Chemical Composition of Rainfall Eastern North Carolina and Southeastern Virginia

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Chemical Composition of Rainfall Eastern North Carolina and Southeastern Virginia

By ARLO W. GAMBELL *and* DONALD W. FISHER

GEOCHEMISTRY OF WATER

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Results are given for analyses of monthly rainfall samples from 27 collection sites for a 1-year period

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CHEMICAL COMPOSITION OF RAINFALL, EASTERN NORTH CAROLINA AND SOUTHEASTERN VIRGINIA

By Arlo W. Gambell and Donald W. Fisher

ABSTRACT

A detailed 1-year study was made of the chemical composition of rainfall over eastern North Carolina and southeastern Virginia. Determinations of the major ions were made on composite monthly samples from each of 27 sampling locations.

Distinct seasonal- and areal-distribution trends are noted for most of the constituents. Chloride, derived primarily from sea salt, decreases sharply inland and shows a marked increase in winter that corresponds to the increase of coastal storms. Calcium reaches a maximum in spring and summer, the increase apparently originating from soil dust associated with agricultural activity. Sodium and magnesium concentrations are slightly higher in winter as a result of the increased supply of sea salt, but soil dust is apparently a significant source of both constituents. Chloride and sodium data indicate that, for the study area, fractionation of sea-salt aerosols is not of any great significance. "Excess" sulfate (sulfate not derived from sea-salt aerosols) increases in concentration with increasing distance from the ocean. The areal trend is probably related in part to variation in the thermal stability of the atmosphere. Gaseous compounds appear to be the principal source of the observed excess sulfate. Variations of nitrate are similar to those of excess sulfate, but factors controlling the occurrence of nitrate are not clear.

The load of each ionic constituent contributed by rainfall is compared with the loads carried by several streams within the precipitation-sampling network. Quantities of sulfate and nitrate supplied by rainfall to the drainage basins exceed the amounts carried by the streams. This seeming anomaly may be evidence of the role of plantlife in affecting composition of natural inland waters. Assimilation by plants can readily account for the loss of both sulfate and nitrate. The quantity of chloride contributed by rainfall constitutes less than one-fourth of the total load carried by the streams. Rock weathering emerges as the most reasonable explanation for the major portion of the stream chloride load.

INTRODUCTION

Some of the numerous investigations on the chemical composition of rainfall have been to evaluate the role of rainfall as a source of nutrients for plant growth; others have been to determine the effectiveness of rainfall as a cleansing agent to rid the atmosphere of pollutants; and still others have been to determine for purely geochemical reasons, the magnitude and significance of the atmospheric transport of water-soluble materials. Such investigations have shown repeatedly that the atmosphere is a source of relatively large quantities of water-soluble material.

This fact has much significance when dealing with the chemistry of natural inland water. In areas where the surface water is very low in dissolved solids, the dissolved material in rainfall can be a major determinant of the water composition.

Further, study of many of the important geochemical and biological processes affecting water quality must begin with certain assumptions about rainfall composition. Hence, the understanding of these processes is closely tied to our knowledge of rainfall composition. The importance of this fact should not be underestimated.

ACKNOWLEDGMENTS

We wish to thank each of the U.S. Weather Bureau Cooperative Observers who assisted in this study, and Mr. George Krahl and others of the Weather Bureau Data Acquisition Division for making the arrangement possible. We are grateful to Marvin Skougstad, Frank Rainwater, and Jack Feth for their critical review of the manuscript.

PURPOSE OF STUDY

The general objectives of this study were as follows: (1) To obtain a detailed description of rainfall composition and of variations in composition both seasonally and areally, over a selected area in an attempt to identify and evaluate the important factors involved and (2) to relate the data on rainfall composition to concurrent stream-quality data and to obtain thereby an estimate of the contribution of rainfall to the dissolved material in the streams.

STUDY AREA

A 34,000-square-mile area in eastern North Carolina and southeastern Virginia was selected for the study. The area consists of five major river basins—the Chowan, Roanoke, Tar, Neuse, and Cape Fear—plus adjacent coastal territory. The area has a number of characteristics desirable for this study. It borders on the ocean; therefore both oceanic and continental effects on rainfall composition can be directly evaluated. Precipitation is abundant—45 to 55 inches annually—and fairly evenly distributed throughout the year.

Furthermore, because only a very small percentage falls as snow, difficulties introduced by the task of collecting and measuring snowfall are minimal.

The predominantly rural nature of the area is also an asset. Industrial air pollution can considerably affect local rainfall composition. Consequently, an area having little industrial air pollution was desired. With a few minor exceptions, the study area fulfills this requirement.

A final and very important consideration is that the concentration of dissolved solids in the streams of the area is very low, generally less than 100 ppm (parts per million).

NETWORK DESIGN AND SAMPLING METHODS

A network of 27 precipitation sampling stations was established covering the study area. The location of each station is shown on plate 1.

Stations were established at existing U.S. Weather Bureau cooperative-observer sites. As daily rainfall measurements are made at these sites, frequent inspection of the sampler and a continuing record of rainfall were ensured.

Placement of the sampling stations was limited by the availability of Weather Bureau observer sites. However, the sites are rather numerous, so that two or three alternative sites were available within most of the desired areas. Hence it was possible to reject sites where local air pollution would obviously introduce spurious results. Large metropolitan areas were avoided, except for Norfolk, Va. There, a sampling station was purposely established in the center of the city. It was believed that data obtained from the Norfolk station would be useful for comparative purposes because the city air usually contains a moderate amount of smoke and other pollutants.

COLLECTOR

The collector incorporates a number of features of the collectors constructed for the Scandinavian precipitation-sampling network (Egner and Eriksson, 1955) except that no provision was made for air sampling.

The device (fig. 1) consists of an aluminum ice chest with a Pyrex glass funnel inserted in one end. The ice chest is very well suited to precipitation sampling in that it provides an inexpensive durable enclosure with excellent insulating qualities.

A ring of spikes mounted on the top of the collector prevents birds from roosting on the rim of the funnel (Egner and others, 1949). A

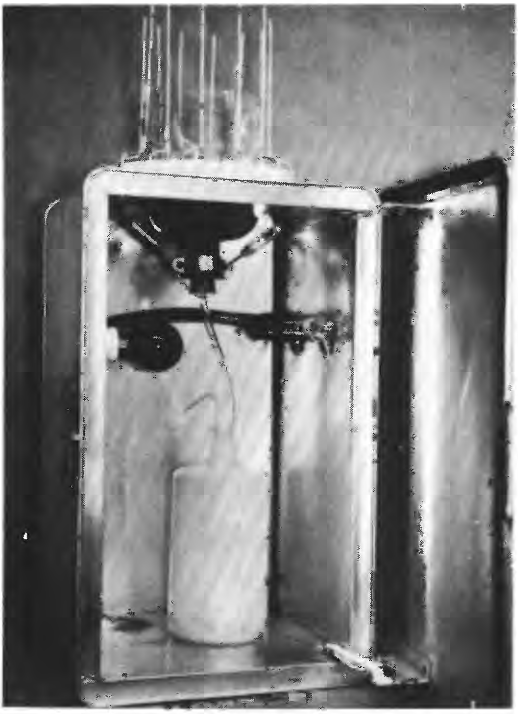

FIGURE 1.—Collector used in the network study.

small pad of Pyrex glass wool in the neck of the funnel acts as a filter.

The glass funnel has a 5-inch diameter and 6-inch vertical sides. It drains through a polyvinyl-chloride tube into a polyethylene bottle. The drain tube and a short air-vent tube are inserted in a polyethylene stopper in the neck of the bottle. The diameter of each of these tubes is kept very small to minimize evaporation losses.

For winter use, the interior of the ice chest is equipped with a thermostatically controlled light bulb designed to keep the temperature between 40° F and 45° F. This facilitates the collection of snow by warming the funnel and keeps the sample from freezing. The light bulb and funnel are blackened to keep the interior of the collector dark, thereby reducing the growth of algae.

The entire device is mounted on a post with the rim of the collecting funnel approximately 5 feet above the ground. Figure 2 shows a mounted collector.

SAMPLING PROCEDURE

Monthly samples were collected at each station from August 1962 through July 1963. On the last day of each month the sample bottle was replaced with a clean empty bottle, and the sample was forwarded for analysis. The glass-wool filter was also replaced at the end of the month.

The observers were instructed to inspect the funnel frequently during the month, remove any debris found there, and make note of any apparent sources of contamination.

FIGURE 2.—Mounted collector at Elizabeth City, N.C.

ANALYTICAL METHODS

An earlier report (Gambell and Fisher, 1964) provides detailed descriptions of the analytical methods used for determinations of sodium, potassium, calcium, ammonium, nitrate, chloride, and sulfate. Briefly, these methods are as follows:

Sodium and potassium: Flame spectrophotometry.

Calcium: Spectrophotometric method based on Kerr's (1960) glyoxal bis-(2-hydroxyanil) procedure.

Ammonium: Nessler ammonia analyses made spectrophotometrically at 400 mμ (millimicrons).

Nitrate: Phenoldisulfonic acid method (Rainwater and Thatcher, 1960).

Chloride: Mercuric thiocyanate-ferric ion method (Iwasaki and others, 1952).

Sulfate: Measurements made on a concentrated sample using spectrophotometric-titration method (Rainwater and Thatcher, 1960).

Magnesium, hydrogen ion, and bicarbonate were also determined for the present study, as follows:

Magnesium: Eriochrome Black T spectrophotometric procedure (described below), using a buffer solution suggested by Pollard and Martin (1956).

Reagents:

Buffer solution (pH, 10.15).—Dissolve 15 grams ammonium chloride in 2 liters of 5 percent (by volume) concentrated ammonium hydroxide.

Dye reagent.—Dissolve 250 milligrams Eriochrome Black T in 1 liter of absolute methanol and filter through Whatman 42 paper or equivalent.

Procedure:

Step 1.—Pipet 5 milliliters of sample into a 10-ml volumetric flask.

Step 2.—Add 2.00 ml of the buffer solution and mix.

Step 3.—Add 2.00 ml of the Eriochrome Black T reagent and mix.

Step 4.—To prepare a blank, pipet 5 ml of de-ionized water into another 10-ml volumetric flask and do steps 2 and 3.

Step 5.—Wait 15 minutes after addition of the dye reagent.

Step 6.—Measure absorbance of samples and standards against blank at 520 mμ in 1-cm cells.

Magnesium concentrations up to 1 ppm can be determined. Calcium interferes; however, a calcium correction can be applied on the basis of the measured absorbance of a calcium standard solution containing buffer and dye, together with a knowledge of the calcium concentration in the sample.

Hydrogen ion: Calculated from pH measurements made on a Beckman Zeromatic pH meter.

Bicarbonate: Potentiometric titration with dilute standard acid (for samples whose pH is greater than 5). Bicarbonate data not treated in detail; determinations made only to permit checks on the reliability of the analyses.

Analytical accuracy for the individual ions may be estimated from the precision of the analytical methods used, since concentrations of interfering ions in most precipitation samples are very low. Standard deviations for the procedures, listed in table 1, were calculated for standard solutions analyzed concurrently with the monthly precipitation samples.

TABLE 1.—*Standard deviation of analytical determinations*

Ion	*Standard deviation (ppm)*	*Ion*	*Standard deviation (ppm)*
Sodium	0. 05	Nitrate	0. 06
Potassium	. 03	Chloride	. 08
Calcium	. 05	Sulfate	. 11
Ammonium	. 06	Magnesium	. 04

Good agreement was obtained between the measured specific conductance of the sample and that calculated as a sum of equivalent conductances contributed by the individual ions (assumed infinitely dilute). This agreement indicates that the analyses were virtually complete for the dissolved ionic constituents. A further check on the adequacy of the analyses was provided by the attainment of good cation-anion balances—in almost all analyses, the value of cations minus anions, in equivalents per million, divided by cations plus anions, in equivalents per million, was less than 0.05.

RAINFALL COMPOSITION

METHOD OF TREATING THE DATA

The collection funnels, being continuously open, collect a certain amount of dry fallout as well as precipitation. Whitehead and Feth (1964) defined the solution resulting from rainfall plus dry fallout as bulk precipitation. Although in the following discussion reference is made to "rainfall composition," the composition of the bulk precipitation is actually implied.

The data for each ionic constituent are presented in three forms. First is a map of areal distribution for the entire network showing precipitation-weighted average concentrations for the year; second is a graph of monthly average concentration computed for the five-basin area; and third is a graph of monthly average load computed for the five-basin area. The graphs pertain only to the area enclosed by the boundaries of the five major drainage basins as shown on plate 1; this area excludes the immediate coastal area. The coastal area was excluded in these computations to avoid undue bias resulting from samples contaminated by direct sea spray.

The monthly average load and monthly average concentration for each ionic constituent were computed in the following manner. Monthly total rainfall at each station, as determined by U.S. Weather Bureau gage measurement, and monthly average concentration of each ion were used to compute a monthly total load, in tons per square mile, for each ion at each sampling station. The load figures were plotted on a map and contoured at convenient intervals. A transparent grid overlay was then used to obtain an average-load figure for the five-basin area. Monthly average rainfall (fig. 3) was determined by plotting the total-rainfall figures and following the procedure used to determine load. This, together with the monthly-average-load figure, was used to compute a monthly average concentration.

RELIABILITY OF THE DATA

Overall accuracy of the data is difficult to assess. By averaging the data in the manner indicated, errors introduced by inaccuracies in the analytical determinations become insignificant. However, microbiological activity in the water samples can alter chemical concentrations before laboratory analyses are made. This fact can be very significant for ammonium and nitrate, but it probably is of much less importance for other constituents.

Addition of chemical agents to the samples to inhibit biological activity was contemplated. Some preliminary experiments were performed using chlorinated hydrocarbons as inhibitors. Results of these tests indicated that the agents were not consistently effective as preservatives; consequently no inhibitor was added.

Another possible source of error is in the sampling apparatus. Collection efficiencies, calculated by comparison of rain-gage readings with measured sample volumes, averaged about 85–90 percent. The disparity can be attributed to differences in the configuration of the gage and the collector, and to the fact that the rim of the collecting funnel was about 2 feet higher than the rim of the gage. The aerody-

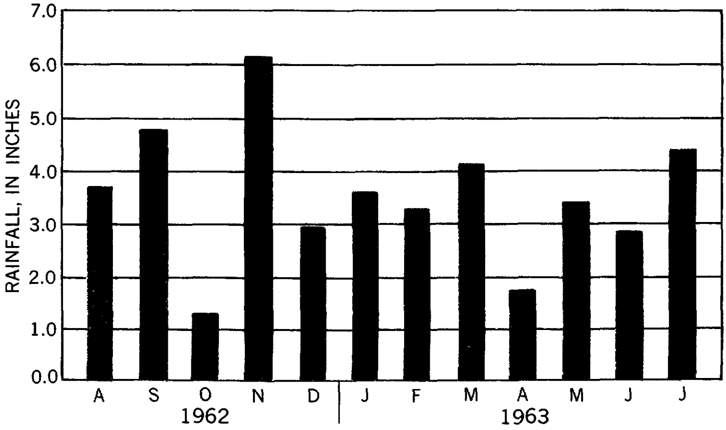

FIGURE 3.—Monthly average rainfall, August 1962–July 1963.

namic effects on collection efficiency, greater for the less streamlined collector, are compounded by increased exposure to wind. Nevertheless the samples are presumably largely integrated samples, so differences in collection efficiency at such high levels of efficiency can be ignored.

Of greater concern is the possibility of error introduced by equating measured rainfall at a sampling station to rainfall over a much larger area around the sampling site. This factor undoubtedly reduces the accuracy of computed monthly averages and patterns of distribution during the summer, when rainstorms are often highly localized.

Soil dust and organic debris, accumulated in the collector funnel in the course of a month, can also contribute ions to the sample and thus lead to errors in interpretation of the resulting data. A rough check on this source of error was made by examining the monthly areal pattern of distribution for each constituent. Values grossly inconsistent with the data from surrounding stations were discarded. However, rejection of data was necessary for only 10 out of the more than 300 samples collected during the study period. The regularity of the patterns of distribution for each constituent, usually even on a monthly basis, testifies to the fact that dry fallout has not greatly influenced the data.

In this same regard, the data in general are surprisingly compatible with the results of large-scale studies—by Junge and Gustafson (1957), Junge and Werby (1958) and Junge (1958)—where collectors were open only during periods of rainfall.

CHLORIDE

It is apparent from previous investigations, such as those by Egner and Eriksson (1955) and Junge and Gustafson (1957), that sea salt is the major and perhaps only significant source of Cl^{-1} in rainfall except in semiarid areas where soil dust also can be important.

A mechanism discussed in earlier reports (Kientzler and others, 1954; Blanchard and Woodcock, 1957) probably explains the presence of sea salt in rainfall. The bursting of the numerous small bubbles at the crest of a wave ejects tiny droplets of sea water into the air. The droplets evaporate, leaving minute sea-salt particles dispersed in the atmosphere. These are carried over land and brought down by rain.

Figure 4 shows the areal distribution of Cl^{-1} over the study area.

The dominant role of sea salt is indicated by the pattern shown. Chloride concentrations, highest along the coast, rapidly decrease inland to a distance of about 200 miles, where the concentrations level off.

Direct sea spray is partly responsible for the very high Cl^{-1} values at the two coastal stations. The northern station, on Bodie Island, was only a few hundred feet from the shore; the southern station, at Cape

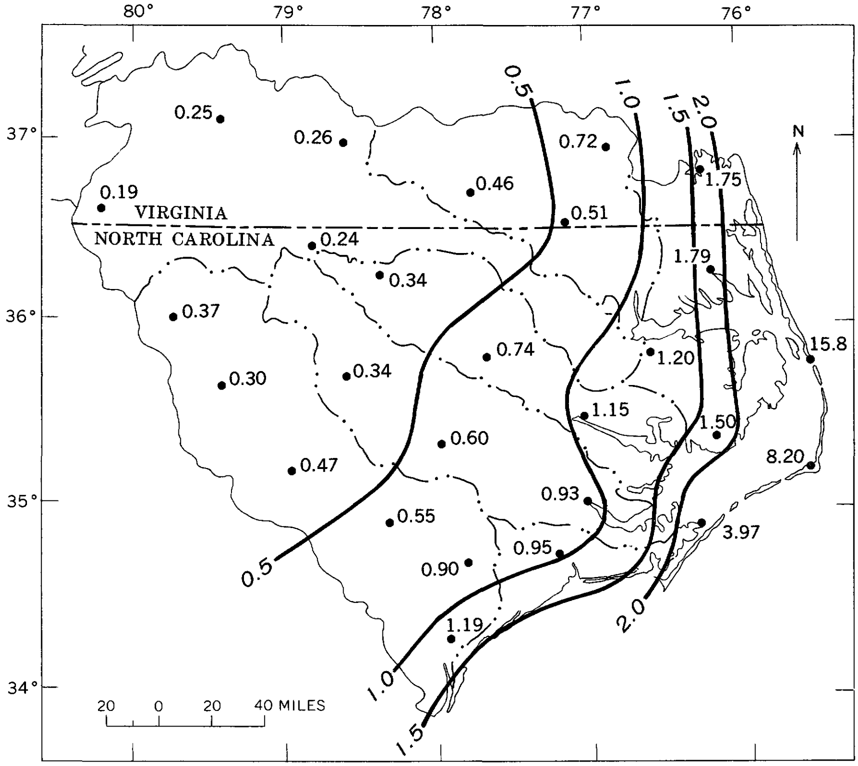

FIGURE 4.—Average Cl^{-1} content of rainfall, in parts per million, August 1962–July 1963.

Hatteras, was approximately one-half mile inland. The difference in location relative to the shore is reflected in the lower Cl^{-1} value at Cape Hatteras.

The rapid decrease inland can be attributed to two factors. First, prevailing winds are from the west, minimizing the oceanic influence. Second, as pointed out by Junge and Gustafson (1957), even when the winds are off the ocean, turbulence and vertical mixing over land surfaces tend to rapidly disperse the sea-salt particles through a greater and greater thickness of the atmosphere. This dispersal reduces the concentration of sea salt in the lower layers of the atmosphere and thus reduces the amount of Cl^{-1} available for washout.

However, the effect of turbulence also seems to ensure a certain low "background" Cl^{-1} concentration in rainfall, regardless of distance from the ocean. Because of the vertical mixing, washout over land is incomplete. The continuous movement and mixing of airmasses assures widespread geographical distribution of the residual sea salt.

Data from the present study agree fairly well with the data collected earlier by Junge and Gustafson, insofar as comparisons are possible.

Junge and Gustafson had only one station in the area, at Cape Hatteras. The annual average Cl^{-1} concentration given in their report is 6.9 ppm, as compared with 8.2 ppm in the present study (fig. 4). For their sampling stations in the interior of the United States, the Cl^{-1} concentrations range between 0.1 and 0.2 ppm, approaching concentrations shown at the westernmost sampling stations in figure 4.

Data on the month-to-month variation of Cl^{-1} over the five-basin area are given in figures 5 and 6. Although absolute concentrations are low (fig. 5), the variations are pronounced and very significant.

By plotting the paths of the major storm centers for any given month, the Cl^{-1} content of rainfall for that month could be generally predicted. This is illustrated by the examples given in figure 7.

Rain having the highest Cl^{-1} content fell during November. Most of the rain in the area during that month was from four major storm systems. Each of the storm centers moved northeastward, passing over, or very near, the network area. Figure 7 (left) shows meteorologic conditions during one of the storms. The storm passed just east of Cape Hatteras and caused a strong northeasterly flow and rain over the entire network area. Any storm following a similar path—whether passing over, just east, or just west of the area—causes flow off the ocean. As a consequence the Cl^{-1} content of the resulting rain is relatively high.

Figure 7 (right) shows a contrasting situation. This storm center was far to the north and rain occurred along the trailing cold front. In such storms, the flow accompanying the rain is from the southwest. Similar situations characterized most of the rain in June. Figure 5 shows the result: rainfall having a very low Cl^{-1} concentration.

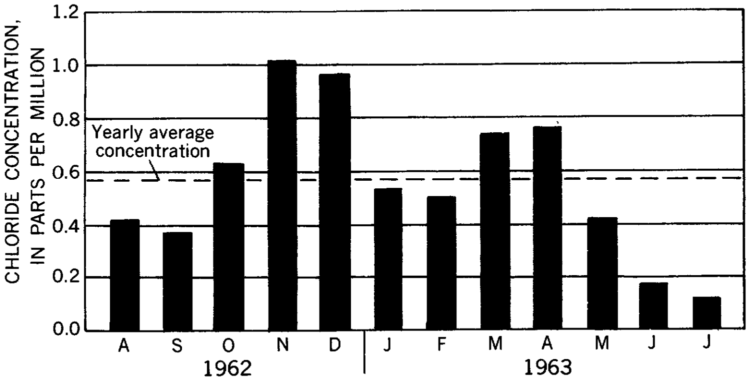

FIGURE 5.—Monthly average Cl^{-1} concentration in rainfall, August 1962–July 1963.

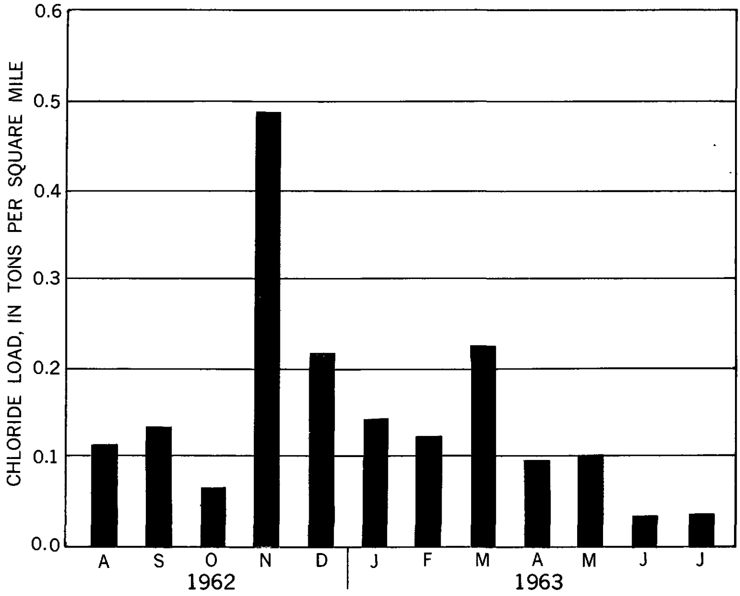

Figure 6.—Monthly average Cl^{-1} loads in rainfall, August 1962–July 1963.

The average Cl^{-1} concentrations for the remaining months can be explained similarly. The important fact is that the Cl^{-1} content of the rainfall responds markedly to changes in the atmospheric circulation pattern. Because the circulation pattern changes seasonally in a generally predictable manner, the seasonal changes in the Cl^{-1} content of rainfall are also predictable.

Figure 7 (left) illustrates a typical wintertime situation. Intense coastal storms, or "northeasters," commonly form over the Gulf of Mexico, move rapidly northeastward, and frequently pass near the network area. In late spring and early summer, storms following this pattern become less and less frequent. Rather, the major storm centers remain farther to the north and the type of situation shown in figure 7 (right) is more common. In the fall the pattern begins a gradual shift back and the cycle is repeated.

A further consideration is that the strength of flow is characteristically greater in winter, and thus the inland transport of sea salt is increased. Strong winds increase agitation of the sea surface and thereby increase the production of sea-salt aerosols. As wind velocity increases, transport capacity also increases.

On the basis of these considerations the Cl^{-1} content of rainfall should be relatively high in winter and low in summer, a contention supported by the data in figure 5.

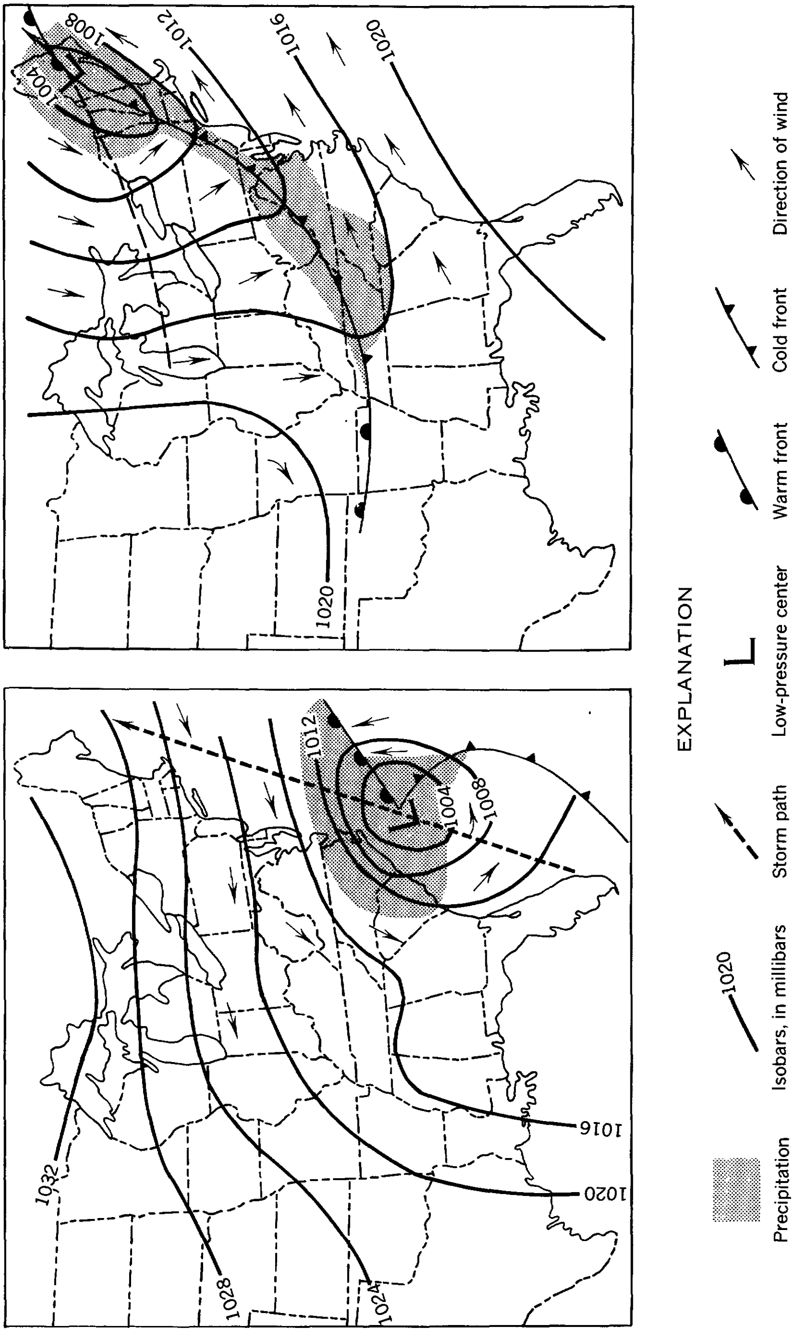

FIGURE 7.—Weather maps for 1:00 a.m. e.s.t., November 3, 1962 (left), and June 21, 1963 (right).

It is believed that the same general pattern applies to the Cl^{-1} content of rainfall along the entire Atlantic coast from the study area northward, because the same meteorological considerations are applicable.

CALCIUM

Potential sources for Ca^{+2} in rainwater are narrowly limited. Soil dust can usually be regarded as the single major source.

Sea water contains relatively low Ca^{+2} concentrations—410 ppm, compared to 18,970 ppm Cl^{-1} (Defant, 1961). Hence, sea-salt aerosols can be disregarded as a source for Ca^{+2}. Industry is also unlikely to be an important source. Some industrial processes add calcium compounds to the atmosphere, but the quantities involved are insignificant except in the immediate vicinity of the source.

Liming of the soils is practiced to some degree in the network area. Some Ca^{+2} may originate from this source, but again, the quantities involved are not likely to have great significance over the network as a whole.

The areal distribution of Ca^{+2}, shown in figure 8, is notable for its

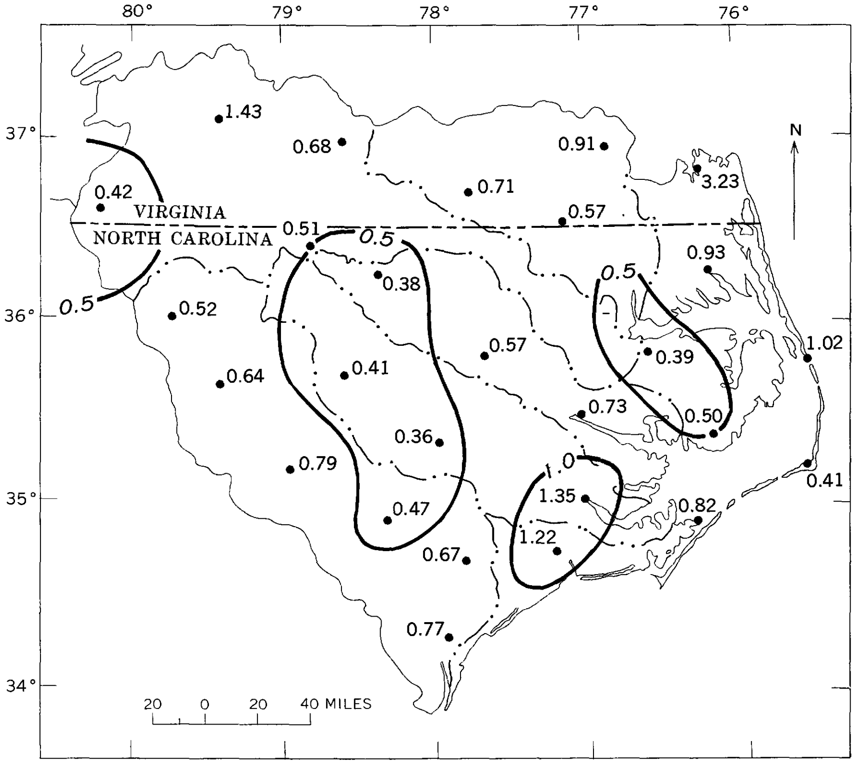

FIGURE 8.—Average Ca^{+2} content of rainfall, in parts per million, August 1962–July 1963.

lack of any well-defined pattern. The only conspicuous feature is a small area of maximum concentration at the southeast edge of the network. This feature appeared every month and is apparently caused by the high calcium content of the soil in this area. The local area is underlain by a very pure limestone formation which has been viewed as the only potentially valuable source of materials for the manufacture of portland cement in North Carolina (Broadhurst, 1955). Residual soils from this formation naturally contain greater amounts of calcium than soils in the surrounding areas.

Examination of figures 9 and 10 provides some insight into factors controlling the Ca^{+2} content of the rain. Figure 9 shows a uniform progression from low Ca^{+2} concentrations in winter to high Ca^{+2} con-

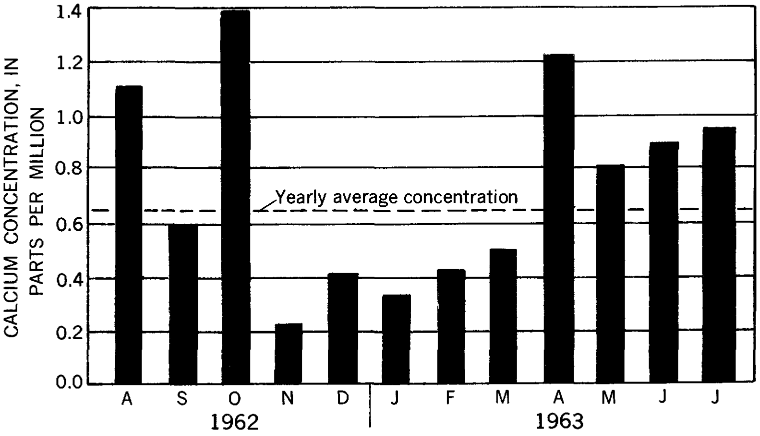

FIGURE 9.—Monthly average Ca^{+2} concentration in rainfall, August 1962–July 1963.

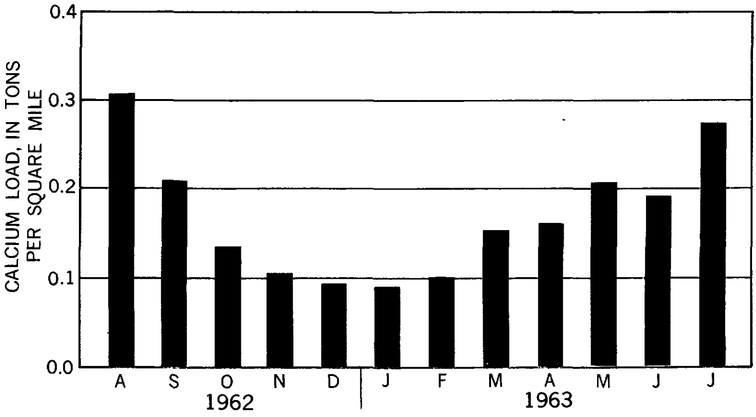

FIGURE 10.—Monthly average Ca^{+2} loads in rainfall, August 1962–July 1963.

centrations in summer, except for October and April, which were very dry months (see fig. 3). Figure 10 shows average loads, and here the pattern is remarkably regular. Presumably, calcium loads are low in winter because agricultural activity is at a minimum. Calcium loads increase in the spring and remain high during the summer because this is the period of greatest agricultural activity.

Junge and Werby's (1958) data indicate Ca^{+2} concentrations between 0.3 and 0.4 ppm over the study area. The computed average for the study period is between 0.6 and 0.7 ppm. In view of differences in sampling methods, the disparity is not large. Dry fallout probably contributes the difference.

SODIUM

Figure 11 shows the areal distribution of Na^{+1}. Figures 12 and 13 show the monthly average Na^{+1} concentration and monthly average Na^{+1} load.

The pattern in figure 11 resembles that shown on the Cl^{-1} map (fig. 4), sea salt thus being indicated as the dominant source for Na^{+1}. However, the gradient is less sharp and the western stations show relatively higher concentrations.

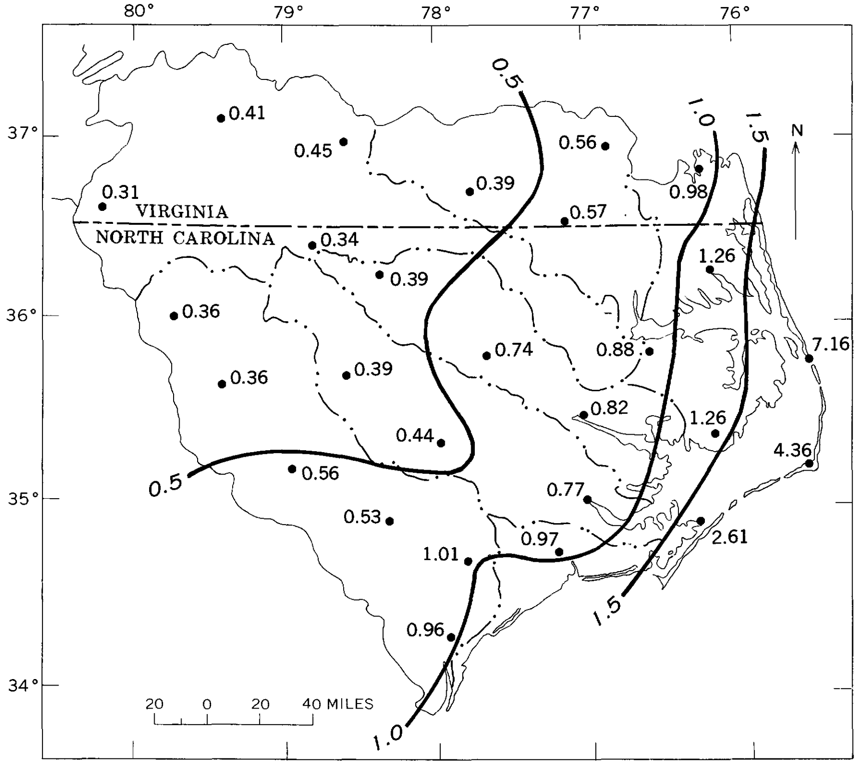

FIGURE 11.—Average Na^{+1} content of rainfall, in parts per million, August 1962–July 1963.

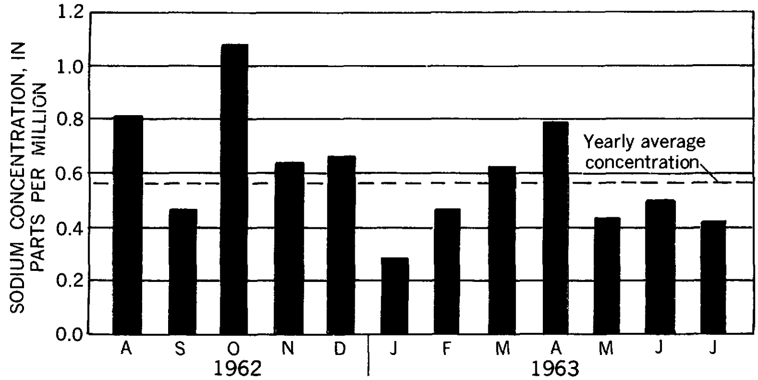

FIGURE 12.—Monthly average Na^{+1} concentration in rainfall, August 1962–July 1963.

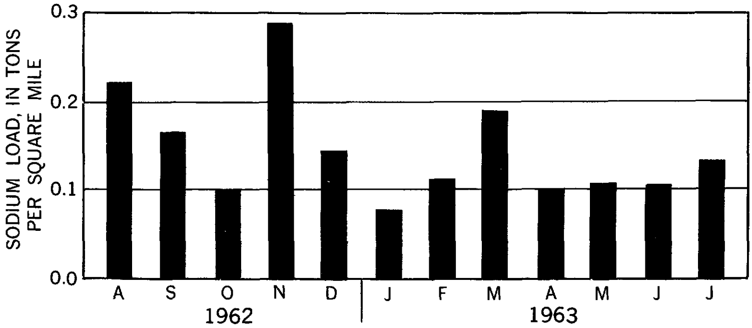

FIGURE 13.—Monthly average Na^{+1} loads in rainfall, August 1962–July 1963.

An estimate of the amount of Na^{+1} derived directly from sea salt can be made by computing the amount of Na^{+1} necessary for a Cl^{-1}/Na^{+1} ratio of 1.8, which is the approximate Cl^{-1}/Na^{+1} ratio in sea water. On the basis of the total Cl^{-1} load deposited on the five-basin area for the year, approximately 60 percent of the Na^{+1} can be attributed to sea salt. The remaining 40 percent is "excess" Na^{+1} (sodium not derived from sea-salt aerosols).

Controversy has arisen concerning whether excess Na^{+1} observed in rainfall is derived from the land surface or whether it only appears to be excess and actually originates from fractionated sea-salt aerosols.

Proponents of the fractionation theory suggest that some chloride is separated from the aerosols, which are thus enriched in sodium. Escape of chloride as gaseous HCl has been offered as one means by which fractionation could occur. If fractionation were to take place, the Cl^{-1}/Na^{+1} ratios imparted by the aerosols to rainfall would then be something less than 1.8.

However, in many areas sodium is abundant in the soil mantle, so that addition of Na^{+1} from soil dust can also explain relatively low Cl^{-1}/Na^{+1} ratios in rainfall. Figure 14, showing the amount of Na^{+1} in excess of that expected from sea salt, indicates that, for the study area, this explanation is to be preferred.

The seasonal variation of monthly average excess Na^{+1} loads in figure 14 is very similar to that shown by Ca^{+2} loads in figure 10. This is good evidence that Ca^{+2} and excess Na^{+1} are derived from a common source—presumably soil dust.

Areal distribution of excess Na^{+1} shows good general agreement with Ca^{+2} distribution, further supporting the contention of a common source. The data of course do not exclude the possibility that some small amount of fractionation is taking place or that fractionation could be of much greater significance for other areas.

The data suggest that normally the average monthly Na^{+1} concentration of the network rainfall has very little seasonal variation. A slight maximum might be expected in winter to coincide with the Cl^{-1} peak. But, for the remainder of the year, variations in continental and marine Na^{+1} sources appear to balance out one another.

MAGNESIUM AND POTASSIUM

Figures 15 and 16 depict areal and seasonal distribution of Mg^{+2} concentrations. Although present in much lower concentrations, Mg^{+2} follows almost the same pattern as Na^{+1} and presumably for the same reasons.

Sea water contains approximately 1,350 ppm Mg^{+2} as compared with 10,470 ppm Na^{+1} (Defant, 1961). Calculations similar to those performed to determine excess Na^{+1} indicate that approximately one-third of the total Mg^{+2} brought down over the network can be attributed directly to sea-salt aerosols. The remaining part is presumably derived from soil dust.

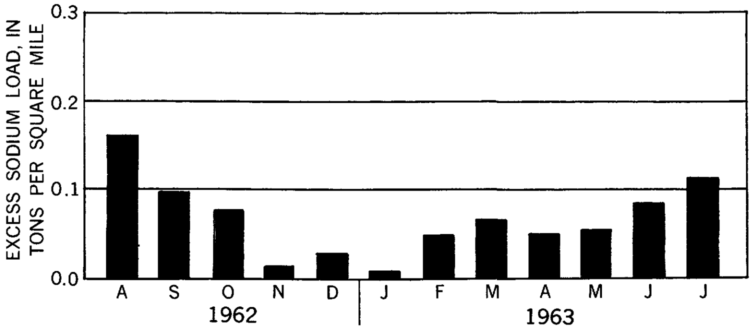

FIGURE 14.—Monthly average excess Na^{+1} loads in rainfall, August 1962–July 1963.

Potassium concentrations were low and very uniform over the entire network area. The average annual K^{+1} concentration was just over 0.1 ppm. The average monthly concentrations ranged from 0.1 to 0.3 ppm. Highest concentrations were observed during the summer.

Soil dust probably is largely responsible for the observed concentrations.

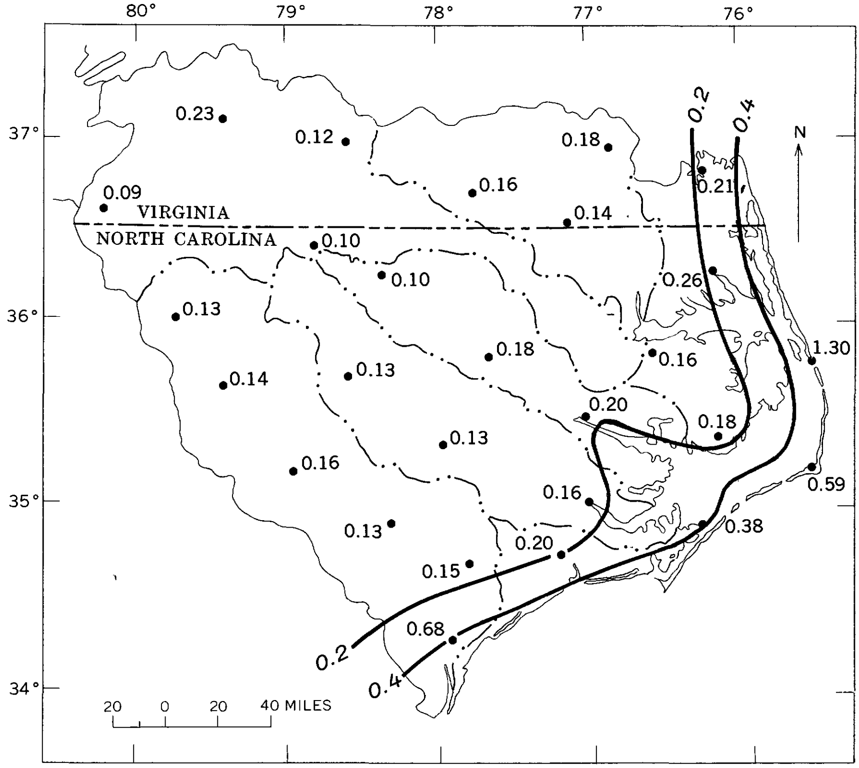

FIGURE 15.—Average Mg^{+2} content of rainfall, in parts per million, August 1962–July 1963.

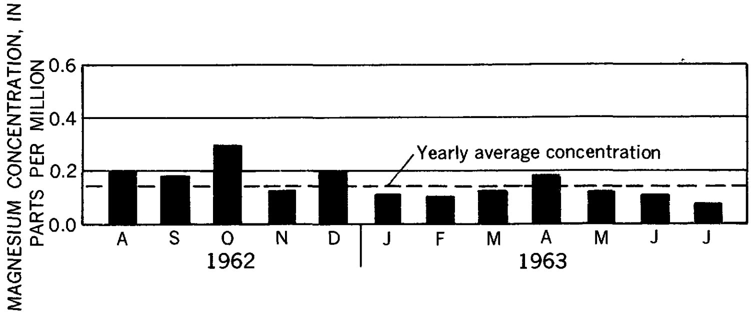

FIGURE 16.—Monthly average Mg^{+2} concentration in rainfall, August 1962–July 1963.

SULFATE

Data on the areal distribution of SO_4^{-2} are given in figure 17. The major features are an area of minimum concentration in the southeast part of the network, an area of maximum concentration along the coast from Cape Hatteras northward, and otherwise generally higher concentrations toward the north and west parts.

Interpretation of SO_4^{-2} data is complicated by the large number of potential sources for atmospheric sulfur compounds. Junge (1960) discussed this topic in some detail. Gaseous sulfur compounds result from the combustion of fossil fuels, from some industrial processes, from the anaerobic decay of organic matter, and from volcanic activity. Particulate sulfur, usually as SO_4^{-2}, is introduced naturally into the atmosphere as soil dust and as sea salt, whereas man contributes industrial sulfur compounds and dust from commercial agricultural fertilizers.

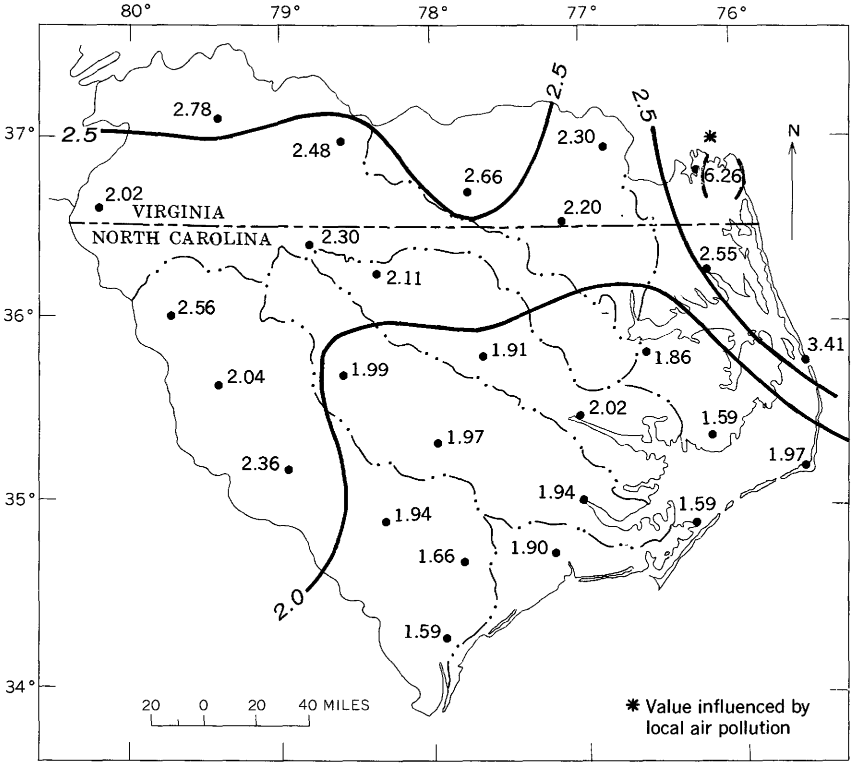

FIGURE 17.—Average SO_4^{-2} content of rainfall, in parts per million, August 1962–July 1963.

PARTICULATE SOURCES OF SULFATE

The effect of sea-salt aerosols on the network SO_4^{-2} data can be readily ascertained by plotting "excess" SO_4^{-2}—total SO_4^{-2} minus that contributed by sea salt—as computed from Cl^{-1} concentrations at each station, the assumed SO_4^{-2}/Cl^{-1} ratio in sea water being 0.14 (Defant, 1961). The result is shown in figure 18. The coastal maximum has been reduced, and the general pattern resulting is a gradual increase in concentration with increasing distance inland.

As computed from the total measured Cl^{-1} load, sea salt constituted less than 5 percent of the total SO_4^{-2} load for the five-basin area for the year. The greatest monthly contribution occurred in November, but even in this month, sea salt was the source of less than 10 percent of the total load.

Soil dust is also unlikely to be a major source of the observed SO_4^{-2}. The network area receives a great deal of rainfall—over 45 inches annually. As a consequence, the soils are thoroughly leached and not likely to contain much soluble material. This condition is reflected in the total dissolved-solids concentration of streams draining the

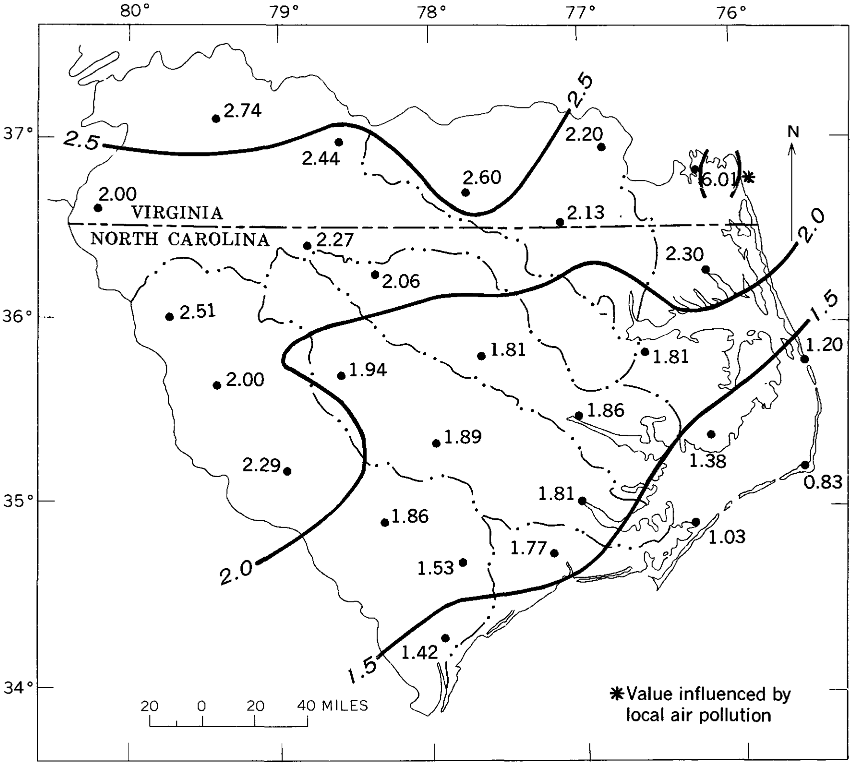

FIGURE 18.—Average excess SO_4^{-2} concentration, in parts per million, August 1962–July 1963.

area, which is generally less than 100 ppm, and their SO_4^{-2} concentration, which is generally less than 10 ppm.

Moreover, if the SO_4^{-2} were derived from soil dust, the likely source mineral would be gypsum—calcium sulfate. Therefore, Ca^{+2} as well as SO_4^{-2} would originate primarily from this source. But the soil parent material in the network area consists largely of marls, sandstones, limestones, and clays, so the calcareous portion of the soil, and hence the soil dust brought down by rainfall, must consist principally of calcium carbonate. Consequently, some other source for the SO_4^{-2} must be assumed.

Contribution from commercial fertilizer cannot be discounted entirely, but a very pronounced spring maximum would be expected if it were a primary source, because fertilizer application occurs largely during the spring. The observed seasonal pattern of SO_4^{-2}, seen in figures 19 and 20, indicates that fertilizer is not a primary source.

Industrial emissions, presumably the only other potential major source of particulate sulfur compounds, may be important for one or two sampling locations. For example, the very high excess SO_4^{-2}

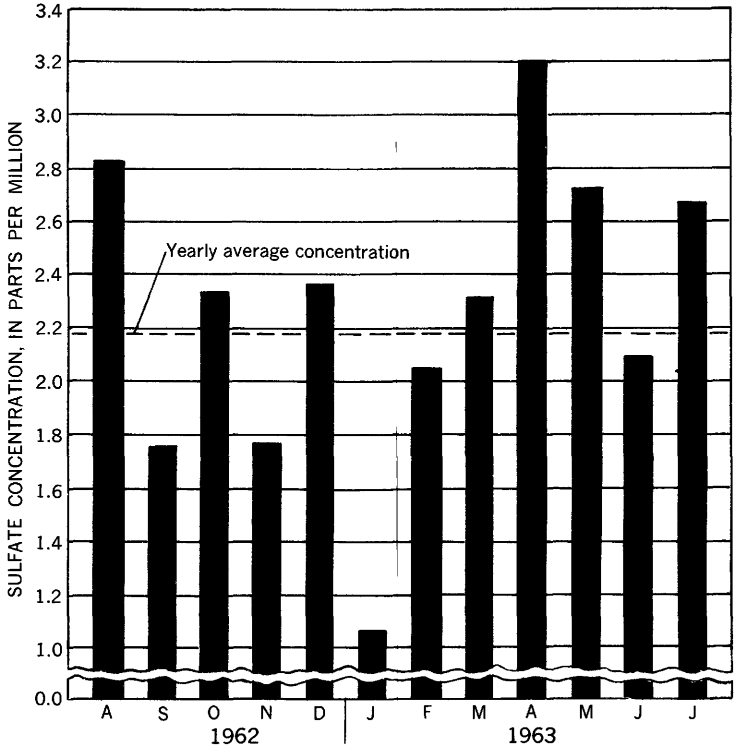

FIGURE 19.—Monthly average SO_4^{-2} concentration in rainfall, August 1962–July 1963.

concentration (6.26 ppm) at Norfolk, Va., a relatively heavily industrialized city, is undoubtedly due in part to particulate matter. However, because of the predominantly rural nature of the network area as a whole, industrial particulate sources should be of minor significance to the total network sulfur budget.

GASEOUS SOURCES OF SULFATE

The question of the origin of atmospheric sulfur was considered by Conway (1942). He concluded that man's activities add relatively little sulfur and that natural processes result in most atmospheric sulfur.

Using newer, more complete data, Junge (1960) computed a global atmospheric sulfur budget and concluded that increased weight must be given to man's activities. He estimated that this is the source for

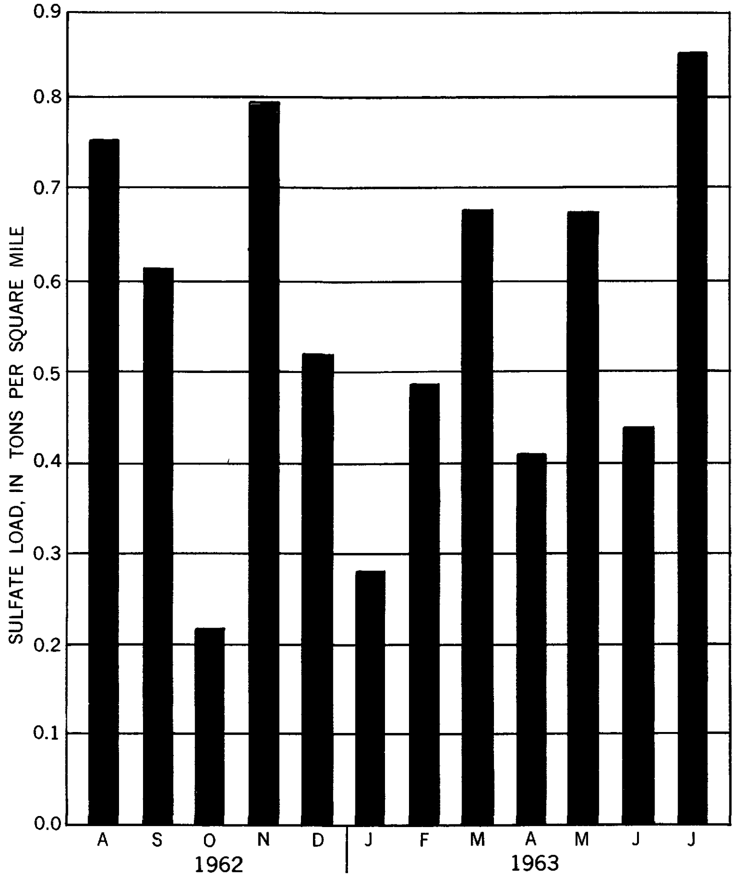

FIGURE 20.—Monthly average SO_4^{-2} loads in rainfall, August 1962–July 1963.

as much as 30 percent of the total global atmospheric sulfur budget. Whichever estimate is correct, very considerable quantities of atmospheric sulfur must be attributed to natural sources.

The primary natural process postulated by Conway is the production of H_2S from the decay of organic matter. This process is known to occur under reducing conditions, often producing high local atmospheric H_2S concentrations over swamps. An additional source suggested by Conway is decaying organic matter in the shallow area along the Continental Shelf.

To account for SO_4^{-2} in rainfall, the atmospheric H_2S must somehow be converted to hexavalent sulfur. No natural process is known whereby this oxidation is accomplished directly. Probably the changes take place very gradually, after wide atmospheric dispersion of the original gaseous sulfide.

An intermediate species in the complete oxidation of sulfur, and one which is known to be a trace constituent of the atmosphere, is gaseous SO_2. It is possible that SO_2 provides most of the SO_4^{-2} observed in network rainfall. A mechanism suggested by Junge and Ryan (1958) involves catalytic oxidation of SO_2 to SO_4^{-2} in cloud droplets. Gambell and Fisher (1964) pointed out that NO_2 would probably serve as an effective catalyst in this reaction, as it does in the lead-chamber process for the commercial production of sulfuric acid. Other reactions, and other catalysts, some considered by Junge and Ryan, may also be capable of forming SO_4^{-2} from gaseous sulfur compounds.

EVIDENCE FOR GASEOUS SOURCES OF SULFATE

Several investigators have suggested the likely importance of gaseous sulfur compounds in regard to the occurrence of SO_4^{-2} in rainfall. The ubiquitous nature of excess SO_4^{-2} in rain in relatively large concentrations is in itself some support for this theory, as is the fact that excess SO_4^{-2} concentrations frequently remain at relatively high levels throughout the course of a storm, even for storms of long duration and large areal extent (Gambell and Fisher, 1964). The implication is that the source of the SO_4^{-2} is not appreciably affected by washout, suggesting a gaseous rather than a particulate source.

Table 2 shows some previously unpublished data which also lend support to the theory of a gaseous origin for SO_4^{-2}. The table shows the chemical composition of rain samples collected in the Pacific on board the USCGS ship *Pioneer*. Samples were collected in a polyethylene-lined trough on the ship's flying bridge. Precautions were taken to keep the collector always upwind from the ship's stack to avoid contamination. Rainfall amounts were not accurately measured, but each sample represents at least several tenths of an inch of rain. During each sampling period, the ship's being several hundred miles from land makes it very unlikely that continentally derived particulate matter contributed significantly to the ionic content of the samples. Yet the measured SO_4^{-2} concentration of each sample is considerably greater than would be expected from sea salt on the basis of a SO_4^{-2}/Cl^{-1} ratio equal to that found in sea water. Fractionation of the sea-salt aerosols does not explain the discrepancy because fractionation would also create an apparent excess of Na^{+1}. The Cl^{-1}/Na^{+1} ratios do not show an excess of Na^{+1}. Hence, the excess SO_4^{-2} must represent true accretion, presumably from the gaseous atmosphere.

TABLE 2.—*Chemical composition of rainfall samples collected in the Pacific Ocean*[1]

Sample	Collection		Concentration (ppm)					SO_4^{-2}/Cl^{-1}	Excess SO_4^{-2} (ppm)	Cl^{-1}/Na^{+2}
	Date	Location	Cl^{-1}	SO_4^{-2}	Na^{+1}	Ca^{+2}	K^{+2}			
1	9-13-61	25°20′ N., 177°31′ W.	51	11	28	1.9	1.8	0.22	4	1.82
2	9-16-61	31°21′ N., 177°22′ W.	54	23	30	1.3	2.1	.43	15	1.80
3	9-17-61	34°46′ N., 177°15′ W.	43	8.0	24	1.3	1.0	.19	2	1.86
4	9-20-61	41°21′ N., 177°02′ W.	258	40	138	5.6	5.0	.16	4	1.86
5	9-24-61	51°45′ N., 177°02′ W.	210	39	112	4.9	6.6	.19	10	1.88
6	9-30-61	51°41′ N., 161°07′ W.	11	2.8	8.3	.2	.6	.25	1	1.33
Average sea-water composition[2]			18,970	2,650	10,470	410	380	.14		1.81

[1] Data collected by Frank H. Rainwater.
[2] Defant (1961).

Figure 21, showing the pH of network rainfall, is also of interest with regard to this question. The pH's were computed from total hydrogen-ion loads for each station. A decrease in pH—increase in H^{+1}—with increasing distance inland is evident and in general parallels the variation in excess SO_4^{-2}. Dissolution of SO_2 and oxidation to SO_4^{-2} would provide H^{+1} by the reaction

$$2SO_2+O_2+2H_2O=4H^{+1}+2SO_4^{-2}.$$

This might well explain the similarity in patterns. There is one anomalous point (pH, 5.5) in the northwest corner of the network. However, it is coincident with an unusually large Ca^{+2} concentration as seen in figure 8. If, as appears likely, the Ca^{+2} results from calcium carbonate soil dust, then a relatively high pH—masking the acidity due to the gas reaction—would be expected.

In all, there appears to be substantial evidence, albeit indirect, that a large part of the SO_4^{-2} brought down by rainfall over the study area is of gaseous origin, most probably formed from SO_2. Moreover, a significant amount must originate from natural sources, although it is not clear whether gaseous sulfur compounds from natural sources or from man's activities predominate.

In this regard, the network area is neither highly industrialized nor densely populated, but the industry and population centers are near the western edge of the network. Atmospheric sulfur from this area and the cumulative effect from man's activities farther inland may partly account for the increase of SO_4^{-2} concentrations with increasing distance inland observed in figure 18. However, meteorologic considerations are probably of equal or greater importance in explaining the observed pattern.

The average monthly SO_4^{-2} concentrations indicate that sulfur from man's activities is not the controlling factor in that the concentrations (fig. 19) are generally lower in winter, the minimum occurring in January. The largest quantities of atmospheric sulfur from man's activities are produced in winter because of increased heating requirements. That this is not reflected by maximum SO_4^{-2} concentrations in winter shows that other factors are of greater importance.

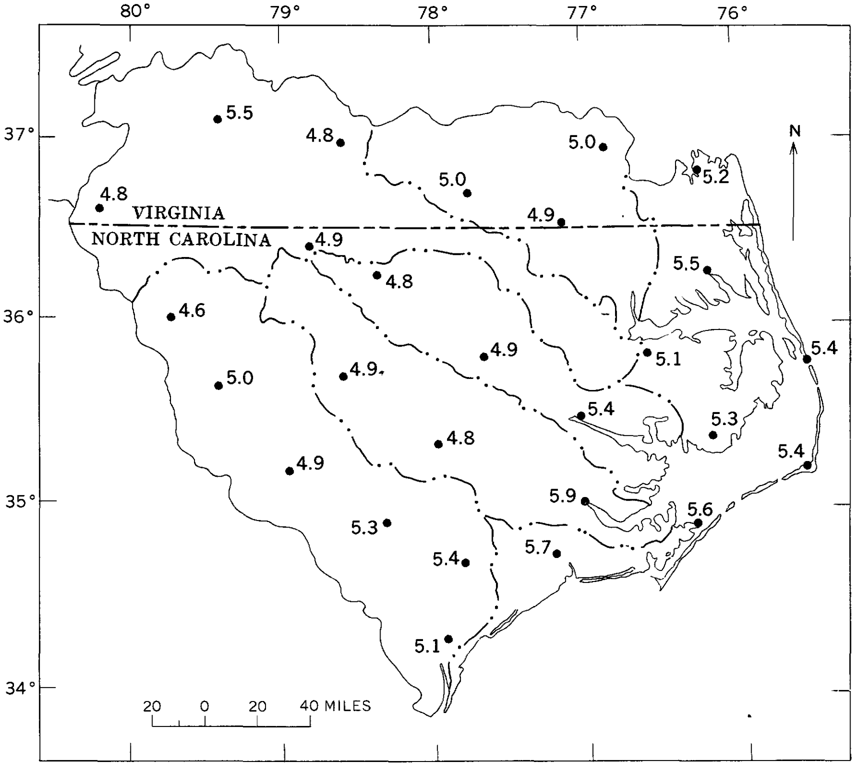

FIGURE 21.—Rainfall pH, August 1962–July 1963.

If previous assumptions about the formation of SO_4^{-2} from SO_2 are correct, then the SO_4^{-2} concentration of rainfall is a function of atmospheric SO_2 concentration. Variation of SO_2 concentration from one part of the network to another should cause corresponding variation in the areal distribution of SO_4^{-2}. Similarly, variation in the average SO_2 concentration over the entire network from one month to another should cause corresponding variation in the monthly average SO_4^{-2} concentration.

During certain periods of the year, notably summer and fall, meteorologic conditions favor accumulation of fairly large pollutant concentrations. (The term "pollutant," as used here, is not meant to differentiate between natural and manmade emissions and is virtually synonymous with SO_2.) In summer and fall, airmass movement is characteristically slow. Frequently, large airmasses stagnate over one area for periods of 4 or 5 days, or even longer. Weak air circulation and thermally stable conditions in the lower layers of such airmasses favor buildup of fairly large pollutant concentrations.

Korshover (1957) made a study of the frequency of occurrence of stagnant airmasses east of the Rocky Mountains for a 20-year period. Criteria indicative of stagnation situations were established, and the United States (from the Rocky Mountains to the east coast) was divided into a set of grid points at every 2° of latitude and 2° of longitude. For each point, the total number stagnation cases and the total number of days of stagnation were determined. The results for the area surrounding and including the precipitation network are shown in figure 22.

The pronounced increase in the number and duration of stagnation cases with increasing distance inland corresponds to the trend of higher SO_4^{-2} concentrations with increasing distance inland shown in figure 18. The tendency for more frequent stagnation situations to occur inland may well be the primary reason for the areal distribution of SO_4^{-2} observed in the network rainfall.

The attempt to compare average conditions over a 20-year period with conditions for one specific year might be questioned. Yet the conditions which gave rise to the pattern in figure 22 are almost invariably present to a greater or lesser degree in any given year, so that the validity of the comparison is not seriously affected. The conditions that result in a lower number of stagnation cases along the coast can be explained simply as follows: Because the surface temperature of the ocean and of the inland water bodies along the coast changes less rapidly than does the temperature of the land surface, the coastal area has less temperature variation from day to night than the area farther inland. Hence nighttime temperature inversions, which favor atmospheric pollution, occur less frequently. Similarly, temperature

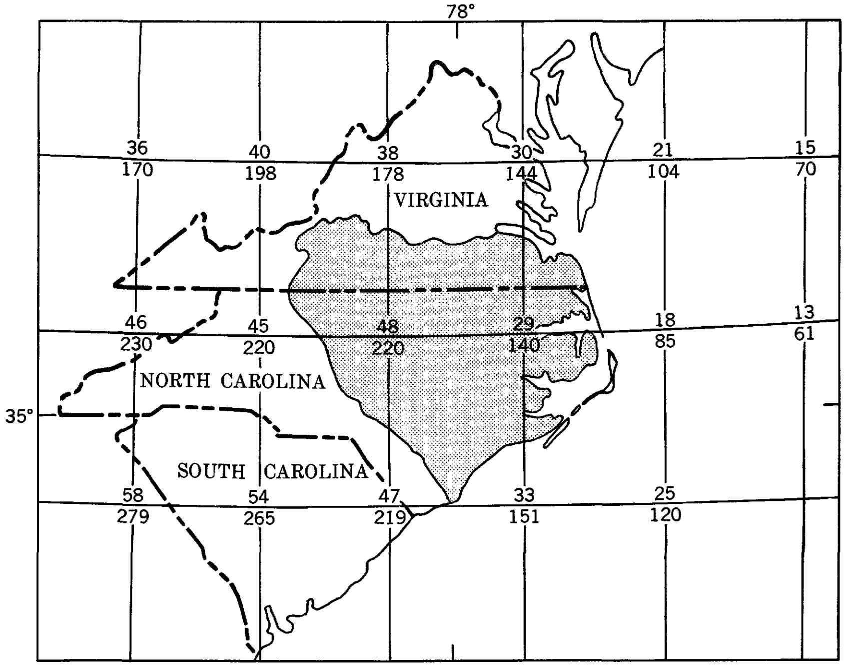

FIGURE 22.—Number (upper grid values) and duration (lower grid values, in days) of stagnation cases, 1936–56. After Korshover (1957).

differences between the land and water surfaces cause higher average wind velocities and fewer calms, which also serve to reduce pollution.

If our assumptions about the effect of stagnation conditions on the SO_4^{-2} content of rainfall are correct, then the seasonal distributions of SO_4^{-2} should relate to the seasonal frequency of occurrence of stagnation conditions.

The seasonal frequency of stagnation cases as determined by Korshover is shown in figure 23. These conditions are shown to be most frequent in late summer and fall, and least frequent in winter. The observed monthly variation of average SO_4^{-2} concentration, as shown in figure 19, and the monthly variation of stagnation cases shown in figure 23 differ in detail, but this might be expected. Korshover's data depict average conditions over 20 years, so that the probability of any given year duplicating these conditions is very small. It appears significant that SO_4^{-2} concentrations were generally lower in winter during the period when stagnation conditions are least likely, but data for a much longer period would be necessary to verify the general relationship suggested.

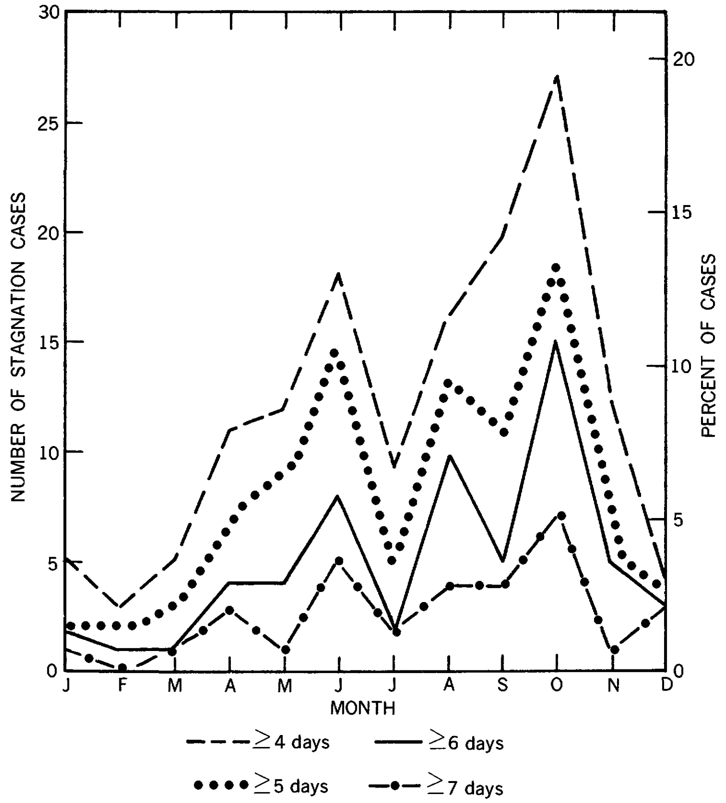

FIGURE 23.—Stagnation cases for 4, 5, 6, and 7 or more days by month in the United States east of the Rocky Mountains, 1936–56. The left scale gives the total number of stagnation cases for the indicated duration for each month during the 20-year period, and the right scale gives the percentage distribution by month of stagnation cases for 4 or more days. After Korshover (1957).

NITRATE

Network NO_3^{-1} data are given in figures 24–26. The primary feature of the NO_3^{-1} map (fig. 24) is a marked increase in concentration with increasing distance inland. Although the indicated concentrations may be inaccurate as a result of biological activity in the samples prior to analysis, it is believed that the geographical trend shown is reliable.

In winter, areal distribution was comparatively uniform throughout the network area. In the summer months a very different pattern developed. High concentrations were observed in the western third of the network and, generally, only trace concentrations were observed at other stations. The boundary often appeared to be very sharp, the gradation from high to low concentration taking place within a distance of 20–30 miles (Gambell, 1963).

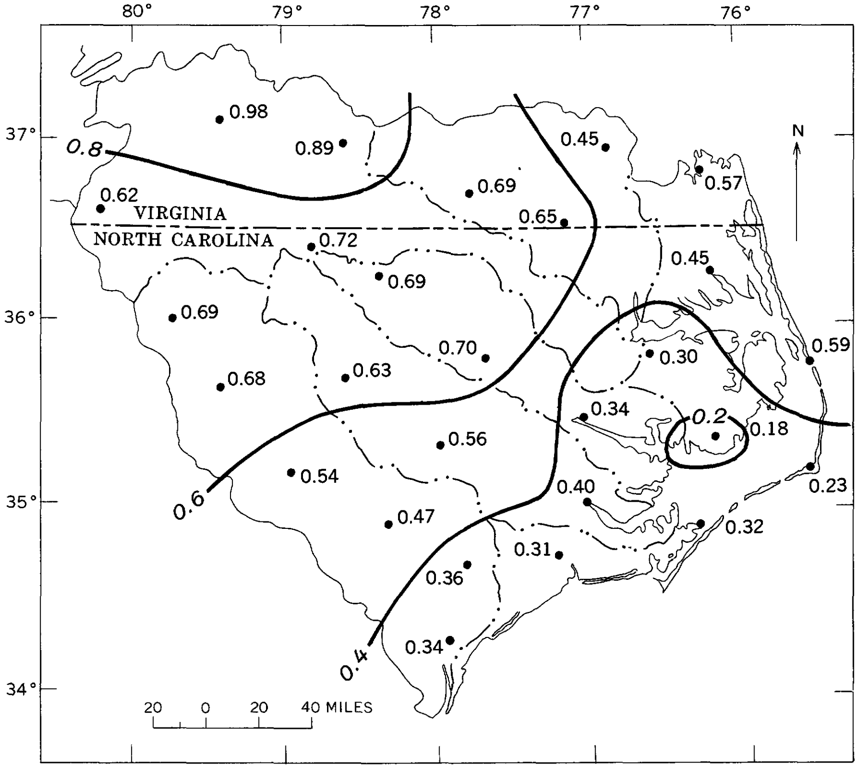

FIGURE 24.—Average NO_3^{-1} content of rainfall, in parts per million, August 1962–July 1963.

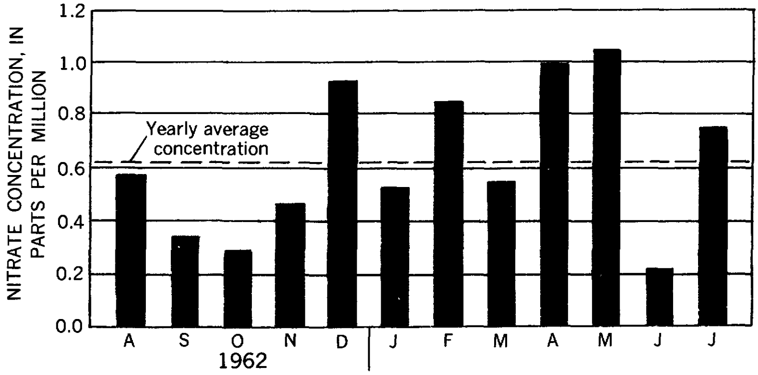

FIGURE 25.—Monthly average NO_3^{-1} concentration in rainfall, August 1962–July 1963.

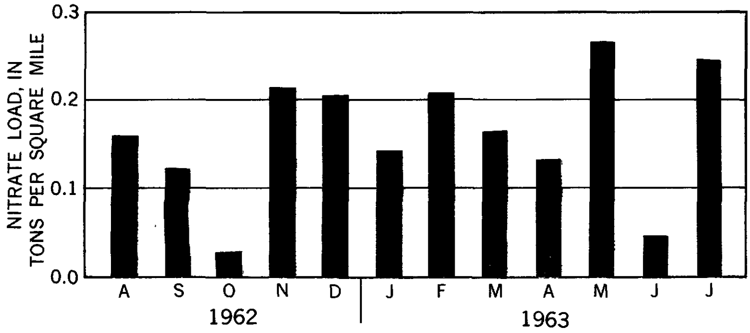

FIGURE 26.—Monthly average NO_3^{-1} loads in rainfall, August 1962–July 1963.

The data on month-to-month variations, shown in figures 25 and 26, are of questionable reliability. The information is presented primarily to allow very general comparison with similar data on the other constituents.

SOURCES OF NITRATE

Most NO_3^{-1} in rainfall is generally presumed to be derived from gaseous compounds. Nitrogen dioxide appears most likely as the primary source. Some particulate sources of NO_3^{-1} exist, such as compounds from industrial processes, commercial fertilizers, and soil dust, but these are not normally of great significance.

Several theories have been offered to explain the origin of NO_2. At one time the most commonly accepted theory was that NO_2 was produced by lightning fixing large quantities of atmospheric nitrogen and that this was the source for much of the NO_3^{-1} in rainfall. However, it gradually became apparent that this process could not be of great importance on a global scale. Investigations by Junge (1958), Viemeister (1960), Wetselaar and Hutton (1963), and others have shown little apparent correlation between the occurrence of thunderstorms and the NO_3^{-1} content of rainfall. Data presented by Gambell and Fisher (1964) showed that NO_3^{-1}/SO_4^{-2} ratios remained almost constant during several thunderstorms. This suggests that both constituents originate in a similar manner and thereby eliminates lightning as a significant source of NO_3^{-1}.

Both the areal distribution and the seasonal patterns shown by the network NO_3^{-1} data tend to discount the influence of lightning.

Virtanen (1952) suggested the possibility of photochemical production of nitrogen oxides in the stratosphere, subsequent diffusion to the troposphere, and eventual assimilation in rainfall as NO_3^{-1}. However, as noted by Junge (1958), this explanation does not appear entirely adequate because the NO_3^{-1} content of rainfall is generally lowest over the ocean and highest over land, suggesting that its occurrence is largely associated with land areas.

The persistence of certain patterns of areal distribution over the network in summer months also suggests that the occurrence of NO_3^{-1} is associated with certain geographical areas.

Junge (1958) suggested that the occurrence of NO_3^{-1} is tied closely to natural processes associated with the soil. Junge noted that decay of organic matter under alkaline soil conditions will release NH_3 to the atmosphere. Oxidation of this NH_3 might explain the presence of NO_3^{-1} in rainfall. A second possibility suggested by Junge is that NO_3^{-1} might originate from nitrogen oxides released directly to the atmosphere by decaying organic matter. Under acid conditions the anaerobic decomposition of certain organic matter releases NO to the atmosphere, which would be rapidly air oxidized to NO_2.

The difficulty with Junge's theory concerns seasonal variation. The microorganisms that cause decay respond markedly to temperature changes. Low temperatures inhibit decay, high temperatures accelerate it. Hence production of gaseous nitrogen compounds by this decay would be at a minimum in winter. If any seasonal variation is apparent in figure 25, it is for higher, not lower, NO_3^{-1} concentrations in winter.

Another possibility is that the NO_3^{-1} is being derived from the gaseous compounds associated with industrial effluents. It is known that nitrogen oxides are formed by high-temperature combustion processes, and that a number of common industrial chemical processes add gaseous nitrogen compounds to the atmosphere. But again, as with SO_4^{-2}, the study area does not appear to be sufficiently industrialized to account for more than a small part of the observed NO_3^{-1}.

Hence, no single present theory seems adequate to explain the characteristics shown by the network NO_3^{-1} data. The occurrence of stagnant airmasses must play a significant part in the distribution, but several features—particularly the sharp discontinuity between the east and west parts of the network in summer—must result from other factors. Despite attempts to identify significant soil or cultural differences in the vicinity of the discontinuity, no satisfactory explanation has been found. The reliability of the data from this study might be suspected, and yet the data of Junge (1958) show the same general features for this area.

It may be that the processes which form NO_3^{-1} are more intricate than previously thought, the NO_3^{-1} resulting from the complex interaction of a number of atmospheric constituents. The general similarity in the distribution of excess SO_4^{-2} (fig. 18) and the distribution of NO_3^{-1} (fig. 24) suggests a relation, but this could result from meteorologic conditions and the fact that both constituents are derived from gaseous compounds.

Complete data on NH_4^{+1} concentrations are not available because of analytical difficulties experienced early in the study. This fact is unfortunate because of the possibility of a relation between NH_4^{+1} and NO_3^{-1}.

The data obtained showed very low concentrations, generally less than 0.05 ppm. However, the available data are insufficient to permit any conclusions regarding seasonal and areal variations.

SUMMARY AND CONCLUSIONS

The data are summarized in table 3.

TABLE 3.—*Summary of data for the five-basin study area, August 1962–July 1963*

Ion	Range of monthly average concentrations (ppm)		Yearly average concentration (ppm)	Yearly average load (tons per sq mi)
	High	Low		
Cl^{-1}	1.1	0.1	0.57	1.8
Ca^{+2}	1.2	.2	.65	2.0
Na^{+1}	1.1	.3	.56	1.7
Mg^{+2}	.2	.1	.14	.6
K^{+1}	.3	.1	.11	.4
SO_4^{-2}	3.2	1.1	2.18	6.7
NO_3^{-1}	1.0	.2	.62	1.9

It was noted in the preceding discussion that the yearly average data of Junge and Gustafson (1957), Junge and Werby (1958), and Junge (1958)—although very general—are verified quite well by data collected in this study. The earlier data excluded dry fallout and the present data does not, so it might be concluded that the contribution of soluble material from dry fallout is comparatively small. The overall coherence of the data also indicates this. Large contributions from dry fallout would create local anomalies in the areal-distribution patterns, but with few exceptions such anomalies were not apparent. Calcium data were probably affected to a greater extent than other data, but even with Ca^{+2} this problem did not appear to be of great concern.

The general agreement with the earlier data also implies that the average composition of rainfall in this area does not vary greatly from year to year.

The average monthly concentrations of most ions considered appear to follow generally predictable seasonal trends. Most of these same trends should be common to precipitation along much of the Atlantic seaboard because many of the same factors, meteorologic and otherwise, apply.

Considerable uncertainty still surrounds the occurrence of SO_4^{-2} and NO_3^{-1}. The importance of man's activities versus natural processes as the source for SO_4^{-2} and NO_3^{-1} is not clear, and this remains a serious obstacle to understanding other factors involved. There seems to be a possibility that the occurrence of SO_4^{-2} and NO_3^{-1} are related, either through a common source or as a consequence of the chemical reactions that form these constituents. However, NO_3^{-1} data that are more reliable are necessary to prove or disprove this contention.

RELATION BETWEEN RAINFALL AND STREAM COMPOSITION

The importance of atmospheric contributions to the dissolved-solids content of dilute natural water has been stressed by Eriksson (1955), Hutchinson (1957), Gorham (1961), and others. However, direct measurements to determine quantitatively the role played by atmospheric sources are very scarce, particularly where stream water is concerned. Hence the present study was designed with one of the major objectives being to obtain comparable rainfall and stream composition data.

Within the study area there are four drainage areas for which stream discharge and stream chemical composition measurements are made on a daily basis. A comparison of the total ionic loads brought down in rainfall with the loads carried by the streams was made for these four areas shown in figure 27. Table 4 summarizes the pertinent stream data.

TABLE 4.—*Discharge data and average stream composition (discharge weighted), August 1, 1962–July 31, 1963*

[Results in parts per million except as indicated. U.S. Geol. Survey data]

Sampling location in North Carolina	Drainage area (sq mi)	Average discharge		NO_3^{-1}	SO_4^{-2}	Ca^{+2}	Mg^{+2}	Cl^{-1}	Na^{+1}	K^{+1}
		Long-term record [1] (cfs)	Study period (cfs)							
Neuse River near Goldsboro	2,390	2,537	2,565	1.6	6.3	4.1	1.5	8.0	7.5	1.9
Haw River at Bynum	1,280	------------	1,206	2.5	10.0	6.3	2.5	10.0	13.0	2.2
Deep River at Moncure	1,412	1,441	1,182	2.0	6.5	4.6	1.8	5.8	6.5	1.5
Tar River at Tarboro	2,140	2,312	1,828	1.0	6.1	4.7	1.6	6.5	6.3	1.8

[1] Based on 33 years of record, or more.

Figure 28 shows rainfall loads and corresponding stream loads in the four-basin area.

The stream loads, computed from daily measurements made throughout the study period, generally can be considered accurate within plus or minus 10 percent. The rainfall loads are less reliable, but probably can be considered accurate within plus or minus 20 percent.

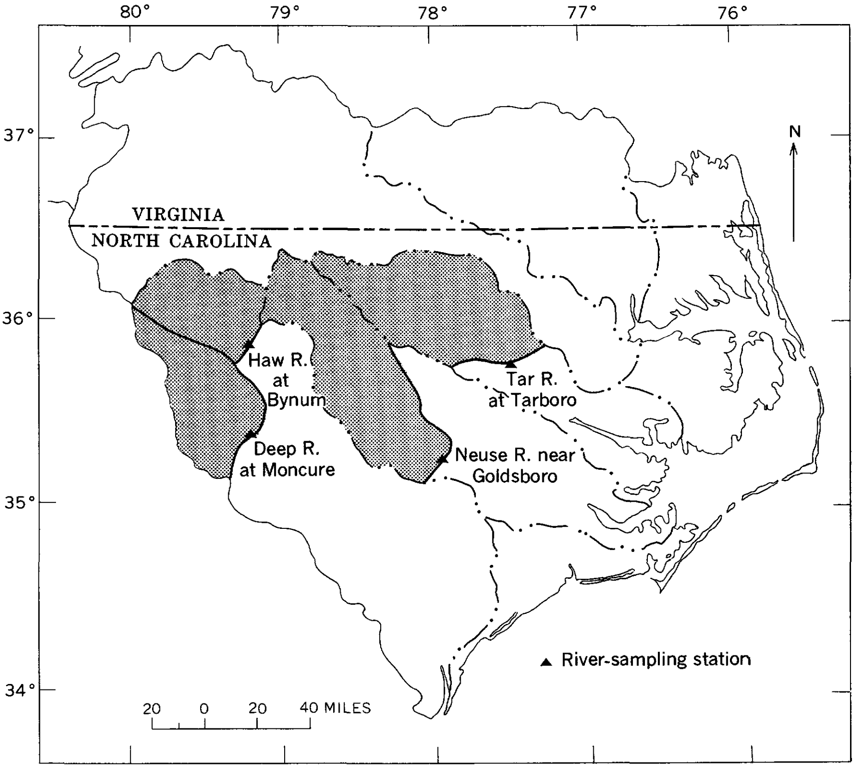

FIGURE 27.—Drainage areas (shaded) for which comparison was made between rainfall composition and stream composition.

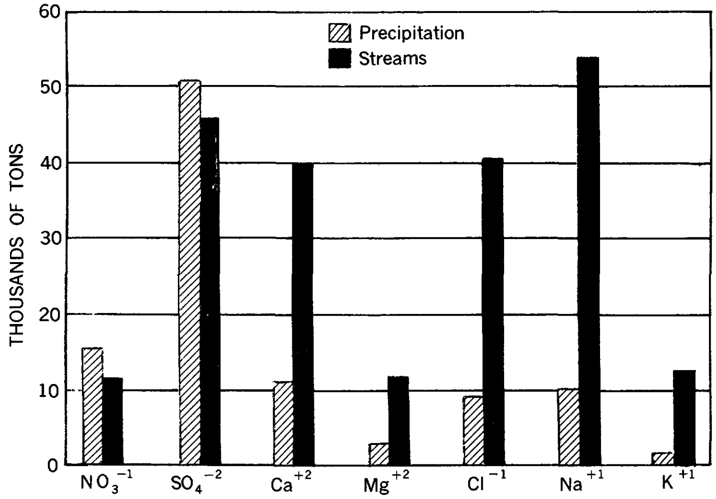

FIGURE 28.—Comparison of loads contributed by rainfall with loads carried by streams draining the areas shown in figure 27, August 1962–July 1963.

The stated limits of accuracy do not apply to NO_3^{-1}. Because of problems of sample preservation, discussd previously, the reliability of the NO_3^{-1} data is uncertain.

DISCUSSION

The following analysis makes no attempt to separate the contribution to the streams made by direct runoff from the contribution made by ground-water inflow. This gross approach is justified if it can be assumed that:

1. All the water passing the discharge-measuring stations is supplied by rain falling within the drainage boundaries of the respective drainage areas;
2. No significant amount of water leaves the basins in liquid form other than by means of the stream channels; and
3. The study period is an average year with respect to rainfall and streamflow.

The four drainage areas lie almost entirely within the Piedmont province. With the exception of a very small percentage of sedimentary rocks in the easternmost parts, the drainage areas are underlain by crystalline rocks. In general these are dense slates, granites, and similar rocks. The rocks are not highly fractured, nor in general does the fracturing appear to extend to great depth. LeGrand (1958) estimated that in this area the linear distance between the point where a drop of water reaches the water table and the point where it is discharged at a spring or seepage area is almost everywhere less than a mile, and commonly less than half a mile. Thus, insofar as it is possible to determine, the first two assumptions—implying no appreciable ground-water flow into or out of the drainage areas—are probably justified.

As to the third assumption, rainfall amounts were slightly below established yearly normals in the northwestern part of the network; however, for the area as a whole, and for the four drainage areas shown in figure 27 in particular, rainfall was near normal. Table 4 indicates that streamflow was near the median value for one drainage area and slightly below median for two others. Thus, with respect to streamflow as well as to rainfall, the study period was close to established normals, and hence the contributions of rainfall to observed stream composition should be reasonably good average values. Moreover, since most other streams in the area are similar in composition to the four studied, the observed relations between rainfall composition and stream composition are probably valid over a large part of the total network area.

Several features of figure 28 are of particular interest. First, it is apparent that the amount of dissolved solids contributed by rainfall is very significant, totalling almost one-half the amount of dissolved solids (excluding bicarbonate) carried by the streams. Obviously any attempt to understand geochemical controls on water quality in an area of dilute water such as this must take into account the dissolved material contributed by the atmosphere.

Second, the data indicate that rainfall supplied more SO_4^{-2} and NO_3^{-1} than were carried by the streams. The apparent loss of SO_4^{-2} and NO_3^{-1} could be explained by errors within the overall estimate of reliability for the data. However, this would not diminish the significance of the general relationship shown. Figure 28 considers only one of several sources for SO_4^{-2} and NO_3^{-1} in the streams. Presumably some SO_4^{-2} is derived from leaching of soils and rocks. An additional source of SO_4^{-2} and also NO_3^{-1} is commercial fertilizers, which are used extensively in the area. A part of the fertilizers is lost by leaching and eventually appears in the streams. Some SO_4^{-2} and NO_3^{-1} from pollution might also be assumed, so that undoubtedly the disparity between the total SO_4^{-2} and NO_3^{-1} supplied from all sources and that carried by the streams is much greater than indicated in figure 28.

With regard to SO_4^{-2}, Laney (1965) found a similar relationship between rainfall and ground-water composition in the Blue Ridge province of North Carolina, west of the network area. The SO_4^{-2} concentration of 33 rainfall samples averaged 2.0 ppm whereas the average SO_4^{-2} concentration in ground-water samples was only 0.4 ppm.

Several explanations might account for the loss of SO_4^{-2} and NO_3^{-1}. Laney suggested that the loss of SO_4^{-2} in the Blue Ridge province may result from anion exchange with clay minerals. Mattson, as quoted by Bear (1955), indicated that the SO_4^{-2} adsorption capacity of kaolinitic clays under suitable conditions of pH can be fairly substantial.

However, the essential role of sulfur as a plant nutrient is well established so that loss of SO_4^{-2} could easily be explained by plant consumption. The fact that the soils of the study area are heavily leached and from an agricultural standpoint are sulfur deficient makes this explanation very plausible. The sulfur utilized for plant nutrition is incorporated in the structure of the plant. Ultimate decay releases the sulfur—some to the soil and some to the atmosphere in gaseous form. A part of the sulfur returned to the soil must ultimately find its way into the streams, but the gaseous sulfur is completely removed from the soil-water system. Some sulfur incorporated in plants is also removed from the system in the harvesting of crop plants.

Direct bacterial reduction of the SO_4^{-2} with subsequent loss as H_2S is a third possibility. Presumably some sulfur is lost in this manner, but the importance of this process is difficult to estimate.

To summarize, the role of plants certainly must be important in explaining the SO_4^{-2} data in figure 28, but other factors, such as SO_4^{-2}

adsorption by clays and direct bacterial reduction of SO_4^{-2}, cannot be entirely discounted.

With regard to NO_3^{-1}, many of the same considerations stated for SO_4^{-2} apply. Nitrate is readily reduced or assimilated by many types of micro-organisms and nitrogen compounds are vital as plant nutrients. Loss of nitrogen compounds to the atmosphere in gaseous form is a well-accepted part of the nitrogen cycle.

Another interesting feature shown in figure 28 concerns Cl^{-1}. The data indicate that rainfall contributed an amount slightly less than one-quarter of the total Cl^{-1} load carried by the streams. This observation deserves some discussion because the atmosphere has been suggested as the primary source of Cl^{-1} in many inland waters.

Since the Cl^{-1} content of most rocks is low, Eriksson (1955) and others have concluded that most Cl^{-1} in river water is of atmospheric origin. Eriksson plotted yearly average Cl^{-1} discharge for a number of rivers over the Eastern United States. His data, supplemented by that of Jackson (1905), showed an approximate logarithmic decrease from the coast inland; this decrease was offered as evidence for the atmospheric origin of Cl^{-1}.

It was noted, however, that the amounts of Cl^{-1} usually observed in rainfall are inadequate to account for the quantities carried by the rivers. To account for the difference, Eriksson suggested that sea-salt particles are "combed" from the atmosphere by vegetation. Spruce and pine needles were suggested as very effective objects for such capture of particulate Cl^{-1}. Rain would then wash the particles from the vegetation and thus carry Cl^{-1} (and other ions) to the rivers.

Very likely some of the Cl^{-1} in the streams of the study area is supplied through this mechanism of vegetative capture. Still, it would seem that only a small percentage of the necessary amount could be accounted for in this manner because of meteorologic considerations. Air passing over the study area usually contains low sea-salt concentrations because prevailing winds are from the west—dictating an overland trajectory. When strong circulation off the ocean does occur, it is frequently accompanied by precipitation. The effect of atmospheric turbulence, discussed previously (p. K10), is also a very important consideration; increased vertical mixing over land reduces sea-salt concentrations in lower layers of the atmosphere and thereby greatly limits the quantity available to vegetation.

Thus it appears that nonatmospheric sources must supply the major portion of the Cl^{-1} to the streams. Pollution, addition of highly mineralized connate water from deep ground-water circulation, and rock weathering must be considered as possible explanations for the bulk of the stream Cl^{-1} load. Of these three, rock weathering appears to be the most reasonable explanation. Pollution of any great significance is not indicated in any of the streams nor does the geology of the area support the explanation concerning deep ground-water circulation.

Because crystalline rocks are supposedly very poor sources of Cl^{-1}, the preceding conclusion may be questioned. However, the total quantity of Cl^{-1} at issue is not great; and despite prevailing views on the subject, very little is actually known about the sources that may release Cl^{-1} from crystalline or sedimentary rocks. These sources may be somewhat underestimated.

It is noteworthy that the rocks of the study area are rich in the mineral biotite—the most common rock-forming mineral known to contain significant amounts of chloride. This may well be the major source of the Cl^{-1} in the streams.

The logarithmic decrease in stream Cl^{-1} loads with increasing distance from the coast inland, shown by Eriksson's data, might be explained by geology. Excluding New England, bedrock along the immediate Atlantic coast is sedimentary. Inland, however, are the crystalline rocks of the Appalachian Highlands. The sedimentary rock, having been deposited under marine environment, would be expected to contain relatively greater amounts of soluble chloride. Hence, a broad-scale trend of decreasing Cl^{-1} discharge with increasing distance inland might reasonably be expected on the basis of rock type. This trend would be reinforced by, but would not be solely the result of, Cl^{-1} from atmospheric sources.

New England presents a different situation in that the entire area is underlain by crystalline rocks. But the area is unique from a meteorologic standpoint because a large number of the major storm systems moving across the United States pass over, or very near, New England. As a consequence, precipitation falling on the area is often accompanied by strong flow off the ocean. Thus, atmospheric Cl^{-1} probably plays a much greater role in this area. But again it may be unwise to completely dismiss the possibility of significant contribution as a result of rock weathering.

CONCLUSIONS

This investigation very concretely reinforces some of the previously stated views regarding the overall importance of the atmosphere as a source for dissolved material in dilute natural water. It also points up graphically the complexity of the relations between rainfall and stream composition. Chemical denudation, biological processes, uptake of mineral nutrients by living plants and release by decaying plant matter, and ion exchange in soil minerals all serve to supplement or alter the original ionic composition of rainfall. It is seldom possible to consider any one of these processes without simultaneous consideration of the others.

Further studies involving the monitoring of rainfall and stream composition over small carefully selected drainage areas would be desirable. The relationships suggested, particularly concerning SO_4^{-2}, NO_3^{-1}, and Cl^{-1} need to be studied in greater detail. Similar data for longer periods of time and from other environments would be very helpful in this regard. Selection of drainage areas with careful regard for geology and climate as well as stream composition could impose the controls necessary to adequately explore the major factors involved.

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