

DOE-EV04327-1
DE-EV04327-1

THE CHEMICAL COMPOSITION OF ATMOSPHERIC
PRECIPITATION IN MINNESOTA AND NORTH DAKOTA

Final Report

for Period 1 July 1977 - 30 June 1980

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July 1980

Prepared For

THE U.S. DEPARTMENT OF ENERGY (FORMERLY ERDA).

UNDER CONTRACT NO. DE-AC02-77EV04327 (FORMERLY EE-77-S-02-4327)

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ABSTRACT

Precipitation chemistry in central North America appears to be controlled by interaction between soil-derived alkaline dust and gaseous NH_3 from the cultivated prairie and anthropogenic acid aerosols from the urban-industrial Lower Great Lakes-Ohio Valley region. Analyses of major ions and trace metals in precipitation event and snow core samples along a 600-km transect from the North Dakota prairie to the northeastern Minnesota forest indicate that loadings and concentrations of Ca^{++} , Mg^{++} , P_{tot} , Al, Fe, M_n , and other soil-derived material decrease with increasing distance from the prairie. Acidity is highest in the east and decreases to the west. Sulfate has natural sources in the west and anthropogenic sources in the east; its concentration was least at sites in the middle of the transect. Acidity increased and inputs of soil-derived elements decreased during winter when snow and freezing temperatures reduced alkaline influxes to the region.

Atmospheric inputs of N and P may be beneficial to nutrient-poor ecosystems. However, precipitation in the eastern portions of the region which are highly sensitive to acid inputs, is approaching levels of acidity known to cause adverse effects. Any increase in acid loading will increase this danger.

INTRODUCTION

The phenomenon of acid precipitation and the problems caused by it have been well documented (see for example Likens et al. 1979 or Galloway et al. 1978). Cogbill and Likens (1974) noted that the extent and severity of acid precipitation in North America was increasing. Recent precipitation chemistry data indicate that an area east of the Mississippi River extending north to the Canadian Arctic is subject to acid precipitation (Whelpdale 1978, Gibson and Baker 1979) on an annual basis. This area is partly coincident with the region of most dense SO_x and NO_x emissions (Likens et al. 1979, Husar and Patterson 1980); other factors must also affect the location and extent of the area subject to acid precipitation.

Two factors potentially affecting the extent of acid rain are the production of alkaline dusts and gaseous NH_3 in the cultivated mid-western prairie. Smith et al. (1970) noted an increase in dust deposition across North America from the humid northeast to the semi-arid central United States. Dust pH also increased from faintly acid to distinctly alkaline along this gradient. Denmead et al. (1974) and Lenhard and Gravenhurst (1980) observed fluxes of NH_3 from the soil to the atmosphere over Australian sheep pastures and rural Western Germany, respectively. Lau and Charlson (1977) calculated atmospheric NH_3 concentrations that were highest over the mid-western United States and decreased toward the coasts. Neutralization by gaseous NH_3 or soil dusts would reduce precipitation acidity even where emissions of acid precursors, SO_x and NO_x , might otherwise be expected to cause acid precipitation.

A gradient in precipitation pH and alkaline dust fall has been observed on a smaller regional scale in and around Minnesota. Gorham and Tilton (1978) found a decline in the mineral content of Sphagnum from west to east across Minnesota. The pH and concentrations of particles, phosphorus,

and all ions measured were much less in snow from the forested Experimental Lakes Area (ELA) of northwestern Ontario (Barica and Armstrong 1971) than in snow from the prairies of North Dakota (Adomaitis et al. 1967). Gorham (1976) found a similar trend in snow samples collected along a transect from North Dakota prairie to eastern Minnesota forests after a blizzard in 1975.

Concentrations of PCBs in Lake Superior sediments, where local sources are minimal (Eisenreich et al. 1980), indicate long-range transport of anthropogenic material to Minnesota from the Lower Great Lakes-Ohio Valley region. Calculations of air mass trajectories and observations from satellites confirm that long-range transport of pollutants, which must include acid precursors, affects Minnesota. The balance between influxes of alkaline material from the west and acid material from the east should therefore control precipitation chemistry in Minnesota.

We initiated a study to generate baseline data on precipitation chemistry across Minnesota and to investigate the effect on precipitation of the interactions between acid and alkaline materials.

SAMPLE COLLECTION AND ANALYSIS

Precipitation samples were collected at three sites shown in figure 1 along a transect from the eastern North Dakota prairie to the remote northeastern Minnesota forests. The western site, at the Tewaukon Wildlife Refuge, is surrounded by a 1 - 2 km buffer of grassland and marsh within an intensely cultivated region, and was chosen to provide precipitation dominated by the alkaline influence of dust and ammonia. The Hovland site, located in a remote forested area of northeastern Minnesota far from serious local pollutant or dust sources, was chosen to provide precipitation influenced primarily by long-range transport of acid anthropogenic material. The Itasca site,

midway between the other two sites and 50 km east of the forest-prairie transition, was chosen to provide precipitation influenced by a mixture of these two influences. Snowpack samples were taken at the collector sites and at intermediate locations as indicated in figure 1.

We used Aerochem Metrics automatic wet-dry precipitation collectors to sample wet-only precipitation and dry fallout. This sampler was also chosen for use in the National Atmospheric Deposition Program network. Wet precipitation was sampled on an event basis; dry fallout was collected over longer intervals. This sampling scheme retained maximum information about variations among individual storms and minimized contamination and chemical alteration of samples in the field.

Personnel at the sites sealed the wet-collection bucket after each precipitation event and shipped the sample to the laboratory. The day it arrived we measured pH and specific conductivity, weighed the sample to determine volume, and filtered an aliquot through a 0.45 μm Nuclepore membrane. Filtered portions of the sample were stored for later determination of Na^+ , K^+ , Ca^{++} , Mg^{++} , Cl^- , NO_3^- , and $\text{SO}_4^{=}$; total P and NH_4^+ were measured in unfiltered aliquots, and trace metals in acidified unfiltered aliquots. We used procedures described in Stainton et al. (1977) or the instrument manuals (Dionex, Varian, Perkin-Elmer). We measured alkalinity by the Gran titration method in samples with $\text{pH} > 5.5$ that had sufficient volume. Dry fallout samples were collected bi-weekly or monthly and those that were not appreciably contaminated by bird feces were dissolved in 250 ml of double-distilled deionized H_2O and analyzed by the same procedures used for wet precipitation samples. Snow-core samples were sealed in plastic bags and stored frozen until they were analyzed. Snow-cores were melted and handled in the same way as event-precipitation samples.

RESULTS AND DISCUSSION

Event-sample Concentrations

During the 14 month study period 47, 79, and 81 event-precipitation samples were collected at Tewaukon, Itasca, and Hovland, respectively. The analytical results for these samples, summarized in tables 1 and 2, indicate a decreasing trend in pH, metal cations and particulates from west to east. The concentrations of NH_4^+ and the acid anions NO_3^- and $\text{SO}_4^{=}$ tended to be lowest at Itasca and higher at the other sites. This was most pronounced for NH_4^+ and $\text{SO}_4^{=}$. Chloride analyses were subject to analytical problems and/or contamination and the concentrations of many samples were unrealistically high. We do not believe that a residue of HCl from the bucket washing was involved since there was no systematic relationship between pH and Cl^- concentration. Total phosphorus concentrations generally declined from Tewaukon to Itasca, but because of a small number of samples at Hovland containing pollen, seeds, or other organic debris, the volume-weighted mean concentration of P_{TOT} was nearly as high there as at Tewaukon. However, the geometric mean concentration was lower than at either Tewaukon or Itasca, as would be expected if the soil was the primary source for P. Most trace metal concentrations decreased from Tewaukon to Hovland, but Pb and Cu had lowest concentrations at Itasca.

Specific conductivity was highest at Hovland because of the high concentration of H^+ ; the lowest conductivity was observed at Itasca. The conductance due to ions other than H^+ was less at Hovland than at Tewaukon, but it was still least at Itasca.

As shown in table 3, the importance of H^+ increased from Tewaukon, where it was least important, to Hovland, where it and Ca^{++} were second only to NH_4^+ . The importance of Ca^{++} relative to NH_4^+ declined from Tewaukon to Hovland. The remainder of the cations had the same relative

order at all three sites. The concentration of $\text{SO}_4^{=}$ exceeded NO_3^- at all three sites, and only at Tewaukon was HCO_3^- more than a minor constituent of precipitation.

Wet Deposition

We estimated monthly wet deposition as the product of monthly precipitation and the volume-weighted mean concentration of all samples analyzed for that month. The average of sums of monthly wet deposition over the three 12-month periods (May-April, June-May, and July-June) was used as an estimate of annual wet deposition.

As indicated in table 4, wet deposition of H^+ , NH_4^+ , and SO_4^- increased from Tewaukon to Hovland. Potassium deposition followed an inverse trend; it was greatest at Tewaukon and least at Hovland, but varied only slightly. Because of the substantially greater precipitation volume at Itasca, deposition of the remaining cations, Ca^{++} , Mg^{++} , and Na^+ , was greater at Itasca than at Tewaukon, even though the concentrations were higher at Tewaukon. The annual deposition of P_{tot} at Hovland was higher than at Tewaukon because of P enrichment during the spring when pollination and seed dispersal occurred.

Dry Fallout

Collection of uncontaminated dry-fall samples proved to be exceptionally troublesome. Bird feces rendered most of the dry fallout samples unusable; NH_4^+ and P_{tot} concentrations were most strongly affected. In addition, the collectors failed to separate fully snow from dry fallout. Extremely light snow and resuspended wind-blown snow were collected in the dry-fall bucket because their moisture content was insufficient to activate the moisture-sensing switch. Power supply and sensor failures reduced the collectors to bulk-deposition collectors for several periods during the winter. The difficulties encountered with very light or resuspended snow point out a problem that is inherent in automatic, moisture-activated

precipitation collectors. During the spring of 1979 we installed a device to discourage birds from perching on the dry-collector bucket rim. This was partially successful, but we had to suspend sample collection before many dry-fall samples free of feces could be collected.

In spite of the sampling difficulties, we were able to get a small number of relatively clean dry fallout samples from each site. Table 5 presents the estimated annual dry deposition calculated from all available measurements at the three sites. Some samples that were only slightly contaminated or that could be cleaned before the dust was dissolved are included in these estimates, so the actual dry fall input of some elements may be overestimated. Total P, Ca^{++} , NH_4^+ , particles and pH decreased from Tewaukon to Hovland. Nitrate and SO_4^- deposition were lowest at Itasca. The reliability of these data is unknown because of contamination and the small sample size, but the observed trends for particles, pH, P_{tot} , and Ca^{++} fit the patterns expected from previous knowledge about dustfall gradients across Minnesota. Dry deposition of NO_3^- and SO_4^- was least at Itasca; this same trend was observed in wet precipitation and snow core concentrations. Our estimates of dry deposition are less than the wet deposition estimates for all ions except K^+ and P_{tot} , which had approximately equal wet and dry depositions.

Seasonal Trends

We compared mean concentrations (see table 6) during the four seasons of the year and found a sharp rise in H^+ , especially at Hovland, during the winter when snow blanketed the soils and freezing temperatures reduced microbial generation of NH_3 . This H^+ increase was accompanied by a drop in Ca^{++} , Mg^{++} , and NH_4^+ concentrations. At Hovland SO_4^- and NO_3^- concentrations also rose during the winter, which may indicate

changes in weather patterns affecting long-range transport of these acid materials.

Snowpack Samples

The concentration data for the snow core samples, summarized in table 7, indicate a decrease from west to east in specific conductivity, pH, and concentrations of particles, P_{TOT} , alkalinity, Cl^- , and the metal cations, Na^+ , K^+ , Ca^{++} , and Mg^{++} . Concentrations of $\text{SO}_4^{=}$, and to a lesser extent NO_3^- , were higher in both the prairie site and northeastern forest site samples than in the transition forest samples. This suggests that these ions are derived from soil dusts as well as from anthropogenic emissions. At the prairie sites $\text{SO}_4^{=}$ was greater on an equivalent basis than NO_3^- , but at the remaining sites NO_3^- was equal to or greater than $\text{SO}_4^{=}$. This contrasts with annual average event-precipitation, in which $\text{SO}_4^{=}$ exceeds NO_3^- .

Correlations

Correlations among the soil-derived elements Ca^{++} , Mg^{++} , Na^+ , K^+ , Fe, Mn, Al, and P_{TOT} , which decreased in concentration from west to east, were generally, but not uniformly, large and significant. (See tables 8,9 and 10) The trace metals Fe, Mn, and Al, which have few non-soil sources (Lantzy and Mackenzie 1979), were highly correlated at all three sites, but they were not consistently correlated with the other major cations derived from soils. The lack of uniformly high correlations among this group of elements and differences among the sites indicates that sources other than soil dust contribute to the input of these elements or that local soil mineralogy varies among the sites. Differences in the abundance of calcium and magnesium carbonates relative to siliceous minerals may well be involved.

Sulfate and NO_3^- , which have anthropogenic sources, were highly correlated at the three sites, but the magnitude of the coefficients decreased from east to west. The decrease suggests that one or both of

these ions may have an additional source in the west, such as soil dust. The increase in $\text{SO}_4^{=}$ concentrations towards the west, where soils rich in CaSO_4 and Na_2SO_4 occur, is in line with this explanation. The $\text{NH}_4^+:\text{SO}_4^{=}$ and $\text{NH}_4^+:\text{NO}_3^-$ correlations also decreased from east to west. The decreasing trend for correlations among NO_3^- , $\text{SO}_4^{=}$, and NH_4^+ is evidence for the existence of an east-to-west gradient of anthropogenic material; as natural sources for these ions become more important in the west the correlations become insignificant.

The high correlation between Pb and NO_3^- suggests automobile emissions as the major source for these substances. This correlation is greatest at Hovland and Itasca, where the long-range transport influence on precipitation is strongest. Some Pb may also be soil-derived; the Pb:Al and Pb:Fe correlations are high and increase from east to west as the soil dust influence increases.

The correlations, either positive or negative, between pH and ions expected to control it were generally small. However, the partial correlations, controlling for NH_4^+ , between pH and $\text{SO}_4^{=}$ or NO_3^- did have large negative values at Hovland, as would be expected if the precipitation pH was controlled by the fraction of acid not neutralized by NH_3 . The partial correlations between pH and $\text{SO}_4^{=}$ or NO_3^- at Tewaukon and Itasca were also negative, but they were not significant.

The correlations among snow-core data shown in table 11, indicate strong associations between the metal cations, P_{tot} , alkalinity, and particulate matter. Sulfate was highly correlated with Ca^{++} , Mg^{++} , and Na^+ , which is in line with its having a soil-source in the cultivated prairies. The ions correlated with particles all had large positive correlations with pH. Only NO_3^- had a small correlation with pH. This suggests that soil dusts are responsible for neutralizing acids in the snow.

Geographic Comparisons

Acidity and $\text{SO}_4^{=}$ in Minnesota are at the low end of the concentration range for sites listed in table 12, where acid rain problems are serious. Sulfate concentrations in North Dakota were also at the low end, but acidities were well below all those listed in table 12. Acid levels in precipitation at Itasca are comparable to those in the Experimental Lakes Area (ELA) of northwestern Ontario. Ammonium concentrations in Minnesota and especially North Dakota were at the high end of the concentration range for sites listed in table 12. Those at Itasca and Hovland were comparable to concentrations at some sites in northeastern North America, Los Angeles, and parts of southern Norway, but greater than at sites in southeastern United States and most of the Norwegian sites. Nitrate in Minnesota and North Dakota is intermediate in concentration, as is Ca^{++} except for Tewaukon, which is at the high end of the concentration range in table 12.

Biological Aspects of Atmospheric Deposition in Minnesota

Atmospheric inputs may have a number of effects on ecosystems in Minnesota. Nutrients in precipitation may constitute a significant portion of the nutrient budgets for lakes, wetlands, and perhaps some forests. Rawson Lake, an oligotrophic lake in the ELA that is similar to many lakes in northeastern Minnesota and northern Wisconsin, received up to 50% of its annual N and P inputs directly from the atmosphere (Schindler et al. 1976). Annual deposition of N and P at Hovland and Itasca are comparable to deposition values at Rawson Lake, so atmospheric inputs of these nutrients to Minnesota and Wisconsin lakes could be as important as they are in Ontario. Large areas of northern Minnesota are covered with peatlands, where the vegetation is dependent on atmospheric inputs for all of its nutrients. As noted previously, the mineral content of Sphagnum is greater in western than in eastern Minnesota. It is also probable that atmospheric inputs, especially of N, are important to forests growing in thin, coarse, acid soils over resistant bedrock.

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In the long run, however, the beneficial effects of nutrients in precipitation may be overcome by deleterious effects of acid. Nutrient leaching, trace-metal mobilization, and soil acidification are potential terrestrial effects of acid precipitation. These effects are most likely to occur in northeastern Minnesota and northern Wisconsin, where thin non-calcareous glacial deposits overlie resistant crystalline bedrock. The most imminent aquatic effects are lake acidification and associated losses of fish populations and changes in species composition at all trophic levels. The geology of those portions of northeastern Minnesota and Wisconsin where precipitation is most acid is similar to the geology in areas such as Scandinavia, the Adirondacks, southern Ontario, and Nova Scotia, where these effects have been observed. Alkalinities in northern Wisconsin lakes are lower and they appear to be in more imminent danger of acidification than do the Minnesota lakes.

SUMMARY

The supply of alkaline dust and gaseous NH_3 available to neutralize acids in the atmosphere controls the western extent of acid precipitation. The acidity of precipitation increased eastward across Minnesota, as the amount of alkaline dust and NH_3 decreased with increasing distance from their sources in the cultivated prairie. Winter snowcover and freezing temperatures, which decreased the evolution of soil dust and NH_3 from the prairie, led to an increase in precipitation acidity at all sites.

Precipitation at Hovland is just reaching acid levels and $\text{SO}_4^{=}$ loadings to cause adverse affects in sensitive regions. The geology of portions of northeastern Minnesota, adjoining Ontario, and northern Wisconsin is similar to that in areas where lake acidification and declines in fish populations have occurred. Such problems may well occur in the North Central U.S. eventually from current levels of precipitation acidity. Any increase in acid loading would increase this danger.

Precipitation inputs of P and N probably have significant beneficial effects on nutrient-poor ecosystems in Minnesota.

Acknowledgements

We acknowledge the collaboration of David Thornton and Professor Steven Eisenreich, who were responsible for the trace metal studies in this project and whose advice on chemical analysis was invaluable. David Thornton was also involved with the snow core sampling. We also thank Forrest Cameron and the staff at Tewaukon Wildlife Refuge, Dave Bosanko at Itasca, Jim Hane and Roy and Judy Stienbrecher at Hovland, and other persons involved with tending the precipitation collectors. Use of computer facilities at the University of Minnesota for data analysis was supported by a grant from the University Computer Center.

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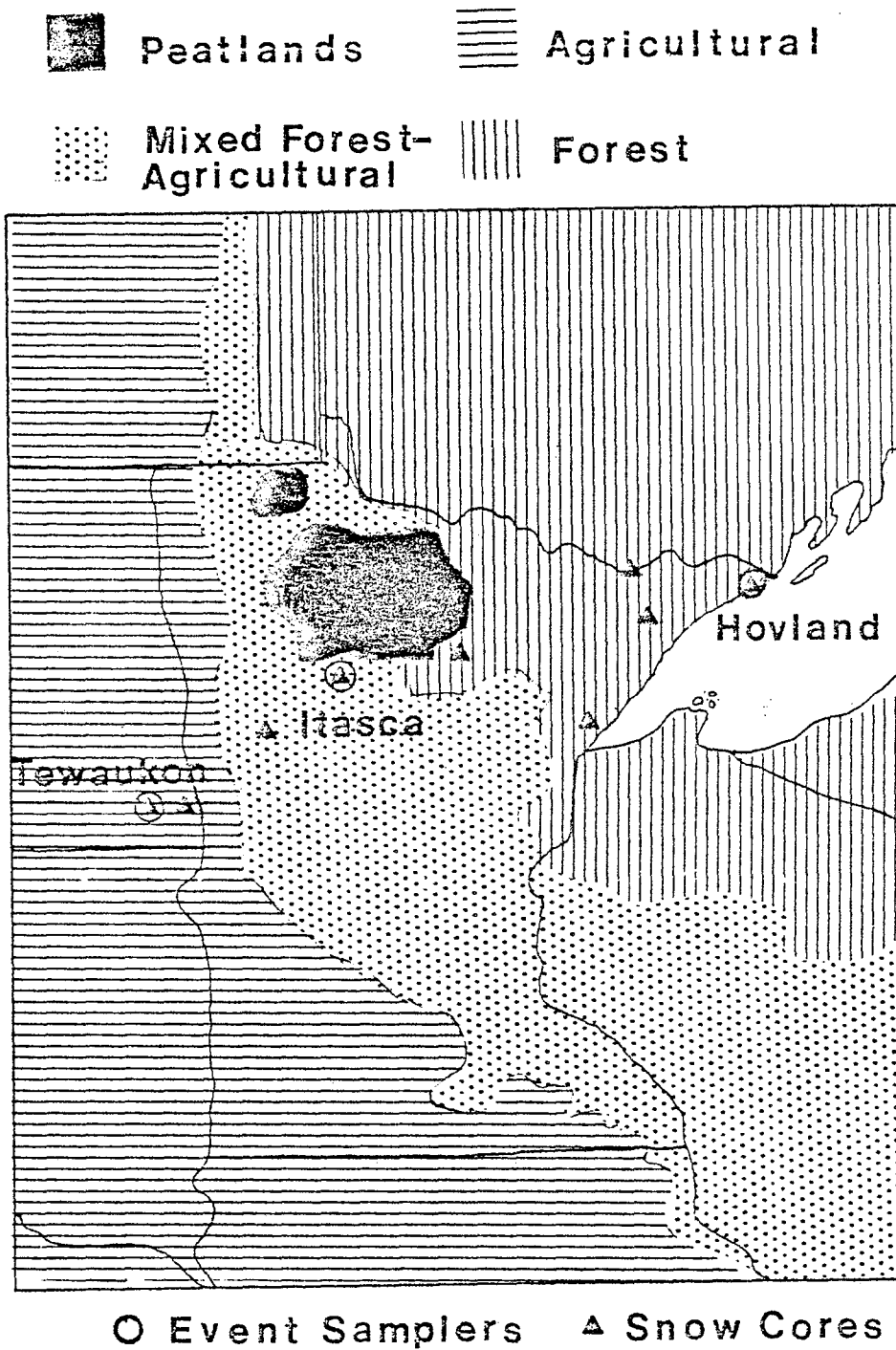


Figure 1. Map showing location of event-sampler and snow core collection sites in relation to agricultural, mixed agricultural - forest, and forest zones.

Table 1. Geometric mean concentrations and number of analyses (n) for major ions, total phosphorus, trace metals, particles > 0.4 μm , and specific conductivity in event - precipitation samples collected at the three collector sites from 15 April 1978 to 30 June 1979. Major ions are given in $\mu\text{eq } \ell^{-1}$, total phosphorus and trace metals are in $\mu\text{g } \ell^{-1}$, particles over 0.4 μm are in $\text{mg } \ell^{-1}$ and specific conductivity is in μS corrected to 25 $^{\circ}$ C. Order from high to low and significant differences are indicated.

T= Tewaukon, I= Itasca, H= Hovland.

	<u>TEWAUKON</u> mean (n)	<u>ITASCA</u> mean (n)	<u>HOVLAND</u> mean (n)	ORDER hi.....low		
H ⁺	1.92 (47)	4.2 (79)	17.8 (81)	H	I	T**
pH	5.79	5.38	4.75			
Na ⁺	10.0 (47)	7.8 (76)	6.5 (75)	T	I	H*
K ⁺	4.9 (47)	3.1 (75)	2.6 (75)	T	I	H**
NH ₄ ⁺	36.4 (36)	22.1 (67)	20.7 (65)	T	I	H*
Ca ⁺⁺	44.0 (38)	30.5 (74)	19.0 (69)	T	I	H**
Mg ⁺⁺	17.5 (44)	13.3 (74)	7.5 (71)	T	I	H**
Cl ⁻	31.0 (46)	35.2 (73)	23.7 (71)	I	T	H
NO ₃ ⁻	26.4 (47)	19.3 (77)	22.1 (75)	T	H	I*
SO ₄ ⁼	33.8 (47)	26.9 (77)	40.0 (75)	H	T	I*
P _{tot}	19.0 (42)	10.5 (70)	9.3	T	I	H**
Al	139 (22)	56.1 (41)	32.1 (36)	T	I	H**
Fe	100.0 (23)	30.6 (40)	21.8 (36)	T	I	H**
Mn	11.7 (23)	3.67 (39)	1.94 (35)	T	I	H**
Pb	6.71 (23)	4.69 (40)	6.46 (35)	T	H	I
Zn	83.8 (23)	54.6 (41)	65.3 (36)	T	H	I
Cd	.34 (22)	.15 (41)	.15 (35)	T	I	~ H**
Cr	<.36 (20)	<.25 (40)	<.28 (35)	T	H	I
Ni	2.16 (22)	<1.11 (40)	<.88 (35)	T	I	H**
Cu	2.11 (21)	1.09 (41)	1.46 (35)	T	H	I
Particles	12.4 (24)	6.5 (42)	5.6 (29)	T	I	H**
Cond	19.0	16.5 (79)	22.6 (81)	H	T	I**
Cond (-H ⁺)	16.8 (47)	12.8 (79)	13.3 (81)	T	H	I

*p < .05
**p < .01

Table 2. Ranges and volume - weighted mean concentrations of major ions, total phosphorus, and trace metals in event-precipitation samples collected at the three collector sites from 15 April 1978 to 30 June 1979. Major ion concentrations are in $\mu\text{eq l}^{-1}$ and total phosphorus and trace metals are in $\mu\text{g l}^{-1}$. Order of concentrations from high to low is indicated.
 T = Tewaukon, I = Itasca, H = Hovland.

	<u>TEWAUKON</u>		<u>ITASCA</u>		<u>HOVLAND</u>		<u>ORDER</u>
	Mean	Range	Mean	Range	Mean	Range	
pH	5.27	4.21-7.42	5.00	4.33-6.88	4.67	3.61-6.77	T I H
H ⁺	5.4	.038-61.7	10.0	.132-37	21.5	.170-246.	H I T
Na ⁺	11.7	1.7-77.	8.7	1.7-456.	6.1	1.3-72.	T I H
K ⁺	5.9	1.0-33.1	4.4	0.5-111	3.3	<0.3-21	T I H
NH ₄ ⁺	47.9	1.4-124.	33.6	<1.4-179	37.1	<1.4-205.	T I H
Ca ⁺⁺	52.5	7.5-211.	34.5	3.0-286	20.0	3.0-197.	T I H
Mg ⁺⁺	22.5	1.7-118.	19.2	1.3-258	10.8	<.2-148	T I H
Cl ⁻	49.9	5.4-256	46.8	5.1-383	26.2	2.8-732	T I H
NO ₃ ⁻	25.7	4.3-133.	20.0	4.3-79.3	20.7	3.6-260	T H I
SO ₄ ⁼	36.3	4.4-229.	31.9	6.3-158	39.4	3.8-315	H T I
P _{tot}	32.9	2.0-600.	14.2	<1-189	28.9	<1. - 611	T H I
Al	249.	13.2-522	103.	3.3-861	56.	6.20-447	T I H
Fe	165.	7.43-669.	50.5	1.0-189	38	4.15-449	T I H
Mn	22.	1.97-66.8	5.6	0.20-47.1	3.2	0.13-22.4	T I H
Pb	8.	1.33-39.9	5.7	0.80-13.3	7.1	0.80-18.9	T H I
Zn	147.	0.3-535	95.	3.18-673	90	9.60-873	T I H
Cd	.73	0.03-3.15	.18	<0.02-1.60	.15	<0.02-2.01	T I H
Cr	.40	<0.20-1.26	.20	<0.20-1.85	.15	<0.20-2.68	T I H
Ni	3.6	<0.50-29.1	1.4	<0.50-15.6	1.3	<0.50-5.09	T I H
Cu	3.9	<0.20-13.5	21.	<0.20-19.5	3.5	<0.20-16.7	T H I

Table 3. Ranking of major ions at the three collector sites based on volume-weighted equivalent concentrations.

<u>Ranking</u>	<u>Tewaukon</u>	<u>Itasca</u>	<u>Hovland</u>
<u>Cations</u>			
1	Ca ⁺⁺	Ca ⁺⁺	NH ₄ ⁺
2	NH ₄ ⁺	NH ₄ ⁺	H ⁺ *
3	Mg ⁺⁺	Mg ⁺⁺	Ca ⁺⁺ *
4	Na ⁺	H ⁺	Mg ⁺⁺
5	K ⁺	Na ⁺	Na ⁺
6	H ⁺	K ⁺	K ⁺
<u>Anions</u>			
1	Cl ⁻	Cl ⁻	SO ₄ ⁼
2	SO ₄ ⁼	SO ₄ ⁼	Cl ⁻
3	HCO ₃ ⁻	NO ₃ ⁻	NO ₃ ⁻
4	NO ₃ ⁻	HCO ₃ ⁻	HCO ₃ ⁻

* H⁺ and Ca⁺⁺ were equal

Table 4. Estimated annual wet deposition of major ions, total phosphorus and trace metals at the three collector sites. Ion depositions are in meq m⁻² yr⁻¹, total phosphorus and trace metals are in mg m⁻² yr⁻¹, and H₂O deposition is in l m⁻² yr⁻¹ (mm yr⁻¹). Sites are ordered from highest to lowest.

	<u>Tewaukon</u>	<u>Itasca</u>	<u>Hovland</u>	<u>Order</u> hi-----low
H ⁺	2.1	6.7	16.4	H I T
Na ⁺	5.1	6.3	4.6	I T H
K ⁺	2.7	2.5	2.2	T I H
NH ₄ ⁺	17.9	21.1	23.1	H I T
Ca ⁺⁺	20.9	21.6	16.2	I T H
Mg ⁺⁺	9.2	13.2	8.2	I T H
NO ₃ ⁻	10.8	13.3	15.2	H I T
SO ₄ ⁼	13.0	19.8	26.8	H I T
P _{tot}	13.3	9.2	15.0	H T I
Al	101.	69.3	39.3	T I H
Fe	66.8	34.0	26.7	T I H
Mn	8.9	3.77	2.25	T I H
Pb	3.2	3.83	4.98	H I T
Zn	59.5	63.9	63.2	I H T
Cd	0.296	0.121	0.105	T I H
Cr	0.162	0.135	0.105	T I H
Ni	1.46	0.942	0.913	T I H
Cu	1.58	1.41	2.46	H T I
H ₂ O	405.1	672.8	702.1	H I T

Table 5. Days sampled, number of samples, and mean deposition (\pm Standard error) of major ions, total phosphorus, and total mass. Ion depositions are in $\text{meq m}^{-2} \text{ yr}^{-1}$, total P is $\text{mg m}^{-2} \text{ yr}^{-1}$ and total mass is in $\text{g m}^{-2} \text{ yr}^{-1}$. pH values are for 250 ml suspensions of particulate matter.

	<u>Tewaukon</u>				<u>Itasca</u>				<u>Hovland</u>			
	mean	std err	n	days sampled	mean	std err	n	days sampled	mean	std err	n	days sampled
Na ⁺	1.04	.23	3	95	.76	.19	5	163	.93	.22	8	245
K ⁺	1.08	.30	3	95	1.65	.48	6	198	2.4	.63	9	275
NH ₄ ⁺	15.9	13.1	3	113	7.8	2.9	6	187	2.5	1.08	4	123
Ca ⁺⁺	13.8	.33	3	95	7.7	1.2	7	248	4.6	.94	7	181
Mg ⁺⁺	3.8	.39	3	95	6.5	2.3	7	170	1.7	.23	8	211
Cl ⁻	1.9	.84	2	61	6.2	3.2	4	148	1.1	.12	5	189
NO ₃ ⁻	4.0	1.98	2	61	1.8	.70	4	148	2.4	.33	5	189
SO ₄ ⁼	9.3	5.2	2	61	3.6	1.5	4	148	5.8	1.46	5	189
P _{tot}	13.0	5.3	2	61	9.2	3.3	7	205	8.9	4.55	6	204
Total mass	6.3	1.6	2	61	3.7	1.9	5	175	3.1	.53	5	189
pH _{250ml}	6.53	-	2	61	6.45	.45	6	198	5.55	.48	4	151

Table 6. Volume weighted mean concentrations of major ions during the four seasons. Numbers in parentheses indicate the ranking of ions. Ions are ordered according to their ranking in mean annual precipitation. Ion concentrations are in meq ℓ^{-1} , total P is in $\mu\text{g } \ell^{-1}$ and H_2O is in $\ell \text{ m}^{-2}$.

<u>Tewaukon</u>								
	Spring		Summer		Fall		Winter	Spring
Ca^{++}	48.0 (2)		72 (1)		169 (1)		32 (1)	28 (2)
NH_4^+	51 (1)		49 (2)		62 (2)		18 (3)	54 (1)
Mg^{++}	21 (3)		22 (3)		35 (3)		24 (2)	17 (3)
Na^+	14 (4)		14 (4)		16 (5)		10 (5)	5 (4)
K^+	5 (6)		8 (5)		22 (4)		2 (6)	5 (5)
H^+	5.8 (5)		2.7 (6)		.15 (6)		13.8 (4)	3.5 (6)
Cl^-	50 (1)		65 (1)		22 (4)		58 (1)	13 (4)
$\text{SO}_4^{=}$	36 (2)		32 (3)		54 (2)		32 (2)	39 (1)
HCO_3^-	22 (4)		35 (2)		137 (1)		.4 (4)	23 (3)
NO_3^-	24 (3)		22 (4)		34 (3)		31 (3)	29 (2)
P_{tot}	29.5		27.9		150.5		15.3	30.5
H_2O	-		125.4		23.8		68.1	118.0
<u>Itasca</u>								
Ca^{++}	119 (1)		24 (2)		27 (1)		25 (2)	28 (3)
NH_4^+	54 (2)		31 (1)		11 (2)		14 (4)	42 (1)
Mg^{++}	29 (3)		8 (4)		11 (4)		26 (1)	29 (2)
H^+	10 (4)		10 (3)		11 (3)		18 (3)	7 (4)
Na^+	15 (5)		6 (5)		10 (5)		4 (5)	6 (5)
K^+	12 (6)		2 (6)		8 (6)		3 (6)	5 (6)
Cl^-	97 (1)		39 (2)		47 (1)		39 (1)	30 (2)
$\text{SO}_4^{=}$	49 (2)		24 (3)		20 (2)		20 (3)	46 (1)
HCO_3^-	13 (4)		226 (1)		.5 (4)		0 (4)	12 (4)
NO_3^-	30 (3)		16 (4)		17 (3)		21 (2)	21 (3)
P_{tot}	19.7		12.2		20.9		8.3	15.1
H_2O	-		336.1		62.8		96.4	213.9
<u>Hovland</u>								
NH_4^+	50 (1)		21 (2)		50 (1)		29 (2)	42 (1)
H^+	17 (2)		14 (3)		19 (3)		58 (1)	12 (4)
Ca^{++}	14 (3)		24 (1)		34 (2)		21 (3)	14 (3)
Mg^{++}	7 (4)		8 (4)		6 (5)		7 (5)	22 (2)
Na^+	6 (5)		6 (5)		10 (4)		8 (4)	3 (6)
K^+	5 (6)		2 (6)		3 (6)		2 (6)	5 (5)
$\text{SO}_4^{=}$	49 (1)		26 (2)		39 (2)		57 (1)	36 (1)
Cl^-	30 (2)		34 (1)		44 (1)		28 (3)	8 (3)
NO_3^-	17 (3)		15 (3)		24 (3)		39 (2)	18 (2)
HCO_3^-	8 (4)		0 (4)		7 (4)		0 (4)	0 (4)
P_{tot}	49.7		8.9		15.0		4.8	52.7
H_2O	-		244.1		94.2		137.4	240.8

Table 7. Standard error and mean concentration of major ions, total P, particulates, and specific conductivity in snow core samples collected during winter 1978-79 grouped according to local vegetation cover. Major ions are in $\mu\text{eq l}^{-1}$, total P is in $\mu\text{g l}^{-1}$, particles are in mg l^{-1} and specific conductivity is in μS corrected to 25°C .

	<u>Prairie</u>		<u>Transition Forest</u>		<u>Northeastern Forest</u>	
	mean	std err.	mean	std err.	mean	std err.
pH	6.68	.25	5.52	.26	4.53	.03
H ⁺	.2	-	3.0	-	29.5	-
Na ⁺	89.1	55.2	7.0	1.7	4.8	1.3
K ⁺	9.7	2.6	6.4	2.8	1.8	.3
NH ₄ ⁺	17.9	3.3	13.6	1.6	13.6	1.9
Ca ⁺⁺	103.0	24.0	21.0	4.0	9.5	1.3
Mg ⁺⁺	63.3	23.7	28.3	17.8	3.3	1.6
Cl ⁻	25.4	13.6	7.6	1.7	6.5	1.5
NO ₃ ⁻	60.7	29.1	26.4	2.9	28.6	1.9
SO ₄ ⁼	162.5	59.3	18.1	1.5	23.8	2.7
P _{tot}	79.6	23.7	14.5	2.1	9.2	1.7
Particles						
>0.4 μm	39.3	12.6	12.2	6.5	6	1.7
Cond	73.8	42.6	13.1	1.8	17.0	1.1

Table 9. Correlation matrices of major ions and trace metals for precipitation collected at each site. Coefficients were computed from logarithms of concentration. Asterisks denote significance level; *p<.05 **p<.01

ITASCA

	Ca ⁺⁺	Mg ⁺⁺	Al	Fe	Mn	Na ⁺	K ⁺	P _{tot}	NH ₄ ⁺	SO ₄ ⁼	NO ₃ ⁻	Ni	Pb	Zn	Cd	Cr	Cu	Cl ⁻	pH
Ca ⁺⁺	1.0																		
Mg ⁺⁺	** .61	1.0																	
Al	** .60	.28	1.0																
Fe	** .57	.22	** .79	1.0															
Mn	** .66	** .41	** .76	** .83	1.0														
Na ⁺	** .58	** .36	** .45	* .39	** .53	1.0													
K ⁺	** .36	.21	.16	.34	** .42	** .56	1.0												
P _{tot}	** .37	.05	** .50	** .53	** .66	.24	** .38	1.0											
NH ₄ ⁺	** .33	.15	** .62	** .62	** .69	.08	.03	.25	1.0										
SO ₄ ⁼	* .28	.28	** .48	** .46	** .57	.14	.19	.22	** .69	1.0									
NO ₃ ⁻	** .47	.23	** .45	** .47	** .66	.18	.32	.46	** .46	** .63	1.0								
Ni	** .45	** .47	* .37	* .35	* .39	* .32	.24	.09	.25	.45	* .37	1.0							
Pb	* .36	.08	** .46	** .42	** .46	.11	.19	.23	* .37	** .55	** .72	.27	1.0						
Zn	* .39	** .46	.24	.06	.25	** .65	.02	.21	.14	.09	-.05	.18	-.18	1.0					
Cd	** .49	* .38	* .31	.17	** .41	** .53	* .33	.19	.17	.12	.19	.06	.16	* .39	1.0				
Cr	* .38	.24	.28	.17	* .36	* .34	.15	.12	-.03	.14	.29	* .39	* .38	.12	* .36	1.0			
Cu	.11	.02	.12	.02	-.04	.29	.01	.09	-.26	-.17	-.20	.22	-.12	** .41	.10	* .39	1.0		
Cl ⁻	** .62	** .59	* .37	.23	* .41	** .48	* .31	-.01	.07	.20	.17	** .44	.07	** .60	* .51	* .34	* .15	1.0	
pH	* .27	.29	** .49	.54	** .62	.19	.22	.42	** .53	* .32	.20	.27	.04	.14	-.05	.17	-.15	.18	1.0

Table 10. Correlation matrices of major ions and trace metals for precipitation collected at each site. Coefficients were computed from logarithms of concentration. Asterisks denote significance level; *p<.05 **p<.01

HOVLAND

	Ca ⁺⁺	Mg ⁺⁺	Al	Fe	Mn	Na ⁺	K ⁺	P _{tot}	NH ₄ ⁺	SO ₄ ⁼	NO ₃ ⁻	Ni	Pb	Zn	Cd	Cr	Cu	Cl ⁻	pH
Ca ⁺⁺	1.0																		
Mg ⁺⁺	.62**	1.0																	
Al	.59**	.61**	1.0																
Fe	.42*	.50**	.87**	1.0															
Mn	.52**	.52**	.72**	.77**	1.0														
Na ⁺	.66**	.49**	.25	.17	.41*	1.0													
K ⁺	.33**	.41**	.35*	.30	.32	.24*	1.0												
P _{tot}	.11	.29*	.38*	.58**	.54**	-.12	.60**	1.0											
NH ₄ ⁺	.09	.22	.21	.31	.27	.01	.39**	.53**	1.0										
SO ₄ ⁼	.25*	.33**	.32	.36*	.41*	.24*	.32**	.39**	.64**	1.0									
NO ₃ ⁻	.24	.17	.32	.35*	.38*	.37**	.20	.20	.58**	.68**	1.0								
Ni	.07	.12	.21	.31	.38*	-.11	.08	.32	.09	.06	.05	1.0							
Pb	.32	.18	.44**	.37*	.39*	.35*	.24	.17	.53**	.72**	.71**	.05	1.0						
Zn	.80**	.38*	.20	.09	.26	.72**	.11	-.06	-.12	.09	.07	-.05	.14	1.0					
Cd	.67**	.60**	.57**	.44**	.50**	.72**	.35*	.14	.04	.32	.28	.05	.48**	.52**	1.0				
Cr	.23	.17	.33*	.27	.17	.40*	.09	.09	.11	.14	.50**	-.10	.42*	-.04	.47**	1.0			
Cu	.16	.18	.27	.26	.43*	.24	.31	.46**	.06	.06	.05	.39*	.04	.19	.39*	.19	1.0		
Cl ⁻	.67**	.54**	.19	.09	.39*	.85**	.16	-.09	-.06	.12	.19	-.04	.15	.79**	.61**	.13	.28	1.0	
pH	.00	.15	.07	.23	.22	-.25*	.32**	.46**	.28*	-.27*	-.37**	.26	-.43*	-.12	-.29*	-.36*	.27	-.19	1.0

Table 11. Correlation matrix of major ions total phosphorus and particulates in snow core samples collected during the winter of 1978-79. Coefficients were computed from logarithms of concentrations, except for particulates which were arithmetic values. Asterisks denote significance level; *p < .05
**p < .01

SNOW CORES

Part.	1.0														
Ca ⁺⁺	.58	1.0													
Mg ⁺⁺	.59	.85	1.0												
Na ⁺	.45	.75	.75	1.0											
K ⁺	.46	.69	.75	.81	1.0										
Cl ⁻	.38	.53	.59	.79	.73	1.0									
P _{tot}	.61	.79	.69	.67	.76	.61	1.0								
HCO ₃ ⁻	.79	.54	.71	.63	.72	.60	.37	1.0							
SO ₄ ⁼	.46	.72	.57	.76	.56	.66	.62	.37	1.0						
NO ₃ ⁻	.22	.42	.10	.29	.26	.05	.39	-.08	.47	1.0					
pH	.63	.88	.88	.77	.77	.55	.75	.84	.59	.29	1.0				
Part.		Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	Cl ⁻	P _{tot}	HCO ₃ ⁻	SO ₄ ⁼	NO ₃ ⁻	pH				

Table 12. Concentrations of major ions and phosphorus in precipitation at selected sites in North America and Scandinavia. All values are volume-weighted mean concentrations over periods of one or more years except the Norwegian values, which are a range of annual volume weighted means from 33 sites. Concentrations are in $\mu\text{eq } \ell^{-1}$ except phosphorus which is in $\mu\text{g } \ell^{-1}$. Superscripts indicate which phosphorus fraction was measured; T = total P, R = dissolved reactive P.
 - indicates data not available.

LOCATION	H ⁺	Na ⁺	K ⁺	NH ₄ ⁺	Ca ⁺⁺	Mg ⁺⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ⁼	P	TYPE	REFERENCE
Pasadena, CA	87	25	2.1	33	2.4	1.6 ⁻	29	75	30	-	wet- only	Liljestrand and Morgan 1978
Muskoka-Haliburton, Ontario	100	16.9	4	31	36	10	9	30	67	24 ^T	wet- only	Scheider et al. 1979
ELA, Ontario	10.9	8.3	3.3	20.9	22.5	9.5	9.9	18.5	89.9	40 ^T	bulk	Schindler et al. 1976
Upstate New York	103.3	8.3	3.3	32	57.7	15.8	33.	51.6	113.2	61.7 ^R	bulk	Likens 1972
Hubbard Brook	72.4	5.2	1.8	12.2	8.0	3.3	13.3	23.7	60.3	8 ^R	bulk	Likens et al. 1977
New York, NY	119	35.8	2.4	11.2	16.1	12.8	43.4	39.1	125.2	-	wet- only	Feely and Larsen 1979
Chester, NJ	79.6	17.8	2.0	13.5	6.4	5.1	16.5	33.4	72.7	-	wet- only	" " " "
Coweeta, SC	-	7.4	2.1	1.4	11.5	4.2	20.7	8.6	-	7 ^R	bulk	Swank and Hendersc 1976
Walker Branch, TN	-	10.9	5.1	9.3	51.5	15.8	-	17.9	-	40 ^R	bulk	" " " "
Southern Norway,	27	-	2	11	5	4	5	11	35	-	bulk	Wright and Henriksen 1978
	55	-	6	30	14	40	169	32	70			
Hovland	21.5	6.1	3.3	37.1	20.0	10.8	26.2	20.7	39.4	28.9	wet- only	This study
Itasca	10.0	8.7	4.4	33.6	34.5	19.2	46.8	20.0	31.9	14.2	"	"
Tewaukon	5.4	11.7	5.9	47.9	52.5	22.5	49.9	25.7	36.3	32.9	"	"