

ACIDIC PRECIPITATION AT A SITE WITHIN THE NORTHEASTERN CONURBATION

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ABSTRACT

Rain and snow were collected in plastic beakers either manually or with a Wong sampler during 58 precipitation events in 1974 at Yonkers, New York approximately 24 km north of the center of New York City. Determinations were made of total dissolved ionic species, free hydrogen ions, total hydrogen ions, sulfate, nitrate, chloride, and fluoride. Conductivity measurements ranged from 618 to 162 μmhos , pH from 3.4 to 4.9, total acidity from 36 to 557 $\mu\text{eq/l}$ sulfate from less than 1 to 20 mg/l, nitrate from less than 1 to 14 mg/l, and chloride from less than 1 to 7 mg/l. All fluoride concentrations were less than 0.1 mg/l.

The results indicate that precipitation at this suburban location adjacent to New York City is consistently acidic and contains concentrations of sulfate, nitrate, and chloride which are similar to values found for other locations in the northeastern United States. Positive correlations were found between nitrate and sulfate concentrations and acidity suggesting that the atmospheric contaminants, sulfur and nitrogen dioxide, are causally-related to the occurrence of acidic precipitation. Further research will be necessary to clarify the relative influence of natural and man-made sources of nitrogen and sulfur compounds and the contributions of gaseous and particulate contaminants in the atmosphere to the acidity of precipitation at this location.

INTRODUCTION

Acidic precipitation is a well-known phenomenon in northern Europe and some of its actual and potential environmental effects have been described (Sweden, 1971) but explanations for its occurrence still are debated. Although a similar problem exists in the northeastern United States, the available data are primarily for bulk deposition (wet and dry) (Pearson and Fisher, 1971; Likens, 1972; Frizzola and

Baier, 1975) and relatively few estimates of the composition of individual precipitation events are available (Cogbill and Likens, 1974; Frohlinger and Kane, 1975). This report presents results of the first phase of a program designed to characterize some of the chemical and physical properties and environmental effects of acidic precipitation. The data include the acidity and anionic composition of individual rain and snow samples collected during 1974 at a site in Yonkers, New York, about 24 km north of the geographical center of New York City.

EXPERIMENTAL

COLLECTION

Wet deposition was collected during 58 events from January through December 1974 at a height of 1.2 m above ground either manually or with an automatic rain sampler (Wong Labs.) with minimum collection of dry deposition between precipitation events. The sampling device consisted of a polyethylene funnel of 25 cm outer diameter placed over a polyethylene beaker of 0.6-liter capacity; two-liter beakers were used later in the study to avoid overflow during heavy precipitation. Samples were stored in tightly-closed polyethylene bottles at 1 to 5° C for periods of up to four weeks prior to analysis.

Precipitation was collected in an open field at an elevation of approximately 100 m above sea level, latitude 40°58'45" north, longitude 73°52'57" west (Figure 1). The nearest bodies of salt water were

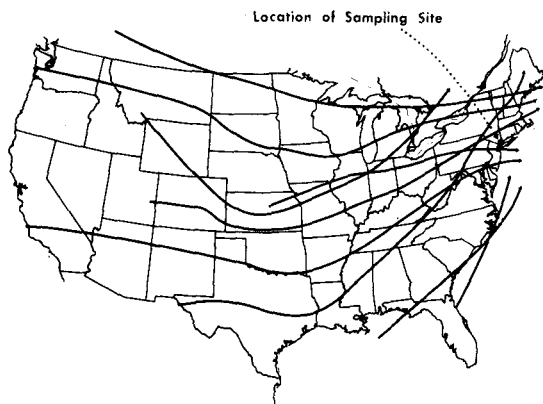


Figure 1. Location of precipitation sampling site in relation to prevailing storm trajectories in the United States.

the lower estuary of the Hudson River (about 1 km to the west) and Long Island Sound (about 11 km to the south-southeast).

Precipitation occurred as snow or a mixture of snow and rain in five of the 58 events sampled. No data are available for several events because they occurred on weekends or because liquid volumes were too low. Partial data were obtained for 16 events because the volume of liquid was insufficient for all analyses.

ANALYSIS OF CONDUCTIVITY AND FREE AND TOTAL HYDROGEN ION CONCENTRATION

Conductivity was measured using a conductivity bridge and pH with an expanded-scale pH meter*. During the measurement of pH and subsequent titration, the surface of the sample was swept with pure nitrogen gas. Samples were stirred during addition of standardized CO₂-free sodium hydroxide (0.008 N) but not during actual pH measurement. Sodium hydroxide was added in 0.06 ml aliquots and pH recorded after each addition until a reading of 9.4 to 9.5 was obtained. Nitrogen was bubbled through representative samples to determine the changes in free and total acidity occurring when volatile gases such as CO₂ are purged from solution.

Free hydrogen ion concentration was calculated from the initial pH; total hydrogen ion concentration was computed from the difference between equivalents of alkali added during titration and the equivalents of hydroxyl ions present at the final pH. The latter value included free hydrogen ions and titratable hydrogen ions of substances with pK values less than about 9.5 (e.g., carbonic acid). Titration curves were constructed both for precipitation samples and for standard samples of pure sulfuric and nitric acids and pure SO₂ and CO₂ bubbled through deionized water.

ANALYSIS OF ANIONS

Sulfate was measured by addition of barium perchlorate to precipitate barium sulfate and spectrophotometric determination of excess barium (II) ions with thorin reagent (Norwegian Institute for Air Research, 1974). Initially, nitrate was measured spectrophotometrically by reaction with brucine (Jenkins and Medsker, 1964). Chloride was determined by the mercury thiocyanate method (Florence and Farrar, 1971) and fluoride with a selective ion electrode (American Society for Testing and Materials, 1973).

*Conductivity measurements were performed with a Model 31 Yellow Springs Instrument Co. meter and pH with either a Model 12 Corning or Model 801 Orion digital electrometer. A No. 14073 Instrumentation Lab. combination electrode or a No. 476139 Corning pH electrode and No. 90-01-00 Orion reference electrode were used for pH measurements.

1971) and fluoride with a selective ion electrode (American Society for Testing and Materials, 1973).

Selected samples were titrated before and after addition of hydrogen peroxide solution to detect the presence of partially oxidized components. Conversion of a weak into a strong acid was clearly shown by titrating SO_2 in water before and after addition of hydrogen peroxide.

DATA ANALYSIS

Frequency distributions of measurements were constructed and joint distribution of paired variates was investigated by plotting one variate against another for all events on an arithmetic scale and by calculating partial correlation coefficients and testing for significance using the t-test.

Total deposition of components in rain and snow for the year were calculated from the measured concentrations and the volume of rainfall for each event. These values represent lower limits of deposition because analyses were not obtained on all events and, infrequently, measurement of rainfall volume was negatively biased due to overflow of the collector.

RESULTS

The minimum, maximum, and mean values for components of precipitation and total wet deposition for 1974 are summarized in Table I. Precipitation at Yonkers was consistently acidic; some samples had hydrogen ion concentrations more than two orders of magnitude greater than expected for a solution of pure water in equilibrium with the atmospheric concentrations of CO_2 . The concentrations of total available hydrogen ions were consistently greater than free hydrogen ions (Figure 2) and the ratio of total to free hydrogen ions tended to rise as pH increased. Free hydrogen ions usually comprised more than half of the total acidity in samples with pH values below 4.2. Values for total deposition of sulfate, nitrate and hydrogen ions (Table I) are similar to those found in northern Europe.

Sulfate was the anion generally in greatest concentration (Table I), but in some samples, concentrations of nitrate were greater than sulfate. On an equivalent basis, the ratio of sulfate to nitrate generally was more than two when the value of sample pH values was greater than 4; when the pH of the precipitation was less than 4, the ratio of sulfate to nitrate was usually less than 2.

Table I. Composition of precipitation collected at Yonkers, New York during 1974

Measurement	Minimum	Mean	Maximum	Total deposition ¹
Amount of precipitation, cm	0.03	1.49	7.1	85.9
Conductance, μmhos	6.8	47.7	162	-
pH	3.4	4.1	4.9	-
Free H^+ , $\mu\text{eq/l}$	13	103	380	0.88
Total H^+ , $\mu\text{eq/l}$	36	148	557	1.27
Ratio of total H^+ to free H^+	1.2	1.7 ²	2.9	-
Sulfate, mg/l	<1	4.8	20	4.12
Nitrate, mg/l	<1	4.4	14	3.78
Chloride, mg/l	<1	1.2	7	1.03
Fluoride, mg/l	<0.1	-	<0.1	-

¹ Data in this column given in kg/hectare except for amount of precipitation (cm).

² Mean ratio calculated only for those events in which both free and total hydrogen ions were measured (47 of 58 samples collected).

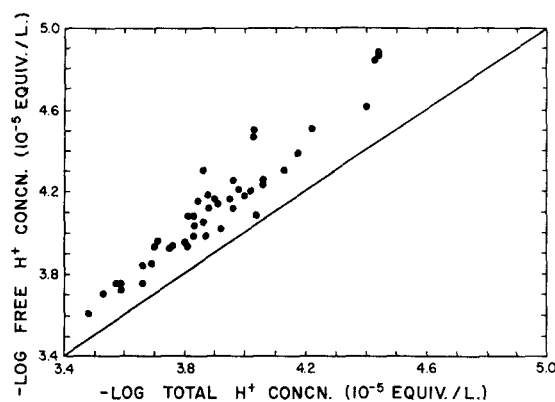


Figure 2. Joint distribution of free and total hydrogen ion concentrations of precipitation samples. The solid line indicates the expected distribution if there were no bound hydrogen ions.

Chloride was present usually in concentrations less than 2 mg/l and the concentration of fluoride seldom exceeded the precision of analyses (± 0.05 mg/l) and never was greater than 0.1 mg/l (Table I).

Frequency distributions for all measurements were skewed with a few data points at high concentrations; cumulative frequency distributions tended to be linear either on arithmetic or on logarithmic scales (free and total hydrogen ion concentrations).

Graphical analysis of the data indicated that there was a similarity between the distributions of certain variates. Free hydrogen ion concentration was positively correlated with total hydrogen ion concentration (Figure 2), conductance (Figure 3), nitrate concentration (Figure 4), and sulfate concentration (Figure 5); but inversely correlated with volume of precipitation event (not shown). Statistical

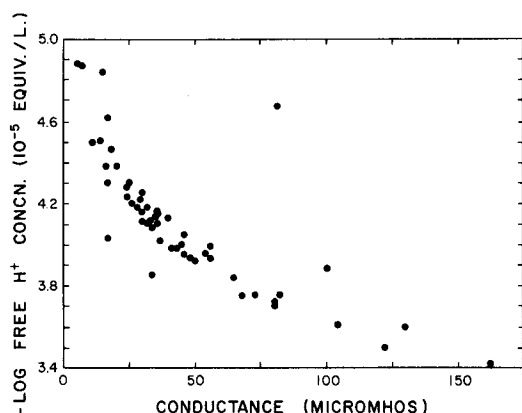


Figure 3. Joint distribution of free hydrogen ion concentrations and conductivity of precipitation samples.

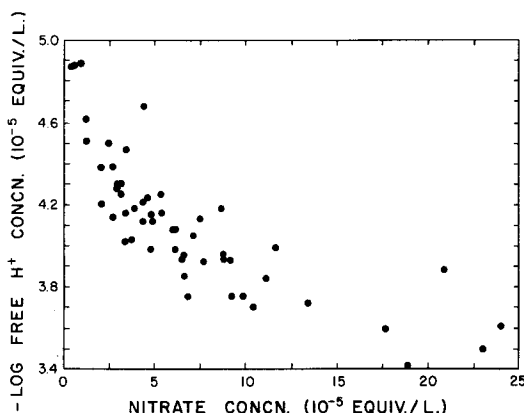


Figure 4. Joint distribution of free hydrogen ion and nitrate concentrations in precipitation samples.

analysis of the data using partial correlation coefficients demonstrated that the most significant correlations with free hydrogen ion concentrations were: volume, conductance, total hydrogen ion concentrations, and nitrate concentrations. Nitrate and sulfate concentrations also were significantly correlated.

All rain samples titrated as though they contained a monoprotic acid with an equivalence point in the vicinity of pH 7 (Figure 6). Synthetic aqueous solutions of carbon dioxide and sulfur dioxide, before and after oxidation to sulfuric acid with hydrogen peroxide, displayed titration curves (Figure 7) typical of carbonic acid (A), a combination of sulfurous and sulfuric acid (B), and sulfuric acid (C).

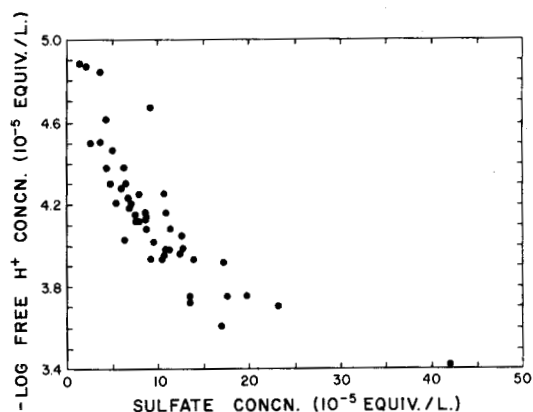


Figure 5. Joint distribution of free hydrogen ion and sulfate concentrations in precipitation samples.

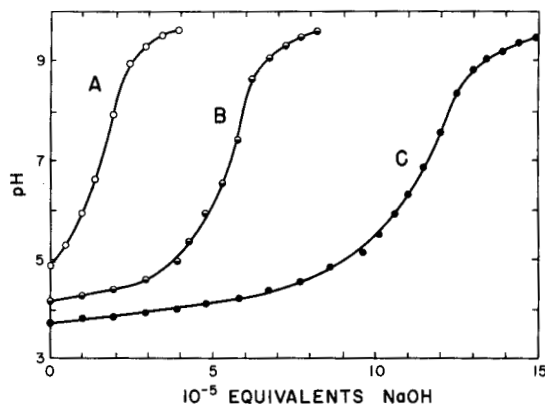


Figure 6. pH titration curves for three representative rain samples (50 ml aliquots) collected at Yonkers, New York in September (A), July (B) and August (C), 1974.

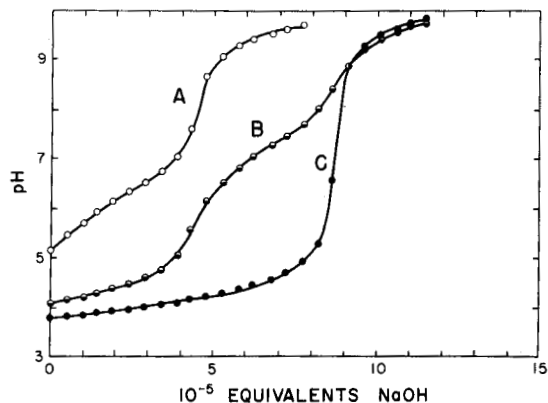


Figure 7. pH titration curves for solutions of carbon dioxide in water (A), sulfur dioxide in water (B), and sulfur dioxide in water (50 ml. aliquots) containing approximately 0.003% hydrogen peroxide v/v (C).

Purging rain samples of volatile gases with nitrogen gas produced only minor changes in free acidity but total hydrogen ion concentrations were reduced by 15 to 25% in different samples.

DISCUSSION AND CONCLUSIONS

The data in Table I demonstrate that precipitation of a consistently acidic nature falls in Yonkers, New York, a suburban site within the northeastern conurbation immediately adjacent to New York City (Figure 1). The sulfate, nitrate, and chloride as well as hydrogen ion concentrations in precipitation at this location (Table I) are similar to those found at other sites in the northeastern United States (Junge, 1963; Fisher et al, 1968; Pearson and Fisher, 1971; Likens and Bormann, 1974). However, the mean sulfate concentration of 4.8 mg/l tends to be toward the upper end of the ranges reported by others and the mean nitrate concentration of 4.4 mg/l is above that reported by others. According to Likens and Bormann (1974), nitrate concentrations in precipitation have increased since 1945. The mean chloride concentration of 1.2 mg/l is intermediate between coastal and continental sites (Pearson and Fisher, 1971).

The range of values found for hydrogen, sulfate, and chloride ion concentrations in precipitation tends to be narrower in previous reports than for Yonkers because bulk sampling for weekly or monthly periods tends to average out the storm by storm variations. In addition, bulk samples contain both wet and dry deposition and are not strictly comparable to event samples which contain only wet deposition.

The chemical form and physical state of sulfur and nitrogen compounds at the time of scavenging by rain are important factors in determining the acidity of precipitation because protons are formed during hydrolysis and oxidation of SO_2 and NO_2 . The correlations found between acidity and nitrate and sulfate concentrations in precipitation at Yonkers (Figures 4 and 5) tend to support the hypothesis that SO_2 and NO_2 are largely responsible for the acidity of precipitation (Junge, 1963; Pearson and Fisher, 1971; Johnson et al, 1972; Cogbill and Likens, 1974). Pearson and Fisher (1974) also have reported a correlation between hydrogen and sulfate ions in precipitation. In addition to entering precipitation in the gaseous form, sulfate and nitrate are components of aerosols and particulate matter. Granat (1972) and Likens and Bormann (1974) have suggested that atmospheric particulate matter has a neutralizing influence on the acidity of rain; however, Frizzola and Baier (1974) found that bulk samples (wet and dry deposition) are more acidic than event samples (wet deposition only) at coastal sites in New York. In addition, Brosset et al (1975) have found that particulate matter on the Swedish west coast is acidic. There is as yet no clear understanding of the relative contributions of atmospheric gases and particulate matter to the composition of precipitation in the northeastern United States.

Alkalimetric titrations of precipitation collected in Yonkers demonstrated the presence of substantial quantities of bound as well as free hydrogen ions (Table I and Figure 2). A portion of this weak

acidity probably was due to the presence of carbonic acid because decreases in total acidity of 15 to 25% were found after removal of volatile gases by bubbling nitrogen gas through rain samples. Other substances such as complexes of heavy metals, organic acids, and clay particles which dissociate weakly to produce protons in aqueous solution may account for the remaining bound hydrogen ion. The ratios of total to free hydrogen ions for precipitation in Yonkers ranged from 1.2 to 2.9 (Table I). Frohlinger and Kane (1975) found ratios of 2 to 100 for rainfall in a rural area of Pennsylvania and have interpreted this to mean that strong acids do not play a major role in determining the pH of rainwater. The high total to free hydrogen ion ratios found by Frohlinger and Kane may be due, in part, to the lower free hydrogen ion concentrations of precipitation in Pennsylvania (pH values ranged from 4.12 to 5.78). Differences in techniques used for titration may also be involved because the latter authors heated their samples and then titrated slowly without using an inert gas to prevent possible absorption of CO_2 from the ambient atmosphere.

Precautions to be taken during the measurement of pH have been published (Barnes, 1964) but there is no agreement or standardization among laboratories in the United States measuring the total acidity of precipitation. The sources of error vary with the method used and each method appears to have some disadvantages. Depending on vapor pressure gradients, volatile components may diffuse out of or into solution during storage or titration. Heating of samples and slow titration procedures may enhance gas exchange with the surrounding atmosphere. Titrations carried out in a laboratory atmosphere may result in absorption of CO_2 because CO_2 partial pressures are frequently above normal indoors. CO_2 also may diffuse into solution from the atmosphere especially when the sample being titrated becomes alkaline. On the other hand, efforts to purge acidic precipitation samples of CO_2 using an inert gas may cause loss of volatile acids including CO_2 derived from bicarbonate or carbonate in atmospheric particulate matter.

In this study we used an inert atmosphere during titration with no purging of CO_2 from samples even though CO_2 will slowly diffuse from solution during the titration. Even if all of the carbonic acid present in rain samples had been lost during these titrations, the maximum negative bias produced in total acidity measurements by this procedure would have been 15 to 25%.

Calculations of free and total hydrogen ions from the titration curves in Figure 6 indicate that strong acids comprise approximately 37% of sample A, 59% of sample B, and 66% of sample C. The lower pH rain samples collected at Yonkers contain the highest proportion of strong acids. Similar calculations for titrations of known substances displayed in Figure 7 indicate that strong acids comprise approximately 7% of sample A (CO_2 in water), 48% of sample B (SO_2 in water), and 97% of sample C (SO_2 in water oxidized to sulfuric acid with hydrogen peroxide). The evidence clearly implies that strong acids are largely responsible for the free hydrogen ion concentrations of rain samples at

this location. The measured concentrations of sulfate and nitrate found in these samples are more than sufficient to account for the accompanying free hydrogen ion concentrations assuming that SO_2 and NO_2 are the original sources of most of the sulfate and nitrate found.

Despite the emissions of fluorides from combustion of coal and other industrial operations in the United States (Committee on Biological Effects of Atmospheric Pollutants, 1971), the fluoride concentration of precipitation in Yonkers was consistently less than 0.1 mg/l (Table I). Fluorides in concentrations as high as 14 mg/l have been found in rain at other locations but mainly in the vicinity of specific industrial operations or where bituminous coal was being used for space heating (Garber, 1970; MacIntire et al, 1952; Harriss, 1969). There are no specific fluoride-emitting industries in Yonkers and bituminous coal has been replaced by anthracite coal, oil, and natural gas in the United States.

Comparisons between concentrations of measured components and conductivity (Table I) indicate that over 90% of the dissolved ionic species are accounted for by hydrogen, sulfate, nitrate, and chloride ions. The remaining conductivity is probably due to cationic species such as calcium, magnesium, sodium, and ammonium ions (Pearson and Fisher, 1971). The correlation between conductivity and acidity (Figure 3) largely reflects the influence of the high concentrations of hydrogen ions in precipitation. Conductivity of precipitation samples also may be influenced by volume of rain because dilution decreases the concentrations of ionic species.

The results of this study indicate that precipitation in Yonkers is equivalent to a dilute solution of sulfuric and nitric acids containing salts of sulfate, nitrate, and chloride in addition to smaller amounts of other inorganic and organic substances. A complete inventory of the composition of rain and snow may require analyses for hundreds of components because of the wide variety of materials present in trace quantities in the atmosphere. Further investigations are needed in order to evaluate the relationships between conductivity, volume of rain events, and cation and anion concentrations. The results of 1974 analyses suggest that there may be a more direct relationship between nitrate concentrations and acidity than between sulfate and acidity but data for at least several years is needed to evaluate these observations and to discover differences in composition with season and type of meteorological event.

The relative contribution of natural vs. anthropogenic sources of pollutants to the composition of precipitation in the northeastern United States is not clear. Junge (1963) has reported that the major sources of naturally-occurring sulfur compounds in the atmosphere are of maritime and coastal origin. The relatively low concentrations of chloride in the majority of precipitation samples taken at Yonkers (Table I) implies a predominately terrestrial origin for precipitation.

The prevailing movement of storm systems and air masses from west to east (Figure 1) also suggests that the major sources of components of rain at Yonkers are terrestrial rather than maritime in origin. However, this information does not indicate the actual course taken by air masses in their anti-cyclonic movement around storm centers. Cogbill and Likens (1975), using wind trajectory data, found that the mid-western region of the country is a major source of components of precipitation in the northeast. This suggestion needs additional verification.

ACKNOWLEDGMENTS

The authors thank L. H. Weinstein for several useful discussions and D. C. McCune for calculation of partial correlation coefficients. This study was financed in part with Federal funds from the Environmental Protection Agency under Grant No. 801070. The contents do not necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

REFERENCES

- American Public Health Assoc. 1965. STANDARD METHODS FOR THE EXAMINATION OF WATER AND WASTEWATER INCLUDING BOTTOM SEDIMENTS AND SLUDGES, New York.
- American Society for Testing and Materials. 1973. TENTATIVE METHODS FOR ANALYSIS OF FLUORIDE CONTENT OF THE ATMOSPHERE AND PLANT TISSUES (MANUAL PROCEDURES), Designation: D 3269-73T, No. 11, Philadelphia.
- Barnes, I. 1964. FIELD MEASUREMENT OF ALKALINITY AND pH, GEOLOGICAL SURVEY, WATER-SUPPLY PAPER 1535-H, U. S. Gov't. Printing Office, Washington, D. C.
- Brosset, C., K. Andreasson, and M. Ferm. 1975. The nature and possible origin of acid particles observed at the Swedish west coast, ATMOS. ENVIRON. 9, 631.
- Cogbill, C. V. and G. E. Likens. 1974. Acid precipitation in the northeastern United States, WATER RESOUR. RES. 10, 1133.
- Committee on Biologic Effects of Atmospheric Pollutants. 1971. FLUORIDES, National Academy of Sciences, Washington, D. C.

- Florence, T. M. and Y. J. Farrar. 1971. Spectrophotometric determination of chloride at the parts-per-billion level by the mercury thiocyanate method, *ANALYT. CHIM. ACTA* 54, 373.
- Frizzola, J. A. and J. H. Baier. 1975. Contaminants in rain water and their relation to water quality, *WATER SEWAGE WORKS* 122, 72 and 94.
- Garber, K. 1970. Fluoride in rainwater and vegetation, *FLUORIDE Q. REP.* 3, 22.
- Granat, L. 1972. ON THE RELATION BETWEEN pH AND THE CHEMICAL COMPOSITION IN ATMOSPHERIC PRECIPITATION, Report AC-18, Institute of Meteorology, University of Stockholm.
- Harriss, R. C. and H. H. Williams. 1969. Specific-ion electrode measurements on Br, Cl and F in atmospheric precipitation. *J. APPL. METEOROL.* 8, 299.
- Jenkins, D. and L. L. Medsker. 1964. Brucine method for determination of nitrate in ocean, estuarine, and fresh waters. *ANALYT. CHEM.* 36, 610.
- Johnson, N. M., R. C. Reynolds, and G. E. Likens. 1972. Atmospheric sulfur: its effect on the chemical weathering of New England, *SCIENCE* 177, 514.
- Junge, C. E. 1963. *AIR CHEMISTRY AND RADIOACTIVITY*, Academic Press, New York, pp. 311-351.
- Likens, G. E. 1972. THE CHEMISTRY OF PRECIPITATION IN THE CENTRAL FINGER LAKES REGION, Technical Report 50, Cornell University Water Resources and Marine Sciences Center, Ithaca.
- Likens, G. E. and F. H. Bormann. 1974. Acid rain: a serious regional environmental problem, *SCIENCE* 184, 1776.
- MacIntire, W. H., L. J. Hardin, and W. Hester. 1952. Measurement of atmospheric fluorine. Analyses of rain waters and Spanish moss exposures. *IND. ENGL. CHEM.* 44, 1365.
- Norwegian Institute for Air Research. 1974. (Rev. Ed.) SPECTROPHOTOMETRIC DETERMINATION OF SULPHATE BY THE BARIUM PERCHLORATE-THORIN METHOD, (LRTAP-4/71), Kjeller.
- Sweden, Royal Ministry for Foreign Affairs/Royal Ministry of Agriculture. 1971. AIR POLLUTION ACROSS NATIONAL BOUNDARIES: THE IMPACT ON THE ENVIRONMENT OF SULFUR IN AIR AND PRECIPITATION, (Sweden's Cast Study for the U. N. Conference on the Human Environment, Stockholm.

Pearson Jr., F. J. and D. W. Fisher. 1971. CHEMICAL COMPOSITION OF
ATMOSPHERIC PRECIPITATION IN THE NORTHEASTERN UNITED STATES.
Geological Survey Water-Supply Paper 1535-P, U.S. Gov't.
Printing Office, Washington, D.C.