THE CHEMICAL COMPOSITION OF ATMOSPHERIC PRECIPITATION FROM SELECTED STATIONS IN MICHIGAN

CURTIS J. RICHARDSON, Resource Ecology, School of Natural Resources, University of Michigan; and GEORGE E. MERVA, Department of Agricultural Engineering, Michigan State University.

ACKNOWLEDGEMENTS

Financial support for this study was provided by the Michigan State University Department of Agricultural Engineering and an NSF-RANN (project GI-34898) to The University of Michigan. We wish to thank M. Quade, Y. Wang, and J. Kruse for precipitation chemistry. D. Kiel and W. B. Rockwell were invaluable in the areas of computer management and statistical analyses. Cooperation of the Michigan Department of Health, The Michigan State Climatologists, The University of Michigan's Biological Station and School of Public Health, and the many wastewater treatment plant operators without whose help this report would not be possible, is gratefully acknowledged.

ABSTRACT

The pH and amount of rainfall from over 60 selected stations throughout northern and lower Michigan was determined from September 1972 to December 1974. Precipitation pH was determined for each station by calibrated electrode meters.

The seasonal weighted average and median pH from all stations in the study was 5.0 and 6.3, respectively. Daily readings from stations throughout Michigan indicate that pH is dependent on the amount of rainfall and that variations in it are often locally controlled. Collectively the pH values suggest carbonic acid control for most of the state.

Annual median pH varied from a high of 8.45 at Dimondale, a

station located 1.5 km from a concrete tile plant in central Michigan to 4.65 at Vassar, a small town located east of several industrial centers in the thumb region of the state.

A comparison of annual nutrient loading for NO_3^-, $SO_4^=$, Cl^-, $PO_4^=$, Ca^{++}, Mg^{++}, Na^+, K^+, and pH of rainwater from selected stations revealed that the eastern U.S. stations reporting pH's $<$ 4.02 have similar loadings for NO_3 but twice the SO_4 input found for rural areas of Michigan.

INTRODUCTION

Air pollution, a product of our highly industrial and mechanized world, is one of the serious environmental problems in the biosphere today. The release of large quantities of sulfur and nitrogen oxides to the atmosphere along with large amounts of contaminants and nutrients have created environmental problems at both the local and global scale.

Scientists in northwestern Europe (Barrett and Brodin 1955, Mrose 1966, Odén 1968, Brosset 1973, and Forland 1973) and the United States (Junge 1958, Junge and Werby 1958, Gambell and Fisher 1964, Fisher et al. 1968, Pearson and Fisher 1971, Likens et al. 1972, and Likens and Bormann 1974) have reported a trend toward increased acidity, NO_x and SO_4 loadings in rainfall due to human activities. Recent work by these scientists indicate a marked decrease in pH during the past two decades. The ecological effects of altering atmospheric chemistry is well documented. Almer et al. (1974) reported a reduction in phytoplankton and zooplankton species and the complete removal of roach, arctic char, trout and perch from many lakes in Sweden as a result of acidification. Johansson et al. (1973) have also noted that frequency of fish hatching in lakes and rivers in northwestern Europe decreased from about 50% at pH 7 to about 4% at pH 4. Jensen and Snekrik (1972) document that acid precipitation due to industrial effects has eliminated brown trout from many lakes and streams in southern Norway. In Ontario, Canada, Beamish and Harvey (1972) and Beamish (1974) traced the loss of lake trout, lake herring, white suckers and other fish to increasing levels of acidity caused mainly by SO_2 emitted by metal smelters in Sudbury.

The effects of increased air pollutants and acidity on increased soil leaching, reduced net primary productivity of coniferous forest species, foliar tissue damage and reduced growth in birch were shown by Overrein (1972), Westman (1974), and Wood and Bormann (1974), respectively. An understanding, documentation and reduction of man's influence on atmospheric chemistry and in turn on species diversity and ecosystem function is thus critical to the future survival of the biosphere as we know it.

The purpose of this investigation has focused primarily on establishing to what extent acidification of precipitation is taking place throughout Michigan. This information coupled with a preliminary estimate of nutrient loadings for key constitutents should aid in determining the present influence of atmospheric inputs to various ecosystems in Michigan. The importance of urban and rural input differences and local influence versus regional effects are also discussed.

SAMPLING PROCEDURE AND METHODS

In 1972, a cooperative project was developed between the Department of Agricultural Engineering at Michigan State University, the Michigan Weather Service and the Department of Natural Resources of the state of Michigan utilizing the facilities of over 100 waste water treatment plants throughout Michigan to determine potential areas of air pollution damage to agricultural vegetation. Data in this report are from 60 stations which have reported at least 12 months. Since the type of pollutants being considered are transported through the atmosphere, it was hypothesized that the removal of pollutants by precipitation could be detected by examining the pH of rainfall.

Each station took daily pH readings and rainfall amounts from samples of rainwater collected during the previous 24 hours in a standardized rainfall collector located one meter above ground level. Precipitation pH was determined by calibrated electrode meters. Selected stations also recorded pH for rainfalls of less than 2.5 mm (0.1 in), 2.5 to 13 mm (0.1 to 0.5 in) and rainfalls of greater than 13 mm (0.5 in). For further discussion of methods see Merva (1974). In 1973 and 1974 fifteen selected stations were established by the School of Natural Resources and the School of Public Health, University of Michigan to determine nutrient loading for rural and industrially influenced areas, respectively. Ten of the stations were located in rural areas of northern lower Michigan and five were located around Saginaw Bay. Additional data from stations in Michigan were supplied by U.S. E.P.A. and the Canadian Government.

Immediately after each precipitation the samples were filtered through cheese cloth and frozen for analysis. Cation analyses (Ca^{++}, Mg^{++}, K^{+}, and Na^{+}) were completed following standard procedures of atomic absorption spectrophotometry (Perkin-Elmer 1973). An autoanalyzer (Technicon) was used to analyze for NO_3^-, NH_4^+, $PO_4^{\equiv}$, and Cl^-. Nitrate was analyzed for by the Greis-Ilsovary reaction and is reported as NO_3-N (E.P.A. 1974). The Berphelot reaction was used to analyze for NH_4-N (E.P.A. 1974). After manual digestion phosphorous was analyzed using molybdate reaction (E.P.A. 1974). All statistical analyses follow Sokal and Rohlf (1969). Acidity was calculated on free hydrogen ion concentrations weighted proportionally to the amount of water and pH during each rainfall. Data are reported by the weighted mean and the median (M) statistic (1972-74). The weighted mean reflects the amount of rainfall while the median statistic reports only directly read pH units. The values for regions are compared by relative frequency in .1 pH units.

RESULTS AND DISCUSSION

An examination of pH values for rainfall from 60 stations in Michigan reveals that wide extremes are found throughout the state (figure 1). The median acidity for the entire state is 6.3. The

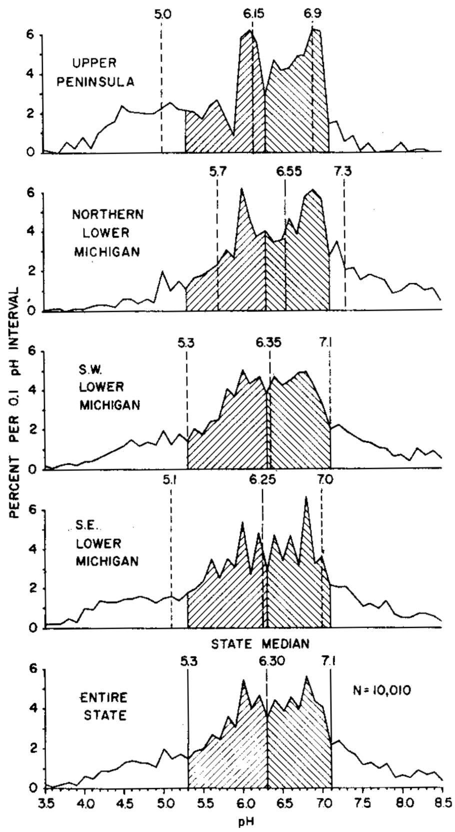

Figure 1. Frequency distribution by region for pH values collected in Michigan (1972-74) from 60 selected stations. The median pH value (±33%) is shown for the entire state by solid lines and hatching. Dashed lines indicate regional pH median values (- - -) and 83.3 and 16.7 percentile (---), respectively. (Note median = 50 percentile, 50 + 33.3 = 83.3, 50 - 33.3 = 16.7).

weighted annual pH is 5.03. This is considerably above the weighted pH values of 4.03, 3.91 and 3.98 reported by Likens et al. (1972) for selected stations in northeastern United States but is less than the average pH of six reported for Iowa (1971-73) by Tabatabai and Laflen (1975). The range of values (pH 3.5-8.5) do compare with those reported for other parts of the country by Whitehead and Feth (1974), Brezonik et al. (1968), and Klein (1974).

On a regional basis northern lower Michigan, an area of low population density and industry, has the highest annual median pH (figure 1). This trend was also found by Klein (1974). The heavily populated and industrialized southern portions of the state closely followed the entire state's frequency distribution and median pH value (figure 1). The Upper Peninsula had only six stations reporting and was heavily influenced by low pH values reported by stations located near pulp and mining industries in the western half of the peninsula.

Collectively the pH values suggest carbonic acid control for most of the state. However, analyses by individual stations reveal the importance of point source inputs and ground loading effects.

The importance of local influence on rainfall acidity is demonstrated by comparing four stations (Reed City, Vassar, Dimondale, and Deerfield) considered representative of locations influenced by forested land, heavy metal industry, a concrete tile plant, and a town adjacent to large population centers, respectively.

Reed City (population 2,296) is located in Oseola County in central Michigan and is bordered by federal and state forest on the west and east sides respectively. The seasonal variation in rainfall pH shows no consistent pattern over the three year period (figure 2). The weighted mean and range of pH's for this station indicate carbonic acid control (figures 2, 3).

The highest median pH (8.45) for the entire state occurred at Dimondale, a small village southwest of Lansing in central Michigan (figure 3). A seasonal trend is lacking through the time period measured (figure 2). The exceptionally high alkaline pH in rainwater is the result of a concrete tile plant located approximately 1.5 km from the collection site. The ecological effects of highly alkaline rainfall on entire systems are not well known, but potentially they add stress to the ecosystem. The tolerances of most species of flora and fauna (including man) to long term extremes in pH are in general low. Thus any variation from normal pH either acid or alkaline should be used as an indication of potential pollution problems.

Vassar (population 2,802) located in Tuscola County in the thumb region of Michigan is due east of several metal industries. There appears to be no seasonal pattern (figure 2) but the weighted annual acidity of 4.2 and the median pH (figure 3) of less than five

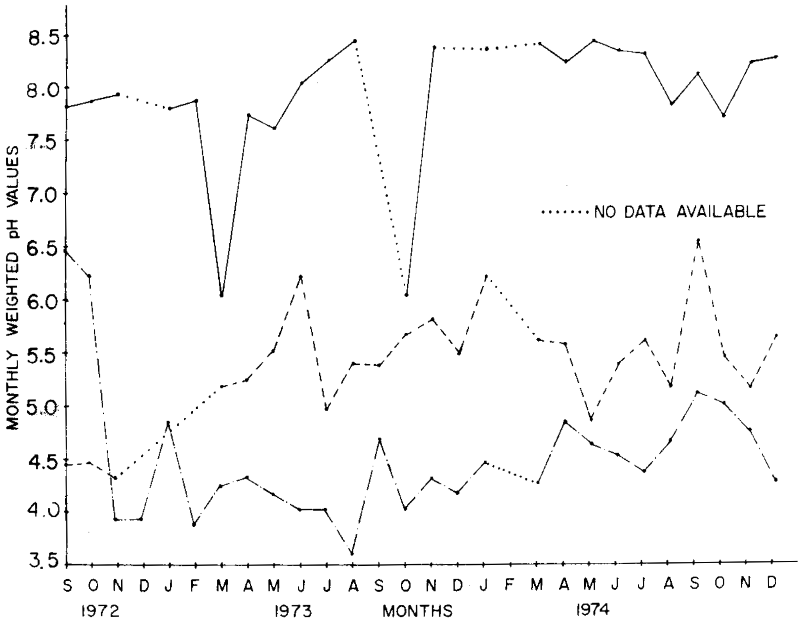

Figure 2. Seasonal trends (1972-74) in weighted monthly pH values for three stations in Michigan (Reed City ---, Dimondale ---, and Vassar -•-•).

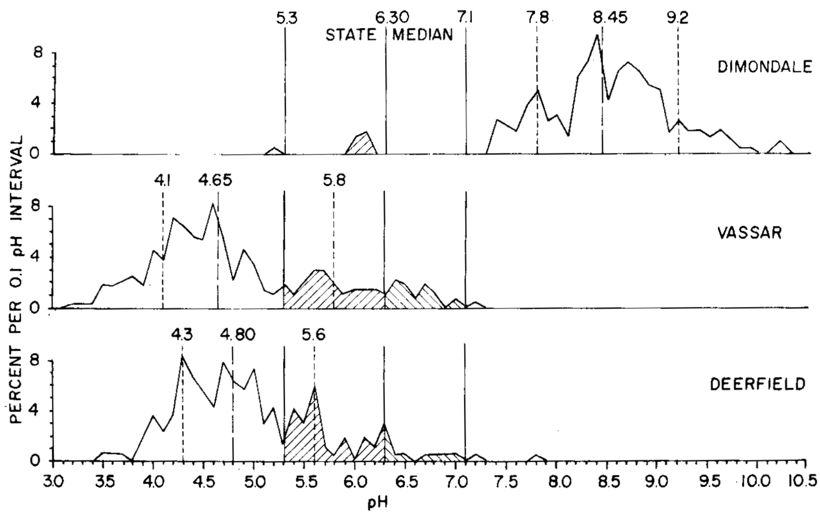

Figure 3. Frequency distribution of pH values for selected stations in Michigan. The median pH value ±33% is shown for the entire state by solid lines and hatching. Dashed lines indicate median station pH values (- - -) and the 83.3 and 16.7 percentile (---), respectively. (Note median = 50 percentile, 50 + 33.3 = 83.3, 50 - 33.3 = 16.7.)

indicates unusually strong acids in the rain (Likens and Bormann 1974).

Deerfield (population 834) reported the second lowest median pH for the state (figure 3). It is located in Lenawee County in the southeastern part of the state between Detroit, Michigan and Toledo, Ohio. Large metropolitan centers which have high emission levels of SO_x and NO_x can produce strong acid rainfalls (Likens et al. 1972). The levels in Detroit and Toledo for NO_x and SO_x emission (thousand tons per year) is estimated to be 1566 and 544, and 200 and 336, respectively (Acres 1975). This is considerably higher than the state's average of 101 and 103 for NO_x and SO_x, respectively (Acres 1975). Further research in meteorology and atmospheric chemistry is needed to help locate sources of nutrient loadings for specific elemental species and determine their role in rainfall acidity for this station and a number of key areas in the state.

Other stations reporting pH values below the "normal" of 5.7 (pH of pure rainwater which is saturated with CO_2 at normal pressure, Barrett and Brodin 1955) are found scattered through the state. At this time, it appears that local influences and ground loading [Michigan glacial soils are high in calcareous material as noted by basic pH values (>7.5) for many unpolluted lakes, streams, groundwater, and soil leachate (Richardson 1975)] are more important than regional influences on precipitation acidity as measured several meters above the ground by our study.

The median pH is dependent on the amount of rainfall (figure 4). A pairwise comparison (t-statistic) between the amount of rainfall (< 2.5 mm, 2.5 to 13 mm and > 13 mm) and acidity (weighted hydrogen ion concentration) indicates that a statistically significant difference ($p<0.01$) does exist between light (<2.5 mm) and heavy (>13 mm) precipitation. Light rainfall is more basic (M pH: 6.36) than heavy rainfall (M pH: 6.15). The ecological significance of these differences seems minimal.

Mean annual nutrient inputs and pH for selected stations in Michigan and New York state are given in table I. The nutrient levels in general follow the values reported for the midwest by Junge (1958), Junge and Werby (1958), Lodge et al. (1968) Hoeft et al. (1972), and Wolaver and Lieth (1972). Because of a lack of long term data from comparable stations a definitive answer on temporal trends is not possible.

A comparison of values from the eastern U.S. (table I) indicates that the loading for most cations is similar except for higher Ca input in Michigan's rural locations and higher Na levels in the Pellston area.

Loading values for NO_3 and NH_4 are similar in both regions, but

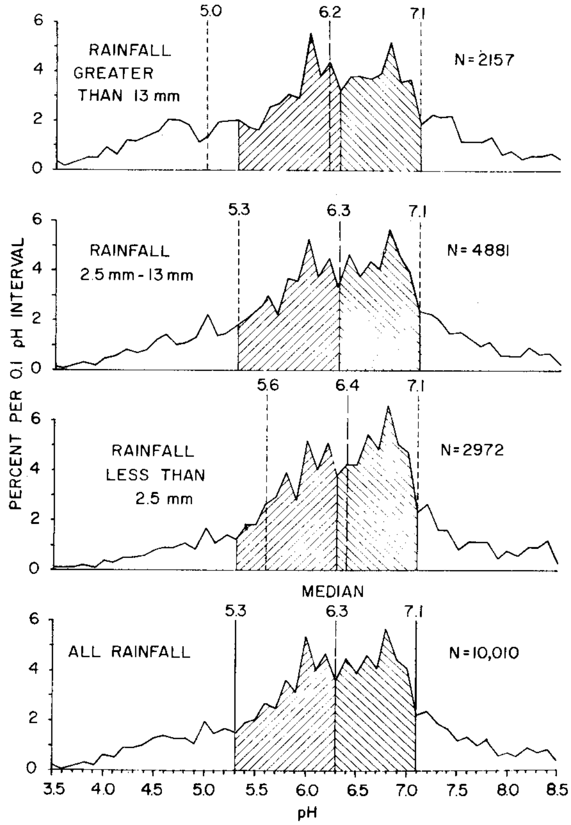

Figure 4. Frequency distribution of pH values for three depths of rainfall. The median pH value ±33% is shown for the entire state by solid lines and hatching. Dashed lines indicate median station pH values (- - -) and the 83.3 and 16.7 percentile (---), respectively. (Note median = 50 percentile, 50 + 33.3 = 83.3, 50 - 33.3 = 16.7.)

Table I. Preliminary estimate of nutrient loading (Kg/ha/yr) for bulk precipitation in selected stations in Michigan and New York.

LOCATION	CONSTITUENT Kg/ha/yr														
	NO_3-N	NH_4-N	NO_2	Total PO_4-P	Soluble P	Ca	Mg	K	Na	Cl	SO_4	Fe	Si	Rainfall[2] Cm	pH
Michigan															
Rural															
Pellston[3] (Northern Lower Mi.)	4.03	3.09	----	0.25	0.20	10.52	1.66	2.66	6.30	9.41	18.25	----	5.80	79.4	5.35[4]
Houghton Lake (Central Mi.)	3.20	2.09	0.01	0.31	0.29	9.46	----	3.20	----	----	----	0.36	----	72.8	5.27
Urban-Industry															
Saginaw Bay[5]	4.40	----	0.33	1.21	1.12	----	----	----	----	----	68.75[6]	----	----	68.9	4.90
New York[7] (1970-71)															
Ithaca	4.22	3.17	----	0.05	----	6.48	1.54	5.64	1.35	9.77	39.49	----	----	96.1	3.98
Aurora	4.28	3.26	----	0.06	----	4.77	0.75	1.09	0.95	12.69	49.65	----	----	98.4	3.91
Geneva	4.77	3.52	----	0.05	----	3.31	0.57	0.41	0.77	7.10	34.86	----	----	95.8	4.02

[1]Nutrient concentrations are weighted averages for bulk samples (rain and dry fall).

[2]Twenty-five year average.

[3]Average loading from ten stations (1973-74).

[4]Average of northern lower Michigan region (station pH 4.8).

[5]Average loading from five stations (six months 1974). Michigan School of Public Health Data.

[6]Sulfate measured on three rainfalls in August 1973 (E.P.A., 1974).

[7]Data from Likens (1972).

the levels of phosphorous are considerably lower in New York (table I). Annual SO_4 inputs in central New York are about double those found in the northern rural areas of Michigan. Likens et al. (1972) reported that higher levels of SO_4 produce strong acid in rainfalls. This coupled with the stronger buffering capacity of Michigan precipitation (table I) may account for the generally higher pH values found in our study.

However, a few samples taken from one region in Michigan (Saginaw Bay, an area downwind of heavy industry and high population centers) indicate that seasonal inputs of SO_4 may be double those of central New York. The mean weighted pH (4.9) for the area is probably the result of strong acid precipitation. Vassar, the station with the state's median low pH (4.65), is also found in this area.

This study although preliminary does indicate potential problems for some locations in Michigan. They seem to be local in origin at the present time but a final answer is not possible until long term regional meterorological and atmospheric chemistry studies are undertaken. The need to establish a statewide sampling network is paramount to our goal in understanding man's long term effects on the ecosystem.

BIBLIOGRAPHY

Acres Consulting Services and Earth Science Consultants. 1975. ATMOSPHERIC LOADINGS OF THE UPPER GREAT LAKES. VOLUME II. Canada.

Almer, B. W., W. Dickson, D. Ekstrom, E. Hornstrom, and W. Miller. 1974. Effects of acidification on Swedish lakes. AMBIO. 3, 30.

Barrett, E. and G. Brodin. 1955. The acidity of Scandinavian precipitation. TELLUS. 7, 251.

Beamish, R. J. 1974. Loss of fish populations from unexploited remote lakes in Ontario, Canada, as a consequence of atmospheric fallout of acid. WATER RES. 8, 85.

Beamish, R. J., and H. H. Harvey. 1972. Acidification of the Cloche Mountain lakes, Ontario, and resulting fish mortalities. J. FISH RES. BD. CAN. 29, 1131.

Brosset, C. 1973. Air-borne acid. AMBIO. 2, 2.

Environmental Protection Agency. 1974. Methods for chemical analysis of water and wastes. NAT. ENV. RES. CENTER PUB. 16020.

Fisher, D. W., A. W. Gambell, G. E. Likens, and F. H. Bormann. 1968. Atmospheric contributions to water quality of streams in the Hubbard Brook Experimental Forest, New Hampshire. WATER RESOURCES RES. 4, 1115.

Forland, E. J. 1973. A study of the acidity in the precipitation in southwestern Norway. TELLUS. 25, 291.

Gambell, A and D. Fisher. 1964. Occurrence of sulfate and nitrate in rainfall. J. OF GEOPHYS. RES. 69, 4203.

Hoeft, R. G., D. R. Keeney, and L. M. Walsh. 1972. Nitrogen and sulfur in precipitation and sulfur dioxide in the atmosphere in Wisconsin. J. ENVIRON. QUALITY. 1, 203.

Jensen, K. W. and E. Snekrik. 1972. Low pH levels wipe out salmon and trout populations in southernmost Norway. AMBIO. 1, 223.

Johansson, N., J. E. Kohlstrom, and A. Wahlberg. 1973. Low pH values shown to affect developing fish eggs. AMBIO. 2, 42.

Junge, C. E. 1958. The distribution of ammonia and nitrate in rain water over the United States. TRANS. AMER. GEOPHYS. UNION. 39, 241.

Junge, C. E. and R. T. Werby. 1958. The concentrations of chlorite, sodium, potassium, calcium and sulphate in rainwater over the United States. J. METEROL. 15, 417.

Klein, A. E. 1974. Acid rain in the United States. THE SCI TEACHER. 41, 36.

Likens, G. E. 1972. The chemistry of precipitation in the central Finger Lakes region. REPORT. 50. CORNELL UNIV WATER RESOURCES.

Likens, G. E., F. H. Bormann. 1974. Acid rain. A serious regional environmental problem. SCIENCE. 184, 1176.

Likens, G. E., F. H. Bormann and N. M. Johnson. 1972. Acid rain. ENVIRONMENT. 14, 33.

Lodge, J. P., J. B. Pate, W. Baskergill, G. S. Swanson, K. C. Hill, E. Lorange, and A. L. Lazrus. 1968. Chemistry of United States precipitation. Final Rept. on the Nat'l Precip. Sampling Network. LAB. OF ATM. SCIENCES. Boulder, Colo.

Merva, G. E. 1974. pH VARIATIONS IN MICHIGAN RAINFALL. Res. Report. Michigan State Univ. 234.

Mrose, H. 1966. Measurements of pH and chemical analyses of rain, snow, and fog-water. TELLUS. 18, 266.

Oden, S. 1968. The acidification of air and precipitation and its consequences on the natural environment. (In Swedish). Nat. Sci. Res. Council of Sweden. ECOLOGY BULL. 1.

Overrein, L. N. 1972. Sulfur pollution patterns observed, leaching of calcium forest soil determined. AMBIO. 1, 145.

Pearson, F. J., and D. W. Fisher. 1971. Chemical composition of atmospheric precipitation in the northeastern United States. GEOL. SURV. WATER-SUPPLY PAPER. 1535 p.

Perkins-Elmer. 1973. ANALYTICAL METH. FOR A. A..SPECTROPHOTOMETRY.

Richardson, C. J. 1975. The effects of land use on water quality in northern lower Michigan. NSF-RANN REPORT. 1. Univ. of Michigan.

Sokal, R. R., and F. J Rohlf. 1969. BIOMETRY - THE PRINCIPLES AND PRACTICE OF STATISTICS IN BIOLOGICAL RESEARCH. Freehman and Co. San Francisco.

Tabatabai, M. A., and J. M. Laflen. 1975. Nutrient content of precipitation over Iowa. FIRST INTER. SYM. OF ACID PRECIPITATION AND THE FOREST ECOSYSTEM. Ohio State. May 1975. (abstract).

Westman, L. 1974. Air pollution indicators and growth of spruce and pine near a sulfite plant. AMBIO. 3, 189.

Wolaver, T. G., and H. Lieth. 1972. U.S. precipitation chemistry theory and quantitative models. ENVIRONMENTAL PROTECTION AGENCY REPORT. Ecol. Research Division. Triangle Park, North Carolina.

Wood, T., and F. H. Bormann. 1974. The effects of artificial acid mist upon the growth of *Betula alleghaniensis* Britt. ENVIRON. POLLUT. 7, 259.