

Annual Variations in
Chemical Composition of
Atmospheric Precipitation
Eastern North Carolina and
Southeastern Virginia

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Annual Variations in Chemical Composition of Atmospheric Precipitation Eastern North Carolina and Southeastern Virginia

By DONALD W. FISHER

G E O C H E M I S T R Y O F W A T E R

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*Results are presented of
chemical analyses of monthly
atmospheric precipitation samples
from 12 collection sites over
a 2-year period*



UNITED STATES DEPARTMENT OF THE INTERIOR

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GEOLOGICAL SURVEY

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GEOCHEMISTRY OF WATER

ANNUAL VARIATIONS IN CHEMICAL COMPOSITION OF ATMOSPHERIC PRECIPITATION, EASTERN NORTH CAROLINA AND SOUTHEASTERN VIRGINIA

By DONALD W. FISHER

ABSTRACT

A 2-year study of precipitation composition over eastern North Carolina and southeastern Virginia has been completed. Chemical analyses were made of the major ions in monthly rainfall samples from each of 12 sampling locations. Areal and seasonal distributions were determined for chloride, calcium, magnesium, sodium, potassium, sulfate, and nitrate.

Annual changes in loads and in geographical distribution of sulfate and of nitrate are small. Yearly rainfall sulfate loads amount to approximately 7 tons per square mile, whereas deposition of nitrate is about 2 tons per square mile per year in the interior of the network and less near the coast.

Areal patterns of chloride content are consistent with the assumption that the ocean is the only major source of rainfall chloride in the area. Chloride loads were 2.1 and 1.8 tons per square mile per year; the difference can be attributed to meteorological conditions.

Cation concentrations in network precipitation appear to depend on localized sources, probably soil dust. Annual loads of the major cations are approximately 2 tons per square mile of calcium, 1.8 tons per square mile of sodium, 0.5 ton per square mile of magnesium, and 0.3 ton per square mile of potassium; considerable year-to-year differences were noted in these values.

Bicarbonate and hydrogen ion in network rainfall are closely related to the relative concentrations of sulfate and calcium. Apparently, reaction of an acidic sulfur-containing aerosol with an alkaline calcium source is one of the principal controls on precipitation alkalinity and pH.

Ions in precipitation contribute substantially to the quality of surface water in the network area. Comparisons between precipitation input and stream export of ions for four North Carolina rivers show that rainfall sulfate is equal to sulfate discharged, whereas nitrate in rain slightly exceeds stream nitrate. Contributions of cations to the streams by way of precipitation range from about 20 percent for potassium to almost 50 percent for calcium.

Chloride deposited by precipitation amounts to about one-fourth of the stream load. Additions of manufactured salt may account for much of the remainder of the surface-water load.

INTRODUCTION

Many investigations have demonstrated the importance of atmospheric precipitation as a source of considerable quantities of water-soluble matter. In areas where surface water is dilute, rainfall can provide a substantial part of the total dissolved solids carried by streams. Quantitative knowledge of this rain-derived part is one prerequisite to better understanding of the natural quality of surface water.

In July 1962 a program of sampling and chemical analysis of rainfall was started in order to determine composition patterns and contributions from precipitation to dissolved-solids loads of streams in the mid-Atlantic States. A network of precipitation-collection stations was established in a 34,000-square-mile area of eastern North Carolina and southeastern Virginia. Chemical determinations were made of the major ions in monthly samples from each collection site, and total loads were calculated from the analytical data together with records of precipitation.

Results of 1 year of operation of the network were compiled and evaluated in an earlier report (Gambell and Fisher, 1966). Operation of 12 of the collection stations was continued to provide data on year-to-year fluctuations in deposition of ions by precipitation over the region. A summary of findings after 2 years of operation of the sampling network is the subject of the present report.

ACKNOWLEDGMENTS

The author is indebted to Arlo W. Gambell for the original design and installation of the sampling network. The assistance of the U.S. Weather Bureau cooperative observers in operation of the network is also gratefully acknowledged. J. H. Feth and Hugh Wilder of the U.S. Geological Survey contributed helpful, critical reviews of the manuscript.

PRECIPITATION-COLLECTION NETWORK

The study region includes a large part of the piedmont and coastal plains of North Carolina and southern Virginia. Five major rivers (Chowan, Roanoke, Tar, Neuse, and Cape Fear), which have a combined drainage area of 34,100 square miles, flow through the area. Drainage boundaries of these rivers are outlined in figure 1.

Choice of the sampling locations indicated in figure 1 was restricted by the need for accurate rainfall measurements in load computations. The samplers were therefore installed near existing Weather Bureau rain gages, for which daily precipitation data are available. The Weather Bureau's cooperative observers were responsible for the main-

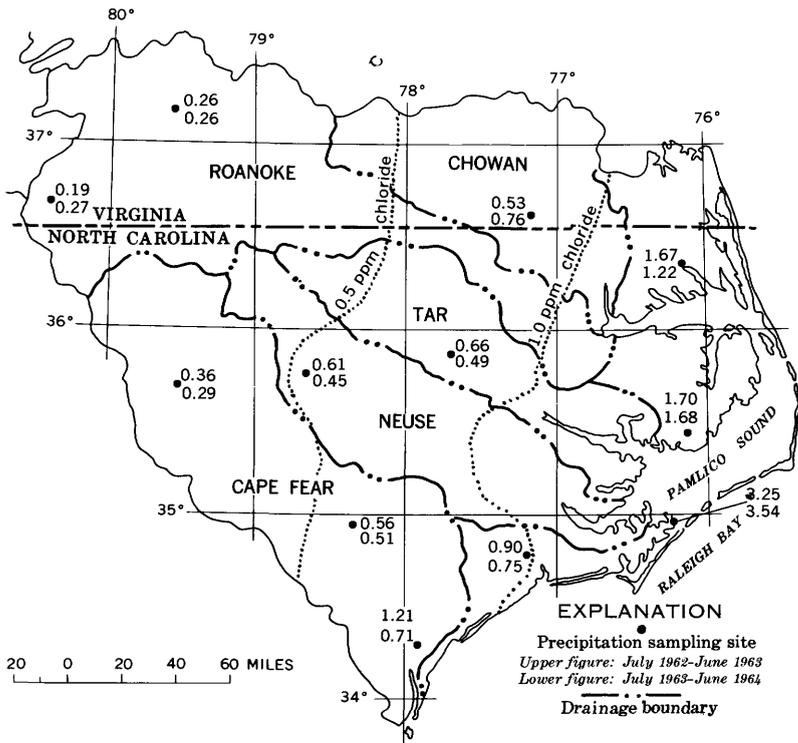


FIGURE 1.—Precipitation sampling area showing river basins, location of sampling sites, and annual chloride concentrations, in parts per million, in rainfall, July 1962-June 1964.

tenance of the samplers and for the collection and shipment of precipitation samples for chemical analysis.

PRECIPITATION-COLLECTION APPARATUS

A detailed description of the collector was presented in a previous report (Gambell and Fisher, 1966). Briefly, the apparatus consists of a Pyrex glass funnel with a Pyrex wool filter plug in the neck. Rain caught by the funnel filters through the glass wool plug, then through a polyvinyl chloride drain tube. The drain tube and a capillary air vent extend through a plastic stopper into a polyethylene collection bottle. Sizes of the tubes are kept as small as possible and the stopper is left in place during the collection period in order to minimize atmospheric contamination and evaporative concentration of the samples.

An insulated aluminum ice chest fastened to a 4- by 4-inch vertical post houses the collection bottle and provides a mounting base for the funnel. A ring of aluminum spikes surrounding the funnel serves as an effective bird-deterrent (Egnér and others, 1949), and a thermo-

statically controlled light bulb maintains temperatures above freezing inside the ice chest and facilitates snow collection by warming the base of the funnel.

ANALYTICAL METHODS

Methods used for the analysis of precipitation samples are described in detail in earlier reports (Gambell and Fisher, 1964 and 1966). 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 determinations made spectrophotometrically at 400 m μ (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: Eriochrome Black T spectrophotometric procedure using a buffer solution suggested by Pollard and Martin (1956).

Hydrogen ion: Calculated from pH measurement.

Bicarbonate: Potentiometric titration with standard acid.

RAINFALL COMPOSITION

TREATMENT OF THE DATA

Areal distributions of ionic rainfall constituents are presented as average annual concentrations in parts per million. These concentrations were determined from individual monthly sample analyses, weighted according to the amount of precipitation.

Seasonal distributions of ion loads were estimated by the Thiessen polygon method applied to precipitation-weighted analytical data. The results, expressed in units of tons per square mile, apply to most of the area within the drainage boundaries outlined in figure 1.

CHLORIDE

Geographical distribution of chloride concentrations for two annual cycles is shown in figure 1. Considerable year-to-year differences are apparent for some stations; however, the trend of decreasing chloride inland from the coast is fixed. Chloride concentrations in excess of 0.5 ppm are confined to areas within about 100 miles of the coast, whereas average values greater than 1 ppm occur only near the ocean or large estuaries.

Figure 2 indicates the monthly distribution of chloride in rainfall

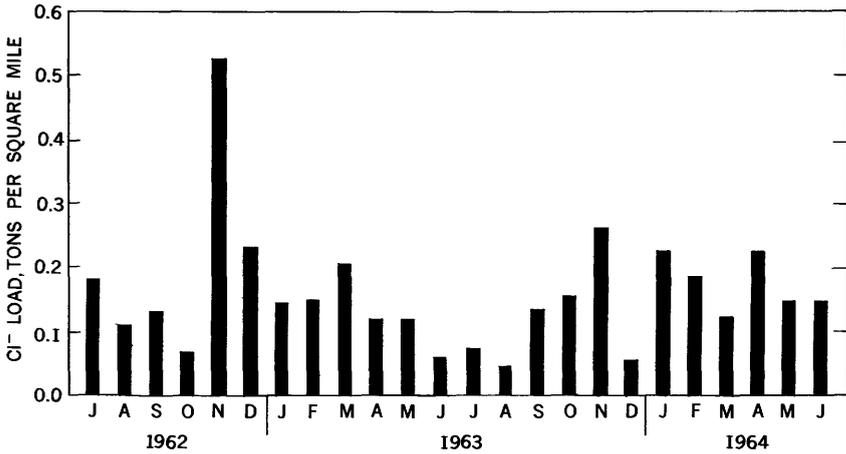


FIGURE 2.—Monthly average chloride loads in rainfall, July 1962–June 1964.

over the area during the study period. Maximum loads were deposited in November of each year; lesser amounts of chloride, usually less than 0.15 ton per square mile, were deposited during each of the summer months.

Several investigations of the effects of meteorological conditions on rainfall composition (Rossby and Egnér, 1955; Gorham, 1955; Junge and Werby, 1958) have demonstrated that sea salts and industrial effluents are the major sources of atmospheric chloride in humid regions bordering the Atlantic Ocean. North Carolina and southern Virginia, however, are not highly industrialized; thus, the ocean is probably the only major source of rainfall chloride in the network area. The consistent pattern of areal distribution noted in figure 1 tends to strengthen this conclusion.

On the other hand, the data in figure 2 show that the deposition of chloride is far from uniform. Variations in meteorological parameters must be considered in accounting for seasonal and annual differences in chloride deposition. Gambell and Fisher (1966) discussed the importance of some of these parameters. In general, centers of major summer storms remain to the north of the network, a phenomenon which induces westerly air movement and little deposition of sea salts over the area. In contrast, winter storms are often accompanied by flow of air off the ocean, which results in the delivery of large quantities of chloride in precipitation. Another important factor affecting sea-salt aerosol concentrations is wind speed. Woodcock (1953) found that the amount of marine aerosols increases exponentially with an increase in wind speed.

The above-mentioned meteorological considerations explain qualitative features of the chloride load distribution shown in figure 2. The

effect of high wind velocity off the ocean accounts for the extremely high value of November 1962. During that month a single "northeaster" dropped almost 4 inches of rain over the entire network. Wind data for the storm period at the Raleigh-Durham Airport indicate a sustained average wind speed of 16.3 miles per hour from the east-northeast. As a result very high chloride loads were found in network rainfall for the month.

A different meteorological situation prevailed in November 1963. Although total monthly precipitation was about the same as that of November 1962 (fig. 3), most of it was associated with westerly winds, a situation which resulted in much smaller chloride loads.

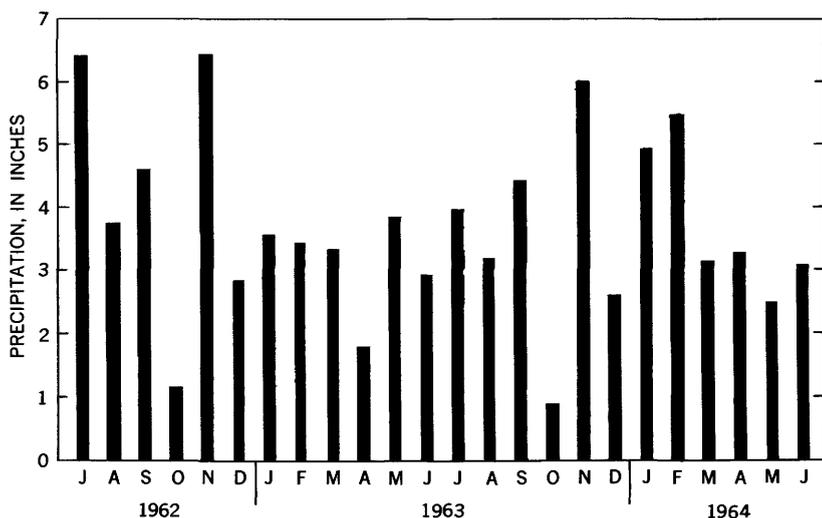


FIGURE 3.—Monthly average precipitation, July 1962–June 1964.

Total chloride loads amounted to 2.10 and 1.80 tons per square mile per year for the two annual cycles. The single intense "northeaster" mentioned above probably deposited at least 0.3 ton per square mile, an amount equal to the difference between annual values.

CALCIUM, MAGNESIUM, SODIUM, AND POTASSIUM

Annual rainfall inputs of the four common cations are listed in table 1. Considerable differences in yearly values are evident for each of the ions. On the other hand, the order does not change; calcium is the principal cation, followed by sodium, magnesium, and potassium.

Concentrations of sodium, the major cation in ocean water, should vary geographically as chloride does, provided the sodium is derived primarily from marine aerosols. Average concentrations of sodium

TABLE 1.—Annual precipitation loads of the common cations

Cation	Annual load (tons per square mile)	
	July 1962-June 1963	July 1963-June 1964
Ca ⁺⁺ -----	2. 24	1. 76
Mg ⁺⁺ -----	. 53	. 42
Na ⁺ -----	1. 99	1. 46
K ⁺ -----	. 35	. 26

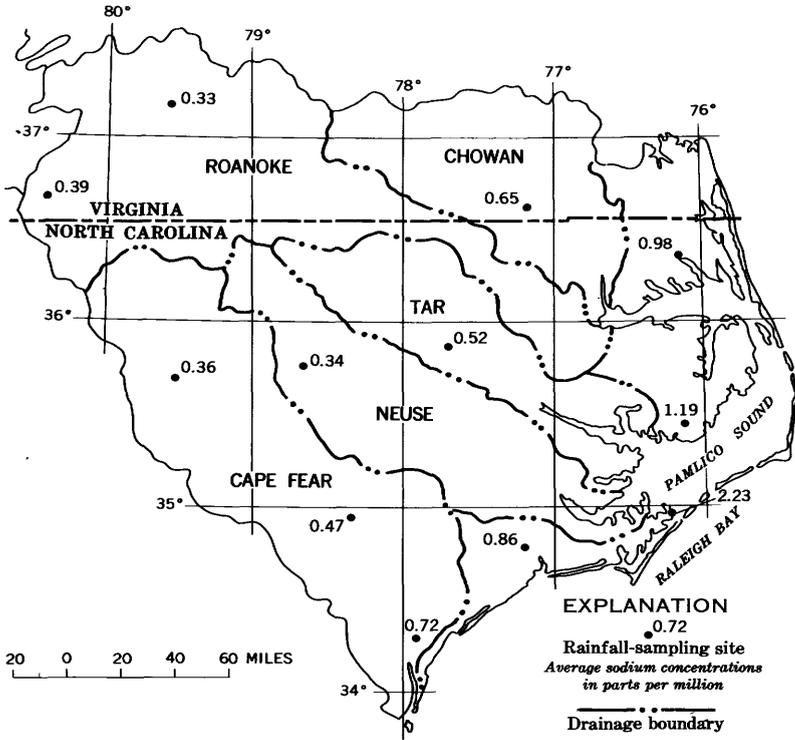


FIGURE 4.—Two-year average sodium concentrations in rainfall, July 1962-June 1964.

over the 2-year period are plotted in figure 4. A general westward decrease in concentration is apparent; however, the ratio of sodium to chloride is distinctly higher than the average sea-water composition ratio of 0.55. This variation indicates the existence of another source of sodium in rainfall.

A "sea-salt" sodium concentration was calculated from the chloride values for each of the network stations. Differences between the resulting values and total sodium concentrations are shown as "excess"

sodium in figure 5. Two-year average potassium concentrations are also plotted in figure 5.

The data in figure 6 represent 2-year average concentrations of calcium and of "excess" magnesium. Excess magnesium values were determined in the same manner as the excess sodium concentrations.

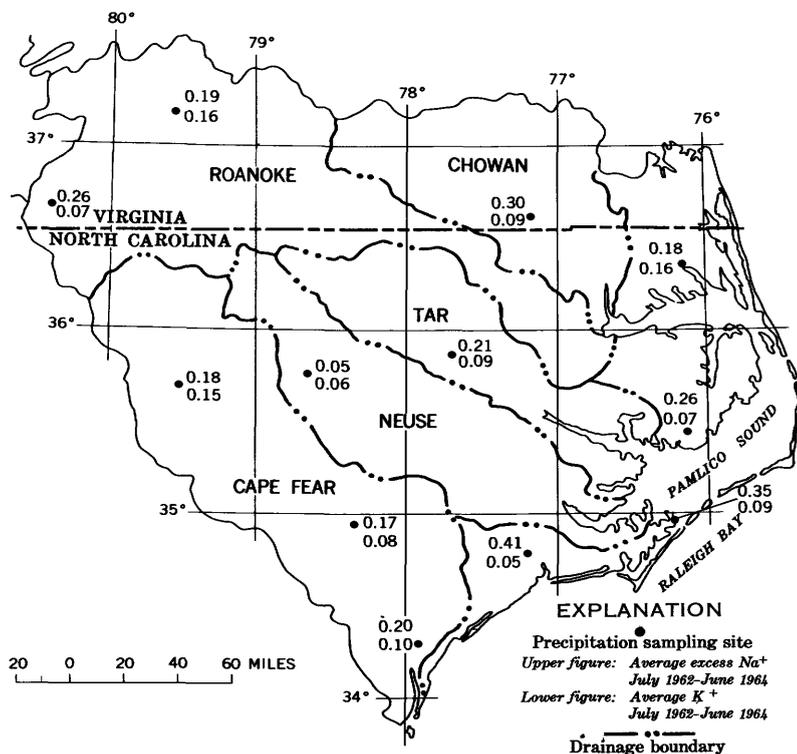


FIGURE 5.—Two-year average concentrations, in parts per million, of excess sodium and of potassium in rainfall, July 1962–June 1964.

No systematic geographical trends are apparent in figures 5 and 6. Precipitation compositions from one station in the northwest corner of the network are consistently high in calcium and magnesium, and calcium concentrations at the stations near the coast are also relatively high. With the exception of these persistent anomalies, average concentrations throughout the network during the 2-year period are as follows: calcium, approximately 0.5 ppm; excess sodium, about 0.25 ppm; and potassium and excess magnesium, each about 0.1 ppm. Individual station values are quite variable from 1 year to the next (some values differing by a factor of 2), and the higher concentrations appear to be localized geographically; hence the probable principal source of these cations is soil dust.

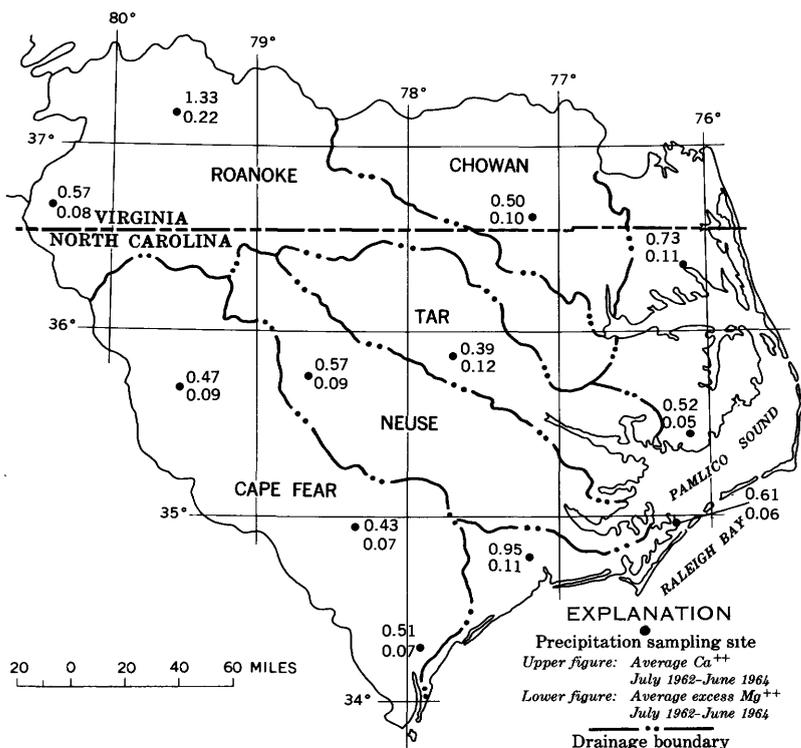


FIGURE 6.—Two-year average concentrations, in parts per million, of calcium and excess magnesium in rainfall, July 1962-June 1964.

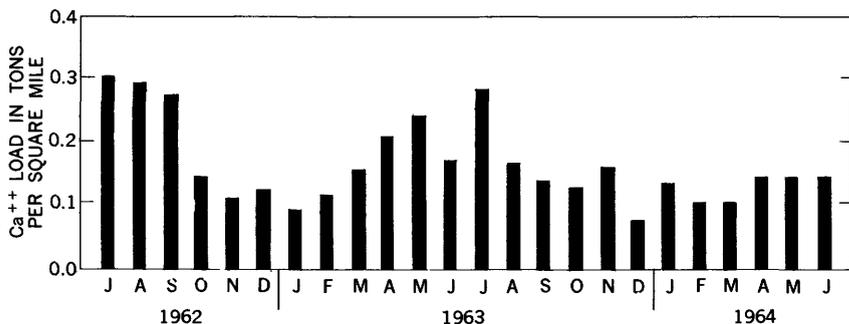


FIGURE 7.—Monthly average calcium loads in rainfall, July 1962-June 1964.

Monthly network input loads of calcium and of excess sodium are shown in figures 7 and 8, respectively. Maximum values occur during the summer, an observation consistent with the assumption of a soil-dust source. Seasonal trends in potassium and excess magnesium loads are similar to the calcium and excess sodium patterns.

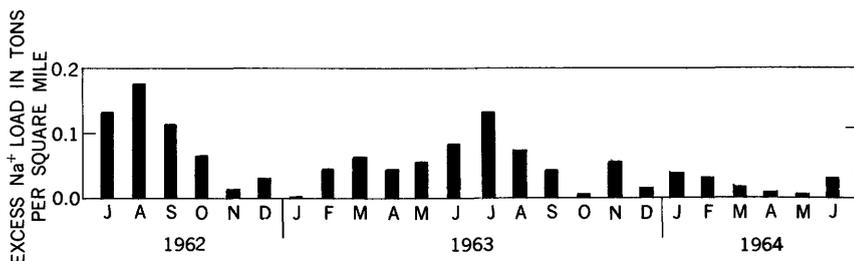


FIGURE 8.—Monthly average excess sodium loads in rainfall, July 1962–June 1964.

It should be emphasized that the composition values reported include a contribution from dry fallout. An estimate of the magnitude of this contribution to observed calcium in precipitation was obtained with the aid of an automatic collector designed to open only during precipitation. The automatic collector was operated side by side with one of the open samplers of the network, and monthly samples from both collectors were analyzed. Over a 21-month period, precipitation-weighted calcium concentrations from the open collector samples averaged 0.6 ppm; those from the automatic collector averaged 0.4 ppm, which is in good agreement with a value reported by Junge and Werby (1958). Thus, dry fallout accounted for approximately one-third of the total calcium in network precipitation at this station. Presumably, comparable ratios of dry fallout to total loads prevail throughout the network.

SULFATE

Sulfate is the dominant anion in precipitation over the network. Average "excess" sulfate concentrations for two annual cycles are shown in figure 9; values plotted were determined by subtracting the expected sea-salt component from total sulfate concentrations. Yearly averages for individual stations do not vary greatly. The most noticeable feature of the geographical pattern is a zone of relatively low excess sulfate concentrations in the southeastern part of the network area.

The seasonal distribution graph of excess sulfate (fig. 10) indicates pronounced maximums in July of each annual cycle. Such a distribution precludes the possibility of any simple dependence of rainfall sulfate on combustion of sulfur-bearing fuels. Although fuel consumption may well be an important source of atmospheric sulfur compounds, the data in figure 10 show that other factors predominate in controlling the deposition of sulfate in this network area.

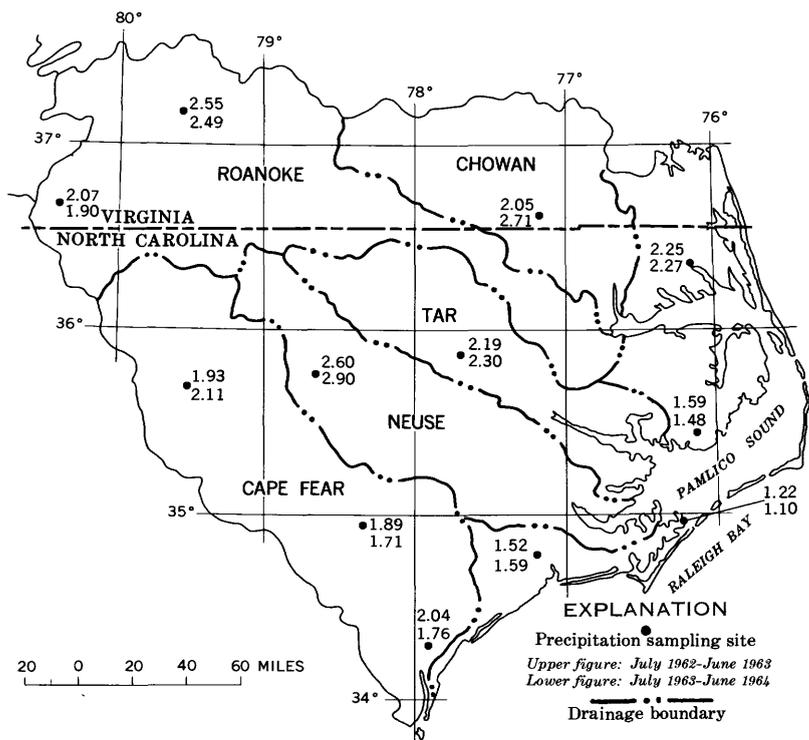


FIGURE 9.—Annual excess sulfate concentrations, in parts per million, in rainfall, July 1962–June 1964.

HYDROGEN ION

Seasonal hydrogen ion loads, estimated from pH measurements of precipitation samples, are shown in figure 11. Weights of hydrogen ion deposited are small in comparison with weights of the other cations considered. On the other hand, in terms of equivalents of cations contained in precipitation, hydrogen ion ranks third, with a 2-year total deposition approximately half as great as the calcium equivalents. Hydrogen ion is thus one of the major rainfall constituents in the network area.

Significant changes can occur in pH of precipitation samples as a result of biological activity during the time between collection and analysis. For this reason, the hydrogen ion loads shown in figure 11 are approximate values only; the accuracy of the load figures is considerably less than the accuracy of measurements of the other major precipitation constituents.

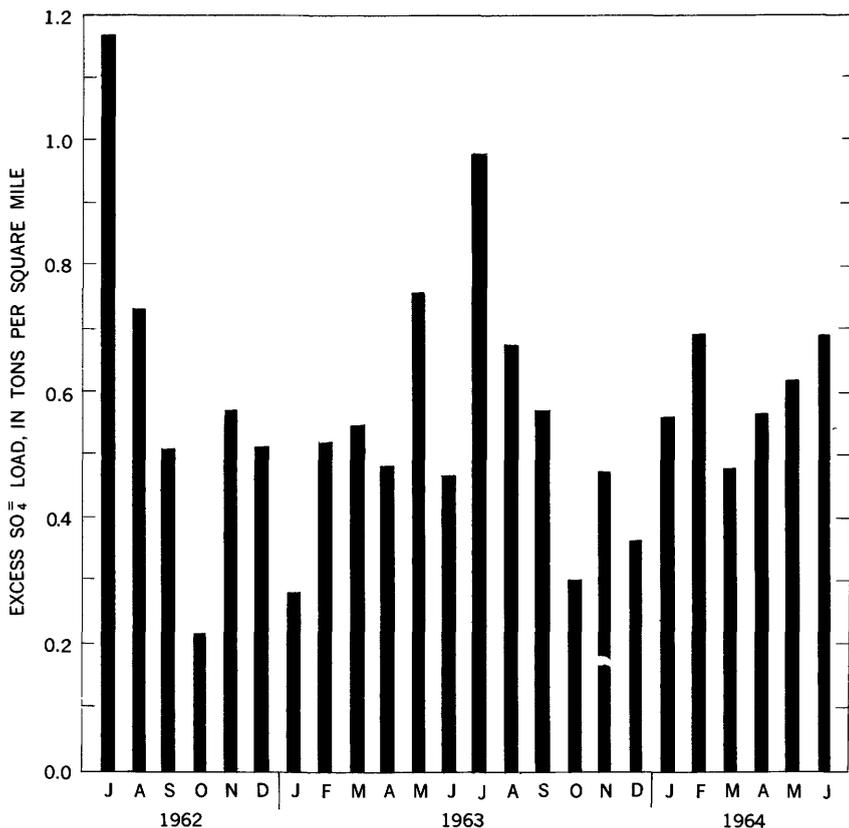


FIGURE 10.—Monthly average excess sulfate loads in rainfall, July 1962–June 1964.

RELATIONSHIPS BETWEEN ACIDITY, ALKALINITY, AND RELATIVE CONCENTRATIONS OF SULFATE AND CALCIUM

Rainfall on much of the study area is distinctly acidic. The source of this acidity has been attributed to sulfur compounds by several investigators, among them Conway (1942), Junge (1958), and Gambell and Fisher (1966). Sulfur oxides and hydrogen sulfide in the atmosphere will provide hydrogen ions upon oxidation and dissolution in water to form sulfuric acid. If these sulfur compounds are the principal source of rainfall acid and if all the sulfate in rain is derived from these oxides and hydrides, then hydrogen ion and sulfate should be present in equivalent amounts in precipitation.

M. D. Edwards, of the Geological Survey's Automatic Data Development Unit, made statistical analyses of the concentration data in order to establish the extent of interdependence of these ions. Data from the

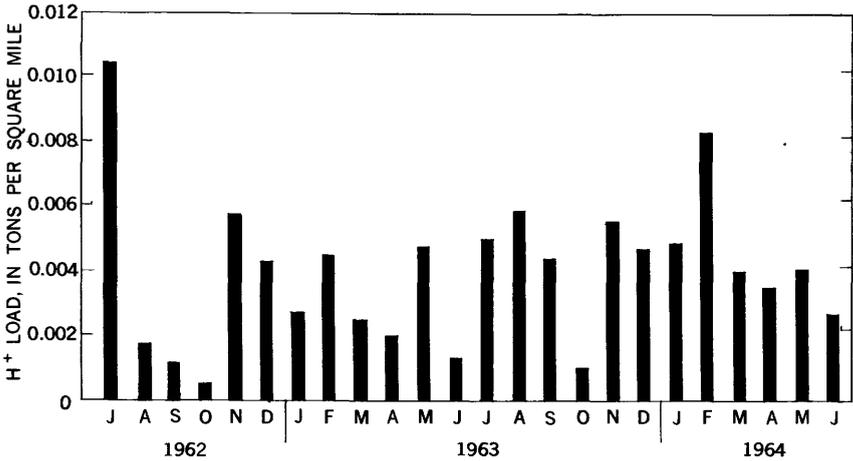


FIGURE 11.—Monthly average hydrogen ion loads in rainfall, July 1962–June 1964.

following types of samples were excluded from the statistical tests: (1) Samples with pH greater than 5 but of insufficient volume for bicarbonate determinations and (2) discolored samples and samples containing visible leaf litter, insects, or other gross organic contamination. All other samples were included in the statistical determinations. Results of these analyses indicate rather poor correlation of hydrogen ion with sulfate alone (correlation coefficient 0.535). However, a much closer correspondence of hydrogen ion with sulfate is obtained if the nonmarine metallic elements are considered. Thus, good correlation (coefficient 0.814) is found between hydrogen ion and sulfate–minus–calcium concentration in samples for which milliequivalents per liter sulfate exceed milliequivalents per liter calcium. Moreover, a comparable relationship (correlation coefficient 0.904) exists between bicarbonate ion concentration and calcium–minus–sulfate concentration for samples with calcium in excess of stoichiometrically equivalent sulfate. A similar correlation has been observed in Illinois rainfall by Larson and Hettick (1956); the general nature of this relationship has been suggested by Junge (1958). Individual sample data and the mean-square regression lines are plotted in figures 12 and 13.

The statistical relationships between hydrogen ion, bicarbonate, sulfate, and calcium in rainfall are quite convincing evidence for the conclusion that much of the sulfate is associated with an acidic source, whereas calcium-containing aerosols are predominantly alkaline. Thus, high sulfate and low calcium concentrations characterize the strongly acidic rain samples in which the acid sulfur-bearing aerosols have not been neutralized by alkaline soil dust. An excess of calcium relative

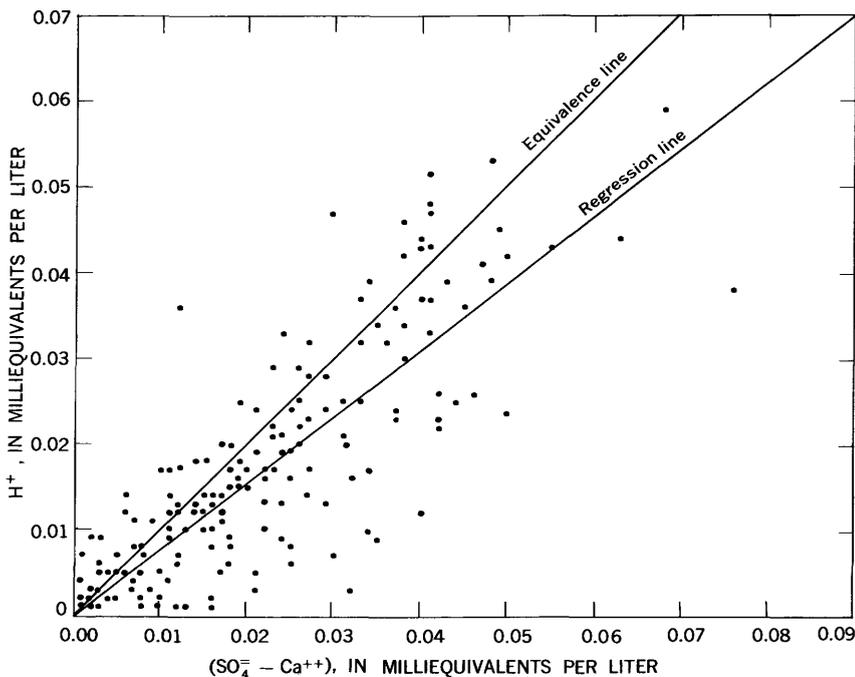


FIGURE 12.—Hydrogen ion versus sulfate-minus-calcium concentrations in samples of network precipitation; 189 observations.

to sulfate, that is, a preponderance of alkaline dust over acidic aerosols, is typical of samples high in bicarbonate. Deviation of the regression lines from stoichiometric equivalence (figs. 12 and 13) can be accounted for in part by the effects of cations not included in the statistical computations. Undoubtedly, potassium and excess sodium and magnesium accompany calcium as alkaline components of aerosols. These additional alkaline constituents would tend to decrease sample hydrogen ion concentration (or increase bicarbonate), thereby lowering the regression line slope in figure 12 (or increasing the regression line slope in fig. 13). The observed divergences of regression lines and equivalence lines are in the directions expected as a result of this effect.

The above considerations demonstrate the existence of at least two types of aerosols which are as important as the sea salts in determining rainfall composition and which appear to have a controlling influence on acidity and alkalinity throughout the network. Possibly the same types of aerosols, along with sea salts, are among the principal controls on rainfall chemistry in other areas.

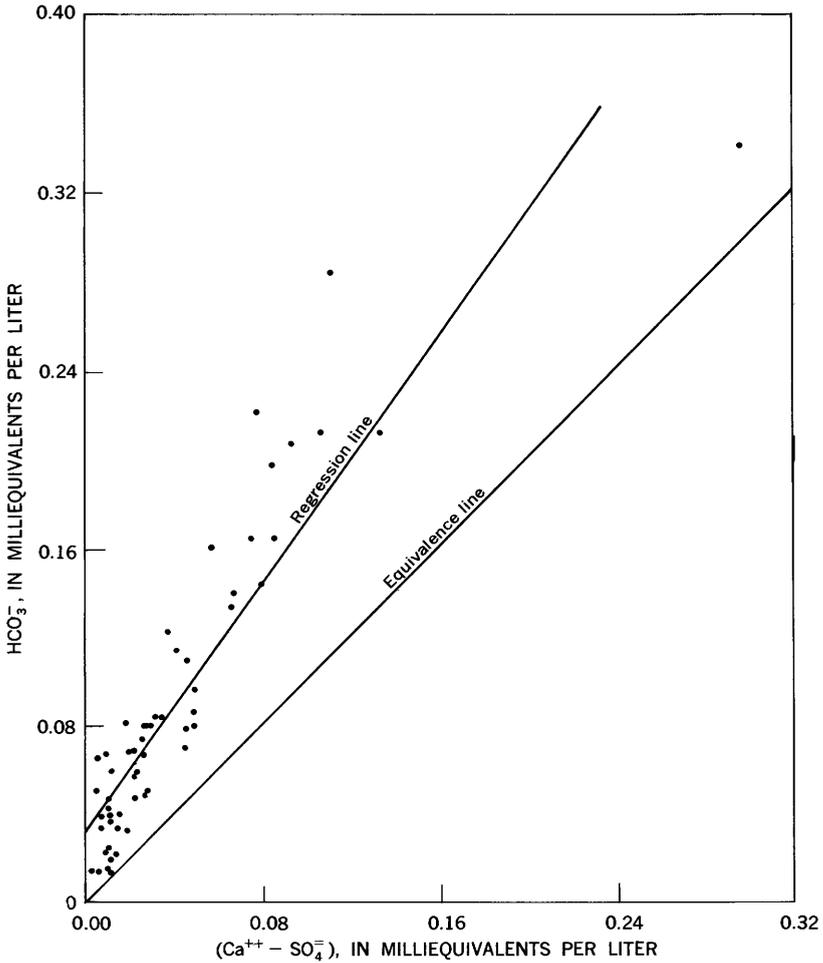


FIGURE 13.—Bicarbonate versus calcium-minus-sulfate concentrations; 61 observations.

NITRATE AND AMMONIUM

Average nitrate concentrations in precipitation over the network are shown in figure 14. Considerable annual variations are apparent for some stations near the ocean; however, the trend of increasing nitrate northwest from the coast is quite definite.

Total deposition of nitrate amounted to about 2 tons per square mile for each year. This total makes nitrate one of the major constituents of precipitation in this area. Monthly nitrate loads fluctuate erratically, as can be seen in figure 15. No simple relationship is apparent between nitrate values and loads of other ions in rainfall. Quite possibly, any

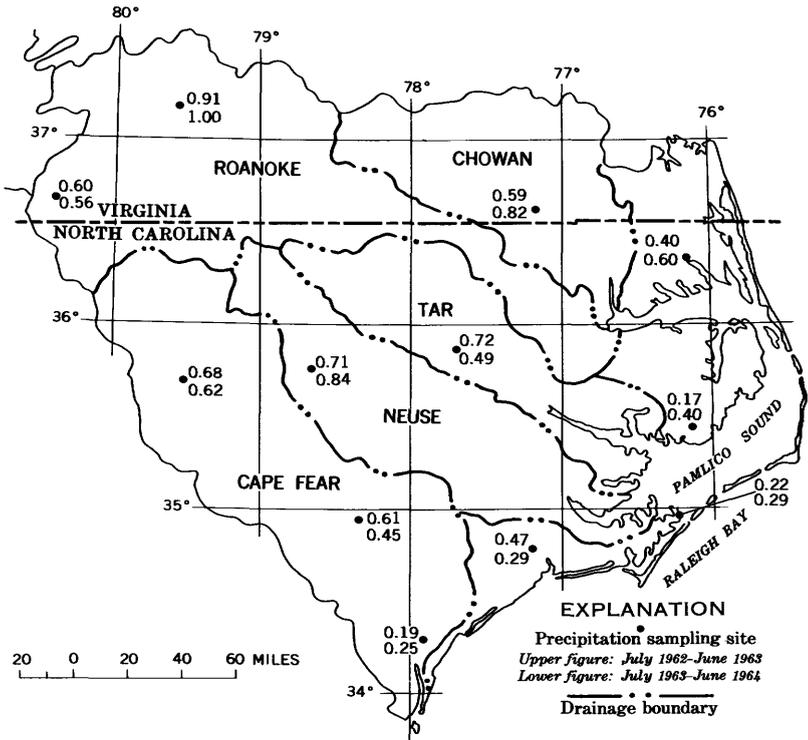


FIGURE 14.—Annual nitrate concentrations, in parts per million, in rainfall, July 1962-June 1964.

such relationship will be masked by changes in fixed nitrogen brought about by biological activity in samples during the collection period.

Ammonium concentrations in network rainfall are generally quite low, averaging about 0.1 ppm. The calculated ammonium ion load over the area was approximately 0.35 ton per square mile per year. However, the highest ammonium concentrations were found in obviously contaminated samples. Although these extreme results were excluded from the total load estimate, reliability of all the ammonium data is questionable, and no inferences can be made concerning natural levels of ammonium ion in precipitation.

CONTRIBUTION OF IONS IN PRECIPITATION TO QUALITY OF SURFACE WATER

Comparisons were made between precipitation input and stream discharge of ions for four drainage basins in the network area for which chemical quality and discharge data are available. River sampling sites include Tar River at Tarboro, Neuse River near Goldsboro, Haw

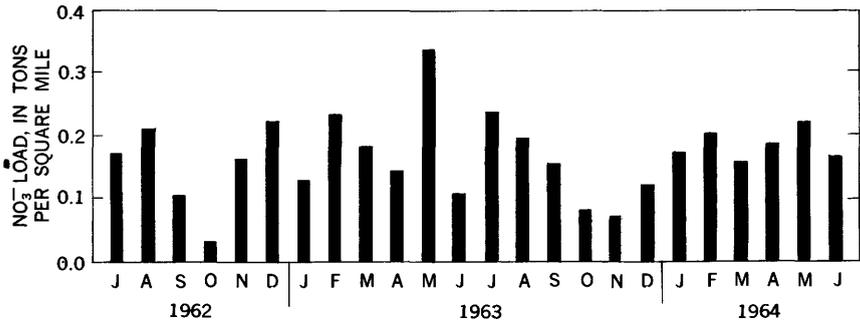


FIGURE 15.—Monthly average nitrate loads, July 1962—June 1964.

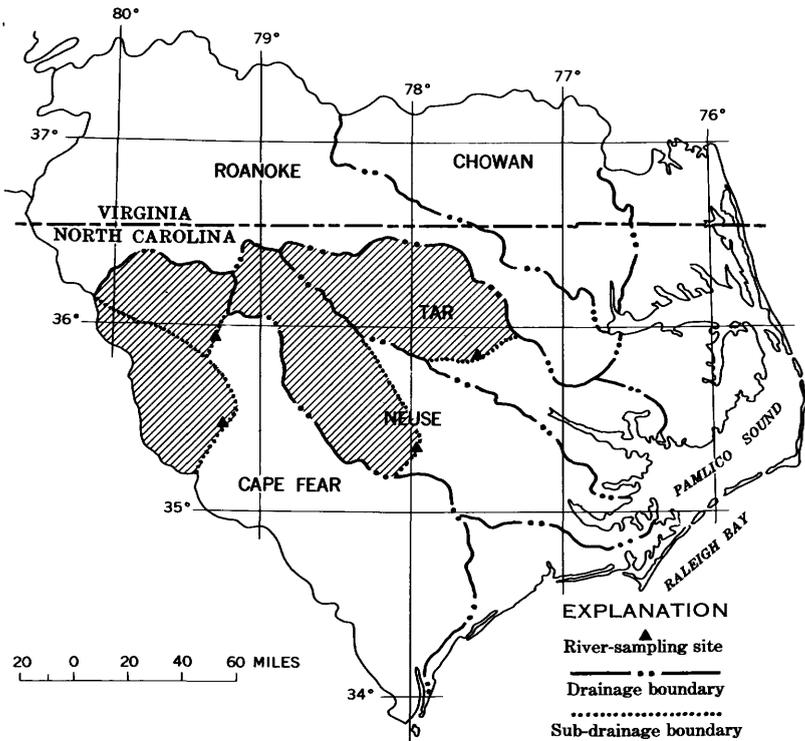


FIGURE 16.—Drainage areas (shaded area) for which comparison was made between precipitation input and stream discharge.

River at Bynum, and Deep River at Moncure. The basins, which are represented by shading in figure 16, have a combined area of 7,200 square miles.

Stream loads were computed from chemical-quality data and concomitant average discharge measurements published in the Geological

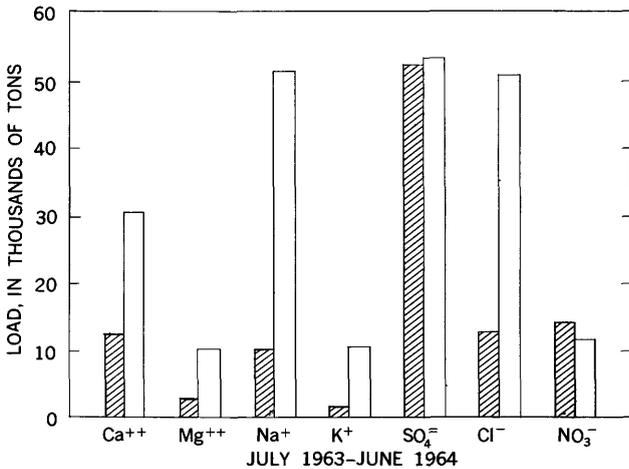
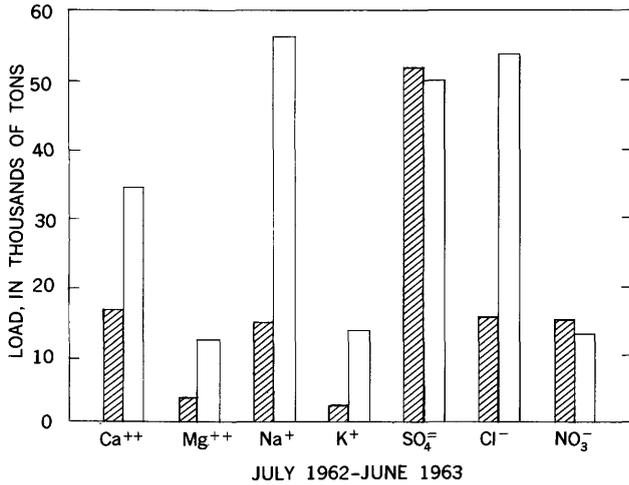


FIGURE 17.—Comparison between annual precipitation input (shaded bars) and stream discharge (open bars) of ions, July 1962–June 1963 and July 1963–June 1964.

Survey's quality-of-surface-water reports. Annual inputs and corresponding stream loads for 2 years are shown in figure 17.

Several features in figure 17 are noteworthy. First, precipitation supplies substantial percentages of the stream loads of the common cations. Relative amounts range from about 20 percent of the potassium to almost 50 percent of the calcium.

Annual precipitation input and stream output of sulfate are approximately equal and apparently quite steady at about 50,000 tons per year. Nitrate input, on the other hand, exceeds stream export by

about 18 percent for each year. Of course, sulfur and nitrogen are essential elements both industrially and biologically. Agricultural, industrial, and biological activity exert major influences on sulfate and nitrate loads in these four rivers, so that no estimates can be made of ecological budgets of these ions from the input and discharge data. Nevertheless, the virtually constant annual loads in rainfall and in the streams indicate the likelihood of a steady state condition with respect to additions and losses of these ions in the river basins.

The data in figure 17 show that atmospheric precipitation supplied only about one-fourth of the total chloride load carried by the four streams. This result is not in accord with the generally accepted idea that rainfall is the major natural source of chloride in streams in the Eastern States (Eriksson, 1955 and others). Gambell and Fisher (1966) suggested that substantial quantities of chloride may be leached from some minerals, notably biotite, which occur widely throughout this area of North Carolina.

An alternative explanation, involving the use of commercial salt, should be considered in accounting for the excess chloride in the streams. The drainage areas above the four stream-sampling sites, although predominantly rural, include several population centers. United States census data for 1960 indicate that the population of the area is approximately 1 million out of a total State population of 4½ million. During the study period, shipments of manufactured salt to North Carolina amounted to 220,000 tons annually according to the U.S. Bureau of Mines Minerals Yearbook data. If distribution of this imported salt within the State was proportional to the population distribution and if all the contained chlorine eventually reached the streams as ionic chloride, then close to 50,000 tons of salt were added annually to the four drainage areas. This quantity of salt would contain about 30,000 tons of chloride, a large fraction of the excess of stream load over precipitation load shown in figure 17. Thus, human activity may be a major factor in chloride budgets of streams in the area.

Hydrogen ion input and export data are not included in figure 17. The pH's of the four rivers range from 6 to 8. Thus, neutralization of acid from precipitation is virtually complete. However, hydrogen ion from rainfall may have an important role in determining the course and rate of weathering of soil minerals.

CONCLUSIONS

The study demonstrates the general features of composition patterns in precipitation over eastern North Carolina and Virginia and provides some data on the extent of annual changes in these patterns. Annual precipitation inputs and areal concentration distributions of

sulfate, nitrate, and chloride appear to be quite steady; the values noted in this report are probably representative for other time spans.

Cation content of rainfall, on the other hand, is quite variable; concentrations and loads depend on local conditions. Values reported herein can be considered only rough approximations to the values extant for other periods of time or for other areas.

The existence of at least three distinct types of aerosols can be inferred from results of the study of rainfall composition. These types are:

1. Marine aerosols, which supply most of the chloride and much sodium to the network area. Supply of these aerosols varies in a predictable manner with changes in meteorological parameters.
2. Acidic aerosols, which contain much of the sulfate in rainfall. Reactions resulting in the formation of rainfall sulfate are not known.
3. Alkaline aerosols, which are very likely derived from soil dust and which provide the bulk of the calcium and potassium, as well as part of the sodium and magnesium, to network precipitation.

Mineral constituents from atmospheric precipitation make up a substantial part of surface-water ion loads in the eastern Carolina-Virginia area. Further investigation of concurrent precipitation and stream compositions in small, well-defined drainage areas would be helpful in determining more precisely the magnitude of the rainfall contribution.

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