

Chemical Composition of Atmospheric Precipitation in the Northeastern United States

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1535-P





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By F. J. PEARSON, JR., and DONALD W. FISHER

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

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1535-P

*Study of the chemical composition of precipitation
and its effect on stream and ground-water content
in the Northeastern United States*



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GEOCHEMISTRY OF WATER

CHEMICAL COMPOSITION OF ATMOSPHERIC PRECIPITATION IN THE NORTHEASTERN UNITED STATES

By F. J. PEARSON, JR., and DONALD W. FISHER

ABSTRACT

Monthly bulk precipitation samples were collected from 18 sites in New York, Pennsylvania, and New England during periods that lasted from 12 to 36 months. The samples were then analyzed for calcium, magnesium, sodium, potassium, ammonium, hydrogen ion, bicarbonate, sulfate, chloride, nitrate, and phosphate. The analytical results were combined with precipitation amounts to get annual average loads of the various ionic species as thousandths of a ton per day per square mile.

The loads of certain species listed above do not vary systematically either with area or with annual precipitation amount. Their loads (ton per day per square mile) are: calcium, 5.3×10^{-3} ; magnesium, 1.0×10^{-3} ; potassium, 1.4×10^{-3} ; and total nitrogen, as N, 2.2×10^{-3} . The phosphate load, 0.37×10^{-3} ton per day per sq mi, was only measured at nine sites for 12 months. Sodium and chloride, the loads of which are 2.4×10^{-3} and 4.0×10^{-3} ton per day per sq mi, respectively, do not vary with precipitation amount among the inland stations; at coastal stations, though, sodium and chloride loads vary with precipitation. Sodium loads range from 4.6×10^{-3} to 13×10^{-3} ton per day per sq mi and chloride from 5.2×10^{-3} to 25×10^{-3} ton per day per sq mi at 25 and 55 inches precipitation per year, respectively. Hydrogen ion and sulfate loads vary with precipitation in both inland and coastal areas. Again at 25 and 55 inches per year, hydrogen ion loads range from 0.16×10^{-3} to 0.46×10^{-3} ton per day per sq mi, and sulfate loads from 25×10^{-3} to 45×10^{-3} ton per day per sq mi. Data from one station suggest that higher calcium, nitrate, and sulfate loads are to be expected near industrial areas.

Those species having loads that do not vary with precipitation amount enter bulk precipitation principally as dry fallout, while those varying with precipitation amount are dissolved in precipitation. The observed load patterns of sodium and chloride in coastal areas are due to sea spray. Bicarbonate, present rarely and erratically, seems to represent windborne dust contamination of individual samples.

Chemical loads in precipitation falling on several basins in the northeastern region were compared with loads carried by unpolluted streams draining the same basins. In all cases, the total nitrogen loads in precipitation entering the basins are greater than the total nitrogen loads being carried out by the streams. In dilute streams substantially all sulfate present is precipitation derived. Comparing the chemistry of precipitation with that of water from the Magothy aquifer, Long Island, N.Y., shows that the precipitation chemistry greatly affects the chemistry of this ground water.

INTRODUCTION

Knowledge of the chemistry of atmospheric precipitation is an important preliminary to the study of controls on surface- and ground-water quality. It has been amply demonstrated that much of the total load of certain ions in many streams has been contributed by atmospheric precipitation (Feth and others, 1964; Fisher, 1968; Fisher and others, 1968; Juang and Johnson, 1967; Likens and others, 1967). The magnitude of these atmospheric contributions must be known before the effects of processes operating on the earth's surface can be isolated for study.

In order to provide this information for present and future hydrologic studies in New England and New York State, results of the 3-year operation (water years 1966-68) of a precipitation-sampling network are made available here. Consideration of the needs of hydrologists and hydrochemists has determined the manner in which the data have been treated and are presented, but the results should also be useful to those concerned with atmospheric processes and to those investigating controls on the chemistry of surface and subsurface waters in other areas.

SAMPLING NETWORK

The New York State precipitation-sampling network includes six stations in upstate New York, one in northern Pennsylvania, and two on Long Island. Locations of these stations are shown in figure 1. All stations have been in operation since September 1965 (except Mineola, Long Island, which was begun in November 1965), and the results given here are based on the first 3 years of record from each station.

A network of nine New England precipitation-sampling stations was also operated from September 1965 through August 1966. The Corinna, Me., station was maintained through August 1967. Location of the New England sampling sites are also shown in figure 1.

The stations are located so that all the climatographic divisions of New York and many of the climatographic divisions of New England are represented. Thus, although the number of stations is relatively small, there is maximum meteorologic diversity among them, and compositional patterns common to them all are applicable to the entire region. All the stations are located at or near U.S. Weather Bureau precipitation-gaging sites, so collateral total-precipitation data are available to use with the chemical data for load computations. The Weather Bureau's cooperative observers maintained the sample collectors and mailed the samples to the U.S. Geological Survey's laboratory in Albany, N.Y., for analysis.

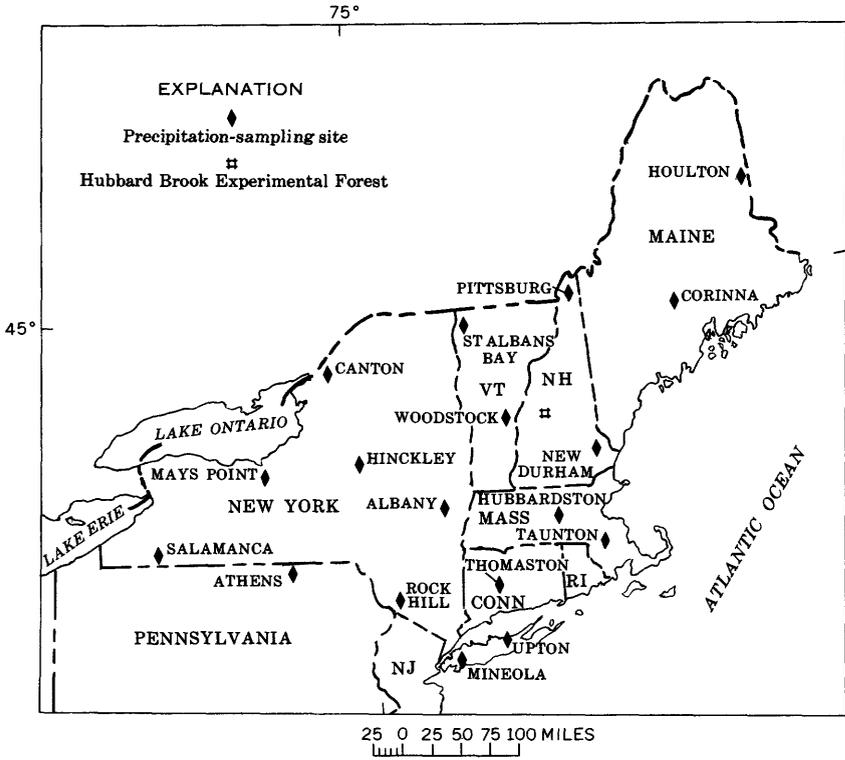


FIGURE 1.—Locations of precipitation-sampling sites in the Northeastern United States.

SAMPLE COLLECTION AND ANALYSIS

Samples were taken monthly from collectors which were continuously open to the atmosphere. The analyses are therefore representative of composite solutions, containing not only material initially dissolved in the precipitation, but also additional dry material falling in the collector during periods of no precipitation and later dissolved by precipitation. This mixture of dry fallout and precipitation, called bulk precipitation by Whitehead and Feth (1964), is what actually reaches the earth's surface and is incorporated in natural waters. It is therefore the proper parameter to investigate in connection with studies of surface- and ground-water chemistry.

The collector at each station is similar to those described by Gambell and Fisher (1966, p. K3). It consists of a straight-sided glass funnel through which precipitation drains into a polyethylene reservoir. The reservoir and the neck of the funnel are housed in an aluminum ice chest which is mounted on steel posts. The funnel is about 5 feet above the ground. A temperature of about 5°C is maintained in the chest by a thermostatically controlled heater. Filtration of the

precipitation samples is accomplished by inserting a replaceable fritted glass disc into the base of the collector funnel. The entire collector is surrounded by an Alter-type windshield designed to increase collection efficiency, particularly for snow.

Precipitation samples were analyzed for calcium, magnesium, sodium, potassium, ammonium, pH, sulfate, chloride, and nitrate. Phosphate was determined in samples collected at nine of the stations in 1967-68, and total phosphate was analyzed by the method described in Rainwater and Thatcher (1960). The metal ions were analyzed by using atomic absorption spectrophotometry, and the other ions were determined by methods described by Gambell and Fisher (1966). Hydrogen ion concentrations were calculated from measured pH values. It is believed that the overall accuracy of the analyses was adequate; rarely did the difference between anion and cation equivalents exceed 10 percent of the total equivalents determined.

TREATMENT OF DATA

This study is meant to provide analytical data that would be useful to water-chemistry investigations throughout the network area. Therefore, features common to all stations were sought first, and then departures of individual stations from the normal pattern were considered. The interpretations in this report are based on visual evidence of trends and correlations between various graphed parameters. Although rigorous statistical evaluation of precipitation-chemistry data will certainly be desirable for future water-chemistry studies, the approximate magnitude of the atmospheric contributions and the relationships between the various constituents will presumably be unchanged.

Laboratory analytical data expressed as concentrations of precipitation constituents cannot be used directly in evaluating the atmospheric contribution to surface- and ground-water chemistry because of water-volume changes resulting from evapotranspiration. Rather, chemical loads, which carry no reference to amounts of water initially present, are desirable for water-chemistry investigations. The load unit in this report is ton per day per square mile and is calculated by multiplying concentration, in milligrams per liter, times inches of precipitation per month times 2.38×10^{-3} .

Knowledge of seasonal variations in the composition of precipitation is important in understanding atmospheric processes (Gambell and Fisher, 1966). But when working with surface- and ground-water chemistry, particularly in a large area, one rarely has enough information to determine chemical budgets, or average concentrations and loads, for periods shorter than a year. For this reason, no analysis of seasonal variations was attempted in this report; instead, only

annual average loads, referred to elsewhere in the report as just "loads," are considered.

PRECIPITATION COMPOSITION

The chemical substances dissolved in bulk precipitation are generally considered to have two atmospheric sources: they may be derived from fairly unreactive dust particles, in which case they are deposited as dry fallout, or they may be present as gases or soluble salts (or their derivatives) which dissolve in the precipitation itself (Fisher, 1968; Gambell and Fisher, 1966). Substances from each of the two sources should have different load-precipitation amount relationships. That is, dry fallout should be deposited in amounts independent of the quantity of precipitation, whereas those substances dissolved in precipitation should have loads that vary with precipitation amounts. The data reported here reflect these relationships.

Annual ionic loads in precipitation are shown in table 1 for each station over the period of record. The values shown are calculated from individual monthly analyses and precipitation values. Many of the monthly data have been presented in various basic-data reports of the U.S. Geological Survey.^{1 2 3}

It is useful to consider the sampling sites in three groups, as follows: (1) coastal stations, including Mineola and Upton, Long Island, N.Y., and Taunton, Mass., (2) the urban station at Albany Airport, N.Y., and (3) the remaining rural inland stations. Conclusions drawn from the last group are most important here, as most of the northeastern region is rural.

INDIVIDUAL IONS Sodium and Chloride

The relationships between annual load and yearly precipitation amount for these species are shown in figure 2. Load patterns for these ions in coastal precipitation differ from corresponding load patterns in inland areas. In the coastal areas the loads of both species vary regularly with precipitation amount, whereas, in the inland areas, the loads are roughly constant from station to station and are independent of precipitation amount.

It is generally held that sea-salt aerosols are the major, if not the only, source of chloride in precipitation and an important source of sodium as well (Gambell and Fisher, 1966, p. K9, K16). Fine droplets of sea water which are dispersed from breaking wave crests evaporate before falling back into the water and leave a residue of sea salt in the air. This residue, carried up into the atmosphere and mixed by

¹ "Water Resources Data for Connecticut [1966-68]," available from U.S. Geol. Survey, Hartford, Conn.

² "Water Resources Data for Maine [1967-68]," available from U.S. Geol. Survey, Augusta, Me.

³ "Water Resources Data for New York [1965-66]—Part 2, Water Quality Records," available from U.S. Geol. Survey, Albany, N.Y.

TABLE 1.—Annual loads and amounts of precipitation at sampling sites in the Northeastern United States

Station	Year ending—	Precipitation (in. per yr)	Annual load (thousandths of a ton per day per sq mi)											
			Calcium nesium	Mag- nesium	Sodium	Potas- sium	Am- monium	Hydrogen ion	Bicar- bonate	Sulfate	Chloride	Nitrate	Total nitrogen, as N	Phos- phate
Rural inland stations														
Houlton, Me.	8-66	30.0	8.36	0.77	1.51	1.84	1.12	0.052	16.68	19.26	3.01	1.45	1.20	---
Canton, N.Y.	9-66	30.8	5.46	1.16	1.28	1.45	1.42	.200	1.54	31.48	2.15	1.55	1.45	---
	9-67	25.7	4.88	1.10	1.79	.85	1.29	.231	.00	27.04	2.71	2.38	1.54	---
	9-68	28.1	4.26	1.08	2.14	.85	1.29	.147	2.30	24.64	2.22	2.05	2.43	0.23
St. Albans Bay, Vt.	8-66	35.1	15.15	1.29	3.40	2.33	4.11	.093	15.81	37.73	5.40	12.57	6.03	---
Pittsburg, N.H.	8-66	41.1	4.38	3.84	1.10	2.05	1.67	4.16	8.16	29.56	3.75	3.51	2.38	---
Corinna, Me.	8-67	36.4	4.58	.74	2.71	2.79	1.40	1.75	4.16	23.78	4.74	2.25	1.59	---
	8-67	38.8	2.30	.50	2.21	1.45	1.40	.196	3.81	23.37	4.54	7.33	2.86	---
Mays Point, N.Y.	9-66	30.8	5.58	1.11	1.46	.96	2.00	.273	.00	32.97	2.90	1.30	1.84	---
	9-67	27.7	5.80	2.27	2.35	.60	.72	.00	.00	30.43	2.78	2.23	1.07	---
	9-68	33.0	14.29	7.04	1.85	1.08	2.06	1.07	13.60	32.73	5.59	6.82	3.14	.28
Hinckley, N.Y.	9-66	42.4	7.04	.92	1.42	1.69	3.32	.380	1.22	36.60	3.97	2.07	1.07	---
	9-67	41.8	8.34	1.46	2.69	.91	.78	.297	1.22	35.52	2.61	1.22	2.75	.50
	9-68	46.2	5.04	.87	2.26	1.46	3.19	.388	1.34	35.52	11.48	4.30	2.90	---
Woodstock, Vt.	8-66	36.0	3.15	.68	6.71	.82	2.49	.334	.36	28.47	3.56	.60	1.41	---
New Durham, N.H.	8-66	35.4	1.70	.38	1.86	.38	1.64	.380	.00	28.47	4.55	1.64	1.43	---
Hubbardston, Mass.	8-66	29.7	3.18	.68	1.75	3.59	1.37	.301	2.36	27.70	5.48	4.93	4.61	---
Salamanca, N.Y.	9-66	40.1	6.36	1.20	4.26	2.50	4.51	.272	2.00	35.20	5.48	2.09	1.84	---
	9-67	47.1	5.35	.71	6.39	2.44	1.76	.497	3.14	49.71	6.38	2.09	1.84	---
	9-68	38.3	4.07	.75	8.02	2.60	2.94	.222	8.08	35.28	4.64	5.12	3.44	.25
Athens, Pa.	9-66	27.0	4.62	.66	1.13	1.23	3.04	.198	.17	27.88	3.07	1.62	2.82	---
	9-67	31.6	4.55	.55	3.18	.82	2.48	.285	1.40	31.77	4.51	1.62	2.29	---
Rock Hill, N.Y.	9-66	25.6	2.80	.47	1.75	1.31	2.63	.346	1.08	27.75	3.33	.89	1.74	---
	9-67	41.7	4.50	.51	2.62	1.31	4.43	.525	.00	38.33	3.33	3.81	3.60	.31
	9-68	46.5	6.10	.96	2.55	3.40	2.44	.506	.00	43.86	5.39	7.04	1.58	---
Thomaston, Conn.	8-66	29.5	3.12	.82	3.15	1.01	1.73	.382	.00	27.64	6.03	1.56	1.58	---
	8-67	49.0	5.53	.19	3.65	.94	3.29	.509	.00	43.94	4.71	2.40	.81	.70
Coastal stations														
Taunton, Mass.	8-66	29.3	1.84	0.88	5.15	1.29	1.48	0.095	0.00	22.82	8.93	1.40	1.46	---
Upton, N.Y.	9-66	33.0	3.99	1.63	9.16	1.27	2.35	.303	.65	31.35	15.34	3.97	2.74	---
	9-67	34.3	2.62	1.34	10.80	.93	1.30	.377	.00	27.33	24.95	3.97	1.74	---
	9-68	40.5	7.32	2.66	7.14	.67	2.35	.203	.00	29.80	16.24	7.52	3.20	0.17
Mineola, N.Y.	9-66	33.5	7.32	2.66	7.14	.67	2.35	.203	.58	31.31	12.65	7.52	3.45	---
	9-67	40.1	7.66	2.61	7.33	.83	1.37	.300	.78	43.02	12.45	4.22	2.02	---
	9-68	33.2	7.43	2.54	9.43	2.52	3.29	.260	.00	43.84	14.76	4.69	3.61	.49
Urban station														
Albany, N.Y.	9-66	31.9	17.53	1.00	3.20	1.26	1.16	0.134	4.91	45.63	6.59	8.41	2.80	---
	9-67	30.3	20.01	1.42	2.66	1.05	2.14	.078	1.65	51.73	5.57	12.34	4.45	---
	9-68	30.1	16.59	1.41	2.58	1.02	1.22	.143	3.71	44.24	4.22	8.32	2.83	0.23

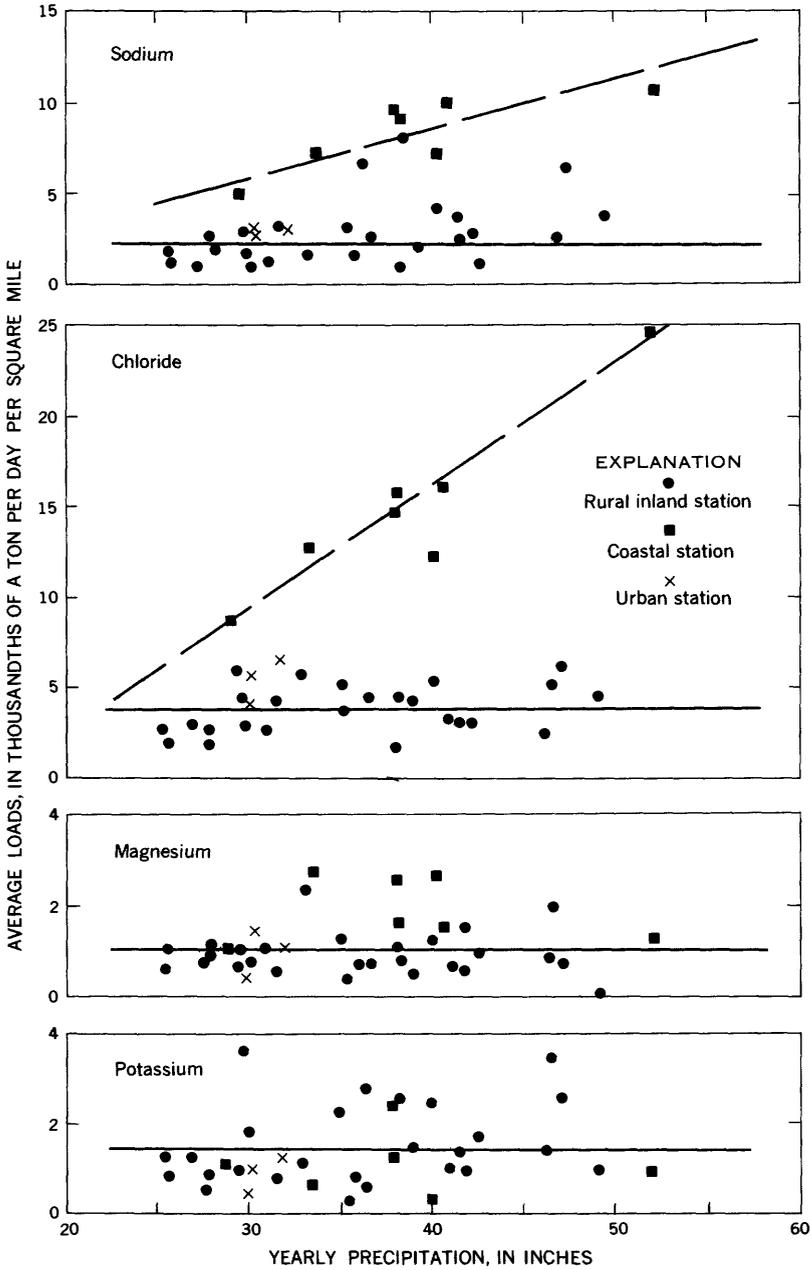


FIGURE 2.—Annual loads of sodium, chloride, magnesium, and potassium in precipitation versus yearly precipitation amount.

turbulence, is dispersed generally and only slowly falls out of suspension. A small amount of the residue is incorporated in precipitation on and near the ocean. Thus the invariant rural chloride loads can be ascribed to the generally dispersed material which enters bulk precipitation as dry fallout. The higher variable coastal loads include this component but are primarily due to the high concentration of sea-spray residue near the ocean which, because it can be dissolved in falling precipitation, causes the loads to vary with precipitation amount.

The fact that sodium and chloride loads in coastal precipitation are notably higher than the same loads in rural precipitation furnishes further evidence for the sea-salt origin of these constituents. From figure 2, the ratio of the excess difference between coastal and rural chloride loads to that between coastal and rural sodium loads is 1.9. This value is close to the chloride-sodium ratio of 1.8 for ocean water and thus indicates a sea-spray origin for the higher sodium and chloride loads observed in precipitation from the coastal stations.

Sodium and chloride loads in precipitation at Woodstock, Vt., were of the same magnitude as the coastal station loads. However, these high annual load values are probably not representative for the area. They can be accounted for by unusually high sodium and chloride concentrations in winter precipitation, which probably resulted from contamination by salt used to melt ice from a nearby highway.

Table 2 compares the loads and concentrations in the northeastern precipitation network with those in other recently studied areas in the Eastern United States. Although others have studied the Hubbard Brook Experimental Forest, N.H. (Fisher and others, 1968; Juang and Johnson, 1967; Likens and others, 1967), which is within the present study area (fig. 1), the sampling frequency, collection apparatus, and some of the analytical techniques used in the other studies differed from those used in the work reported here. These differences may account for some of the discrepancies between the results of the two studies.

As table 2 shows, the chloride loads in the first two areas of study are higher than the rural inland loads of the northeastern stations but lower than loads at the coastal sites. These differences are consistent with the assumption of an oceanic origin for the chloride.

The sodium-load values for North Carolina and Virginia are also intermediate between those of rural inland and coastal stations in the Northeast. This effect could result from greater coastal influence in the mid-Atlantic coastal plains and piedmont than in the hilly Northeastern States. However, sea salts are not the only source of sodium in precipitation; local atmospheric dust can contribute appreciably to loads of this ion (Gambell and Fisher, 1966). The explanation for the

TABLE 2.—Composition of atmospheric precipitation in various areas in the Eastern United States

(Chemical values are first given in milligrams per liter, then in thousandths of a ton per day per square mile)

Location	Period	Precipitation (in. per yr)	Calcium	Magnesium	Sodium	Potassium	Ammonium	Hydrogen ion	Sulfate	Chloride	Nitrate	Total nitrogen	Phosphate
Eastern North Carolina and southeastern Virginia ¹	7-62-6-63	44.4	0.69	0.17	0.62	0.11	0.1	0.014	2.3	0.65	0.65	0.23	---
	7-63-6-64	43.7	6.1 .55 4.8	1.5 .15 1.3	5.5 .46 4.0	1.0 .08 .7	1 1 1	.12 .017 .15	20 2.3 20	5.7 .56 4.9	5.7 .61 5.3	2.0 .22 1.9	---
Hubbard Brook Experimental Forest, N.H. ²	6-63-5-64	46.2	.42	.06	.09	.21	---	---	---	---	---	---	---
	6-64-5-65	37.4	3.9 .48 3.6	.6 .12 .9	.8 .22 1.6	1.9 .19 1.4	---	---	3.1 23 3.3	---	---	.32 2.4 4.7	---
Northeastern stations ³	9-65-8-66	53	---	---	---	---	2.1	---	---	.64	---	---	---
	45	45	.60 5.3	.11 1.0	.22 2.7	.16 1.4	.22 2.0	.042 .37	4.3 38	6.8	.84 3.0	.25 2.2	0.04 .37
Rural inland stations	45	45	---	---	2.4	---	---	---	---	4.5	---	---	---
Coastal stations	45	45	---	---	1.13	---	---	---	---	4.0	---	---	---
			---	---	10	---	---	---	---	19	---	---	---

¹ Fisher (1968).
² Likens, Bormann, Johnson, and Pierce (1967); Fisher, Gambell, Likens, and Bormann (1968); Juang and Johnson (1967).
³ This report; average concentrations and loads at stated precipitation amount.

low sodium loads in the Hubbard Brook area may be the procedural differences mentioned above, or it may be that the Hubbard Brook area is completely forested and further removed from roads, towns, and open areas than the majority of stations in this network and thus further removed from sources of atmospheric particulate matter.

Magnesium and Potassium

Soil dust is generally considered to be the source of most of the potassium and much of the magnesium in precipitation (Gambell and Fisher, 1966). These elements should then enter bulk precipitation as dry fallout, and their loads should be independent of precipitation amount. Figure 2 shows this to be true for the northeastern network.

The average potassium load of 1.4×10^{-3} ton per day per sq mi (ton per day per square mile) is slightly higher than that in North Carolina and Virginia, and slightly lower than that at the Hubbard Brook forest (table 2). The differences, though, are small and may result from analytical errors.

The magnesium load, 1.0×10^{-3} ton per day per sq mi, is slightly lower than the loads in North Carolina and Virginia. Like sodium loads, magnesium loads in the Hubbard Brook forest are significantly lower than in the northeastern network (table 2). Again, this may be due to differences in methods of collection or analysis between this work and that at Hubbard Brook. It may also be caused by the presence of less dust in the atmosphere over the completely forested, uninhabited Hubbard Brook watersheds. Magnesium concentration in ocean water is as much as one-eighth that of sodium: precipitation over the coastal stations should therefore be magnesium enriched. Coastal precipitation may have slightly higher magnesium loads (fig. 2); however, magnesium was quite low during the excessively wet 1966-67 year at the Upton station. Because magnesium loads at stations in the inland and coastal sections overlap, determining averages by section does not seem warranted.

Sulfate

Sulfate in precipitation results primarily from the solution of sulfate aerosol particles and of various atmospheric gaseous sulfur compounds in falling precipitation (Junge, 1960; Gambell and Fisher, 1966). The gaseous sulfur compounds, predominantly H_2S and SO_2 , are released to the atmosphere by combustion of fossil fuels and also by such natural processes as forest fires, volcanic emanations, and biological reduction of sulfates. These gases are oxidized in the atmosphere and the product, hexavalent sulfur, appears in precipitation as sulfate. Because of its origin, sulfate loads in precipitation should vary with precipitation amount. Figure 3 shows that this is the case in the Northeast, where sulfate loads, from the line through the data points, range from 25×10^{-3} ton per day per sq mi at 25 inches per

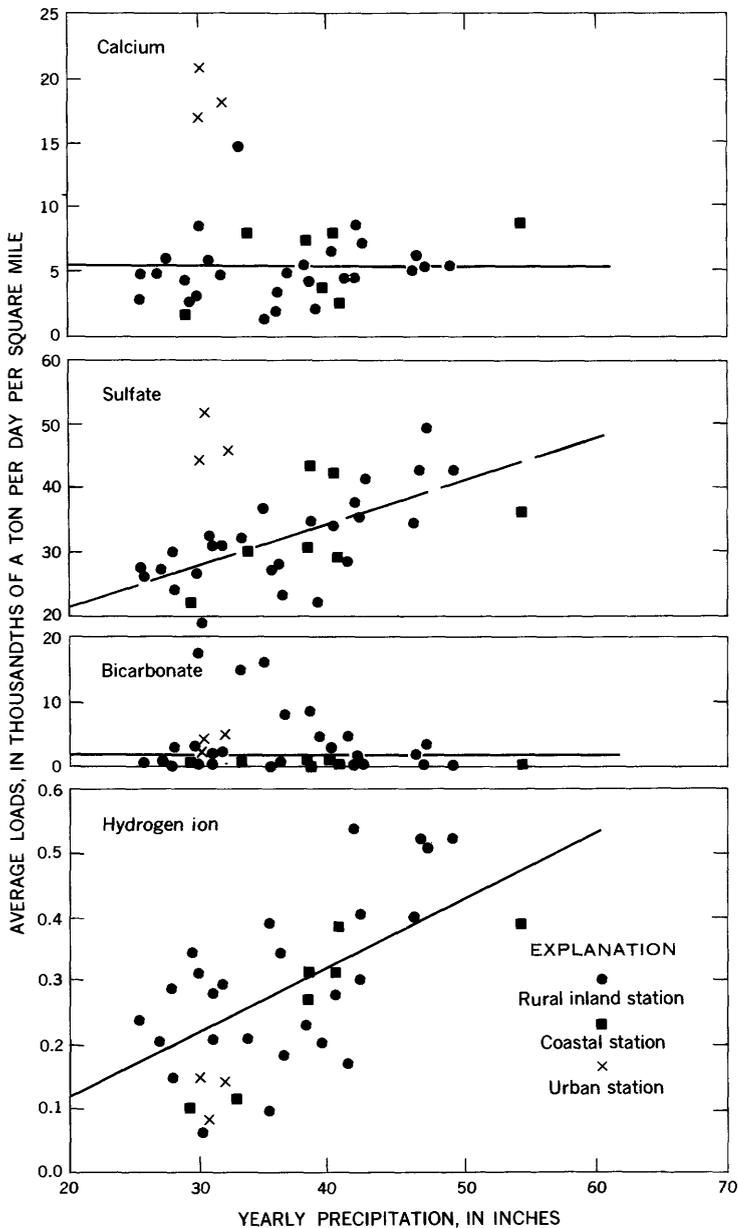


FIGURE 3.—Annual loads of calcium, sulfate, bicarbonate, and hydrogen ion in precipitation versus yearly precipitation amount.

year precipitation to 38×10^{-3} ton per day per sq mi at 45 inches per year precipitation. These loads, converted to average concentrations, are 5.2 and 4.3 mg/l (milligrams per liter) SO_4 respectively.

Considerable quantities of sulfur compounds are released to the atmosphere from the human-controlled combustion of fossil fuels. The amount of sulfate so released has been estimated to contribute about 50 percent of the global atmospheric sulfur budget (Junge, 1960). Although some of this sulfur from fuel is mixed in the atmosphere and causes higher-than-natural sulfate levels in precipitation on a regional and global scale, the effects of fuel sulfate are most marked in smaller areas, close to major industrial or urban centers. At the urban station at Albany Airport, the average sulfate loads are about 25 percent higher than the rural loads (fig. 3). There is not sufficient information to permit estimation of the size of the area over which this higher sulfate level occurs or of the average sulfate loads that might be expected in more heavily industrialized areas such as Buffalo or New York City.

There is information, though, on the effect of a single storm on such an area. Figure 4 shows the concentrations of sulfate in fresh snow from a storm which passed to the east across the heavily industrialized Tonawanda-Buffalo-Lackawanna region of western New York (Archer and others, 1968). South of the industrial area, the sulfate concentrations average about 4.5 mg/l, essentially the annual average for the network. To the east of the industrial area, very much higher SO_4 concentrations were observed. As indicated in figure 4, the detailed sulfate pattern is very complex, presumably because of vagaries of the wind patterns within the storm itself, but the industrial region's area of influence is clear.

Extremely high sulfate concentrations such as those in figure 4 are not the rule, even near heavily industrialized areas. Samples of snow from other storms near Buffalo, for instance, showed no unusual sulfate concentrations (Archer and others, 1968). Likewise, a series of precipitation samples taken around the city of Binghamton, N.Y., showed no discernible sulfate enrichment (R. D. MacNish, oral commun., 1968).

As table 2 shows, sulfate in the rural northeastern precipitation is considerably higher than that in the North Carolina-Virginia precipitation. Sulfate concentrations in samples from the Maine stations (Corinna and Houlton) were significantly lower than the network average. These stations, the farthest removed from densely populated areas, are apparently outside the region of high atmospheric sulfur concentrations.

Calcium

Soil dust is one source of the calcium in precipitation, as it is for magnesium and potassium. The average calcium load for the rural and coastal stations in the Northeastern States, 5.3×10^{-3} ton per day per sq mi (table 2), is not dependent on precipitation volume

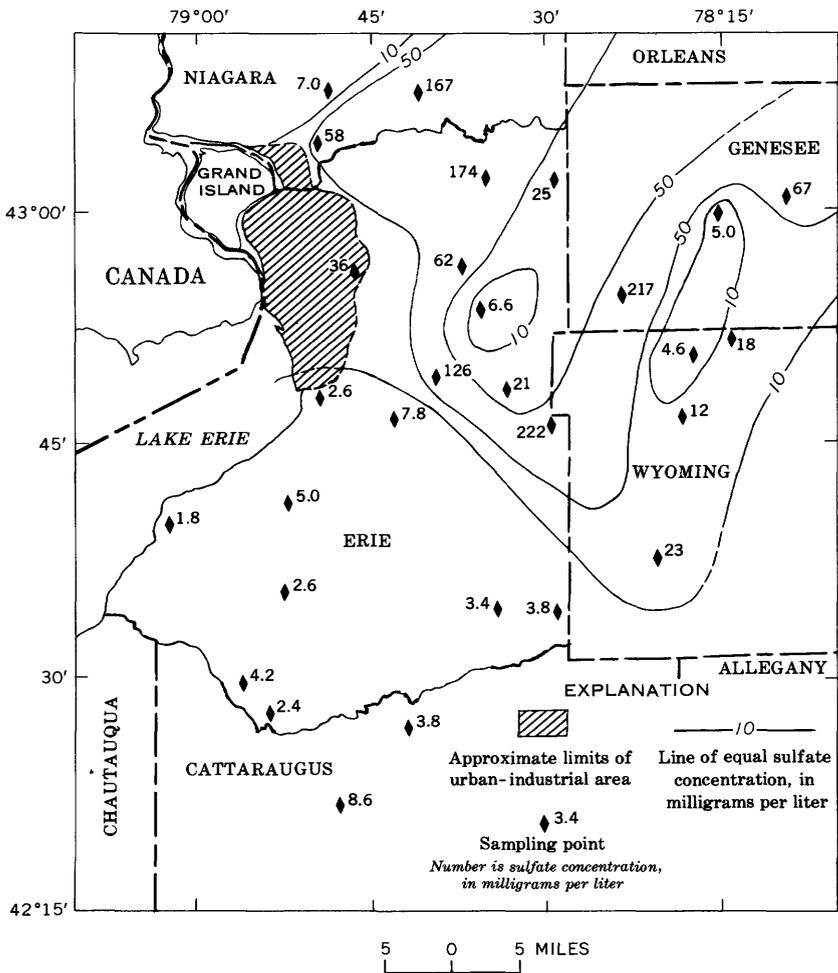


FIGURE 4.—Sulfate concentrations in snow from storm of February 16, 1964, in the vicinity of Buffalo, N.Y.

(fig. 3). This value, while it is close to the 2-year average calcium load of 5.4×10^{-3} ton per day per sq mi in precipitation on North Carolina and Virginia (table 2), is considerably greater than the loads reported by Likens and others (1967) for the Hubbard Brook region. The lower calcium values observed in the Hubbard Brook watersheds probably reflect a lower soil dust content in the atmosphere over that isolated forest area.

By weight, calcium is usually the dominant cation and sulfate the principal anion in precipitation on the Northeastern States and on eastern North Carolina and southeastern Virginia as well. In terms

of equivalents, hydrogen ion is also an important constituent of precipitation in the same regions. Fisher (1968, fig. 12) reported good correlation between hydrogen ion and sulfate-minus-calcium concentrations for the North Carolina-Virginia network. A similar relationship exists between these ions in precipitation on the Northeastern States (fig. 5). In both regions calcium is equivalent to approximately two-thirds of the sulfate in excess of hydrogen ion. That is, the sulfate in acidic precipitation samples may be considered a mixture of sulfuric acid and sulfates, two-thirds of which are associated with calcium. Presumably the same relationship applies to precipitation over much of the Eastern United States.

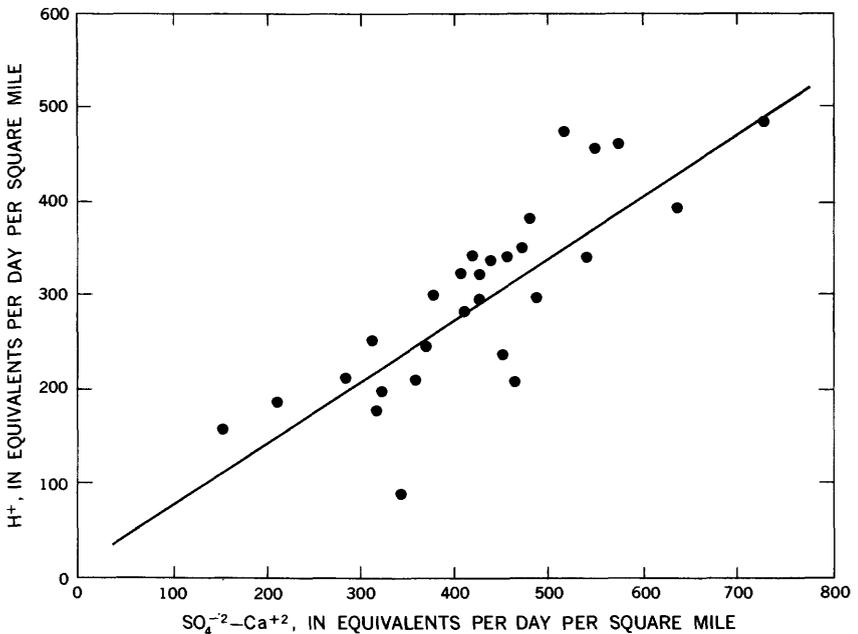


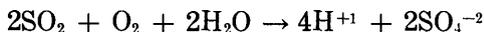
FIGURE 5.—Hydrogen ion versus sulfate-minus-calcium concentrations.

Calcium loads at the Albany Airport site are almost four times as high as the average loads at rural stations. The large open area in and around the airport could contribute calcium to local dust. At Albany, as well as at other urban areas, industrial activity may increase the calcium content of atmospheric particulates. At Norfolk, Va., for example, calcium concentrations in precipitation were nearly five times greater than the average value for the more rural stations in the North Carolina-Virginia network (Gambell and Fisher, 1966). High atmospheric levels of calcium and of sulfate seem to be typical of urban areas. Sumi, Corkery, and Monkman (1959) found gypsum

(CaSO₄·2H₂O) to be the principal crystalline constituent of urban dust. Settling or washing out and subsequent solution of this gypsum is the most probable explanation for the consistently high calcium and sulfate contents of urban precipitation.

Hydrogen Ion and Bicarbonate

The origin of hydrogen ion in precipitation was touched on in the discussions of sulfate and calcium. It seems that part of the sulfate is derived from the solution of gaseous sulfur compounds. Such solution can be grossly represented by a reaction such as



which produces the hydrogen ion present in precipitation. Because it originates through the solution of gases, the hydrogen ion load should vary with precipitation amount. Figure 3 shows this to be true of northeastern precipitation. Hydrogen ion loads at the northeastern stations are considerably higher than those reported for the North Carolina-Virginia area (table 2); northeastern sulfate loads are correspondingly high. The high northeastern hydrogen ion loads are probably due to the high atmospheric (gaseous) sulfur level in the Northeast.

CO₂ is present in the atmosphere at a partial pressure of about 10^{-3.5} atmospheres. This will dissolve in precipitation as a mixture of CO₂(aqueous) and H₂CO₃(aqueous), the total concentration of which will be about 10⁻⁵ M (0.6 mg/l H₂CO₃) (Garrels and Christ, 1965, p. 76). However, the dissociation of H₂CO₃ to produce significant quantities of bicarbonate is minimized by the high hydrogen ion concentrations resulting from the oxidation and solution of SO₂. Because of this, atmospheric carbon dioxide does not ordinarily control precipitation alkalinity.

The most likely alternate source of bicarbonate is atmospheric dust. This is supported by the fact that the highest bicarbonate noted in New York is in samples from the urban Albany Airport station (table 1) where the dust level probably would be highest. Fisher (1968) has shown that when bicarbonate occurs in North Carolina-Virginia precipitation, it seems to be chemically balanced by calcium, as if CaCO₃ dust were the source. The few stations in the northeastern network that had any significant bicarbonate (fig. 3 and table 1) also showed anomalously high calcium.

Ammonium and Nitrate

These nitrogen-containing ionic species are known to be particularly susceptible to changes in concentration incident to biological activity (Rainwater and Thatcher, 1960, p. 28). Therefore, in samples

such as the monthly composites in this study, the analyzed ammonium and nitrate values may differ from the values in the precipitation itself. The magnitude of this difference cannot be estimated, and therefore no estimate of the accuracy of the data can be made.

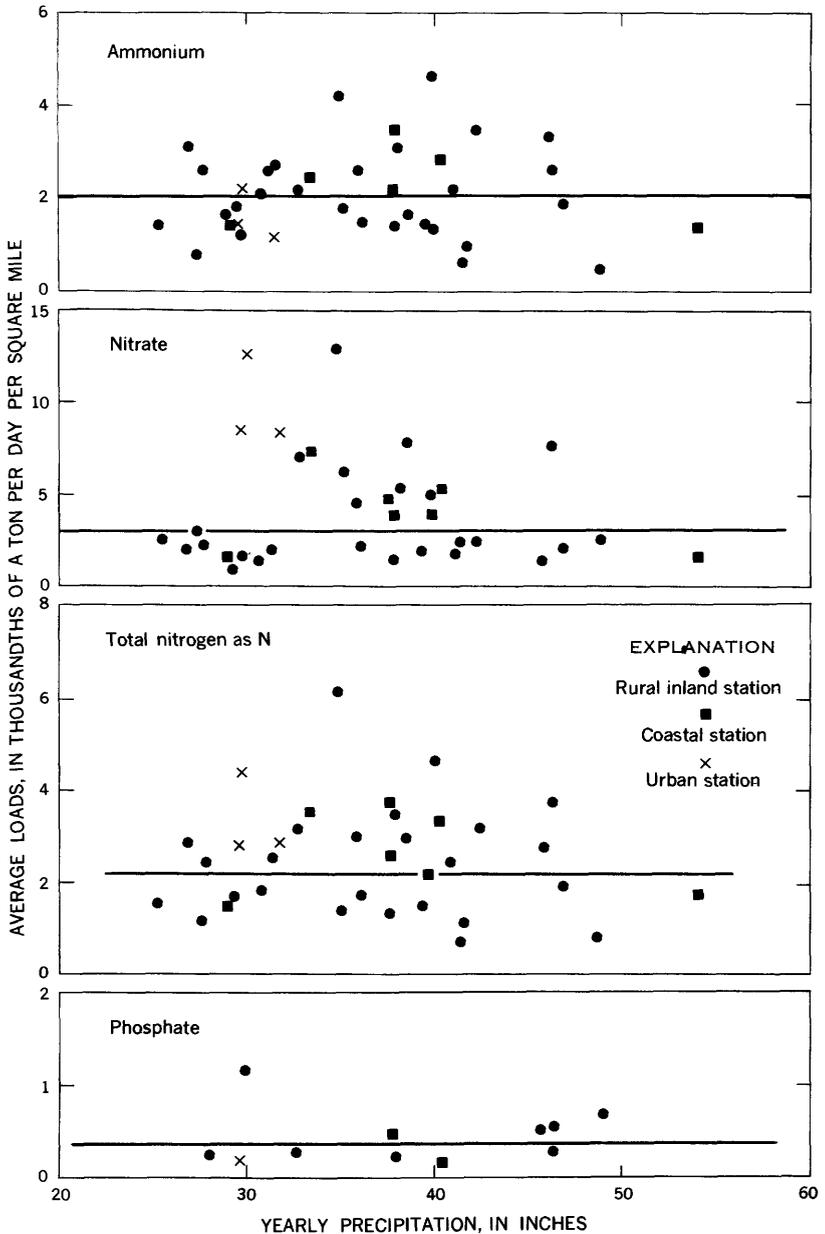


FIGURE 6.—Annual loads of nitrogen species and phosphate in precipitation versus yearly precipitation amount.

The variations of loads of the nitrogen species with precipitation amount are shown in figure 6. There is considerable scatter among the ammonium and nitrate loads, which could be due to changes during sampling and storage as well as to real variations in the precipitation itself. For ammonium, the average load in the Northeast, which does not vary with precipitation amount, is 2.0×10^{-3} ton per day per sq mi, a value consistent with those reported from other areas in table 2.

Although nitrate is presumed to have a gaseous origin (Gambell and Fisher, 1964, 1966) and should have loads varying with precipitation, the data of figure 6 only warrant drawing a horizontal average line. The average, 3.0×10^{-3} ton per day per sq mi for rural northeastern precipitation, is much lower than either the Hubbard Brook or the North Carolina-Virginia precipitation (table 2). Urban Albany Airport nitrate is about 10×10^{-3} ton per day per sq mi, within the range of Hubbard Brook values.

It is often convenient to consider the concentrations, not of the individual nitrogen-bearing ionic species, but of the total nitrogen, expressed as milligrams per liter N, in all analyzed species. By so doing, some of the errors introduced by interactions between the individual nitrogenous species may be eliminated. The values of total nitrogen in precipitation are shown for the northeastern stations in figure 6 and table 1, and for other areas in table 2. Figure 6 shows that there is still about as much scatter in the rural total nitrogen loads as for the individual ions. It also shows that, high urban nitrate loads notwithstanding, urban total nitrogen is not substantially higher than rural total nitrogen. Gambell and Fisher (1964) have noted a positive correlation between sulfate and nitrate concentrations in storm rainfall. The high nitrate content and sulfate values in the Albany Airport samples may result from similar atmospheric chemical processes.

In the northeast total nitrogen load values from network precipitation agree with those from the North Carolina-Virginia study and with values from the first year of the Hubbard Brook study (table 2). The second year of the Hubbard Brook study, though, showed a much greater load. The Hubbard Brook load values may be more nearly correct for the area studied than those for the northeast and North Carolina-Virginia networks, for, in the Hubbard Brook area, samples were collected and analyzed weekly, and in the northeast and North Carolina-Virginia areas, monthly. There is thus less chance for loss of nitrogen species during the sample collection period in the Hubbard Brook work.

Phosphate

Analyses for phosphate were performed on samples collected at nine stations during the 1967-68 year. The calculated loads are shown in

table 1 and figure 6. The limited data available do not allow an accurate estimate of average phosphate loads in the northeast region. The mean of the loads listed in table 1, 0.37×10^{-3} ton per day per sq mi, should be considered an order-of-magnitude figure only. Confirmation of any trend of increasing phosphate with increasing precipitation must await further data.

PRECIPITATION CONTRIBUTION TO STREAM- AND GROUND-WATER CHEMISTRY

Loads of various ions in precipitation can contribute much or all of the stream loads of these ions. Figure 7 shows precipitation and sur-

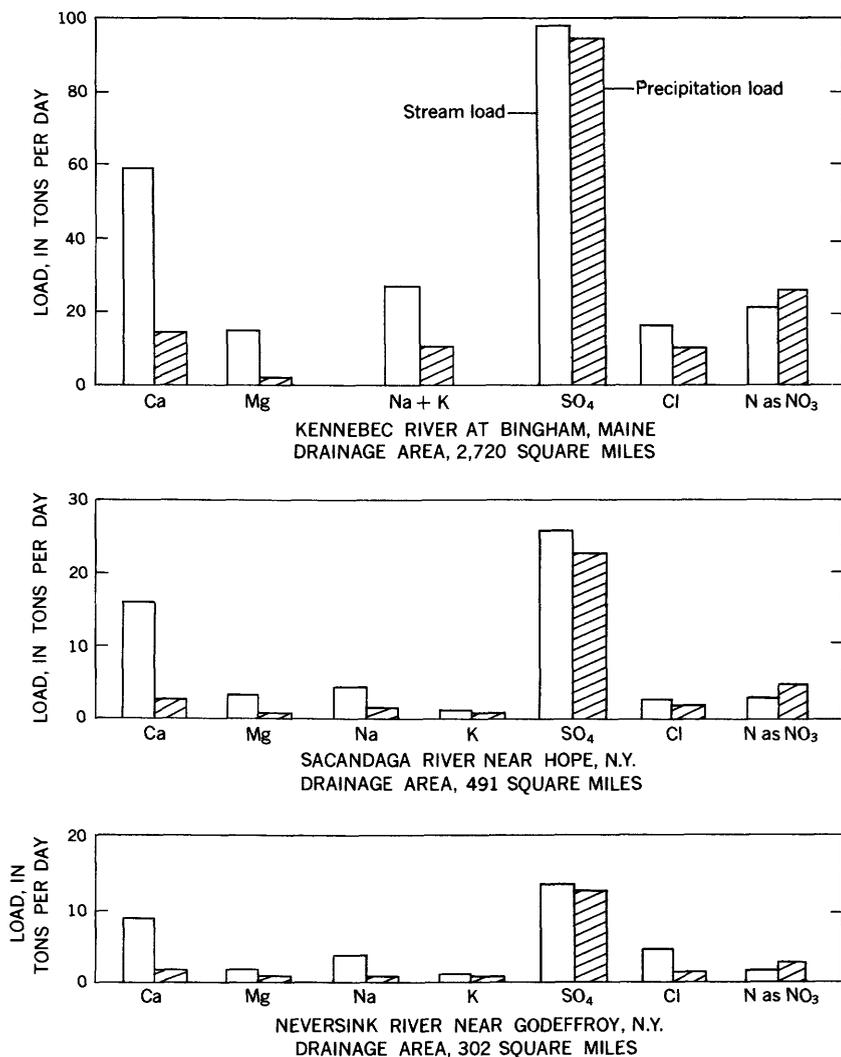


FIGURE 7.—Contribution of precipitation to chemical loads of three northeastern streams.

face-water loads for three stream basins in the northeast region. Above the gaging stations these streams drain areas which are relatively free from industrial and urban pollution. Moreover, the geology of the basins is such that it is highly unlikely that any significant amount of water leaves the basins except by the gaged stream. Thus, the load comparisons indicate fairly well the precipitation and watershed mineral contributions to the stream loads.

The stream loads shown in figure 7 were calculated from the average annual discharge recorded at the station and the chemical composition at that discharge (for data sources, see footnotes 2 and 3 on p. P5). The average composition was defined by U.S. Geological Survey analyses which were made on grab samples. These were taken at least once a month over a minimum period of 1 year. None of the streams showed substantial variation of stream chemistry with discharge. This fact justified the load-calculation method used. The precipitation loads were calculated from the average network or rural loads shown in table 2 multiplied by the drainage area of the stream basin. The sulfate loads used were those for the average amount of precipitation falling on the drainage basin (Dethier, 1966; Knox and Nordenson, 1955).

As figure 7 shows, nearly all the stream loads of sulfate and of the nitrogen species are derived from precipitation. In fact, the nitrogen loads in precipitation exceed the stream loads. This phenomenon, which has also been noted in streams in North Carolina (Fisher, 1968) and the Hubbard Brook region (Fisher and others, 1968), is not well understood but, presumably, is due to biological activity which results in the direct return of elemental nitrogen or volatile nitrogen compounds to the atmosphere.

In the Kennebec River in western Maine and the Sacandaga River in New York, most of the chloride is precipitation derived, whereas the drainage basin apparently contributes most of the chloride to the Neversink River, also in New York. The proportion of precipitation-derived magnesium load of the Neversink River, however, is higher than that of the other two rivers.

These differences are in keeping with the regional geology of the basins drained by the streams. The Neversink River drains sedimentary rocks of the southern Catskill region, while the Sacandaga River, on the southern flank of the Adirondack Mountains, and the Kennebec River drain regions of nonsedimentary rocks. Sedimentary rock ordinarily contains more chloride and less soluble magnesium than nonsedimentary rock, so the differences in stream loads are reasonable.

The contribution of precipitation to the chemical loads of streams which drain regions of more chemically reactive rock is less than its contribution to the three streams mentioned previously but may still

be significant to the loads of certain ions. For example, Pearson and Meyers (1971), considered the contribution of precipitation to the chemical loads of streams flowing into Oneida Lake in central New York State. These streams drain rocks, ranging from fairly inert sandstones and shales to limestones, and highly organic, peaty soils. The basin is mantled by glacial debris which includes fragments of a gypsum-bearing shale. For all natural streams, including those which drain the peaty areas, the total nitrogen input, from precipitation, to the basins exceeded the streams' output load by about 30 percent, the same relation as that shown in figure 7 for the extremely dilute streams. Also, the precipitation-sulfate contribution to the streams is as much as 70 percent of their total sulfate load, in spite of the traces of gypsiferous shale in the glacial deposits. Even in streams draining limestone, where average dissolved-solids contents range from 180 to 240 mg/l, the sulfate from precipitation contributes from 30 to 50 percent of the total sulfate load. This shows the need to consider the chemistry of atmospheric precipitation when describing the chemistry of concentrated stream water, as well as that of dilute streams.

Most ground water has enough contact with reactive minerals to mask the effects of precipitation on its chemistry. However, the Magothy aquifer, which underlies Long Island and supplies water to the eastern two-thirds of the island, consists largely of unreactive quartz (Cohen and others, 1968) and yields water having a very low dissolved-solids content. The contribution of precipitation is therefore particularly important to the chemistry of the water in this system.

Concentrations, rather than loads, are meaningful chemical descriptors of ground water. The concentrations of ions in the water entering the formation will be equal to those measured in the precipitation times the factor $P/(P-E)$, where P is precipitation amount and E is amount of evapotranspiration. Precipitation and evapotranspiration values for Long Island are given by Cohen, Franke, and Foxworthy (1968, p. 58). From these and the coastal precipitation chemistry data in table 2, the concentrations of ions in the recharge water were calculated. These, along with the average composition of a number of representative samples from the Magothy aquifer, are given in table 3.

Several striking comparisons can be made between the two sets of values. For example, the lack of substantial differences between the concentrations of calcium, magnesium, potassium, and chloride ions indicates a steady state in the geochemical cycling of these elements in the system. Among the cations there are differences in the sodium and hydrogen ion concentrations, but the sums of all the cations, in milliequivalents per liter, are the same. This suggests modification of the precipitation chemistry by an exchange reaction. In fact, the sodium

TABLE 3.—*Chemistry of evaporation-concentrated precipitation and water from the Magothy aquifer, Long Island, N.Y.*

[Magothy aquifer: Data from "Water Resources Data for New York, 1965—Part 2, Water Quality Records," available from U.S. Geol. Survey, Albany, N.Y.; U.S. Geol. Survey, unpub. data. Data expressed in milligrams per liter and milliequivalents per liter]

Substance	Precipitation concentrated by evapotranspiration		Magothy aquifer	
	mg/l	me/l	mg/l	me/l
Calcium.....	1.1	0.06	1.2	0.06
Magnesium.....	.2	.02	.4	.03
Sodium.....	2.0	.09	3.4	.15
Potassium.....	.3	.01	.4	.01
Hydrogen ion.....	---	.07	---	.00
Sum of cations.....	---	.25	---	.25
Bicarbonate.....	0	0	6	.10
Sulfate.....	7.5	.15	2.2	.05
Chloride.....	3.7	.10	3.5	.10
Sum of anions.....	---	.25	---	.25
Silica.....	---	---	7.3	---
Sum of dissolved solids.....	14.8	---	24.4	---

to hydrogen ion ratio and the silica content of Magothy water are as if they were controlled by the mineral kaolinite, as expected in this area (B. F. Jones, oral commun., 1969).

The sulfate content of Magothy aquifer water is less than half that of precipitation. This could result from reactions, in the soil or within the formation, that remove sulfate from the water. An additional explanation might be that the chemistry of 20th-century precipitation does not reflect that of the recharge water. The regional hydrochemistry is sufficiently well known to make the first possibility unlikely. Certain sulfate losses do occur in the formation, by reduction to sulfide and subsequent precipitation with iron, but the region of the aquifer in which these processes take place is deep, farther from the recharge area than the region being considered here.

Because of its much slower rate of movement, a ground-water body responds less rapidly to changes in its recharge than does a stream to changes in precipitation on its basin. Thus the water from the Magothy, described by the analyses summarized in table 3, probably represents recharge and precipitation that occurred several hundreds to several thousands of years ago. This water certainly antedates the industrial revolution and its accompanying increase in atmospheric sulfate from fossil fuel combustion; the sulfate concentration of the water should therefore be lower. The fact that water in the shallow aquifer on Long Island, while otherwise similar to water in the Magothy, has a sulfate content of about 6 mg/l (O. L. Franke, oral commun., 1969) supports this explanation for the differing sulfate concentrations. Thus it does appear that the chemistry of ground-water in Long Island is largely determined by the chemistry of atmospheric precipitation.

CONCLUSIONS

Data from sampling stations in the Northeastern United States show that atmospheric precipitation in this region is composed of a dilute calcium-hydrogen sulfate water having additional sodium and chloride near the coast. In the inland and coastal sections, excepting only the highly industrialized areas, variations among the precipitation chemical loads measured at various sites show no systematic differences that suggest sectional changes in precipitation chemistry.

In the rural inland section, the average loads of all measured constituents except sulfate and hydrogen ion are independent of precipitation amount. In the coastal section, sodium and chloride loads vary with precipitation, presumably owing to the effects of sea spray. Limited data show that industrial regions are marked by the presence of higher calcium, sulfate, and nitrate loads.

Atmospheric precipitation contributes substantially to the chemical loads of streams, particularly those draining basins underlain by unreactive rock. Essentially all the sulfate- and nitrogen-bearing ions and much of the chloride and potassium in such streams are supplied by precipitation. Even in areas of more chemically reactive rock, the stream loads of the nitrogenous species may still be largely from precipitation.

Most ground water contains enough material dissolved from its containing rock to mask the effect of precipitation on its recharge. However, because the Magothy aquifer on Long Island is so unreactive, the chemistry of its water appears to be controlled in large part by the chemistry of the atmospheric precipitation recharging it.

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