH and moisture content were found to have a major bearing on the release of gaseous ammonia from soils in the region.

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I. INTRODUCTION

Purpose

In July 1980 a grant from the National Aeronautics and Space Administration (NASA) was awarded to Old Dominion University (principal investigator: Dr. G.E. Copeland) to conduct research into the temporal distribution of gaseous ammonia in the air of Southeastern Virginia. Since the late summer of 1980 measurements of ambient ammonia have been taken with an experimental measurement system housed at NASA Langley Research Center in Hampton, Virginia. This paper will present those measurements and will investigate various factors which may have influenced the variations in ammonia concentrations noted during the course of this research. An attempt will also be made to place the measurements in a proper perspective. That is, results of a thorough review of the current knowledge concerning atmospheric ammonia will be presented. The review will contain information on the role of ammonia in the nitrogen cycle, aspects of ammonia's atmospheric chemistry that may have deleterious consequences in the environment, and the results of other research programs which included measurements of atmospheric ammonia. In addition, the measurement technique used for this study

will be described in some detail--and other methods of monitoring atmospheric ammonia will be discussed--so that the existing technologies can be compared with the experimental technique employed in this study. It has been recognized for some time that gaseous ammonia is an important trace constituent of the atmosphere; yet accurate measurement of it has proven to be extraordinarily difficult. As a result, relatively little is now known about ammonia in the atmosphere. The primary purpose of this paper will be to increase our knowledge and help pave the way for future research in this area.

Atmospheric Ammonia and the Nitrogen Cycle

Gaseous ammonia, the familiar compound consisting of a nitrogen atom bound to three hydrogen atoms, is a ubiquitous trace constituent of the atmosphere. Although poisonous in high concentrations, gaseous ammonia rarely constitutes a health hazard outside of the laboratory. In the environment the ammonia molecule, together with the ammonium ion (NH4+), represent the most common forms of fixed nitrogen, which is essential to life [1]. Ammonia is therefore generally considered a beneficial substance. Ammonia is so essential for food production that in the last fifty years man has increasingly supplemented the enormous amount of ammonia produced by natural processes with manufactured ammonia. He has also planted large

numbers of nitrogen-fixing plants to augment natural production of fixed nitrogen. Man's activities account for a large and increasing share of the total quantity of fixed nitrogen produced each year. Although estimates vary widely, by most accounts the quantity of nitrogen fixed annually by industry and legume crops approximately equals that fixed "naturally" [1]. How much of this fixed nitrogen actually finds its way into the atmosphere as gaseous ammonia is not known. Better understanding of the nitrogen cycle, and especially of soil processes, is necessary before scientists can assay what effect the increase in fixed nitrogen production will have on the atmospheric pool of ammonia.

Natural production of ammonia occurs as an integral part of the nitrogen cycle. Organic nitrogen in soil and in water is mineralized by microorganisms into ammonium or nitrate ions, forms of nitrogen suitable for assimilation by plants. In plant tissues the nitrogen is converted to organic form again, only to be returned to the soil or water by death and decay. However, the cycle is complicated by the action of some species of microbes, which extract energy by converting nitrate to gaseous nitrogen or nitrous oxide. This process, called denitrification, must be balanced by an input of fixed nitrogen for the cycle to remain in equilibrium. Most fixed nitrogen in the soil is provided by certain species

of microorganisms, usually existing in symbiotic relationships with plants, which metabolically convert atmospheric nitrogen to ammonium. A smaller amount of fixed nitrogen is created in the atmosphere by ionizing processes such as lightning.

The processes which lead to denitrification are a major sink for fixed nitrogen in the soil. Moreover, volatilization of ammonia from the soil into the atmosphere also constitutes a large sink for fixed nitrogen in the soil and represents the major source of atmospheric ammonia. According to Dawson [8] some 50 million metric tons per year of ammonia are released by volatilization from the soil. Once in the atmosphere gaseous ammonia resides there for comparably short periods. Research indicates that the average residence time is approximately five to ten days [1] [27] [42]. Ammonia, a chemical base, readily reacts with a number of acidic substances abundantly present in the atmosphere, frequently forming aerosols. It is also extremely soluble in water. Therefore, it is not surprising that fallout, washout, and rainout processes rapidly scavenge ammonia from the air. Concern for the amount of ammonia released into the atmosphere as a result of man's intervention into the nitrogen cycle would seem unjustified in light of such efficient mechanisms for removal of this gas. Unfortunately, some of the chemical products which result

in removal of gaseous ammonia from the atmosphere have deleterious effects on the environment.

Acid Rain

Atmospheric ammonia plays a key role in the chemical processes which lead to the formation of acid precipitation. Acid precipitation, hereafter referred to as acid rain, is defined as precipitation containing an excessive concentration of hydrogen ions. In terms of pH, acid rain is described as precipitation having pH below 5.6, which is considered the minimal pH for pure water in the presence of atmospheric carbon dioxide [28]. A remarkable decline in the average pH of precipitation in North America and in Europe since the industrial revolution has been noted by numerous authors [10] [23]. The most significant changes in pH have occurred within the last thirty years. The pH of rain and snow in many parts of the eastern United States and northern Europe now averages around 4.0; pH values as low as 2.1 have been measured in some storms [28]. Anthropogenically produced sulfur and nitrogen oxides, products of industry and combustion, are largely responsible for the drastic increase in the acidity of precipitation over widespread areas [1].

Chemical analyses of rainwater indicate that ammonium ions are present in significant quantities [9]. Researchers have examined possible chemical interactions

between ammonium and other ionic species present in raindrops and have reached somewhat surprising conclusions. A strong chemical base, ammonium acts to increase pH in raindrops. This effectively neutralizes some of the acidity caused by sulfate and nitrate ions also present in rainwater. However, other processes in which the ammonium ions participate apparently enhance the acidity of raindrops. According to Scott and Hobbs [39], Junge and Ryan [22], and others, ammonium acts as a chemical promoter within raindrops, speeding conversion of dissolved sulfur dioxide into acid sulfate. By controlling the pH of the system, ammonium ions also increase the solubility of gaseous sulfur dioxide in cloud droplets [12]. Ammonium's role in enhancing the solubility of gaseous sulfur dioxic and promoting its oxidation to sulfate apparently supercedes its role as a neutralizing agent. Gaseous ammonia, which readily dissolves in raindrops to form ammonium ions, is now considered an important precursor to the phenomenon known as acid rain.

Other Chemical Interactions and Their Effects

Ammonia is known to undergo both aqueous-phase and gas-phase reactions with atmospheric pollutants to form aerosols such as ammonium nitrate and ammonium sulfate [1]. These particulates may affect the earth's radiation balance; more importantly, they constitute a health hazard

in high concentrations. The Donora, Pennsylvania episode in 1948 is an example of the health hazards brought about by such "smog."

Ammonia molecules may also migrate to the stratosphere and participate in photochemical interactions with ozone, resulting in depletion of this essential stratospheric component. Such destruction of ozone molecules is thought to be of secondary importance compared to catalytic destruction of ozone by nitric oxide. At this time it is suspected that atmospheric ammonia may be a source for nitric oxide [32], but definite conclusions have not been reached.

II.   LITERATURE REVIEW

Early Measurements of Atmospheric Ammonia

The role of ammonia in acid precipitation was not defined until Junge [22], Scott and Hobbs [39], and other pioneers in atmospheric chemistry published their results in the nineteen fifties and sixties. Therefore it is not surprising that attempts to measure gaseous ammonia were few and far between until fairly recently. The lack of interest in gaseous ammonia was also due in part to the widely held notion that ammonia was chiefly fixed to dust particles and did not occur in gaseous form at significant concentrations [21].   Early measurements of total ammonia (gaseous ammonia plus ammonium) in the nineteenth century reflect curiousity about the cycling of nitrogen compounds in the atmosphere, but after the turn of the century research all but ceased until the nineteen fifties [21]. In 1953 a network of sampling stations was established in Scandinavia.   These stations produced monthly averages of gaseous ammonia concentrations. According to Junge [21] the results indicated a rather uniform distribution of ammonia--in the neighborhood of several micrograms per cubic meter ($\mu g/m^3$)--with evidence of summer maxima and winter minima in ammonia levels at most stations.   Junge

[21] also conducted his own measurements during 1954 in Florida, Hawaii, and Massachusetts. At these locations he obtained average ground-level concentrations of 5.1, 2.5, and 6.1 $\mu g/m^3$, respectively. Junge tentatively concluded that the oceans are a source for gaseous ammonia, and suggested that thin organic films at the sea surface may release ammonia into the air.

Almost twenty years later Georgii and Muller [11] published the results of their investigation of gaseous ammonia and ammonium-containing aerosols in the air over northern Europe. This study was the first comprehensive study of atmospheric ammonia. From 1969 until 1972 monitoring was conducted over both land and water areas from aircraft outfitted with automatic sampling apparatus. Georgii and Muller reported that gaseous ammonia concentrations at ground level averaged 7 $\mu g/m^3$ on "cold" days (temperatures below 10°C) and 18 $\mu g/m^3$ on "warm" days (above 18°C). Seasonal differences in ammonia levels were still noticeable aloft. At 3000 meters concentrations were, on the average, approximately 2 $\mu g/m^3$ on cold days and 5 $\mu g/m^3$ on warm days. Georgii and Muller found that ammonia concentrations generally reached constant "background" levels at 1500 meters on cold days and 3000 meters on warm days. They concluded that atmospheric ammonia originated at the ground, and that temperature inversions as well as convection strongly affect the

vertical transport of ammonia.

While most of the aircraft flights were centered over western Germany, measurements were also taken over the North Sea and over Bavaria. Ammonia levels were much lower over open water--as low as 0.3 $\mu g/m^3$. Hence they concluded that ammonia is largely of continental origin. Georgii and Muller witnessed a classic example of rainout of ammonia over Bavaria. Upwind of their sampling area the intensification of a foehn wind system caused rainclouds to form over the Alps. From one day to the next ammonia concentrations in the lower troposphere fell from 20 $\mu g/m^3$ to 4 $\mu g/m^3$.

Georgii and Muller showed that meteorological parameters such as air temperature, lapse rates, and rainfall exert a strong influence on gaseous ammonia concentrations. No other investigation into atmospheric ammonia has been so thorough and informative. A number of other scientists, however, have made valuable contributions to our knowledge of atmospheric ammonia. For example, in 1974 Lodge and coworkers [29] published results of their investigation into trace atmospheric constituents in the American tropics. Measurements were taken in 1967 and 1968; these included seasonal and diurnal profiles. Lodge et al. found that gaseous ammonia concentrations averaged 15 parts per billion (10^{09}) by volume (1.0 ppb=0.7 $\mu g/m^3$ for ammonia at STP), a level considerably higher than in

temperate climates. Their data indicated that ammonia concentrations were generally higher at night than during the day, perhaps reflecting inversion conditions. A "burst" of high concentrations at the beginning of the dry season was also noted by Lodge et al.

Another important investigation was conducted by Tsunogai [41] in 1971. He found that the concentration of atmospheric ammonia was much lower over the ocean--averaging around 0.85 $\mu g/m^3$--than over land, where concentrations increased to approximately 3.4 $\mu g/m^3$. Tsunogai also measured the ratio of particulate ammonium to gaseous ammonia over open ocean and compared it to data obtained near land. From his results he concluded that gaseous ammonia is mainly of continental origin and has an average residence time in the atmosphere of five to ten days [42].

Healy [15] [16] conducted several investigations of ammonia levels at both rural and urban locations in England. At rural Harwell he found that ammonia was present typically at 0.85-1.70 $\mu g/m^3$. Healy concluded that domestic animals were responsible for most of the gaseous ammonia found over England.

In the United States early measurements of gaseous ammonia were obtained by Breeding and his coworkers [6]. In 1971 and 1972 they conducted an investigation into

background levels of various trace atmospheric constituents. The sampling was done in rural areas around St. Louis, and attempts were made to pinpoint local sources of contamination. Breeding et al. reported that background concentrations of ammonia varied between 2 and 6 ppb in the area, with variations in this range due to "natural mechanisms." They detected no diurnal trends in ammonia levels. Interestingly, during a rainfall they measured higher concentrations than most of the samples obtained under sunny skies.

Most early research into atmospheric ammonia in the United States was conducted in urban areas near strong sources of the gas [1]. As would be expected, widely varying concentrations were reported. For example, one study obtained measurements as high as 450 ppb in the vicinity of a major dairy farm. Typically, it was reported that urban ammonia concentrations were significantly higher than those in rural areas.

No federal or state agency in America has routinely monitored ambient ammonia. The unavailability of a continuous and reliable method for measuring ammonia at low concentrations contributed to the paucity of measurements [1].

Recent Measurements Using New Techniques

Continued interest in gaseous ammonia has spurred development of more sensitive and accurate measurement techniques. Most of these new methods are still in experimental development, but very recently results of some of these measurements have begun to appear in scientific publications. Many of these reports involve measurements taken in Southeastern Virginia--both by remote and in situ techniques--and thus form an excellent basis for comparison with the measurements which will be reported in this paper.

Using a new in situ technique in 1978, McClenney and Bennett [30] measured gaseous ammonia at two sites in North Carolina. Near Research Triangle Park, where five measurements were made, the average ammonia concentration was 4.1 ppb. McClenney and Bennett also sampled at Cedar Island, North Carolina. No attempt was made to delineate diurnal trends in ammonia levels (all sampling took place in the afternoon), but an effort was made to sample near possible local sources of ammonia. Samples were taken from a ten foot height over land (average ammonia concentration: 1.0 ppb), from a height of six feet over marsh grass (one sample: 0.9 ppb), from a height of two inches over marsh grass at the water's edge (average: 2.9 ppb), over land at a height of two feet (0.3 ppb), and from within a shelter during rain (average concentration: 0.3 for six samples). McClenney and Bennett avoided drawing any broad conclusions

from such sparce data. Moreover, their main objective was to test the efficacy of their sampling methods and analytical technique.

A team of researchers at NASA Langley in Hampton, Virginia and at Old Dominion University began conducting both in situ and remote measurements of ambient ammonia in 1979. One of their reports [18] compared in situ data obtained from an aircraft measurement platform with vertical profiles of ammonia concentrations from a Remote Infrared Heterodyne Radiometer (IHR). Results from the in situ data were in good agreement with the remotely obtained profiles. Both techniques indicated that on the day the measurements took place (June 12, 1979) ammonia levels were approximately 1 ppb near the ground and slowly decreased with increasing altitude.

In another report [19] these researchers compared vertical ammonia profiles taken in March of 1979 with profiles obtained in August of that year. They found that ammonia concentrations were significantly lower throughout the lower troposphere in August than in March. The latter measurement indicated that ground-level concentrations of gaseous ammonia were approximately 1.3 ppb, while March levels were around 10 ppb. These results were contrary to Georgii and Muller's in situ measurements in Europe, which indicated that ammonia release from the soil was dependent on soil temperature. The measurements, however,

qualitatively agreed with measurements obtained on Long Island in 1976 by Peyton et al. [36] during a preliminary test of a similar IHR instrument. Peyton and coworkers had found that ammonia levels near the ground had decreased from 12 ppb in March to 0.2 ppb in July. These results indicated to the researchers at Langley that other factors beside temperature influenced ammonia emission from the soil. It was concluded that rapid volatilization of ammonium nitrate fertilizer which had been applied to nearby fields several weeks earlier had contributed to the high ammonia concentrations found at Langley in March of 1979 [27].

Extensive in situ measurements in 1979 and 1980 at Langley (some of which overlapped this study's research) indicated to Hoell et al. [20] that soil moisture was a factor which also influenced local ammonia levels in the atmosphere. They found that background ammonia levels in the late summer of 1980 were much lower than during the corresponding period of 1979. Abundant rain fell in both August and September of 1979, when ammonia levels averaged nearly 2 ppb. In 1980, however, severe drought apparently contributed to much lower ammonia concentrations, which averaged only around 0.5 ppb in August and September. It is also noteworthy that the spring maximum in 1980 was much less pronounced with the in situ data than would be expected from the previously reported March 1979 levels

recorded by remote means. The authors noted that the entire year of 1980 was relatively dry, and hence a variety of climatological conditions may be operating simultaneously to influence concentrations of ammonia in the atmosphere.

III.   STATEMENT OF THE PROBLEM

Current Requirements for In Situ Ammonia Measurements

Research into the distribution and chemical interactions of atmospheric ammonia has been hampered by a lack of data concerning this important trace gas. Most of what we know about ammonia in the atmosphere comes from the handful of articles and reports outlined in the foregoing discussion. In the past few years federal regulatory agencies, atmospheric chemists, and other concerned groups and individuals have expressed the desire for more information on the temporal and spatial distribution of gaseous ammonia, its sources and sinks, its residence time in the atmosphere, and concentrations of related trace species. For example, in 1979 the Subcommittee on Ammonia (of the Committee on Medical and Biologic Effects on Environmental Pollutants, National Research Council) recommended that accurate estimates of the emission, movement, and degradation of ammonia in the atmosphere be obtained. It also listed as a high priority further study of ammonia's complicated atmospheric chemistry. Toward this end:

Simultaneous measurement of ammonia and of particulate hydrogen (acidity), ammonium, sulfate, and nitrate content are needed to elucidate further the role of ammonia in the formation of particulate ammonium, nitrate, and sulfate and to formulate improved strategies for the control of these major inorganic pollutants [1].

Furthermore, the Subcommittee recognized that current monitoring methods for ammonia are woefully inadequate and stated that "methods should be developed or refined for the routine measurement of ambient ammonia at parts-per-billion concentrations. These methods should be suitable for continuous measurement of ambient ammonia as part of a limited monitoring network." [1]

The existence of a monitoring network would be a boon to scientists interested in modeling the complicated atmospheric chemistry of ammonia. Under non-steady-state conditions, validation of a model's output is impossible without extensive spatially and temporally resolved data. Under the simplifying (if somewhat unrealistic) assumption of steady-state, horizontall homogeneous distributions of gaseous ammonia, modelers can "make do" with vertical profiles of ammonia concentrations. In fact, vertical profiles obtained by IHR have been used by a team at NASA Langley in conjunction with a steady-state model they developed. Using the data thay were able to derive rate constants for heterogeneous reactions (including gas to particle conversions, dry deposition, and rainout)

involving ammonia [27].

At the present time the IHR can yield data useful to numerical modelers at Langley with less cost and bother than available _in_ _situ_ techniques. However, _in_ _situ_ monitors are still needed to provide ground truthing of the data f om the IHR and to extend measurement capabilities. The IHR system at Langley has limited sensitivity (0.5 ppb) and cannot be used when direct sunlight is not present [20].

An automated _in_ _situ_ ammonia monitor is the only practical method for obtaining continuous data. If such a monitor were to exist, it could be easily integrated into existing monitoring networks which have been established by various state and federal agencies. Without such a network scientists cannot accurately pinpoint sources of the gas or reach definite conclusions about the influence of various meteorological parameters on the temporal and spatial distribution of ammonia and related atmospheric species. While the utility of a single, isolated monitoring station is limited, inferences can be drawn where conclusions cannot. The present data base is so sparce that any information about ammonia, however fragmentary, would be welcomed by the scientific community.

Available Measurement Techniques

Most methods of measuring atmospheric ammonia involve a period of sampling (by bubbling or some other form of preconcentration), followed by an analysis of ammonia content in the sample. Collection of ammonia is complicated by a number of difficulties. Contamination of samples by ammonia emanated from nearby personnel is a problem which many investigators have encountered. Because ammonia adsorbs onto almost any surface, care must also be taken to minimize contact of the air stream containing ammonia with the walls of tubing. An additional problem arises out of the fact that ammonia and ammonium aerosols are generally both present in air. Differentiation between the two is impossible with most analytical techniques. The inclusion of particulate prefilters in the sampling stream may result in either positive or negative errors in measurement, depending on the aerosol content of the air and the type of filter used [1]. Sampling efficiency is yet another problem. Most sampling techniques rely on the high solubility of ammonia in acidified water. But studies have shown that bubblers are usually less than 100% efficient in dissolving ammonia. Efficiency also decreases with low ammonia concentrations [1].

Assuming valid samples of ammonia have been obtained, any of several wet chemical techniques can be used to analyze the samples for ammonia. The Nessler method,

involving the reaction of ammonium ion with Nessler's reagent, is considered the classic colorimetric technique. It has been demonstrated, however, that interfering substances frequently invalidate the measurement of ammonia by this method [34]. Alternatives to the Nessler method have been developed and widely used in recent years. The two most popular colorimetric techniques are the indophenol method and the pyridine-pyrazolone method. Breeding et al. [6] and Georgii and Muller [11] relied on the former technique to determine ammonia concentrations for their extensive investigations. Okita and Kanamori [34] have extolled the virtues of the latter method.

Several reservations about these and other aqueous techniques immediately come to mind. As mentioned earlier, none of the aqueous methods is capable of separating the gaseous ammonia from species containing ammonium ions. Indeed, to avoid the problems inherent in the use of prefilters, some investigators have contented themselves with simply measuring the total ammonium concentrations present in the air. The three techniques discussed above are generally considered among the most sensitive of all colorimetric methods. Yet their sensitivity limits lie in the range of 0.01-0.05 mg/liter of solution [1]. Using standard bubbling apparatus, less than ten liters per minute (l/min) of air per liter of solution can be sampled with high efficiency. This implies sampling times of two

hours or longer for valid determination of background ammonia concentrations (less than ten nanograms/liter). Breeding et al. [6] sampled for one hour, but they gave standard deviations for accuracy of the measurements larger than the approximate average concentration of ammonia in many cases. Other researchers report that a sampling period of anywhere between one and two hours was necessary to obtain measureable amounts of ammonia [11] [34].

Other wet chemical analytical methods reported in the literature include the specific-ion electrode method and ion chromatography [1]. Both claim sensitivity limits only slightly greater than the colorimetric techniques (approximately 0.1 mg/liter of solution). Moreover, bubbling apparatus must still be used for sampling before employing either of these means of analysis.

To avoid the pitfalls associated with bubbling apparatus, Shendrikar and Lodge [40] adapted the so-called ring oven technique for analysis of ammonia. Basically the sampling technique involves the impinging of ammonia (and ammonium ions as well) on a filter paper impregnated with oxalic acid. Final determination of ammonia content depends on visual comparisons of sample spots on the paper with the intensities of spots obtained from known amounts of ammonia. Not only is the procedure complex, but long sampling times (approximately two hours) are necessary to obtain measureable quantities of ammonia. Interference by

formaldehyde is also a problem, according to the authors.

It is readily apparent that all of the wet and quasi-wet analytical techniques have their shortcomings. The most fundamental of these which all of the above share is that ammonia in its gas phase is never measured directly, but is instead converted into a form (ammonium ion) which may be detected by chemical means. Many direct methods of measuring gaseous ammonia now exist, but almost without exception these lack the sensitivity to accurately assess the minute quantities of ammonia present in the air of most environments.

One possible exception was alluded to earlier. The technique involves the use of an IHR, which measures the solar absorption due to atmospheric ammonia. One such system is being used at the NASA Langley Research Center. Its current sensitivity limit (0.5 ppb) makes it only marginally suitable for detecting background levels of ammonia. However, improvements in sensitivity are possible [13]. Since it relies on the sun for a radiation source, the IHR's use is restricted to relatively clear days. Offsetting this disadvantage is the system's capability to obtain virtually instantaneous profiles of ammonia concentrations from ground level up to 30 km [19].

Among the other direct techniques which have been experimentally employed in attempts to measure ambient

ammonia are Fourier-transform long-path infrared spectroscopy, second derivative spectroscopy, chemiluminescence, and laser photo-acoustic spectroscopy (LPS) [1]. These techniques currently cannot detect low background concentrations of ammonia. However, new methods of preconcentrating ambient ammonia now exist which make routine monitoring of atmospheric ammonia by either chemiluminescence or LPS practical. It was stated earlier that gaseous ammonia has the propensity to adhere to almost any available surface. Ironically, this characteristic has opened up new avenues of research into substances which adsorb and subsequently can be induced to desorb ammonia molecules.

Two substances, tungsten oxide and small teflon beads (known by the trade name "Chromosorb T"), have thus far been found which are suitable for preconcentrating ammonia. Both substances exhibit a strong tendency to "trap" ammonia molecules on their surfaces at room temperature; upon heating they release the ammonia at an accelerated rate. Tungsten oxide has emerged as the preferred substance for most purposes. The teflon beads are easily fused by excessive temperatures, so the ammonia may not be driven off as rapidly as is the case with tungsten oxide. This results in a lower factor of preconcentration for the teflon beads. Furthermore, the teflon beads are packed in quartz tubing while the tungsten oxide merely coats the

inside of the tubes. Ammonium-containing particles pass through the tungsten oxide-coated tubes so long as the flow is nearly laminar within the tubes [5]. The particles must be prefiltered from the teflon bead-packed tubes, and this introduces the uncertainties alluded to earlier.

The ammonia, once driven off from the tubes, may be analyzed by a specially modified oxides of nitrogen analyzer, which utilyzes the chemiluminescent reaction between nitric oxide and ozone. The ammonia molecules are first converted to nitric oxide by a catalyst (platinum at 1000 $^{\circ}$C is most frequently employed) before being passed through the analyzer. Unfortunately, many other nitrogen compounds which may be present in the air stream are also converted. Studies have shown that nitric acid and some amines are collected by both the teflon-packed and tungsten oxide-coated tubes, and these constitute a positive interference when the tubes are used with a chemiluminescent oxides of nitrogen analyzer [5].

The chemiluminescent technique uses commercially available gas analyzers which have been specially modified. These instruments are easy to use and relatively portable. In addition, excellent sensitivity has been reported [5]. These advantages are offset by the lack of selectivity of the chemiluminescent oxides of nitrogen analyzers, which allows possible interference by a number of common atmospheric contaminants.

A more specific physical method for determination of ammonia is still in experimental development. A brief history of the discovery and development of the principles underlying this technique follows.

Laser Photo-acoustic Spectroscopic Measurement of Atmospheric Ammonia

The science of acoustics owes a great deal to the work of Bell, Tyndall, and Roentgen in the late nineteenth century. In 1881 they first reported on a phenomenon which became known as the photo-acoustic effect [23]. As its name implies, the photo-acoustic effect occurs when some of the energy absorbed by gas molecules from a beam of radiation results in the net heating of the gas. If the beam is made to vary in intensity, the temperature of the gas in turn fluctuates. As a result the pressure exerted by the gas will undergo fluctuations if the volume of the gas is held constant. Pressure fluctuations in the gas medium propogate as sound waves. A pressure transducer, which is no more than a sensitive microphone, may be used to convert the sound into electrical signals.

Many uses have been found for the photo-acoustic effect since its discovery. Commercial detectors which use the photo-acoustic effect to measure carbon dioxide, carbon monoxide, or water vapor have been around for a number of years [23]. They rely on conventional black-body emitters

of radiation and employ optical filters to select the region of the electro-magnetic spectrum where the gas being measured strongly absorbs radiation. Ammonia is generally too scarce to be successfully monitored by such methods, although it does strongly absorb certain wavelengths of infrared radiation. Other gas species which absorb in the nearby wavelengths effectively "drown out" any slight response which may be due to ammonia molecules alone. But gas lasers produce virtually monochromatic radiation. Isolated absorption features (single absorption lines rather than wide bands in which absorption takes place) can be used to detect minute amounts of absorbing gas. The technique employing gas lasers to produce the photo-acoustic effect has come to be known as laser photo-acoustic spectroscopy. Its rapid development in the last ten years is attributable to the increasingly powerful and reliable carbon dioxide lasers which have only recently become commercially available.

One of the pioneers in the application of laser photo-acoustic spectroscopy (LPS) to pollutant monitoring has been L.B. Kreuzer. In the early nineteen seventies he developed a prototype multiple gas analyzer which relied on a discretely tunable carbon dioxide gas laser and a photo-acoustic effect detector cell [23]. The gas laser could be tuned to a number of wavelengths which roughly correspond to absorption lines of pollutant molecules.

Multiple pollutant gas analysis was accomplished by solving a set of simultaneous linear equations containing information on the signal response, absorptivity of individual gases, path length, and power of the infrared beam at each wavelength. This chore was done by a microcomputer. Uncertainties in the calculation of absorptivities and limitations to the sensitivity of the detector cell limited the instrument's sensitivity to the 1 ppb range for most gases. Still, for ammonia at least, this was a considerable improvement over previously existing systems.

Kreuzer's shotgun approach to pollutant detection (the laser was tuned to 200 different wavelengths in a five minute time span) was aimed at replacing a whole bank of gas analyzers with one device which could almost simultaneously measure up to ten gases. A team at NASA Langley working with an EPA group from Research Triangle Park, North Carolina needed a more sensitive instrument for measuring background concentrations of gaseous ammonia. They developed their own LPS system in the late nineteen seventies for this purpose. The use of preconcentrator tubes and other technological refinements incorporated into this LPS system make it possible to monitor ammonia concentrations of less than 0.1 ppb on an hourly basis.

IV. PRINCIPAL FOCUS OF THIS STUDY

Parameters of Interest Relating to the Measurements

A measurement program for any trace atmospheric constituent gains significance if attempts are made to relate the measurements to parameters which may have a bearing on its distribution in space and time. An attempt will be made in this paper to analyze ammonia concentrations in terms of several meteorological, climatological and soil parameters. Limitations in the data may prevent positive conclusions concerning possible cause-and-effect relationships, but inferences can certainly be drawn where conclusions cannot.

Therefore the ammonia measurements will be categorized by ambient temperature intervals, in order that a possible relationship between ammonia concentrations and air temperature may be investigated. In addition, a regression analysis of ammonia concentrations versus air temperature will be performed.

Further, the data will be divided into eight groups corresponding to the prevailing wind directions at the times of sampling. In this way the suspected continental origin of most gaseous ammonia may be demonstrated.

Perhaps local sources of the gas can be inferred from the data as well.

Seasonal variations in ammonia levels will be described, the results will be compared to other ammonia measurements obtained at Langley, such as those reported by Hoell et al. [20]. If it is determined that local ammonia levels repeatedly peak in the early spring, as Hoell et al. claim, a possible explanation for the peculiar early springtime maximum will be further investigated.

Other data obtained by previous measurement programs at NASA Langley will be compared to data from this program to ascertain if systematic variations exist in ammonia levels from year to year. If such discrepancies do occur, they may be due to differences in soil moisture. A soil water budget model has been developed at Old Dominion University which will be used to estimate soil moisture levels in both 1979 and 1980. In this manner a causitive link between moisture levels in nearby soils and local ammonia production may be inferred.

Moisture in the air may also affect ammonia concentrations. The measurements will be analyzed in terms of both water vapor mixing ratio and relative humidity in an attempt to ascertain what, if any, relationship exists between ammonia concentrations and moisture content of the air.

An Evaluation of the Merits and Limitations of This
Technique

Several promising new methods for measuring
atmospheric ammonia have emerged in recent years, but none
of these has yet been proven superior for all purposes or
situations. Remote techniques such as infrared heterodyne
radiometry, while they hold great promise, may never be
able to totally supplant _in situ_ methods, especially where
continuous monitoring is desired. Modified
chemiluminescent oxides of nitrogen monitors may now
possess the necessary sensitivity and selectivity to
differentiate gaseous ammonia from other ambient nitrogen
compounds, but continuous, routine measurement using
chemiluminescence has not yet become a reality. The same
is true of laser photo-acoustic spectroscopy. The method
is still in experimental development and further
improvements are needed. A second focus of this paper will
therefore center on an evaluation of the system's
performance during the measurement program. The aim will
be to determine where further improvements are necessary
and to suggest possible modifications to the existing
design or measurement procedure. Toward this end a
narrative discussion of the problems and discoveries
encountered during the course of the research will be
presented.

V.   THE MEASUREMENT SYSTEM

Theoretical Background

The ammonia molecule has a pyramidal structure and behaves as a symmetric-top rotor [1]. While the gas is virtually transparent in the visible and near-ultraviolet regions of the electromagnetic spectrum, it exhibits strong absorption in the near-infrared. In the ten micron wavelength region particularly, the gas has large absorption coefficients [37]. This spectral region corresponds to a series of strong absorption bands caused by the molecule's vibrational-rotational characteristics. Figure 1 shows line strengths of individual lines for ammonia and several other molecules. Several strong absorption lines for ammonia are present in the region around 10.78 microns, or 927 Kaysers (1 Kayser = 1 cm-1). In order to isolate absorption of radiation due to the presence of ammonia from absorption by other molecules which may be present, a strong absorption feature which does not significantly overlap with the absorption lines of other molecules must be isolated. One such absorption feature is centered at 927.32323($\pm$0.00012) Kaysers. This corresponds to the aQ(6,6) ν 2 fundamental vibrational-rotational transition of the ammonia molecule
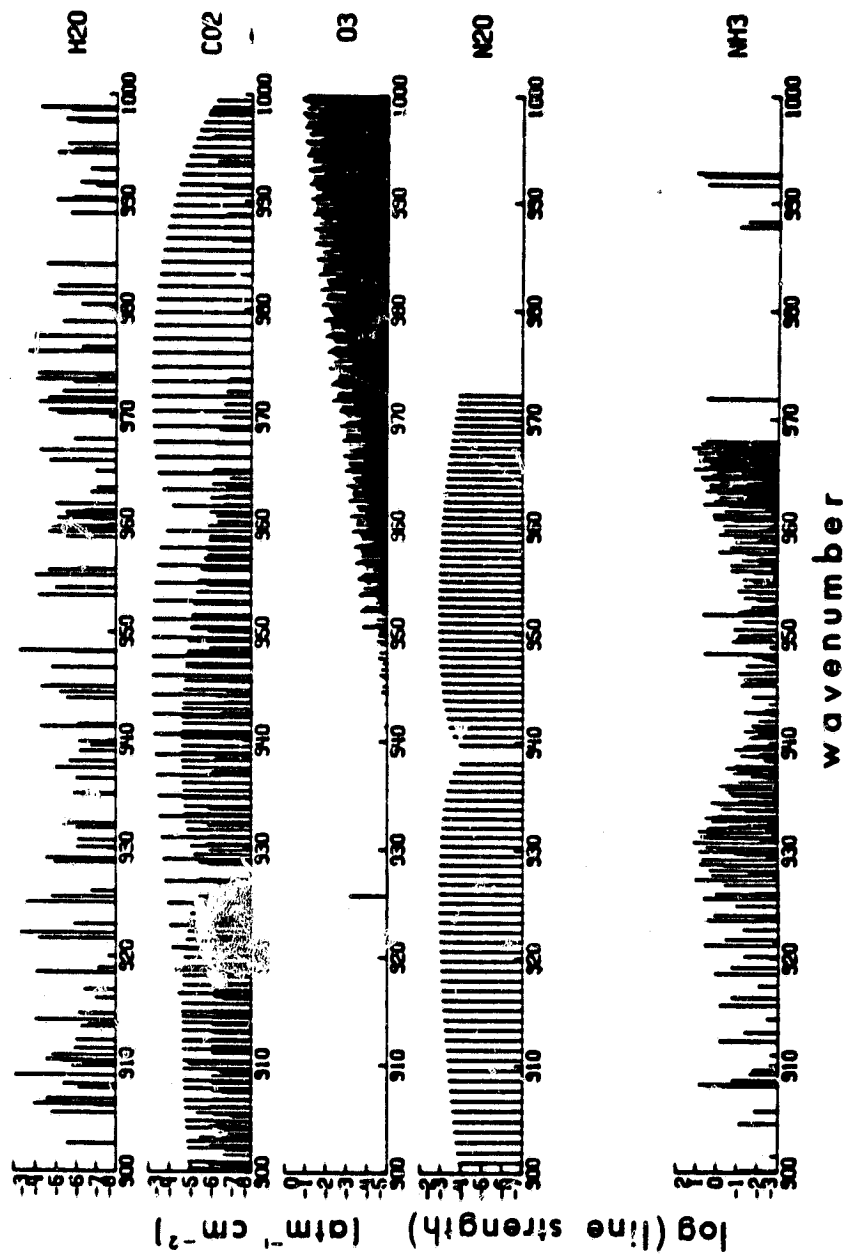
Figure 1. Absorption line strengths for ammonia and other selected gases in the 900 – 1000 cm -1 region. (From [35])

[17]. The absorption feature has a line strength of 4.09*10-19 Kaysers/(molecule cm**2) [19]. Nearby absorption lines of other gases are generally several orders of magnitude weaker. Water vapor, a much more abundant gas in the atmosphere, may cause interference when ambient air is being analyzed for ammonia. The sampling method used in this study, however, virtually eliminates the possibility of water vapor causing errors. Evidence for this assertion will be presented in another section.

Since the spectrum is crowded with absorption lines, a means must be found to provide radiation across a very narrow spectral interval. Lasers provide virtually monochromatic radiation of great intensity. For this LPS system an isotopic carbon dioxide laser (carbon 13, oxygen 16) was chosen which lases continuously with power on the order of several watts at 927.300406 Kaysers [19]. (This corresponds to the R18 line in the $(00^{0}1-10^{0}0)$ band.) Since the half-width of the absorption feature of interest is 0.08 Kaysers [19], and the incident radiation is within 0.023 Kaysers of the line center, strong absorption is assured.

When dealing with minute amounts of ammonia, direct measurement of absorption (or beam attenuation) is impractical, if not impossible. Fortunately an indirect means of determining absorption exists: the photo-acoustic effect. Once incident radiation has been absorbed by an

ammonia molecule, there is a large probability that collisional deactivation will occur before the molecule has a chance to reradiate the absorbed energy [7]. Collisional deactivation occurs at normal atmospheric pressures and temperatures because of the large number of molecular collisions taking place over a short time in the crowded gas medium. Excited molecules donate their increased vibrational-rotational energy to the colliding molecules, resulting in larger kinetic energies for the latter. When the incoming radiation is "chopped" (made to fluctuate), thermal energy and pressure within the detector cell in turn fluctuate. Sound waves are thus produced which propagate through the medium.

For small concentrations of ammonia , pressure waves resulting from absorption of radiation could easily be obscured by the overall "noise" within the detector cell. Additional steps must be taken to enhance and isolate the sound produced by the action of the ammonia molecules alone. The photo-acoustic cell may be so designed to operate as a Helmholtz resonator at certain sound frequencies. The addition of a lock-in amplifier to the system further enhances the sensitivity by reducing the bandwidth.

A Helmholtz resonator is an acoustic enclosure whose geometry allows the gas within a cavity to "communicate" with a second chamber through a narrow neck. Viscous

dissipation of the sound waves in the secondary chamber is thus minimized because they "feed back" into the main cavity of the resonator, which returns most of the energy to the neck in the form of reflected waves. There is a fundamental resonant frequency for a given resonator, which is a function of the speed of sound, the cross sectional area and length of the neck, and the volume and geometry of the cavities [38]. In the LPS system the light chopper at the proper frequency creates resonance within the detector cell.

The lock-in amplifier is a specialized ac amplifier which synchronously demodulates only certain frequencies of an incoming "noisy" signal at a reference frequency. It filters out electrical impulses not in phase with or at the same frequency as the reference signal. An electrical signal from the mechanical light chopper acts as a reference signal. Since the microphone signals have a frequency component (due to molecular absorption) that is the same as that of the light chopper, the signal-to-noise ratio of the detection is greatly increased.

Theoretical limits to the amount of ammonia which may be detected by LPS are eventually encountered and must be mentioned briefly here. After Kreuzer [23], the signal (S) which is measured by the microphone within the detector may be mathematically expressed as a function of the laser power (P) and the absorbance (A) of the ammonia molecules:

$S=P*[1-\exp(-A)]$. This expression shows that the signal is directly proportional to the laser power. The exponential term results from Beers's Law. The absorbance in turn effects the power transmitted through the sample (T): $T=P*\exp(-A)$. Combining these equations and solving for sample absorbance: $A=\ln(S/T+1)$; and, according to Beer's Law, the absorbance may also be described as a function of the path length l, absorptivity of the gas a, and gas concentration C: $A=laC$. Therefore, the concentration of ammonia is given by $C=(a/l)*\ln(S/T+1)$.

This last equation defines the basic parameters which must be dealt with in designing a LPS system. Moreover, since the detector used in this study operates as a Helmholtz resonator, other factors also influence the sensitivity of the apparatus. These include the geometric configuration of the resonator, connecting neck, and absorption chamber, the frequency of the chopped radiation, the molecular viscosity coefficient of the gas, and the speed of sound within the gas medium [31]. The combination of photo-acoustic cell and Helmholtz resonator increases the system's responsivity to absorption by ammonia molecules, but the "window signal" due to absorption of radiation at interior surfaces of the cell is also amplified. Therefore the magnitude of the "window signal" essentially establishes the minimum detectable limit for this system [31]. Currently around four nanograms of

ammonia can be detected by the LPS system. This is adequate for obtaining hourly averaged ammonia concentrations under almost any conditions.

Apparatus

In its present stage of development the LPS system used for this study does not directly sample ambient air for determination of ammonia concentration. Measurements are made in a two step process: a period of sampling or preconcentration of ammonia is followed by subsequent analysis of the sample for ammonia content. It is therefore convenient to describe the sampling equipment, analytical apparatus, and calibration system separately.

Limitations in the sensitivity of the analytical apparatus necessitate some method of preconcentration of the ambient ammonia before analysis. Hollow quartz collection tubes coated on the inside with tungsten oxide have been used exclusively during the course of this study. The tubes are approximately 40 cm long, 35 cm of which has been coated. The inside diameters measure approximately 0.4 cm. These tubes were developed by Dr. Robert Braman of the University of South Florida during a similar measurement program. A likely mechanism for the action of the tubes in selectively adsorbing ammonia has been described by Braman [5]. The tungsten oxide interacts with water vapor to create tungstic acid (H_2WO_4). This weak

acid in turn reacts with gaseous ammonia, forming NH_4HWO_4. At temperatures above $350^{\circ}C$ the reaction is reversed, liberating the ammonia. The tubes are wrapped with nichrome wire so that electrical power may be applied to heat the tubes at the time of analysis. More observations on the tubes' performance will be presented in a later section.

The remainder of the sampling apparatus consists of a suction pump and associated tubing with three calibrated flowmeters and control valves incorporated into the air stream. Multiple valves and flowmeters allow replicates to be taken. The entire sampling apparatus is portable and requires only standard 110 Vac electrical outlets for operation. Sampling times are monitored by means of a stopwatch.

If the sampling system is simple and compact, the analytical apparatus compensates for this by virtue of its complexity and bulkiness. Figure 2 is a simplified diagram of the basic components of the LPS analytical system. Mechanically chopped (approximately 1000 Hz) radiation from the laser (GTE Sylvania Model 950) is directed by a series of mirrors and a focusing lens through the narrow opening of the photo-acoustic detector. After passing through the detector, the beam is divided by a beam splitter. A portion of the beam is directed into a power meter, as shown in the diagram. The remaining radiation finds its
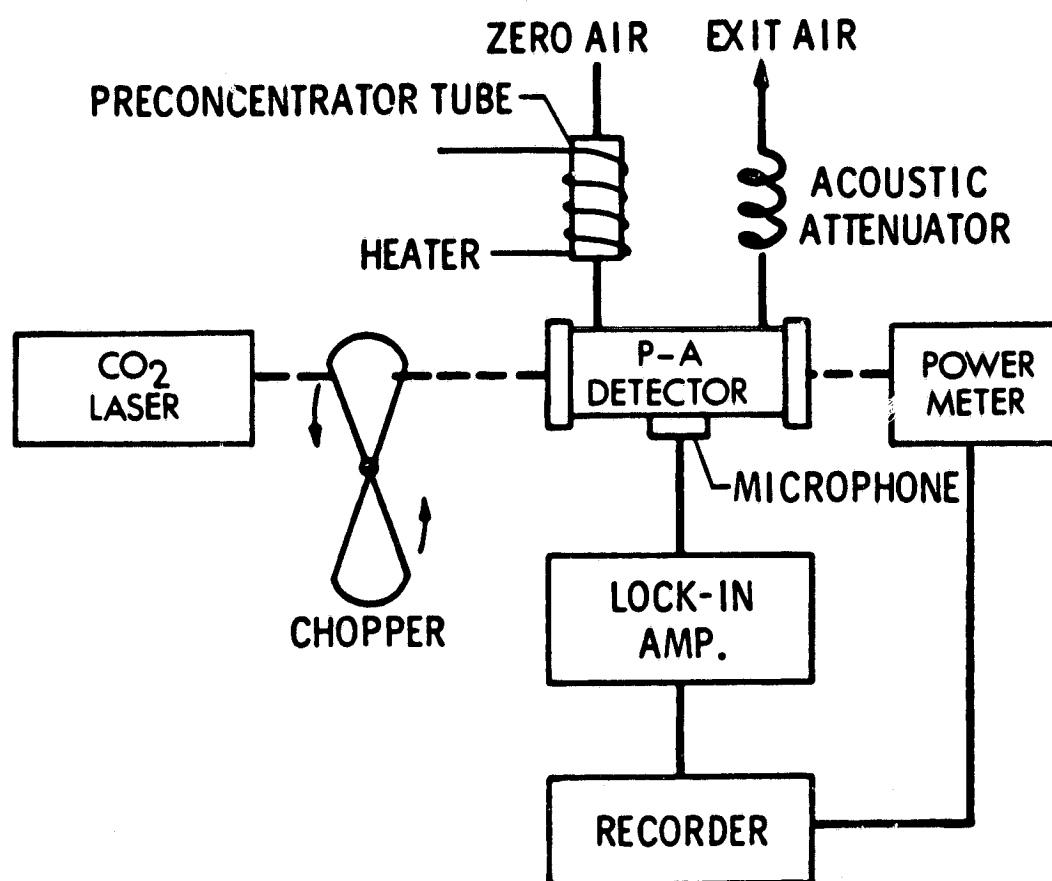
Figure 2. Simplified diagram of the basic components of the LPS analytical system.

way into a spectrum analyzer (Optical Engineering CO2 Spectrum Analyzer), so that the wavelength of laser radiation may be monitored and adjusted, if necessary. Ammonia passes into the detection cell directly from the heated tubes. Helium (technical grade: 99.995% pure) is used as a carrier gas (flowrate: 0.1 l/min) because of its inert and nonabsorbing qualities. The photo-acoustic detector is coated with teflon and is heated (approximately 50°C) to minimize retention of ammonia by its walls. Dimensions of the cell through which the gas stream passes are approximately 25 cm long by 0.6 cm in diameter. The microphone (Bruel and Kjoer Model 4138 with Type 2801 power supply) is mounted on top of the Helmholtz resonator. Its signal is synchronously demodulated by the lock-in amplifier (EG and G Princeton Applied Research Model 510) with the chopper frequency as a reference. Any signal in phase with the chopper is amplified and fed to the recorder. Simultaneously the laser power as measured by the power meter (Molelectron Corp. Pyroelectric Radiometer) is also recorded.

Early in this study it became apparent that fluctuations in laser power produced signal fluctuations from the photo-acoustic detector, creating noise and producing large errors in the measurements. This problem was eventually solved by including a ratiometer (Princeton Applied Research Model 193 Multiplier/divider) in the

processing system. This instrument electronically divides the signal from the detector by the power reading from the power meter. Inclusion of the ratiometer greatly enhanced the performance of the system and allowed accurate measurement and calibration even when the laser power was markedly oscillating. The "transparent" apertures at both ends of the photo-acoustic detector created a slight "window signal" because of absorption of radiation by the aperture material. This constituted no great problem, since the recorder could be offset to compensate for the window signal.

The two channel recorder (Linear Instruments Corp. Integrator/recorder Model 282) is equipped with an electronic integrator with adjustable baseline response and three "count rate" settings. The count rate recorded by the electronic integrator is governed by the signal received from the lock-in amplifier. As ammonia is driven off from the collector tubes, a curve is described on the recorder paper. The area under this curve before it returns to baseline is proportional to the amount of ammonia which passed through the detector. The integrator counts the number of area units contained within the envelope of the curve, eliminating the need for determining the area by graphical means.

The remainder of the system's components consists of calibration equipment. See figure 3 for a diagram of the
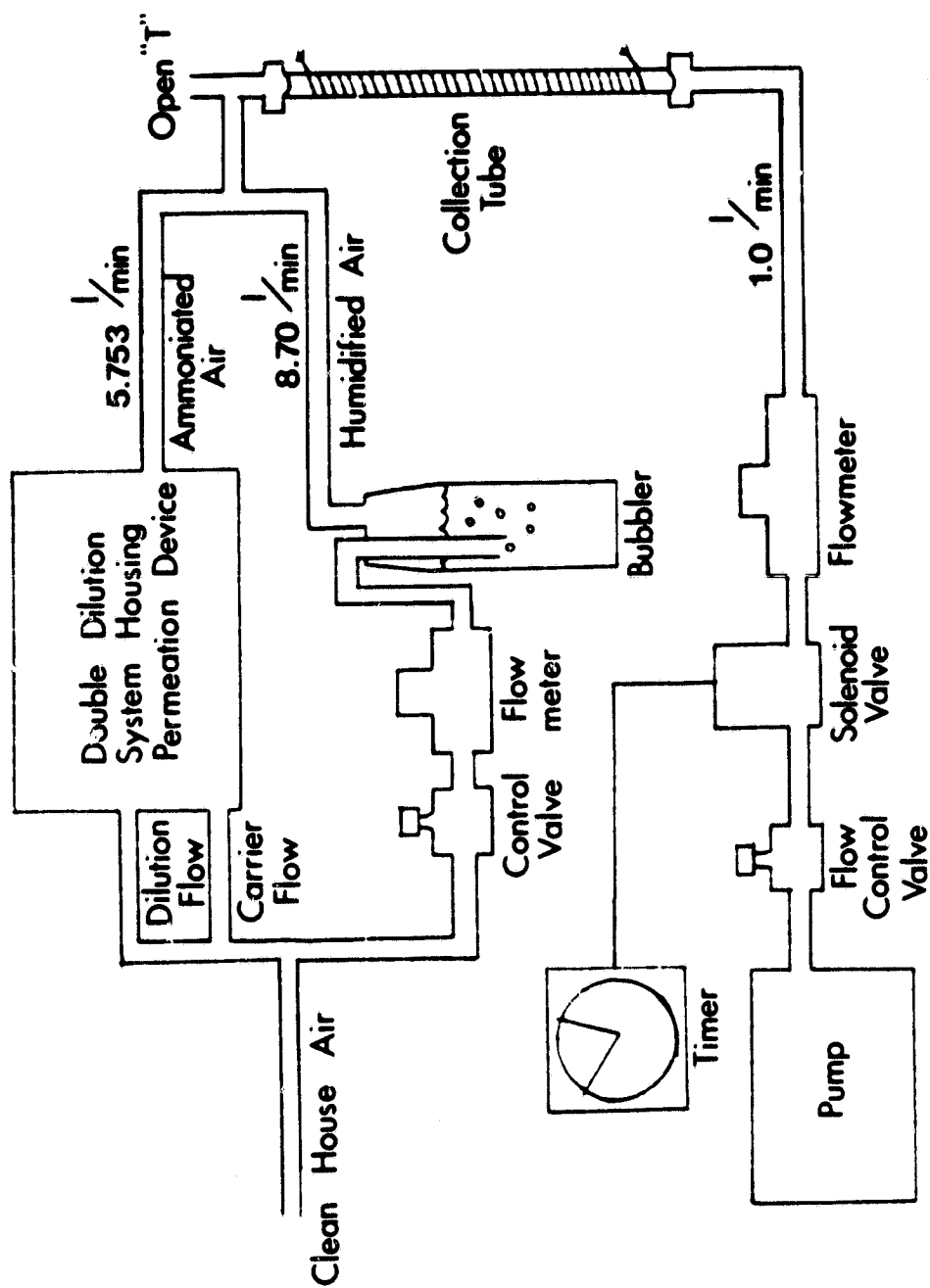
Figure 3. Diagram of the calibration system.

calibration system. Sorbants are used to clean and dry pressurized "house" air, which then passes into a triple dilution system. Ammonia is added to the air by means of a commercial double dilution device (Metronics Model 340 Dynacalibrator) containing an ammonia permeation tube (Metronics wafer type) housed in a temperature-controlled chamber. Triple dilution is achieved by the addition of a flowmeter and control valve to regulate another air stream. Clean house air is humidified while passing through this third circuit by inclusion of a bubbler containing distilled water. Humid air is used (relative humidity: 60%) because this at least partially duplicates the ambient environment, and because the sampling tubes apparently require at least a minute amount of water vapor to maintain their sensitivity. (Water vapor must be available to allow conversion of tungsten oxide to tungstic acid.)

Other calibration equipment includes a timer connected to a shutoff valve to control calibration sampling time, a pump used to pull air through the tubes when performing calibration sampling, a valve and flowmeter to regulate the flow through the tubes, and various connectors and brackets for mounting the tubes. Tubes are mounted in a teflon "tee" connector during calibration sampling. One outlet of the "tee" remains open to the room. This prevents a pressure buildup due to differences between the flowrates of the calibration air stream and the sampling air stream.

Since the calibration air stream is over ten times that demanded by the tubes when samping takes place, no backwash of room air can take place through the open "tee."

Calibration

Calibration of the instrument was accomplished by linear regression analysis of the integrated recorder response to several different "loads" of ammonia in a collection tube. Each collection tube was separately calibrated, although frequently different tubes' regression equations were very similar. Absolute calibration was traced to the permeation of ammonia through teflon [33]. Since the permeation rate is dependent on air temperature, the permeation device was kept at a constant temperature of 30°C throughout this study, except for brief periods when the device was being weighed. Periodic weighings allowed the permeation rate to be determined gravimetrically. Figure 4 shows the data, best linear fit, and regression equation for a permeation device used during most of this study. The nearly linear weight loss (linear correlation coefficient: -0.9999051) corresponds to an average elution rate of 58.664452 nanograms per minute (ng/min). For the great majority of calibration runs flow rates through the permeation chamber, the secondary dilution, and the tertiary (humidified) dilution were fixed at 0.333, 5.420, and 8.70 l/min, respectively. This resulted in an ammonia
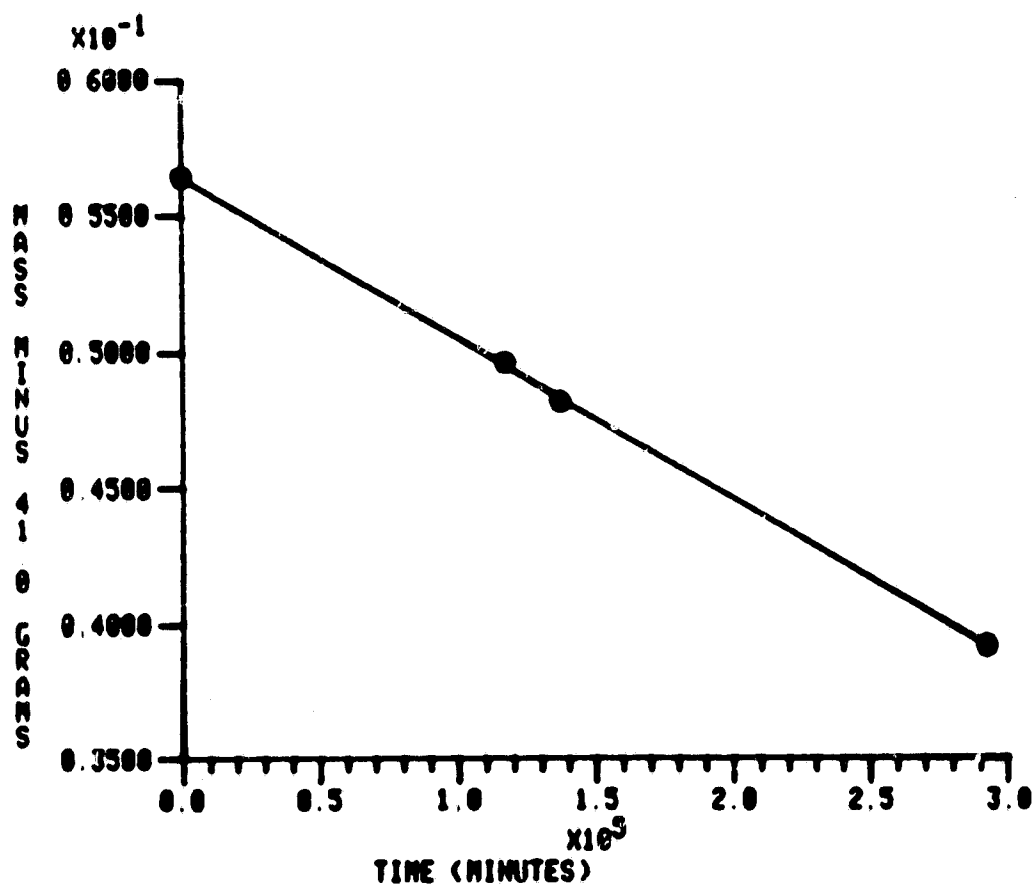
Figure 4. Weight loss of ammonia permeation device used in calibrations. The line's slope corresponds to a permeation rate of 56.664452 ng/min.

concentration of 4.05 ng/l in the calibration air stream. A propagation of errors analysis has been performed which estimates the magnitude of errors in the gas flow measurements. The analysis indicates that the concentration may have varied by $\pm3.5\%$ from the 4.05 ng/l mean value. For simplicity in calculations the concentration was assumed to be 4.0 ng/l. Ammonia loading was varied by pulling 1 l/min of the calibration mixture through the tubes for various periods of time. For example, a 24 ng load of ammonia was achieved by sampling for six minutes. Since the tubes tended to exhibit some changes in response over varying lengths of time, frequent recalibrations were performed on the tubes to maintain accuracy. Frequently checks were also made after measurement runs to ensure that sudden response changes had not occured. Whenever it was felt that a new calibration was required for a given tube, at least five and often more runs at various loads were made in order to derive a new regression equation. Linearity of the regression equations was generally excellent: linear correlation coefficients averaged over 0.98 for some 60 calibrations. Tubes that exhibited poor reproducibility were not used for measurements until reproducibility was restored. Linear correlation coefficients less than 0.9 (95% confidence level for 5 data pairs) were considered unacceptable.

In order to arrive at an estimate of the errors in deriving regression equations, a "worst case" experiment has been performed for an individual tube. Several individual calibrations were lumped together into an overall regression analysis covering several months of sampling. Figure 5 illustrates the results of this experiment. An envelope representing the slope and intercept errors (two standard deviations from the mean) has been drawn around the regression line. Inspection reveals the uncertainty in the slope and intercept values to be tolerably small (less than 2.5% uncertainty in the slope). However, for small loads the relative errors in calibration might be proportionally larger than for large loads. Another experiment confirmed this suspicion. A calibrated tube that had been used for measurement was later subjected to a follow-up analysis of its reproducibility for small loadings of ammonia. It was found that the mean of the area units corresponded to a 7.7 ng average loading, according to the previous calibration. This systematic error implies a slight loss of sensitivity, although the standard deviation about this mean value--0.6 ng--was large enough to indicate that the error may not have been significant. In similar studies using this equipment the calibration precision was given as the ratio of the standard deviation to the mean. Using that criterion the results of the foregoing experiment would imply an uncertainty in calibration precision approaching
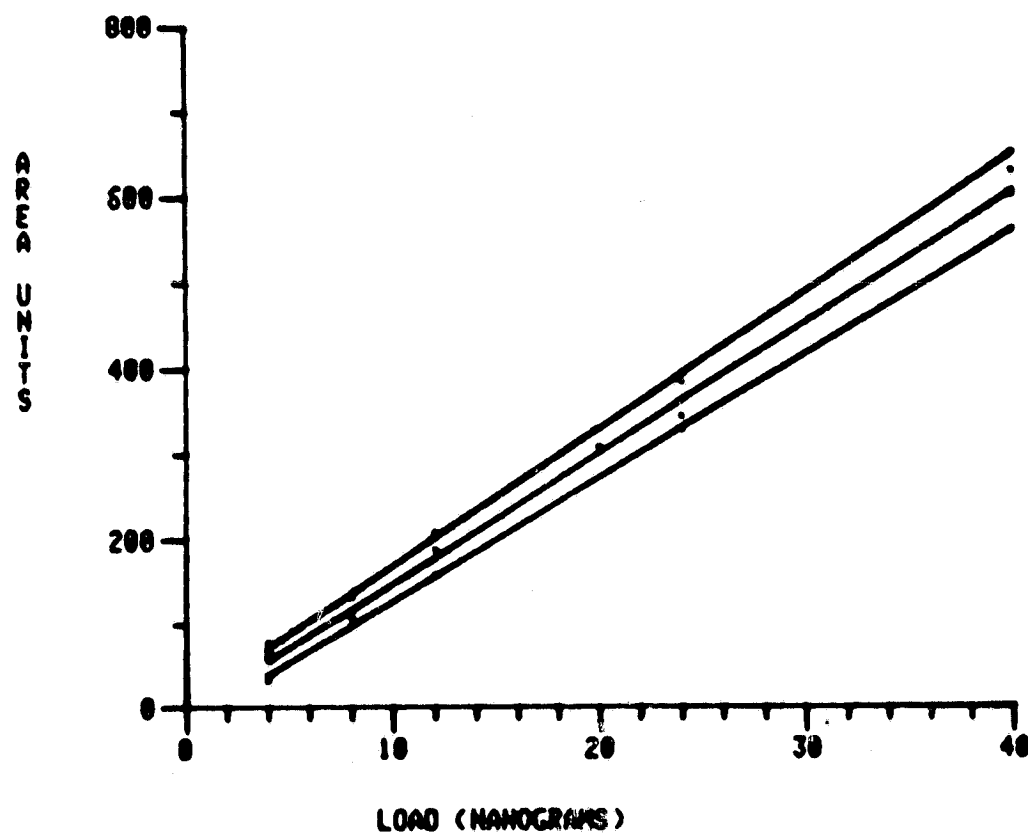
Figure 5. Worst case test for errors in calibrations.
The envelope represents slope and intercept
uncertainties (two standard deviations from
mean values).

8% for small loads.

Figure 6 represents a regression line for a typical calibration. Note that the intercept on the ordinate is negative. This is the case for most of the tubes. The negative offset is due to the method of determining the area under response curves. A slight upward shift in the background signal from the detector occurs when the tubes are heated, because the warmer gas causes the acoustic resonance to be increased in frequency inside the detector cell. Therefore baselines at the end of a analytical run are higher than at the start. The shift in baseline response results in the negative offset in area. Figure 7, an example of a typical analysis, illustrates this characteristic.

Sampling Method

While sampling for ammonia is relatively simple using this technique, precautions must be taken to ensure that representative samples of the ambient air are obtained. Contamination by nearby personnel or other sources (such as vehicles) is always a possibility. For this reason the sampling apparatus must be left largely unattended or situated upwind of the observer, and handling of the tubes must be minimized. Replicate samples help reduce the possibility of spurious measurements due to contamination. Unfortunately, for this study a shortage of collection
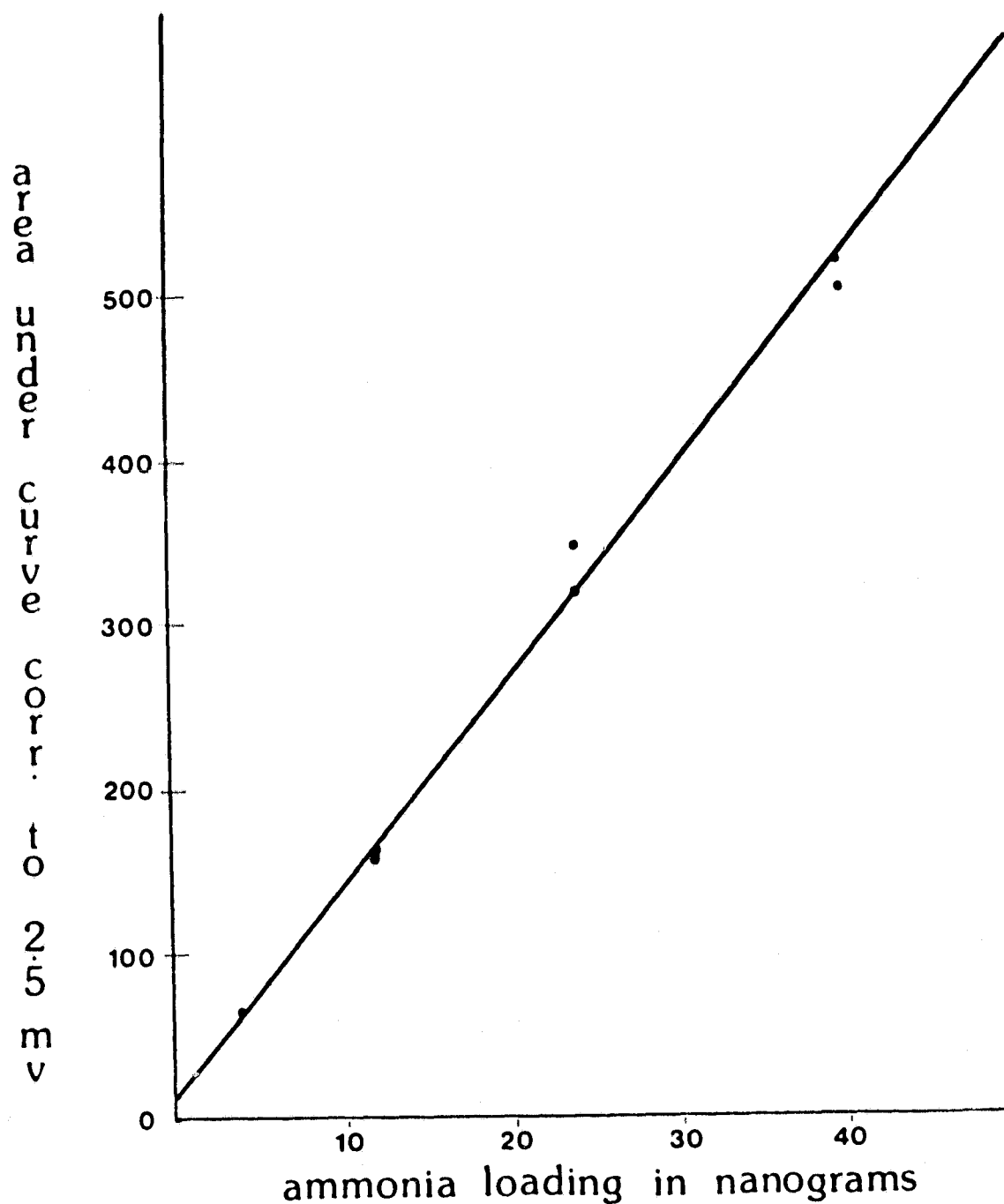
Figure 6. Point plot of a typical calibration of an individual collection tube, accompanied by the best fitting line for the data.

Sample Recorder Response

time (minutes)
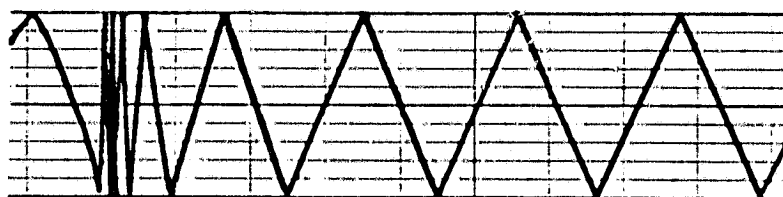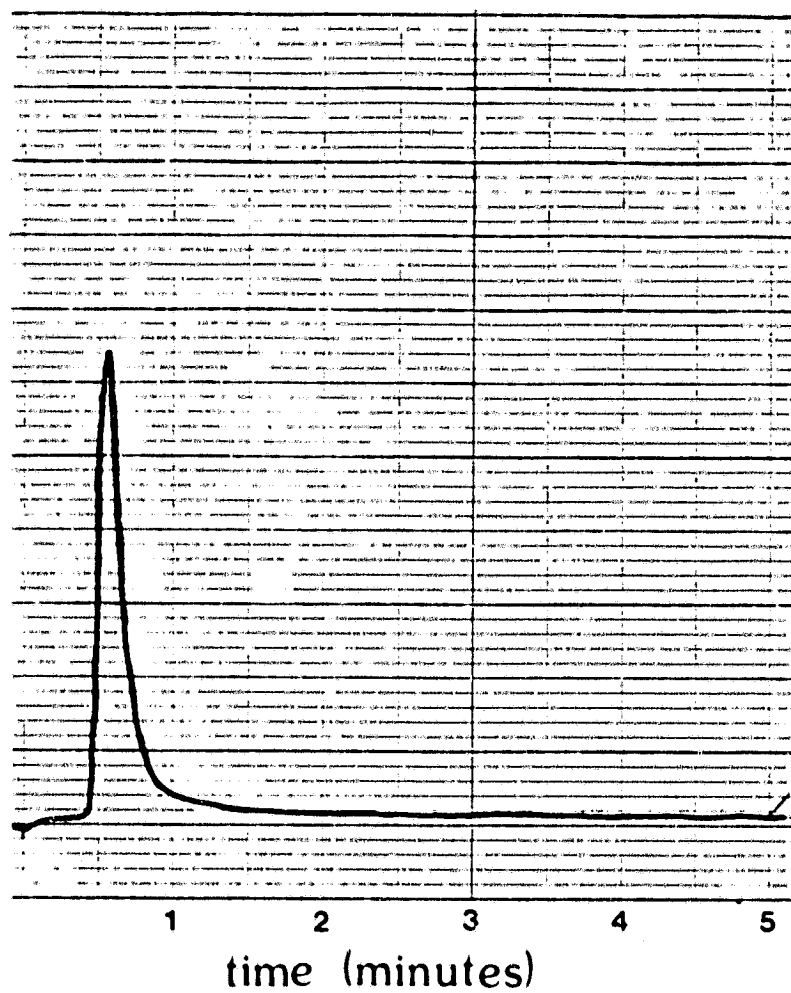
area

Figure 7. An example of a typical analytical run, showing
the response curve and the trace from the
integrator.

tubes frequently prevented simultaneous sampling. Therefore extra attention was given to avoiding contamination wherever possible.

To prevent leakage of ambient air into the tubes, they were sealed with parafilm prior to and following each measurement or calibration run. Blank tubes were periodically checked for seepage over extended periods. Generally little response was noted, even after weeks of storage. To eliminate the possibility that samples might deteriorate while awaiting analysis, an experiment was performed to test for loss of response of a loaded tube after being stored overnight. The results were negative, indicating the tubes could be put aside for several days after sampling for later analysis.

Determination of ammonia concentrations was accomplished by dividing the estimated load (derived for the relevant regression equation) by the volume of air pulled through the tube during the course of sampling. Therefore particular care was exercised in ensuring that the flow remained at 1 l/min through the tubes. Whenever it was noted that flow rates at the end of sampling varied by more than 5% from this value, corrections for this variation were included in the calculations. Sampling times varied a great deal, depending on the suspected concentration of ammonia. For extended sampling times of 30 minutes or more periodic checks of the flow rates were

made.

A flow rate of 1 l/min ensured that laminar flow was maintained throughout the the length of the coated portion of the tubes [4] [30]. Laminar flow helped prevent particles containing ammonium from impinging on tube walls and subsequently affecting the analysis. Migration of particles to the tube walls because of gravitational effects was prevented by orienting the tubes vertically within the mounting bracket. While particles, because of their inertia, were pulled directly through the tubes, collection efficiency for ammonia was excellent. Experiments made during this study confirmed that collection efficiency exceeded 99%, even for large loads.

Two sites were used for sampling the ambient air. One of these was from the roof of the building where the analytical apparatus was housed (bldg. 1201 at NASA Langley, North latitude: 37.09 degrees and West longitude: 76.39). Samples were taken in September 1980, January, February, and March 1981 were from this location, situated approximately eight meters above ground level. During the fall sampling took place two meters above the ground from a location one-half mile north of the original site. The move was made for two reasons: to avoid interfering with the work of other personnel using the roof, and to negate any effects which pollutants from a nearby steam plant might have had on the measurements. Transportation

problems necessitated the return move to the original site
after the end of 1980.

VI.   RESULTS AND CONCLUSIONS

Data Reduction and Analysis

Table I in Appendix A presents the results of over 230 measurements taken from September 1980 until mid-March 1981. Times for initiation of sampling and estimated wind directions are included alongside the data. The raw data have been graded according to the relative accuracy of the given concentrations. On many days when samples were gathered, especially in late fall and early winter, ambient ammonia levels were too low to be detected by the system. Sampling time was extended in order to draw more air through the tubes and thus increase sensitivity. Yet even when sampling for one or two hours, frequently no ammonia was detected in the tubes. At other times the extended sampling resulted in unexpectedly large loads and caused off scale responses on the recorder. The former cases have been assigned a grade of "C." The values given represent one half of the minimum concentration which could be detected by the equipment under the circumstances. This is admittedly a crude estimate of the actual amount of ammonia present at the time, but it was felt that this information would be better than none at all. Those cases which are graded "B" correspond to off scale readings. The actual

loads were subsequently estimated by giving the tubes large calibration loads and qualitatively comparing the off scale responses on the recorder to those from the measurement runs. The estimates are better than those graded "C," generally representing less than 30% uncertainty in the accuracy of the measurements. Those measurements graded "A" lay within the dynamic range of the analytical equipment. The uncertainty intervals for these measurements are the sum of the uncertainties in calibrations (approximately 8% for small loads) and sampling flow rates (less than 5%). Therefore these values should differ at most from actual concentrations by 13%. However, a series of replicates taken in February and March of 1981 tend to refute this figure, since they differ form one another by an average of nearly 25%, suggesting that contamination of samples was a bigger problem than had been suspected.

Table II in Appendix A gives the average daily concentrations when samples were taken. These have also been assigned grades: "A" for days when all measurements lay within detection limits, "B" for days when one or more off scale responses were noted, and "C" for days when concentrations were at least once below the detection limits. Accompanying the measurement data are the average daily temperatures, wind directions, and dewpoint temperatures, as well as the number of samples gathered

each day.

Meteorological data appearing in these tables were obtained from two sources. Prior to January 1981 the NASA Langley Energy and Environmental Monitoring System provided the information. Instrument failure prevented any data from being obtained from NASA sources after December. Nearby Langley Air Force Base furnished meteorological data during the remainder of the study. In addition, on-site meteorological observations were made at sampling times. Close inspection reveals that the furnished data differ little from wind and temperature estimates made at the measurement sites.

Relationships with Various Meteorological Parameters

From the data an obvious conclusion can be drawn: ammonia concentrations locally reach a minimum value in early winter. Figure 8 graphically depicts average daily concentrations during the six and one-half months of this study. Superimposed on this point plot are lines connecting the monthly means of ammonia concentrations. The January minimum is followed by a distinct upward trend in February, when some of the highest recorded concentrations for the entire period occurred. A possible explanation for the early winter minimum follows from an examination of the relationship between air temperature and ammonia concentrations. In table III in Appendix A daily
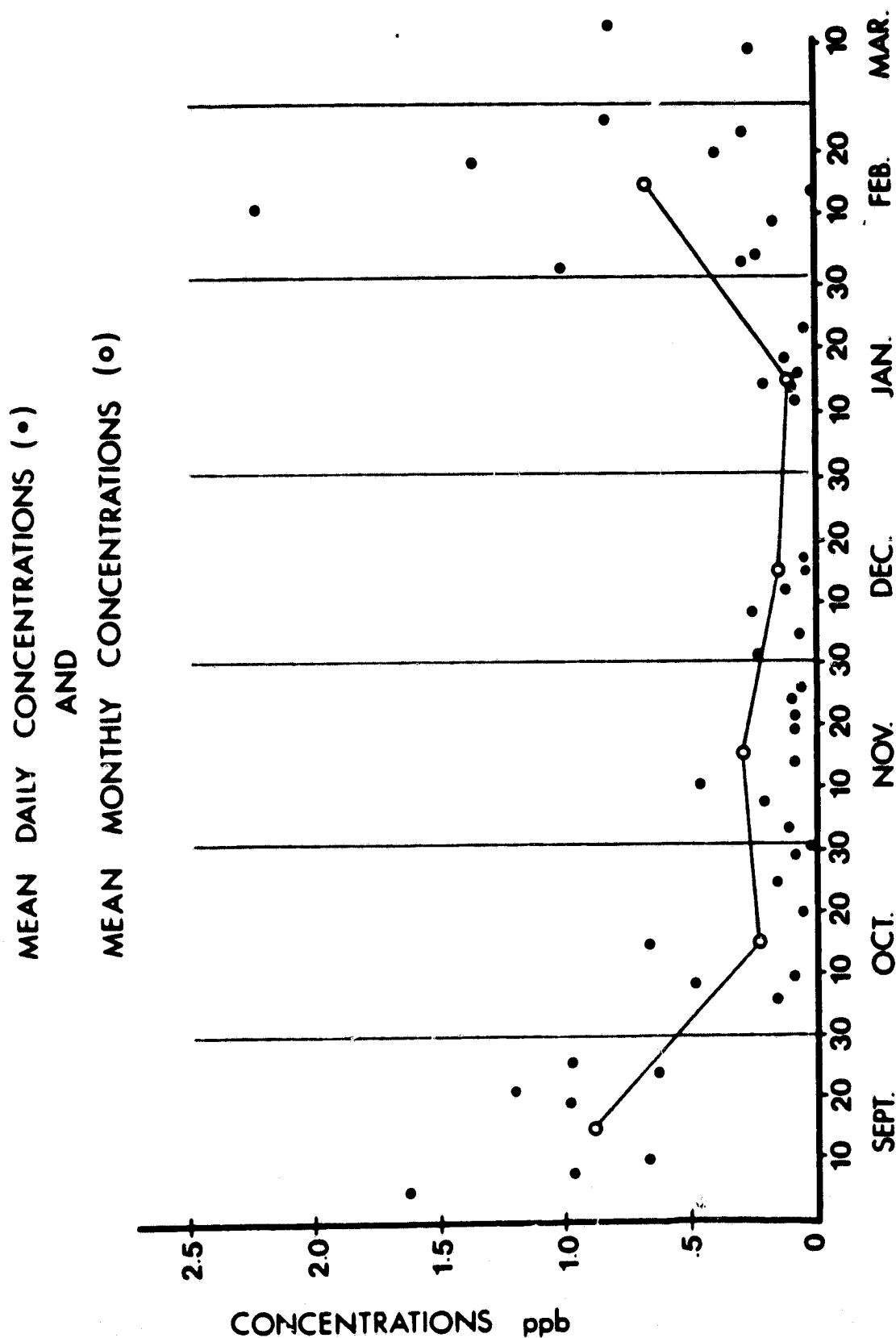
Figure 8. Mean daily and monthly ammonia concentrations.

average concentrations have been categorized according to five temperature intervals and the mean value within each category has been presented. An upward trend in ammonia concentrations is discernable as temperatures increase. The higher mean concentration for the 50 to 59° F interval compared to the mean for the $60-69^\circ$ F interval may be due to some seasonal bias in the data. Many of the days where temperatures averaged in the fifties were in February, a month of anomalously high ammonia concentrations. From the table there is some indication that temperatures below 50°F are not conducive to ammonia production.

While table III is suggestive of some relationship between ammonia concentrations and air temperatures, more meaningful results can be obtained by means of a graphical presentation of the data. In figure 9 daily mean concentrations have been plotted against mean daily temperatures. A linear regression analysis has also been performed for this data and the resulting best fitting line plotted on the same graph. While ammonia concentrations may not be a linear function of air temperature, the results of the analysis point to some relationship. In fact a linear correlation coefficient of 0.5346 for these data indicates that there is a 99.9% probability that the dependent and independent variables are correlated [3]. In light of these findings a partial explanation for the upward trend in February concentrations may be inferred if

Figure 9. Mean daily concentrations plotted against mean daily temperatures, accompanied by the best fitting line for the data.

the meteorological record for that month is examined closely. February 1981 was notable for several abnormally warm periods following unusually cold weather in January and late December. The mean temperature for February was 43.1°F (6.2°C), compared to 32.6°F (0.3°C) in January and 41.6°F (5.3°C) in December.

Scientists are acutely aware of the danger of inferring a cause-and-effect relationship between two parameters simply because they appear correlated. If ammonia levels were a function of air temperature alone, then measured ammonia amounts would have been significantly higher in October and November 1980 (mean temperatures: 61.5°F and 49.1°F, respectively) than in February. Other factors must be considered as well as air temperature.

Hoell et al. [20] noted a similar increase in local ammonia concentrations in March of 1979, when levels as high as 10 ppb were measured. It was tentatively concluded that volatilization of gaseous ammonia from nearby fields where fertilizers had been recently applied largely contributed to the March maximum in that year. An attempt was made for this study to further investigate the prevailing agricultural practices of surrounding areas regarding fertilizer application. Several calls were placed to agricultural agents in nearby Virginia localities. Mr. Jim Belote [2], an agricultural extension agent for Virginia Beach, stated that most fertilizers were

applied in April through May. However, a top dressing of fertilizer (approximately 80 lbs. per acre) was applied to winter wheat beginning in late February. He estimated that 13,000 acres are given to winter wheat production in Virginia Beach. Mr. Ben S. Lee [26] in Southhampton County stated that some farmers applied fertilizer in fall, while most waited until March. But he also indicated that large amounts of fertilizer were applied to winter wheat crops in February. Mr. Lee estimated that the total acreage in winter wheat was nearly 10,000 acres in Southhampton County. While other extension agents could not be reached, office personnel in several county agricultural extension offices agreed that significant amounts of fertilizer are generally applied to winter wheat crops, weather permitting, beginning in February.

Since most of the fertilization of winter wheat in surrounding areas appears to have taken place after high ammonia concentrations first appeared in early February, positive conclusions cannot be drawn about about any link between the two events. It may be useful to examine other factors besides temperature or agricultural practices that could have affected local ammonia production in February 1981.

Dawson [8] cited soil moisture as well as soil temperature as an important parameter regulating the release of ammonia from the soil by microbiological

activity. He indicated that saturated soils release little ammonia, while completely dry soils cannot support the microorganisms which convert organic substances into gaseous ammonia. Intermediate levels of soil moisture are required for optimal volatilization of ammonia from the soil. The best method for determination of the water content of a particular soil is to continuously monitor moisture levels. Unfortunately such data was not available for this research. Instead a water budget model which estimates soil moisture based on evapotranspiration rates has been used to determine whether soil moisture levels may have varied significantly during the course of this study. The model requires information on soil field capacity (a measure of how much water the soil can hold), monthly mean temperatures, and monthly rainfall amounts in order to arrive at estimates of soil water content. When soil field capacity is reached (80% of saturation, according to Dawson) any excess rainfall is categorized as runoff. Field capacity for this case was estimated by referring to soil surveys for nearby counties [43]. Research has shown that the model successfully predicts actual water runoff [24]. However, no attempt was made to verify the model's estimates of soil moisture. Results of the model should therefore not be interpreted too narrowly.

For the fall to late winter period covering this study, the model showed that water levels rose from near

zero in late September to 25% of field capacity by November first. In contrast moisture was nearly 30% of field capacity by the end of February. Dawson estimated that ammonia volatilization peaks at moisture content corresponding to 20% of field capacity. Model results tend to refute the hypothesis that the February ammonia levels were due in part to soil moisture.

The water budget model may not be very useful for interpreting February's relatively high ammonia concentrations. But it can be applied with more conclusive results when comparing the data presented here for September 1980 with similar measurements for September 1979 published by Hoell et al. [20]. Ammonia levels in September 1979 averaged around 2 ppb, over twice as high as those found in September 1980 at the same location. The model shows that extensive rainfall throughout the summer of 1979 resulted in soil moisture remaining at nearly 57% of field capacity for September of that year. By contrast severe drought in 1980 completely depleted the soil of available moisture by July. Dry conditions continued until moderating temperatures and more plentiful rainfall brought soil moisture levels back up in the fall. The drought must have had a significant effect on microbiological activity in local soils. (See Appendix B for model output.)

Results presented here confirm the importance of air temperature and rainfall (and therefore soil temperature

and moisture) in regulating ammonia production and ambient ammonia concentations. While rainfall tends to increase ammonia production from previously dry soils, it also may scavenge large amounts of ammonia from the air. Georgii and Muller [11] witnessed this effect, as did Harward et al. [14]. Results from this study, however, proved inconclusive. On several occasions ammonia concentrations indeed dropped following rain; on others concentrations apparently increased. Insufficient data also inhibit the formation of any conclusions. Lack of a suitable shelter prevented any sampling during rainfall. Furthermore, since most rainstorms during the study were not showers, but prolonged rainfalls, follow-up sampling during normal work hours was frequently prevented.

Other meteorological parameters besides temperature or rainfall may have an impact on ambient ammonia concentrations. In a theoretical study Lau and Charlson [25] concluded that high humidities may reduce the amount of gaseous ammonia in the air by promoting its conversion to dissolved ammonium sulfate in haze or cloud droplets. Data on dewpoint temperatures were made available for this study. Therefore the average water vapor mixing ratios and relative humidities could be calculated, and both were correlated with mean ammonia concentrations as was done for air temperature. The results appear in graphical form in figures 10 and 11.
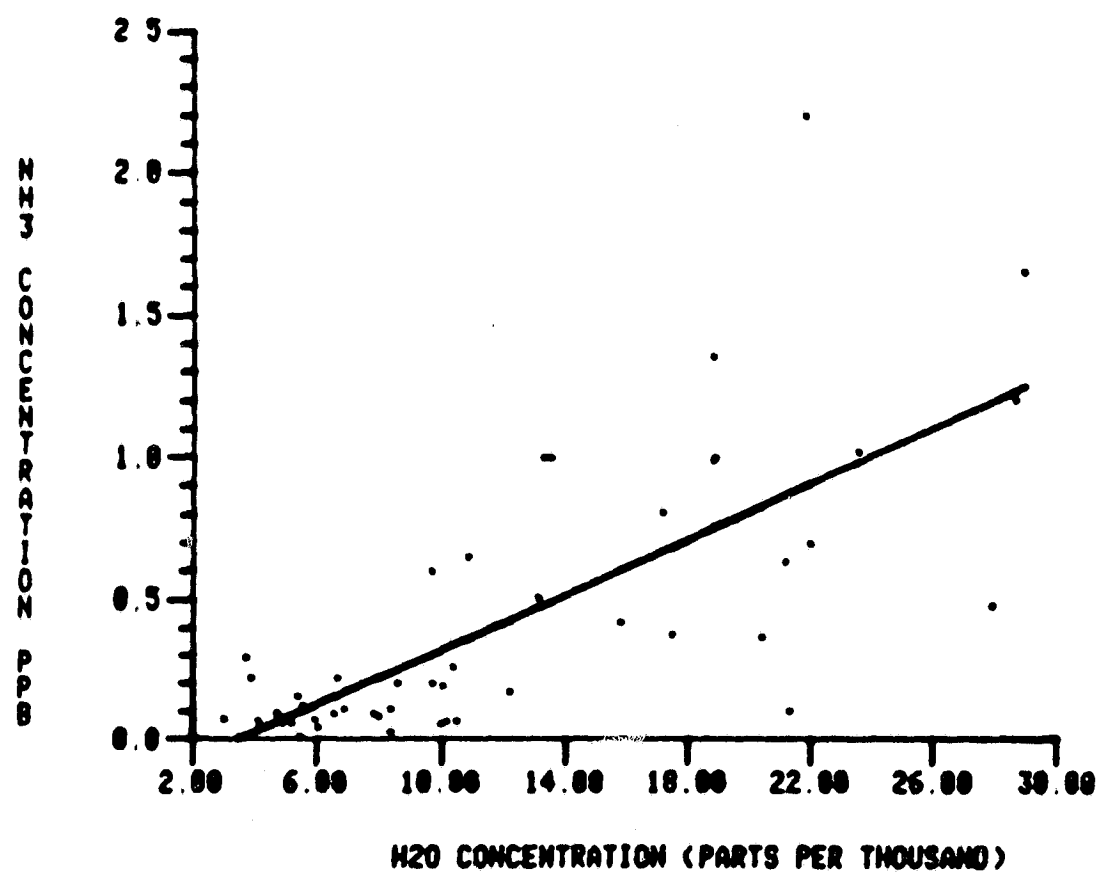
Figure 10. Mean daily concentrations plotted against mean
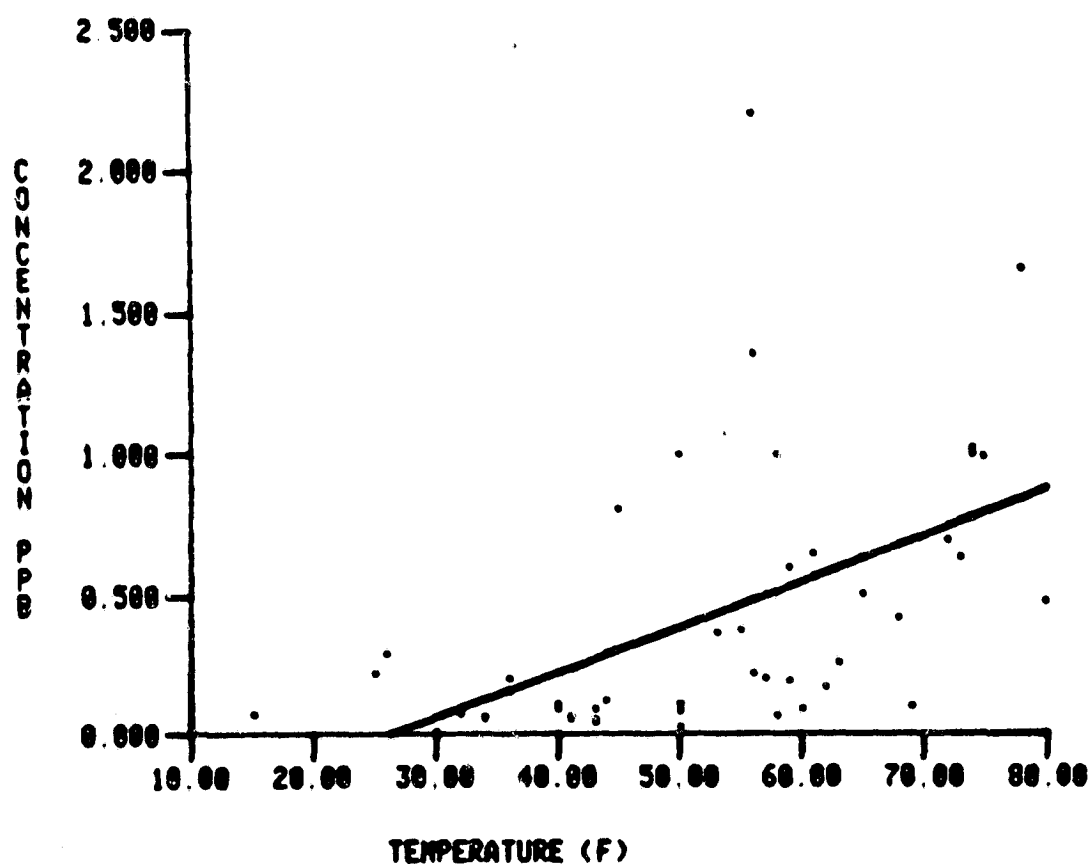daily water vapor mixing ratios, accompanied
by the best fitting line for the data.
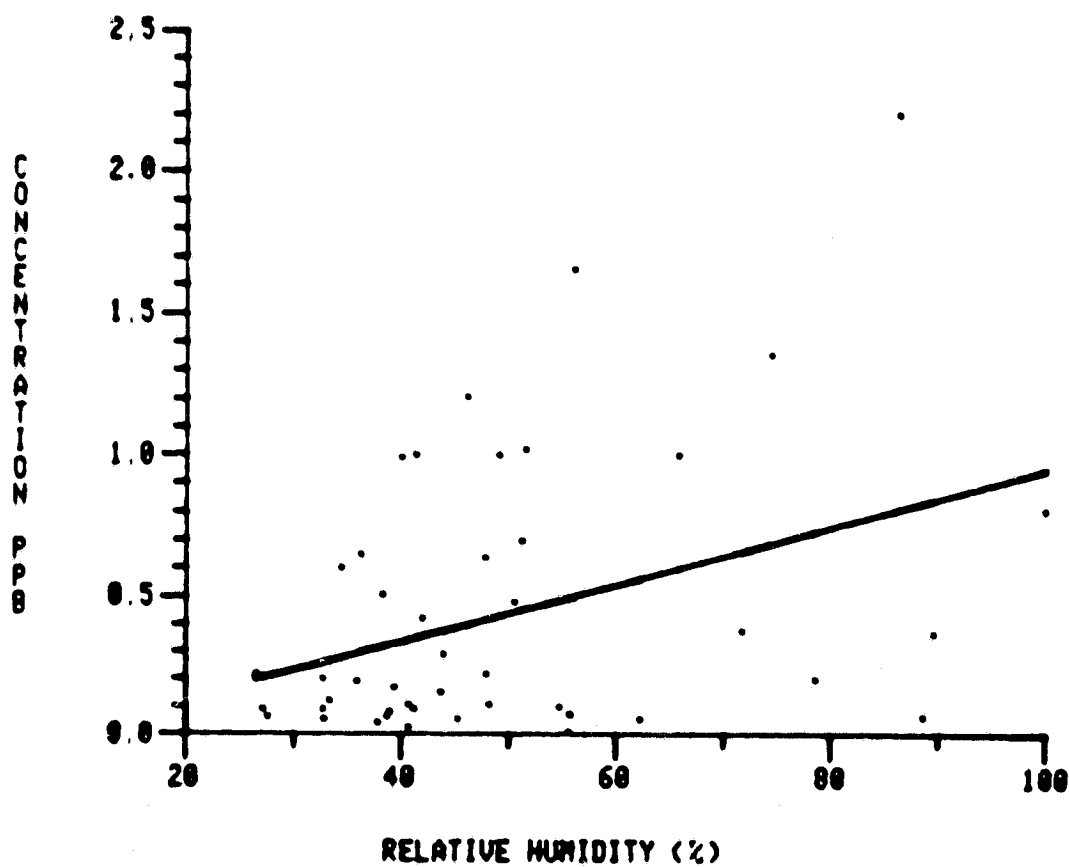
Figure 11. Mean daily concentrations plotted against mean daily relative humidities, accompanied by the best fitting line for the data.

Contrary to the assertion of Lau and Charlson, ammonia levels seemed to actually increase with higher relative humidities. The correlation coeficient for the regression line in figure 11 is approximately 0.367, which for N=47 implies a high probability (greater than 95%) that relative humidity and ammonia concentration were directly correlated. Even more interesting is the high correlation between the water vapor mixing ratio of the air and ambient ammonia levels. The linear correlation coefficient here (0.722) was much higher than those for either relative humidity versus concentration or temperature versus concentration. This relationship was not due to measurement errors caused by collection of water on the sampling tubes. Experiments were performed on the tubes' sensitivity to various humidities, both during this study and others [14], and results were negative.

Although explanations for the strong relationship between water vapor mixing ratio and ammonia concentration must remain in the realm of speculation, an hypothesis can be advanced here. Ammonia levels seem to be related to air temperature and relative humidity separately. When correlating water vapor mixing ratio and ammonia concentrations, we are essentially adding these two effects. In other words, if ambient ammonia tends to increase as either the relative humidity or air temperature increases, then it should certainly be high under warm,

humid conditions. This still does not explain the relationship between relative humidity and ambient ammonia levels. One clue may come from the frequently observed high variations in ammonia content from one sample to the next. Ammonia often seems to arrive in "puffs" or events, rather than remaining at similar concentrations. On humid days when clouds are present, evaporation at cloud bases creates "dry" aerosols from dissolved species (consisting of at least some ammonium nitrate) in the cloud droplets. Research has shown that the equilibrium chemistry of ammonium nitrate is highly temperature dependent. Warming of the ambient air (for example, by adiabatic descent) results in formation of gaseous ammonia and nitric acid from the dissociation of the solid ammonium nitrate [4]. Thus "clouds" of gaseous ammonia and nitric acid may frequently descend to the surface from the condensation level. This effect would be most prevalent on warm days when vigorous mixing takes place. Indeed, some of the highest concentrations were noted on partly cloudy days.

No quantitative data can be presented here to further examine the high variations in ammonia content within an individual air mass. Such a study would require an extensive monitoring network. But from a single station different air masses can at least be crudely categorized according to ammonia levels. This is usually accomplished by means of concentration wind roses. The sampling

locations for this research offer an opportunity to
investigate the contention that most atmospheric ammonia is
of continental origin.   If the continents constitute the
major source for atmospheric ammonia, air masses having
long trajectories over open water would therefore contain
less ammonia than those which generally passed over land
before reaching coastal Southeastern Virginia.   Table IV
(in Appendix A) presents the mean ammonia concentrations
for individual measurements classified according to
prevailing wind directions at the time of sampling.   Figure
12 illustrates these results by means of a concentration
wind rose superimposed on a map of the area.   Ammonia
concentrations were significantly higher when winds were
from the south or southwest than when winds were from the
east, northeast, or north.   However, air masses arriving
from the west or northwest did not contain significantly
more gaseous ammonia than those coming off open water.
Furthermore, highest concentrations were found when
southeasterly winds prevailed.   This anomalous maximum was
probably due to anthropogenic sources.   In particular, an
industrial source for gaseous ammonia--a fertilizer
plant--is situated roughly 10 km southeast of NASA Langley.
Air arriving from the other seven wind directions was
comparatively pristine.   Of course surronding areas are by
no means undeveloped, and the least development has
occurred to the north and west of Langley.   This may
partially explain the comparatively low ammonia content
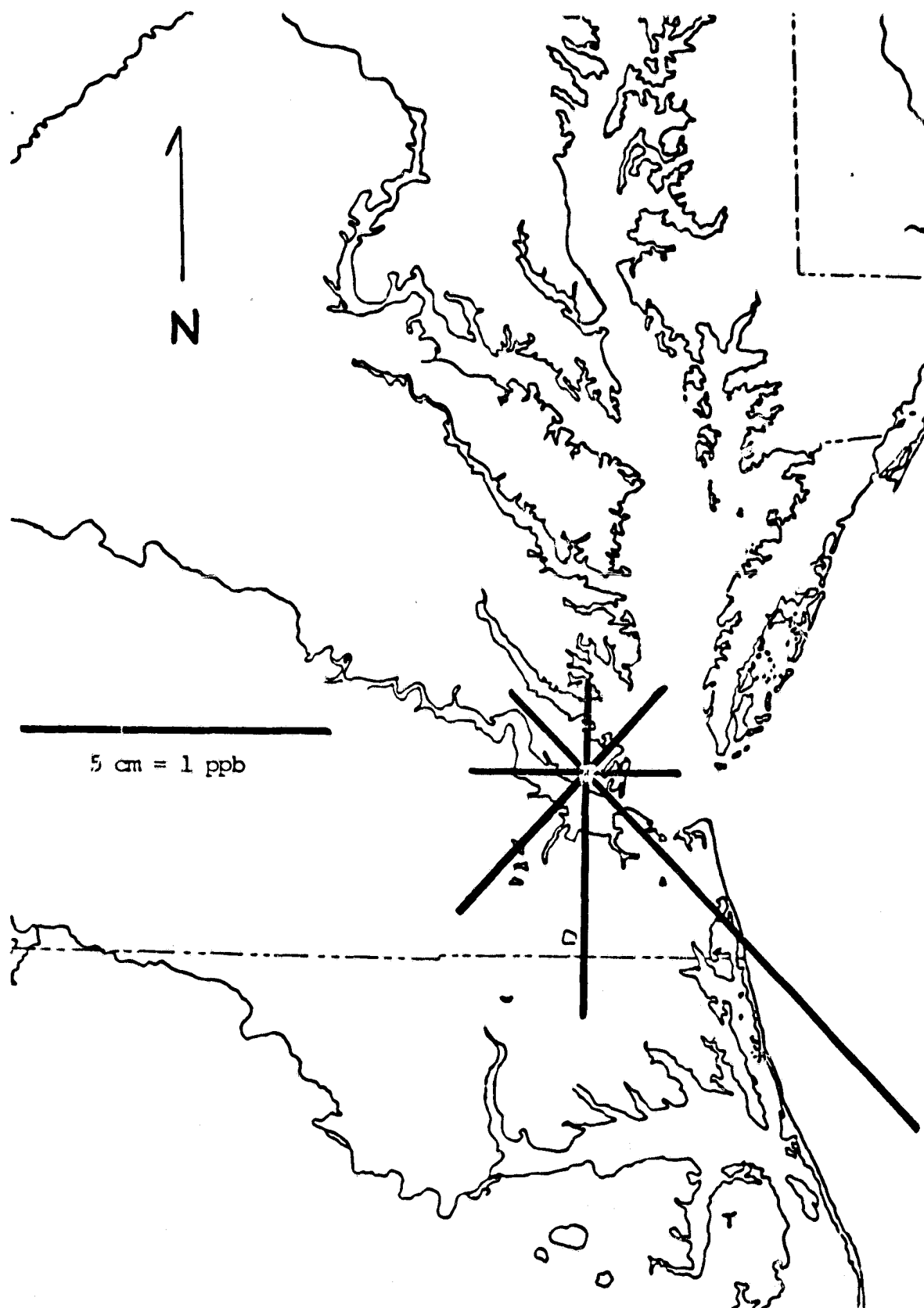
Figure 12. Concentration   wind rose for individual
                  measurements.

found in the air arriving from the west, northwest, or north. The humidity factors mentioned above may also have influenced the results. Cool temperatures and low humidities generally prevailed under north or northwesterly winds, while winds from the south or southwest were usually accompanied by warmer and moister conditions. A further biasing of the data may be inferred when examining those days when easterly or northeasterly winds prevailed. Most of these cases occurred in the early fall, when ammonia levels were generally higher overall. By contrast the winter sampling was characterized by an overabundance of northerly and northwesterly winds.

Because of these reservations about the available data base, any conclusions about the sources for most of the "natural" ammonia in the air of Southeastern Virginia must remain tentative. Yet continental air masses arriving from the south and southwest did contain significantly more gaseous ammonia than maritime air masses. Man's participation in the production of atmospheric ammonia, at least around this locality, was also quite apparent from the data.

Implications of Results

One of the major problems encountered during this research involved selecting appropriate sampling intervals and adjusting the sensitivity of the analytical apparatus

so that ammonia could be measured accurately. Large, short-term variations in ammonia concentrations were frequently encountered that exceeded the dynamic range of the equipment. This demonstrates that gaseous ammonia simply cannot be thought of or treated as a uniformly distributed background constituent. This is especially true near the ground, the source of virtually all gaseous ammonia. When numerical modelers talk of steady-state conditions in the atmosphere, they almost always are oversimplifying actual conditions. Of course they are acutely aware of this, and would respond that there is usually no better way to analyze atmospheric behavior, whether it be of a dynamical or chemical nature. Ammonia's heterogenous chemical interactions with other atmospheric constituents present an almost intractable problem even when steady-state conditions are assumed. Once these problems are solved, scientists can move on to more realistic assumptions. At that time they will require accurate information about the real-time variations in concentrations of a host of trace species in the air. For measurement of ammonia, at least, such capabilities simply do not exist. Integral results such as those from this technique may be adequate for now, but a reliable fast-response monitoring system with a large dynamic range in sensitivity must be developed.

Besides finding that concentrations of ammonia vary a great deal, this study has shown that ammonia levels in southeastern Virginia are much lower than those reported from other measurement programs in both Europe and other places on this continent. Some of the higher measurements given for other areas may reflect inaccurate measurement techniques. For example, some have cited evidence that measurement errors with wet chemical techniques may approach 1 ppb [25]. On the other hand, the measurements generally found in this study do have a physical explanation (which hinges on soil conditions).

Junge [21], when examining rainwater analyses made in this country, noticed that dissolved ammonium in rainwater was much less (sometimes almost absent) across the entire Southeast than elsewhere in the United States. He attributed this to systematically lower gaseous ammonia concentrations in the air, and hypothesized that some factor may prevent the escape of ammonia from soils in the Southeastern U.S.A. He found that a yellow-red lateritic soil type is predominant throughout the Southeast. Soils in the area have an average pH of less than six [21]. Soils of low pH inhibit both microbiological activity and the release of gaseous ammonia into the air. Coastal Virginia also has markedly acidic soils. According to soil surveys [43] pH values of less than 4.5 prevail for most soils in the Dismal Swamp region, while soils in much of

the rest of Tidewater Virginia have pH values varying from 3.6 to 6.0.

Since natural emissions of gaseous ammonia may be inhibited by soil acidity, anthropogenic sources are likely to be more noticeable locally than where background levels of ammonia are higher. Such was the case with this study. A small fertilizer plant situated miles from the sampling locations apparently produced some of the highest concentrations that were encountered. Systematically higher levels of ammonia in late winter may have been caused by man's intervention in natural soil processes. By applying fertilizers to fields farmers directly introduce ammonia into the air by increasing volatilization of ammonia from soils saturated with nitrogen. They may indirectly affect long-term emissions of ammonia by altering the pH of the soil through fertilization. Efficient and economical use of limited resources, as well as concern for possible effects of this vast dumping of nitrogen compounds into the air, should lead agriculturalists to closely examine existing practices with an eye toward reducing ammonia emissions from agricultural areas.

Comments on the Efficacy of This Technique for Routine Monitoring

It was unfortunate that more could not be said in this paper about short-term variations of ammonia content in the atmosphere. It was hoped that links could be established between ammonia concentrations and specific meteorological events, such as frontal passages or rainstorms. Such was not the case, however, and some of the shortcoming in the data must be attributed to the measurement technique itself. Although LPS is far superior to most other techniques of measurement, some of its limitations and drawbacks should be commented on briefly.

It is apparent that low ammonia concentrations (as low as a few tens of parts per trillion by volume at times) make real-time measurements with existing technology extremely difficult. Integral methods employing preconcentration of some kind are the only available alternative. Yet some refinements to the system are quite possible without significantly altering the basic technique. Automated sampling would be an important improvement. As the disappointing results of replicate sampling have shown, contamination by contact with the collection tubes may constitute a major problem. Poor replicate results may also stem from inconsistencies in the collection tubes' performance. Early in this study a gradual loss of sensitivity for some of the tubes was

noticed. This necessitated frequent and time-consuming recalibration of the tubes. Eventually some tubes' lack of sensitivity or reproducibility made rejuventation by oxidation necessary. This wasted further time and did not always work. Eventually serendipity led to the discovery that a simple washing with distilled water completely restored a tube's performance. This was especially fortunate because longer sampling times had made it necessary to rejuvenate the tubes more often.

More distressing than gradual aging of the tubes was their tendency to occasionally become "poisoned" by the action of some unknown agent. Rejuvenation restored them but did not restore confidence in the accuracy of measurements taken with poisoned tubes. This may explain some of the poor reproducibility noted in replicate sampling. The possibility of poisoning also made constant monitoring of each tube's performance an absolute necessity, which wasted still more precious time better spent sampling. The exact cause for sudden loss of sensitivity has not been determined. It is suspected, however, that sulfur compounds may have contributed to this phenomenon. A steam generating plant was located only a few hundred meters from the original sampling site. Sudden poisoning was more frequently encountered when winds carried the plume containing large amounts of sulfur dioxide from this plant toward the sampling station. For

this reason the tubes' usefulness in extremely polluted environments must be questioned.

It is possible to envision the entire LPS system being incorporated into a single monitoring device no larger than conventional monitors for other trace gases. The technology is presently available, but modifications such as a smaller laser and the inclusion of a computer to allow automated analysis would require considerable ingenuity and technical expertise, not to mention large sums of money. The overall performance of the system was encouraging enough to merit its further development. There remains the possibility of incorporating basic design changes into the system to permit real-time measurements of ammonia. Perhaps interferometry could be used to detect minute changes in the index of refraction within the gas cell as ammonia molecules absorb radiation and heat the medium. Eventually an attempt must be made to bypass the currently necessary step of preconcentration. Fast response in real-time monitoring is the goal of any in situ measurement technique.

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APPENDIX A

Tables of Data

TABLE I.

INDIVIDUAL AMMONIA MEASUREMENTS

Date	Time	Concentration (ppb)	Wind Direction	Grade
09-03-80	9:35	0.20	N	C
	9:58	0.20	N	C
	11:55	0.20	N	C
	12:56	0.66	NE	A
	1:20	0.20	NE	C
	1:42	0.20	NE	C
	2:05	1.08	E	A
09-05-80	10:26	1.68	SE	A
	11:48	2.22	SE	A
	12:33	1.26	SE	A
	1:17	1.18	SE	A
	1:58	1.98	SE	A
09-08-80	9:50	1.50	SW	A
	10:22	1.32	NW	A
	10:53	1.16	NW	A
	12:22	0.20	N	C
	12:54	1.10	NE	A
	1:26	1.08	NE	A
	1:57	1.56	NE	A
	2:29	0.20	NE	C
	3:00	0.20	NE	C
09-10-80	8:40	0.80	SW	A
	9:49	0.88	SW	A
	10:29	0.20	SW	C
09-19-80	9:26	1.26	N	A
	10:11	1.12	N	A
	12:23	0.96	N	A
	1:09	0.86	NE	A
	1:56	1.12	NE	A
	2:40	0.80	NE	A
09-22-80	9:30	0.90	SW	A
	9:52	2.44	SW	A
	10:20	0.90	SW	A
	10:42	1.20	SW	A
	11:11	1.20	SW	A
	11:32	1.62	SW	A
	11:54	1.08	SW	A
	1:08	1.02	W	A
	1:49	0.62	W	A
	2:28	1.08	W	A
	3:12	1.30	W	A
09-24-80	9:05	0.72	N	A
	9:51	0.46	N	A
	10:36	0.62	NE	A

TABLE I.

CONTINUED

Date	Time	Concentration (ppb)	Wind Direction	Grade
09-24-80	11:46	0.74	NE	A
	12:34	0.76	NE	A
	1:15	0.48	NE	A
	1:45	0.62	NE	A
	2:31	0.70	NE	A
	3:13	0.66	NE	A
09-26-80	8:40	1.22	SW	A
	9:20	1.08	SW	A
	10:00	0.86	W	A
	10:40	0.80	NW	A
	12:20	1.10	NW	A
	1:00	0.94	NW	A
	1:40	0.90	W	A
	2:20	0.62	NW	A
	3:00	1.40	N	A
09-29-80	9:20	0.16	NE	A
	10:00	0.18	E	A
	10:40	0.40	E	A
	12:30	0.36	NE	A
	2:00	1.02	E	A
	2:50	0.70	E	A
	3:30	0.10	E	A
10-06-80	12:20	0.04	NW	C
	12:45	0.10	NW	C
	1:10	0.36	NW	A
	1:35	0.27	NW	A
10-08-80	10:48	0.45	S	A
	11:10	0.55	S	A
	12:17	0.48	S	A
	12:40	0.56	S	A
10-10-80	8:40	0.19	NE	A
	9:02	0.05	NE	C
	9:25	0.10	NE	C
	9:47	0.10	NE	C
	10:09	0.04	NE	C
10-15-80	9:30	0.04	S	C
	9:52	0.05	S	C
	1:16	0.82	S	A
	1:39	1.03	S	A
	2:01	1.32	S	A
10-20-80	1:28	0.05	NW	C
	1:51	0.10	W	C
	2:19	0.04	W	C
10-22-80	9:50	0.50	W	A

TABLE I.

CONTINUED

Date	Time	Concentration (ppb)	Wind Direction	Grade
10-22-80	10:11	0.10	W	C
	10:36	0.24	W	A
	12:31	0.05	NW	C
	12:52	0.10	W	C
	1:16	0.04	W	C
10-29-80	1:37	0.11	NW	A
	2:39	0.04	NW	A
10-31-80	9:43	0.03	SW	C
	10:44	0.01	SW	C
	1:03	0.01	SW	C
	2:05	0.04	SW	C
11-03-80	9:12	0.20	SW	A
	10:14	0.12	E	A
	12:18	0.06	E	A
	1:20	0.04	E	C
11-07-80	9:13	0.12	SW	A
	10:15	0.20	SW	A
	12:13	0.18	SW	A
	1:15	0.29	SW	A
11-10-80	9:17	0.41	SW	A
	10:19	0.70	SW	A
	12:50	0.70	W	A
11-14-80	9:12	0.04	SW	C
	10:14	0.09	SW	C
	12:00	0.08	SW	A
	1:01	0.13	SW	A
11-19-80	12:48	0.09	NW	C
	1:19	0.09	NW	C
11-21-80	12:25	0.09	N	C
	1:27	0.09	NW	C
11-24-80	12:10	1.00	SE	B
11-26-80	11:08	0.05	N	C
	12:10	0.05	NW	C
	1:12	0.05	N	C
12-01-80	11:56	0.28	SW	A
	12:57	0.33	S	A
	1:59	0.05	SW	C
12-05-80	12:04	0.05	W	C
	1:06	0.07	N	A
	2:07	0.05	N	C
12-08-8?	11:57	0.22	W	A
	12:59	0.33	SW	A
	2:03	0.24	W	A
12-12-80	12:21	0.12	SW	A

TABLE I.

CONTINUED

Date	Time	Concentration (ppb)	Wind Direction	Grade
12-15-80	11:14	0.03	E	A
	12:15	0.05	E	C
	1:16	0.05	E	C
12-17-80	12:21	0.05	NW	C
	1:22	0.05	NW	C
01-12-81	12:18	0.07	SW	A
	12:18	0.07	SW	A
01-14-81	11:01	0.08	W	A
	1:03	0.06	W	C
01-15-81	1:04	0.20	E	A
01-16-81	9:15	0.06	SE	A
01-19-81	10:03	0.12	SW	A
	12:04	0.14	SW	A
	1:05	0.06	S	A
	2:06	0.10	S	A
01-23-81	9:16	0.03	W	A
	11:18	0.07	W	A
02-02-81	3:33	3.40	W	A
	3:49	0.20	W	C
	5:43	0.42	W	A
	6:43	0.48	W	A
	9:04	0.49	W	A
02-03-81	9:44	0.02	W	C
	10:15	0.65	W	B
	1:30	0.44	W	A
	2:30	0.04	W	C
02-04-81	10:02	0.30	SW	B
	11:03	0.03	SW	C
	12:05	0.09	SW	A
	2:08	0.07	W	A
	2:08	0.01	W	A
02-09-81	10:04	0.28	W	A
	12:04	0.13	W	A
	2:00	0.08	W	A
	2:00	0.10	W	A
02-11-81	9:14	1.44	SE	A
	9:55	2.80	SE	A
	10:30	10.09	SE	A
	11:14	1.96	SE	A
	11:14	2.00	SE	A
	12:53	1.04	S	A
	12:53	1.15	S	A
	1:23	0.97	S	A
	1:23	0.93	S	A

TABLE I.

CONTINUED

Date	Time	Concentration (ppb)	Wind Direction	Grade
02-11-81	2:35	0.98	S	A
	2:35	0.99	S	A
02-13-81	10:15	0.01	N	C
	10:15	0.01	N	C
	11:18	0.03	N	A
	11:18	0.01	N	A
	1:21	0.01	N	A
02-18-81	10:02	0.55	SW	A
	11:01	1.39	SW	A
	11:58	0.56	S	A
	11:58	0.67	S	A
	3:11	0.85	SE	A
	3:11	0.85	SE	A
	3:44	2.99	S	A
	3:44	3.13	S	A
02-20-81	9:58	0.23	W	A
	9:58	0.37	W	A
	12:03	0.33	W	A
	12:03	0.21	W	A
	1:04	0.21	SW	A
	1:04	0.26	SW	A
	3:06	0.68	W	A
	3:06	0.70	W	A
02-23-81	11:17	0.28	SE	A
	11:17	0.28	SE	A
	12:17	0.60	SE	A
	12:17	0.50	SE	A
	1:17	0.62	SE	A
	1:17	0.58	SE	A
	2:55	0.11	S	A
	2:55	0.05	S	C
02-25-81	10:52	0.53	SW	A
	10:52	0.56	SW	A
	11:26	0.99	SW	A
	12:00	1.15	SW	A
	12:33	1.87	SW	A
	12:33	2.26	SW	A
	1:05	0.41	W	A
	1:05	0.25	W	A
	1:38	0.01	W	A
	1:38	0.08	W	A
03-09-81	10:06	0.01	N	C
	10:06	0.14	N	A
	12:07	0.04	N	A

C - 2

TABLE I.

CONTINUED

Date	Time	Concentration (ppb)	Wind Direction	Grade
03-09-81	12:07	0.07	N	A
	1:46	0.27	N	A
	1:46	0.19	N	A
03-13-81	3:02	1.95	SW	A
	3:40	0.41	SW	A

TABLE II.

MEAN DAILY CONCENTRATIONS AND METEOROLOGICAL DATA

Date	Ave. Concen. (ppb)	Ave. Temp. (F)	Ave. Wind Dir.	Ave. Dewpoint (F)	No. of Runs	Grade
09-03-80	0.48	80	NE	60	7	C
09-05-80	1.66	78	SE	61	5	A
09-08-80	1.00	74	NE	49	9	C
09-10-80	0.70	72	SW	53	3	C
09-19-80	1.02	74	N	55	6	A
09-22-80	1.21	84	SW	61	11	A
09-24-80	0.64	73	NE	52	9	A
09-26-80	0.99	75	W	49	9	A
09-29-80	0.42	68	E	44	7	C
10-06-80	0.19	59	NW	32	4	C
10-08-80	0.51	65	S	39	4	A
10-10-80	0.10	69	E	52	5	C
10-15-80	0.65	61	S	34	5	C
10-20-80	0.06	58	NW	33	3	C
10-22-80	0.17	62	NW	37	6	C
10-29-80	0.08	50	N	26	2	A
10-31-80	0.02	50	W	27	4	C
11-03-80	0.11	50	E	27	4	C
11-07-80	0.20	57	SW	28	4	A
11-10-80	0.60	59	W	31	3	A
11-14-80	0.09	60	SW	26	4	C
11-19-80	0.09	40	NW	13	2	C
11-21-80	0.09	43	N	21	2	C
11-24-80	1.00	58	SE	39	1	B
11-26-80	0.05	41	N	14	3	C
12-01-80	0.22	56	SW	22	3	C
12-05-80	0.06	41	NW	10	3	C
12-08-80	0.26	63	SW	33	3	A
12-12-80	0.12	44	W	17	1	A
12-15-80	0.04	43	E	19	3	C
12-17-80	0.05	34	N	15	2	C
01-12-81	0.07	15	NW	2	2	A
01-14-81	0.07	32	SW	18	2	C
01-15-81	0.20	36	W	30	1	A
01-16-81	0.06	34	SE	31	1	A
01-19-81	0.11	40	S	22	4	A
01-23-81	0.05	43	W	31	2	A
02-02-81	1.00	50	W	39	5	C
02-03-81	0.29	26	W	7	4	C
02-04-81	0.22	25	W	8	5	C
02-09-81	0.15	36	W	16	4	A
02-11-81	2.21	56	SE	52	11	A
02-13-81	0.01	30	NE	16	5	C

TABLE II.

CONTINUED

Date	Ave. Concen. (ppb)	Ave. Temp. (F)	Ave. Wind Dir.	Ave. Dewpoint (F)	No. of Runs	Grade
02-18-81	1.36	56	S	48	8	A
02-20-81	0.37	53	W	50	8	A
02-23-81	0.38	55	S	46	8	C
02-25-81	0.81	45	SW	45	10	A
03-09-81	0.12	NA	NA	NA	6	A
03-13-81	0.93	NA	NA	NA	2	A

TABLE III.

MEAN DAILY CONCENTRATIONS ACCORDING TO TEMPERATURE INTERVALS

Mean Temperature (^{O}F)	Mean Concentration (ppb)	Number of Days
< 40	0.12	9
40 - 49	0.16	9
50 - 59	0.56	14
60 - 69	0.31	7
70	0.96	8

TABLE IV.

CONCENTRATION WIND ROSE BY INDIVIDUAL OBSERVATIONS

Wind Direction	Mean Concentrations	Number of Observations
N	0.30	26
NE	0.38	25
E	0.31	13
SE	1.61	20
S	0.81	22
SW	0.63	51
W	0.40	46
NW	0.37	20

APPENDIX B

Program THORN and Its Output

Appendix B contains the results of the water budget model used in this study to estimate the water content of the soil. For purposes of comparison the model has been run for a five year period from 1977 to 1981. Data for the months after February of 1981 were of course not available, but dummy data were inserted to allow the model to run through the entire year. Folowing the output is a listing of the FORTRAN code comprising the model.

TDEGF=TEMPERATURE IN DEGREES F
TDEGC=TEMPERATURE IN DEGREES C
PPTIN=MONTHLY PRECIPITATION IN INCHES
PPTCM=MONTHLY PRECIPITATION IN CENTIMETERS
SMALLI=MONTHLY HEAT INDEX
UPETCM=UNADJUSTED POTENTIAL EVAPOTRANSPIRATION IN CM
CORPHI=CORRECTION FACTOR FOR LENGTH OF DAYLIGHT AT STATION
APETCM=ADJUSTED PET (=CORPHI*UPETCM)
RMNDR=PRECIPITATION-ADJUSTED PET
STRCHG=STORAGE CHANGE
STRAGE=WATER IN SOIL (CM)
%CAP=PER CENT OF SOIL FIELD CAPACITY
WTRDEF=WATER DEFICIT (NO MORE WATER IS STORED IN SOIL)
WTRSPL=SURPLUS OF WATER BEYOND FIELD CAPACITY
ACTEVP=ACTUAL EVAPOTRANSPIRATION IN CM

LANGLEY FIELD, VIRGINIA

LATITUDE 37.08 N
LONGITUDE 76.35 W
ELEVATION 10.00FT
WATER HOLDING CAPACITY 22.00CM
YEAR 1977

	JAN	FEB	MAR	APR	MAY	JUNE	JULY	AUG	SEPT	OCT	NOV	DEC
TDEGF	28.60	41.40	55.20	61.40	67.80	74.50	81.10	80.40	76.60	61.50	55.00	43.30
TDEGC	-1.89	5.22	12.89	16.33	19.89	23.61	27.28	26.89	24.78	16.39	12.78	6.28
PPTIN	3.73	3.06	4.77	1.55	4.00	2.27	5.71	3.88	1.44	5.35	4.61	3.41
PPTCM	9.47	7.77	12.12	3.94	10.16	5.77	14.50	9.86	3.66	13.59	11.71	8.66
SMALLI	0.00	0.00	4.19	6.00	8.09	10.49	13.05	12.77	11.28	6.03	4.14	1.41
UPETCM	0.00	0.00	3.86	5.82	8.19	11.02	14.15	13.80	11.98	5.86	3.81	1.11
CORPHI	0.00	0.00	1.02	1.09	1.21	1.21	1.23	1.16	1.03	0.95	0.84	0.82
APETCM	0.00	0.00	3.93	6.32	9.88	13.31	17.36	15.99	12.28	5.59	3.21	0.91
RMNDR	0.00	0.00	8.19	-2.38	0.28	-7.55	-2.86	-6.13	-8.63	8.00	8.50	7.75
STRCHG	0.00	0.00	0.00	-2.38	0.28	-7.55	-2.86	-6.13	-3.36	8.00	8.50	5.50
STRAGE	0.00	22.00	22.00	19.62	19.90	12.35	9.49	3.36	0.00	8.00	16.50	22.00
%CAP	0.	100.	100.	89.	90.	56.	43.	15.	0.	36.	75.	100.
WTRDEF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-5.27	0.00	0.00	0.00
WTRSPL	0.00	0.00	8.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.25
ACTEVP	0.00	0.00	3.93	6.32	9.88	13.31	17.36	15.99	7.01	5.59	3.21	0.91

1978

	JAN	FEB	MAR	APR	MAY	JUNE	JULY	AUG	SEPT	OCT	NOV	DEC
TDEGF	37.20	30.70	44.60	56.70	64.80	75.20	76.90	82.90	73.10	59.50	56.20	44.60
TDEGC	2.89	-0.72	7.00	13.72	18.22	24.00	24.94	28.28	22.83	15.28	13.44	7.00
PPTIN	4.76	1.33	7.21	3.93	6.22	3.57	3.39	2.25	1.59	2.28	4.06	3.19
PPTCM	12.09	3.38	18.31	9.98	15.80	9.07	8.61	5.71	4.04	5.79	10.31	8.10
SMALLI	0.44	0.00	1.66	4.61	7.08	10.75	11.40	13.78	9.97	5.43	4.47	1.66
UPETCM	0.37	0.00	1.55	4.63	7.34	11.47	12.21	14.97	10.58	5.51	4.48	1.55
CORPHI	0.84	0.83	1.02	1.09	1.21	1.21	1.23	1.16	1.03	0.95	0.84	0.82
APETCM	0.31	0.00	1.58	5.03	8.85	13.85	14.98	17.33	10.85	5.26	3.77	1.27
RMNDR	11.78	3.38	16.73	4.96	6.95	-4.79	-6.37	-11.62	-6.81	0.53	6.54	6.83
STRCHG	-0.00	-0.00	-0.00	-0.00	-0.00	-4.79	-6.37	-10.84	0.00	0.53	6.54	6.83
STRAGE	22.00	22.00	22.00	22.00	22.00	17.21	10.84	0.00	0.00	0.53	7.07	13.90
%CAP	100.	100.	100.	100.	100.	78.	49.	0.	0.	2.	32.	63.
WTRDEF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.78	-6.81	0.00	0.00	0.00
WTRSPL	11.78	3.38	16.73	4.96	6.95	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ACTEVP	0.00	0.00	3.93	6.32	9.88	13.85	14.98	16.56	4.04	5.26	3.77	1.27

1979

	JAN	FEB	MAR	APR	MAY	JUNE	JULY	AUG	SEPT	OCT	NOV	DEC
TDEGF	38.70	33.50	49.90	57.00	67.20	71.00	77.80	78.60	71.50	59.00	54.70	42.50
TDEGC	3.72	0.83	9.94	13.89	19.56	21.67	25.44	25.89	21.94	15.00	12.61	5.83
PPTIN	6.13	4.77	4.62	5.81	8.64	3.84	3.53	5.58	15.51	2.60	6.51	0.45
PPTCM	15.57	12.12	11.73	14.76	21.95	9.75	8.97	14.17	39.40	6.60	16.54	1.14
SMALLI	0.64	0.07	2.83	4.70	7.88	9.21	11.74	12.06	9.39	5.28	4.06	1.26
UPETCM	0.60	0.06	2.85	4.84	8.32	9.79	12.63	12.99	9.99	5.47	4.15	1.22
CORPHI	0.84	0.83	1.02	1.09	1.21	1.21	1.23	1.16	1.03	0.95	0.84	0.82
APETCM	0.50	0.05	2.89	5.25	10.04	11.83	15.50	15.04	10.24	5.22	3.50	1.00
RMNDR	15.07	12.07	8.84	9.51	11.90	-2.07	-6.54	-0.86	29.15	1.39	13.04	0.74
STRCHG	8.10	0.00	0.00	0.00	0.00	-2.07	-6.54	-0.86	9.47	-0.00	0.00	0.06
STRAGE	22.00	22.00	22.00	22.00	22.00	19.93	13.39	12.53	22.00	22.00	22.00	22.00
%CAP	100.	100.	100.	100.	100.	91.	61.	57.	100.	100.	100.	100.
WTRDEF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
WTRSPL	6.96	12.07	8.84	9.51	11.90	0.00	0.00	0.00	19.68	1.39	13.04	0.14
ACTEVP	0.50	0.05	2.89	5.25	10.04	11.83	15.50	15.04	10.24	5.26	3.50	1.00

1980

	JAN	FEB	MAR	APR	MAY	JUNE	JULY	AUG	SEPT	OCT	NOV	DEC
TDEGF	38.00	36.00	48.00	60.00	69.00	74.10	81.90	81.90	75.90	61.50	49.10	41.70
TDEGC	3.33	2.22	8.89	15.56	20.56	23.39	27.72	27.72	24.39	16.39	9.50	5.39
PPTIN	4.26	2.81	4.90	2.44	3.46	0.56	1.85	4.48	1.01	4.28	1.88	1.78
PPTCM	10.82	7.14	12.45	6.20	8.79	1.42	4.70	11.38	2.57	10.87	4.78	4.52
SMALLI	0.54	0.29	2.39	5.58	8.50	10.34	13.37	13.37	11.01	6.03	2.64	1.12
UPETCM	0.40	0.20	2.12	5.47	8.76	10.90	14.53	14.53	11.70	5.97	2.38	0.91
CORPHI	0.84	0.83	1.02	1.09	1.21	1.21	1.23	1.16	1.03	0.95	0.84	0.82
APETCM	0.34	0.17	2.16	5.93	10.57	13.17	17.83	16.83	12.00	5.70	2.00	0.75
RMNDR	10.48	6.97	10.29	0.26	-1.78	-11.74	-13.13	-5.45	-9.43	5.17	2.77	3.78
STRCHG	-0.00	0.00	0.00	-0.00	-1.78	-11.74	-8.47	0.00	0.00	5.17	2.77	3.78
STRAGE	22.00	22.00	22.00	22.00	20.22	8.47	0.00	0.00	0.00	5.17	7.94	11.72
%CAP	100.	100.	100.	100.	92.	39.	0.	0.	0.	23.	36.	53.
WTRDEF	0.00	0.00	0.00	0.00	0.00	0.00	-4.66	-5.45	-9.43	0.00	0.00	0.00
WTRSPL	10.48	6.97	10.29	0.26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ACTEVP	0.50	0.17	2.16	5.25	10.57	13.17	13.17	11.38	2.57	5.70	2.00	0.75

1981

	JAN	FEB	MAR	APR	MAY	JUNE	JULY	AUG	SEPT	OCT	NOV	DEC
TDEGF	32.60	43.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TDEGC	0.33	6.17	-17.78	-17.78	-17.78	-17.78	-17.78	-17.78	-17.78	-17.78	-17.78	-17.78
PPTIN	0.72	1.68	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PPTCM	1.83	4.27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SMALLI	0.02	1.37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
UPETCM	2.51	11.37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CORPHI	0.84	0.83	1.02	1.09	1.21	1.21	1.23	1.16	1.03	0.95	0.84	0.82
APETCM	2.11	9.43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RMNDR	-0.28	-5.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STRCHG	0.00	-5.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STRAGE	11.72	6.56	6.56	6.56	6.56	6.56	6.56	6.56	6.56	6.56	6.56	6.56
%CAP	53.	30.	30.	30.	30.	30.	30.	30.	30.	30.	30.	30.
WTRDEF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
WTRSPL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ACTEVP	1.83	9.43	2.16	5.25	10.57	13.17	13.17	11.38	2.57	5.70	2.00	0.75

```
C   THIS PROGRAM COMPUTES POTENTIAL
EVAPOTRANSPIRATION (USING
C   THE THORNTHWAITE METHOD), THEN COMPUTES
ACTUAL EVAPOTRANSPIRATION
C   MONTHLY AT A GIVEN SITE.
C
C   PLEASE NOTE: AT LEAST TWO DATA FILES ARE
REQUIRED TO RUN THIS
C   PROGRAM: DAYDEC.DAT AND A DATA FILE
CONTAINING MONTHLY TEMPERATURES
C   AND PRECIPITATION AMOUNTS.
C
        DIMENSION AVMDEC(24), DAYSM(24),
TDEGF(24), TDEGC(24),
     1  PPTIN(24), PPTCM(24), SMALLI(24),
UPETCM(24),CORPHI(24),
     2  APETCM(24), RMNDR(24), STRCHG(24),
STRAGE(24), WTRDEF(24),
     3  WTRSPL(24), SNAME(8), ACTEVP(24)
        DIMENSION FNAME(1),PCMAX(24)
        DOUBLE PRECISION FNAME
C   AVMDEC=AVERAGE MONTHLY SOLAR DECLINATION
FOR THE STATION
C   DAYSM=NUMBER OF DAYS IN A MONTH
C   TDEGF=TEMPERATURE IN DEGREES FARHENHEIT
C   TDEGC=TEMPERATURE IN DEGREES CENTIGRADE
C   PPTIN=MONTHLY PRECIPITATION IN INCHES
C   PPTCM=MONTHLY PRECIPITATION IN
CENTIMETERS
C   SMALLI=MONTHLY HEAT INDEX
C   UPETCM=UNADJUSTED POTENTIAL
EVAPOTRANSPIRATION IN CENTIMETERS
C   CORPHI=CORRECTION FACTOR FOR LENGTH OF
DAYLIGHT AT STATION
C   APETCM=ADJUSTED PET (=CORPHI*UPETCM)
C   RMNDR=PRECIPITATION-ADJUSTED PET
C   STRAGE=WATER IN THE SOIL (CM)
C   STRCHG=STORAGE CHANGE
C   WTRDEF=WATER DEFICIT (NO MORE WATER IS
STORED IN SOIL).
C   WTRSPL=SURPLUS OF WATER BEYOND THE
MAXIMUM STORAGE CAPACITY
C   ACTEVP=THE ACTUAL EVAPOTRANSPIRATION IN
CM

OPEN(UNIT=21,ACCESS='SEQIN',FILE='DAYDEC.DAT')
        READ (21,300) (AVMDEC(I),I=1,12)
        READ (21,400) (DAYSM(I),I=1,12)
  300   FORMAT (12F6.2)
  400   FORMAT (12F5.1)
        CLOSE (UNIT=21)
  962   WRITE(5,789)
  789   FORMAT (///,' TYPE NAME OF DATA FILE
```

```
      (IF YOU WANT TO STOP
         1TYPE NONE):')
            READ (5,796) FNAME(1)
     796    FORMAT (A10)
            IF (FNAME(1).EQ.'NONE')RETURN

   OPEN(UNIT=21,ACCESS='SEQIN',FILE=FNAME(1))
            PI=3.14159
            PIRAD=PI/180.
            DO 200 I=1,12
            AVMDEC(I)=AVMDEC(I)*PIRAD
   C  AVERAGE MONTHLY DECLINATION IS NOW IN
   RADIANS!
      200    CONTINUE
            P=1./PIRAD
            READ (21,936) IYEARS
            READ (21,101) NY
     101    FORMAT (I3)
     936    FORMAT (I4)
            DO 4 I=1,12
            TDEGF(I)=0.
            TDEGC(I)=0.
            PPTIN(I)=0.
            PPTCM(I)=0.
            SMALLI(I)=0.
            UPETCM(I)=0.
            APETCM(I)=0.
            CORPHI(I)=0.0
            RMNDR(I)=0.
            STRCHG(I)=0.
            STRAGE(I)=0.0
            WTRDEF(I)=0.
            WTRSPL(I)=0.
            ACTEVP(I)=0.
       4    CONTINUE
            SUMI=0.
            SUMTF=0.
            SUMPIN=0.
            SUMTC=0.
            SUMPCM=0.
            SUMAPE=0.
            SUMDEF=0.
            SUMSPL=0.
            SUMACT=0.
            READ (21,2) SNAME, SLAT, NORS, SLONG,
   EORW, SELEV, Z, WHC, UNIT
       2
   FORMAT(8A4,F7.2,A2,F7.2,A2,F7.2,A2,F7.2,A2)
            STRAGE(2)=WHC
            DO 102 JNY=1,NY
            IF (JNY.GT.1) GO TO 601
            WRITE (5,99)
   SNAME,SLAT,NORS,SLONG,EORW,SELEV,Z,WHC,UNIT,IY
```

```
EARS
  99       FORMAT (///,1X,8A4,//,1X,'LATITUDE',
F7.2,A2,/,1X,'LONGITUDE',
      1
F7.2,A2,//,1X,'ELEVATION',F7.2,A2,//,1X,'WATER
HOLDING
      2 CAPACITY', F7.2, A2,/,' YEAR
',I4,///)
          GO TO 602
 601      WRITE(5,603)IYEARS
 603      FORMAT(///,36X,I4)
 602      JI=1
          IF (JNY.EQ.1) JI=3
C    THIS SOLVES AN INITIALIZATION PROBLEM
WITHIN THE PROGRAM.
C     IN THE SECOND MONTH STORAGE SHOULD BE AT
CAPACITY.
          READ (21,5) (TDEGF(I), I=1,12)
          READ (21,753) (PPTIN(I),I=1,12)
    5     FORMAT (12F 5.2)
  753     FORMAT (12F 6.3)
          DO 999 I=1,12
          PPTCM(I)=PPTIN(I)*2.54
          TDEGC(I)=(5./9.)*(TDEGF(I)-32.)
  999     CONTINUE
          SUMI=0.0
          DO 8 I=JI,12
          IF (TDEGC(I) .LE.0.) GO TO 6
          SMALLI(I)=(TDEGC(I)/5.)**1.514
          GO TO 7
    6     SMALLI(I)=0.
    7     SUMI=SUMI+SMALLI(I)
    8     CONTINUE

A=(0.000000675*(SUMI**3.))-(0.0000771*(SUMI**2
.))
      1  +(0.01792*SUMI)+0.49239
C        THE ABOVE CALCULATES THE STATION
CONSTANT FROM THE
C        SUM OF THE HEAT CONSTANTS OF EACH
STATION
          DO 10 I=JI,12
          IF (TDEGC(I).LE.0.) GO TO 9

UPETCM(I)=1.6*((10.*TDEGC(I)/SUMI)**A)
C     THE ABOVE CALCULATES THE UNADJUSTED
POTENTIAL EVAPOTRANSPIRATION
          GO TO 10
    9     UPETCM(I)=0.
   10     CONTINUE
          PHIRAD=SLAT*PIRAD
C
C         DO LOOP 11 CALCULATES THE CORRECTION
```

```
FACTOR FROM LATITUDE,
C         LENGTH OF DAY, AND SOLAR DECLINATION
AND THEN
C         CALCULATES THE ADJUSTED VALUES FOR
POT EVAPOTRANSPIRATION
C
          DO 11 I=JI,12
          Q=DAYSM(I)
          R=AVMDEC(I)
          S=-SIN(PHIRAD)/COS(PHIRAD)
          T=SIN(R)/COS(R)
          U=S*T
          V=ACOS(U)
          CORPHI(I)=(Q*V*P)/2700.
          APETCM(I)=UPETCM(I)*CORPHI(I)
   11     CONTINUE
          IF (JNY.GT.1)GO TO 80
C
C         DO LOOP 18 CALCULATES THE MONTHLY
WATER BUDGET FOR THE
C         STATIONS FOR THE FIRST YEAR
C
          DO 18 I=JI,12
          STRMAX=WHC
          RMNDR(I)=PPTCM(I)-APETCM(I)
   12     IF (RMNDR(I).GE.0.)GO TO 13
          IF (STRAGE(I-1).GT.0.)GO TO 13
          STRCHG(I)=0.
          GOTO 14
   13     STRCHG(I)=RMNDR(I)
   14     STRAGE(I)=STRAGE(I-1)+STRCHG(I)
          IF (STRAGE(I).GT.STRMAX) GOTO 15
          WTRSPL(I)=0.
          GOTO 16
   15     WTRSPL(I)=STRAGE(I)-STRMAX
          STRAGE(I)=WHC
          STRCHG(I)=STRCHG(I)-WTRSPL(I)
   16     IF (STRAGE(I).LE.0.) GOTO 17
          WTRDEF(I)=0.
          GOTO 18
   17     WTRDEF(I)=RMNDR(I)+STRAGE(I-1)
          STRAGE(I)=0.
          STRCHG(I)=STRCHG(I)-WTRDEF(I)
          IF
(STRAGE(I-1).GT.0..AND.RMNDR(I).GT.0.) GOTO
18
          STRCHG(I)=-STRAGE(I-1)
          WTRDEF(I)=RMNDR(I)-STRCHG(I)
   18     CONTINUE
          GOTO 118
   80     DO 118 I=1,12
          STRAGE(0)=0.0
          RMNDR(I)=PPTCM(I)-APETCM(I)
```

```
112      IF (RMNDR(I).GE.0.) GOTO 113
         IF (STRAGE(I-1).GT.0.) GOTO 113
         STRCHG(I)=0.
         GOTO 114
113      STRCHG(I)=RMNDR(I)
114      STRAGE(I)=STRAGE(I-1)+STRCHG(I)
         IF (I.GT.1) GOTO 224
         STRAGE(I)=STRAGE(12)+STRCHG(1)
224      IF (STRAGE(I).GT.STRMAX) GOTO 115
         WTRSPL(I)=0.0
         GOTO 116
115      WTRSPL(I)=STRAGE(I)-STRMAX
         STRAGE(I)=WHC
         STRCHG(I)=STRCHG(I)-WTRSPL(I)
116      IF (STRAGE(I).LE.0.) GOTO 117
         WTRDEF(I)=0.
         GOTO 118
117      WTRDEF(I)=RMNDR(I)+STRAGE(I-1)
         STRAGE(I)=0.
         STRCHG(I)=STRCHG(I)-WTRDEF(I)
         IF
(STRCHG(I-1).GT.0..AND.RMNDR(I).GT.0.) GOTO
118
         STRCHG(I)=-STRAGE(I-1)
         WTRDEF(I)=RMNDR(I)-STRCHG(I)
118      CONTINUE
C
C        DO LOOP 20 CALCULATES THE YEARLY SUMS
OF THE INDICATED
C        QUANTITY
C
         SUMTF=0.
         SUMPIN=0.
         SUMTC=0.
         SUMPCM=0.
         SUMAPE=0.
         SUMDEF=0.
         SUMSPL=0.
         SUMACT=0.
         DO 20 I=1,12
         SUMTF=SUMTF+TDEGF(I)
         SUMPIN=SUMPIN+PPTIN(I)
         SUMTC=SUMTC+TDEGC(I)
         SUMPCM=SUMPCM+PPTCM(I)
         SUMAPE=SUMAPE+APETCM(I)
         SUMDEF=SUMDEF+WTRDEF(I)
         SUMSPL=SUMSPL+WTRSPL(I)
         IF
(PPTCM(I).GT.APETCM(I).AND.STRCHG(I).GE.0.)
     1   ACTEVP(I)=APETCM(I)
         IF
(APETCM(I).GT.PPTCM(I).AND.STRCHG(I).LE.0.)
     1   ACTEVP(I)=PPTCM(I)+ABS(STRCHG(I))
```

```
            SUMACT=SUMACT+ACTEVP(I)
   20       CONTINUE
            ADEGF=SUMTF/12.
            ADEGC=SUMTC/12.
            DEXARD=(100.*SUMDEF)/SUMAPE
            DEXHUM=(100.*SUMSPL)/SUMAPE

AMSTDX=((110.*SUMSPL)+60.*SUMDEF)/SUMAPE
            RUNOFF=SUMPCM-SUMACT
C    THE ABOVE THREE STATEMENTS CALCULATE THE
CLIMATIC INDICES
C    OF THORNTHWAITE
C
C    TRYING TO GET % OF CAPACITY HERE
            DO 456 II=1,12
  456       PCMAX(II)=(STRAGE(II)/STRMAX)*100.
            WRITE(5,21)
   21       FORMAT (7X,'    JAN    FEB    MAR    APR
   MAY   JUNE   JULY
      1 AUG  SEPT   OCT    NOV    DEC ')
            WRITE(5,22)(TDEGF(KP),KP=1,12)
   22       FORMAT(' TDEGF ',12F6.2)
            WRITE (5,23) (TDEGC(KP),KP=1,12)
   23       FORMAT(' TDEGC ',12F6.2)
            WRITE (5,24) (PPTIN(KP),KP=1,12)
   24       FORMAT(' PPTIN ',12F6.2)
            WRITE (5,25) (PPTCM(KP),KP=1,12)
   25       FORMAT(' PPTCM ',12F6.2)
            WRITE (5,26) (SMALLI(KP),KP=1,12)
   26       FORMAT(' SMALLI',12F6.2)
            WRITE (5,27) (UPETCM(KP),KP=1,12)
   27       FORMAT(' UPETCM',12F6.2)
            WRITE (5,28) (CORPHI(KP),KP=1,12)
   28       FORMAT(' CORPHI',12F6.2)
            WRITE (5,29) (APETCM(KP),KP=1,12)
   29       FORMAT(' APETCM',12F6.2)
            WRITE (5,30) (RMNDR(KP),KP=1,12)
   30       FORMAT(' RMNDR ',12F6.2)
            WRITE (5,31) (STRCHG(KP),KP=1,12)
   31       FORMAT(' STRCHG',12F6.2)
            WRITE (5,32) (STRAGE(KP),KP=1,12)
   32       FORMAT(' STRAGE',12F6.2)
            WRITE(5,567) (PCMAX(KP),KP=1,12)
  567       FORMAT(' %CAP  ',12F6.0)
            WRITE (5,33) (WTRDEF(KP),KP=1,12)
   33       FORMAT(' WTRDEF',12F6.2)
            WRITE (5,34) (WTRSPL(KP),KP=1,12)
   34       FORMAT(' WTRSPL',12F6.2)
            WRITE (5,35) (ACTEVP(KP),KP=1,12)
   35       FORMAT(' ACTEVP',12F6.2)
            WRITE(5,36)
   36       FORMAT('0',22X,'ANNUAL SUMMARY')
            WRITE(5,37)
```

```
  37      FORMAT(2X,'TDEGF    TDEGC     PPTIN
PPTCM   APETCM  WTRDEF
     1WTRSPL   ACTEVP')
         WRITE(5,38)
ADEGF,ADEGC,SUMPIN,SUMPCM,SUMAPE,SUMDEF,
     1SUMSPL,SUMACT
  38
FORMAT(1XF6.2,2X,F6.2,2X,F6.2,2X,F6.2,2X,F6.2,
2X,F6.2
     1,2X,F6.2,2X,F6.2)

WRITE(5,39)AMSTDX,DEXARD,DEXHUM,RUNOFF
  39      FORMAT('0','THE FOUR THORNTHWAITE
CLIMATIC INDICES: MOISTURE'
     1,F7.2,'  DRYNESS',F7.2,'
HUMIDITY',F7.2,' RUNOFF',F7.2)
         IYEARS=IYEARS+1
 102     CONTINUE
         CLOSE (UNIT=21)
         GO TO 962
         STOP
         END
```