Precipitation Chemistry at the Marcell Experimental Forest in North Central Minnesota

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Concentration (milligrams and microequivalents per liter) values are presented for major ions occurring in rain and snow from July 1978 to July 1980. Ammonium, sodium, and calcium are the largest equivalent weight cations which are largely balanced by sulfate and nitrate anions. Hydrogen is the fourth most abundant cation; but high combined concentrations of other cations in 27% of the sample events mask positive correlations with high hydrogen concentrations. Field-measured pH averaged 4.3, but the range (3.5 to 6.5) fluctuated with a combination of earth and air mass conditions. When high cation (and anion) data are deleted, low pH correlates well with high nitrate. Sulfate concentrations are similar to those measured in 1936 and do not correlate with pH. Calcium and, to a lesser extent, ammonium tend to increase pH values. High nitrate values also correlate positively with high excess acidity, while high sodium and calcium values correlate with high excess alkalinity.

INTRODUCTION

Acid rain and acid snow are operationally defined as rain and snow with pH less than 5.6 [Likens, 1976]. This value results from the reaction of carbon dioxide with water in the air to form carbonic acid and is assumed to be normal, although alkaline dust can increase precipitation pH above this level in drier parts of the country. Acid precipitation is caused by the reaction of sulfur dioxide and nitric oxides with water to form sulfuric or nitric acids which freely disscoiate and yield high hydrogen concentrations and lower pH values [Likens, 1976].

Precipitation pH was measured or estimated from ion balance in the northeastern United States, southeastern Ontario, and Scandinavia in the mid-1950's and again in the early 1970's when the degree of acidity and affected area increased [Likens, 1976]. Concern was expressed that acid precipitation would cause lake pH to decrease in areas where thin soils over hard bedrock lacked sufficient buffering capacity to keep lakes above pH 6. Below pH 6, invertebrate foods for fish and fish reproduction are adversely affected. Such effects were measured in 1975 for 110 Adirondack lakes [Schofield, 1977].

Since northeastern Minnesota and north central Wisconsin have extensive hardrock watersheds with thin soils, we joined the north central region of the state agricultural experiment stations and other government agencies to implement a nationwide network of precipitation quality–sampling stations. This committee (IR-7) is referred to as the National Atmospheric Deposition Program (NADP) and began sample collection in 1978.

This paper summarizes NADP data at the Marcell Experimental Forest located in north central Minnesota (47°32'N, 93°28'W) to test the hypothesis that acid precipitation occurs this far west and to document what constituents are associated with high and low pH values. Mean concentrations by weight and equivalents are analyzed and interpreted for a 2-year period (July 11, 1978, through July 10, 1979, and July 11, 1979, through July 15, 1980). These data are compared to earlier partial data developed in 1971–1973 at the Marcell Experimental Forest and to other data in the literature. The collection site

is in an extensive aspen-birch and conifer forest that extends north into Canada, west 130 km, south 160 km, and east 160 km to Lake Superior. A 1000-MW coal-generating plant is located 23 km SW of the site, and the Mesabi Iron Range and taconite (low-grade iron ore) processing plants are located to the east and northeast. The closest distance to the southern end of the Mesabi Range is 29 km.

METHODS

Precipitation samples were collected weekly in the NADP standard Aerochemetric double bucket gage located in an aspen forest opening with a clearance angle of 30° from the horizontal. (Mention of trade names does not constitute endorsement by the U.S. Department of Agriculture.)

Field collection and field measurement of pH and specific conductance followed standard NADP protocol [Bigelow, 1982]. Sample conductance and pH were measured again at the NADP Central Analytic Laboratory (CAL). Other analyses done at the CAL include calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), ammonium (NH_4), nitrate (NO_3), chloride (Cl), sulfate (SO_4), and phosphate (PO_4). Metals were determined by flame atomic absorption with lanthanum added for Ca and Mg determinations; other ions were determined with the Technicon Auto Analyzer II System using methods detailed by Stensland et al. [1980].

Concentration means for rain and snow samples were calculated for each year along with their 5% confidence interval. Volume-weighted means without statistics are also given. All mean values reported as pH were calculated on the basis of hydrogen ion concentration and then converted back to pH. All volume-weighted values use weekly storm volume as the weight. Correlation matrices were developed between microequivalents per liter values of the various anions and cations as an indirect estimate of the type of cation-anion combinations occurring in precipitation.

As an alternative to pH measurements, excess acidity (or excess alkalinity if the resultant term is negative) can be determined by subtracting the equivalent concentration sum of major cations from the equivalent concentration sum of major anions [Reuss, 1975]. Long-term effects on soil systems are more easily evaluated in these terms because excess acidity will leach bases from the soil, while excess alkalinity is a measure of the rain's ability to add bases to the soil.

TABLE 1a. Specific Conductance, Hydrogen, and pH Values in Precipitation at the Marcell Experimental Forest

	1978–1979		1979–1980		1978–1980, All Precipitation
	Snow	Rain	Snow	Rain	
			Specific Conductance, μmho/cm		
Field	(18)	(22)	(14)	(20)	(74)
Mean ± 5% C.I.	9.3 ± 2.3	10.8 ± 3.2	11.5 ± 2.8	14.8 ± 3.3	11.6 ± 1.5
Volume-weighted mean	10.2	9.9	10.6	14.4	11.3
CAL	(19)	(22)	(17)	(24)	(82) ·
Mean ± 5% C.I.	17.1 ± 5.6	12.3 ± 3.4	18.9 ± 7.0	19.0 ± 3.9	16.8 ± 2.4
Volume-weighted mean	16.7	9.5	13.2	16.9	13.2
			Hydrogen Ion, μeq/l		
Field	(18)	(22)	(14)	(20)	(74)
Mean ± 5% C.I.	116.90 ± 38.77	59.23 ± 27.31	12.87 ± 5.82	21.33 ± 10.47	54.24 ± 15.13
Volume-weighted mean	128.18	42.89	12.57	28.27	50.36
CAL	(19)	(22)	(17)	(24)	(82)
Mean ± 5% C.I.	29.29 ± 15.51	3.93 ± 1.31	12.62 ± 2.94	7.48 ± 4.29	12.61 ± 4.33
Volume-weighted mean	32.38	3.77	12.08	14.59	12.42
			pH		
Field	(18)	(22)	(14)	(20) ·	(74)
Mean	3.93	4.23	4.89	4.67	4.27
5% C.I.	3.81–4.11	4.06–4.49	4.72–5.15	4.50–4.96	4.16–4.41
Volume-weighted mean	3.89	4.37	4.90	4.55	4.30
CAL	(19)	(22)	(17)	(24)	(82)
Mean	4.53	5.41	4.90	5.13	4.90
5% C.I.	4.35–4.86	5.28–5.58	4.81–5.01	4.93–5.49	4.77–5.08
Volume-weighted mean	4.49	5.42	4.92	4.84	4.91

Numbers in parentheses are sample size. C.I. is confidence interval. CAL is Central Analytic Laboratory.

Excess acidity and excess alkalinity values were estimated as the microequivalents per liter sums of NO_3^-, Cl^-, SO_4^{2-}, and PO_4^{3-} minus the microequivalents per liter sums of Ca^{2+}, Mg^{2+}, K^+, Na^+, and NH_4^+ for each weekly sample and summed for rain and snow periods in each of the 2 sample years. In addition, each individual anion and weekly sample size (in centimeters) was correlated with excess acidity. Also, each cation and weekly sample size was correlated with excess alkalinity so that the ions most responsible for excess acidity or excess alkalinity could be identified.

TABLE 1b. Ionic Concentrations in Precipitation at the Marcell Experimental Forest

	1978–1979		1979–1980		1978–1980, All Precipitation
	Snow	Rain	Snow	Rain	
	(19)	(22)	(17)	(24)	(82)
Calcium					
Mean ± 5% C.I.	0.20 ± 0.11	0.49 ± 0.22	0.48 ± 0.21	0.76 ± 0.31	0.50 ± 0.12
Volume-weighted mean	0.15	0.33	0.28	0.34	0.30
Magnesium					
Mean ± 5% C.I.	0.04 ± 0.02	0.08 ± 0.04	0.08 ± 0.03	0.13 ± 0.06	0.09 ± 0.02
Volume-weighted mean	0.02	0.06	0.05	0.06	0.05
Potassium					
Mean ± 5% C.I.	0.06 ± 0.03	0.09 ± 0.04	0.08 ± 0.05	0.13 ± 0.07	0.09 ± 0.03
Volume-weighted mean	0.04	0.08	0.06	0.06	0.07
Sodium					
Mean ± 5% C.I.	0.27 ± 0.20	0.44 ± 0.33	1.34 ± 1.43	0.60 ± 0.41	0.63 ± 0.32
Volume-weighted mean	0.20	0.24	0.69	0.48	0.35
Ammonium					
Mean ± 5% C.I.	0.18 ± 0.18	0.49 ± 0.17	0.30 ± 0.20	0.71 ± 0.27	0.44 ± 0.11
Volume-weighted mean	0.14	0.43	0.20	0.51	0.39
Nitrate					
Mean ± 5% C.I.	1.73 ± 0.62	1.53 ± 0.54	1.98 ± 0.84	2.27 ± 0.75	1.89 ± 0.33
Volume-weighted mean	1.53	1.14	1.52	1.71	1.41
Chloride					
Mean ± 5% C.I.	0.18 ± 0.05	0.17 ± 0.06	0.32 ± 0.12	0.25 ± 0.09	0.23 ± 0.04
Volume-weighted mean	0.13	0.14	0.29	0.20	0.17
Sulfate					
Mean ± 5% C.I.	1.19 ± 0.54	1.96 ± 0.53	2.11 ± 1.12	2.90 ± 0.68	2.09 ± 0.36
Volume-weighted mean	1.13	1.62	1.32	2.37	1.73
Phosphate					
Mean ± 5% C.I.	0.004 ± 0.002	0.015 ± 0.027	0.014 ± 0.018	0.004 ± 0.001	0.009 ± 0.008
Volume-weighted mean	0.002	0.012	0.006	0.003	0.007

Values are in milligrams per liter. Numbers in parentheses are sample size. C.I. is confidence interval.

TABLE 2. Mean Concentrations of Ions in Precipitation for Selected Areas of North America

| Location	Date	Specific Conductance, μmhos	pH units	Ca, mg/l	Mg, mg/l	K, mg/l	Na, mg/l	NH₄ Ion, mg/l	NO₃ Ion, mg/l	Cl, mg/l	SO₄ Ion, mg/l	PO₄ Ion, mg/l	Source
Marcell Experi-	1978–1980	11.3	4.30	0.30	0.05	0.07	0.35	0.39	1.41	0.17	1.73	0.007	this paper
mental Forest	1971–1973	...	...	0.45	0.09	0.14	0.31	0.46	1.30	...	...	0.009	*Verry and Timmons* [1977]
Tewaukon, North Dakota	April 1978 to June 1979	19.3	5.27	1.05	0.27	0.23	0.27	0.86	1.59	...	1.74	...	*Munger* [1981]
Itasca Park, Minnesota	April 1978 to June 1979	16.2	5.00	0.69	0.23	0.17	0.20	0.61	1.24	...	1.53	...	
Hovland, Minnesota	April 1978 to June 1979	20.3	4.67	0.40	0.13	0.13	0.14	0.67	1.28	...	1.89	...	
Cloquet,	1977	...	...	1.67	0.23	0.54	...	...	...	...	...	...	*Comerford and White* [1977]
Minnesota	1975	...	...	...	...	...	...	...	...	...	3.09	...	*White and Kramer* [1980]
International Falls, Minnesota	1956–1957	...	...	...	...	...	...	0.12	0.90	...	...	...	*Stensland* [1979] [after *Junge, 1958*]
Bemidji, Minnesota	1936–1937	...	...	...	...	...	...	...	...	...	2.44	...	*Alway et al.* [1937]
Becida, Minnesota	1936–1937	...	...	...	...	...	...	...	...	...	2.10	...	*Alway et al.* [1937]
Watersmeet, Michigan	1972–1975	...	...	0.46	0.13	...	...	...	...	...	3.20	...	*Tabatabai et al.* [1981]
Ontario	1970–1972	...	4.93	0.69	0.13	0.50	...	...	1.64	...	...	...	*Foster* [1974]
	1976–1977	...	4.17	...	...	...	...	...	...	...	...	...	*Scheider et al.* [1979]
Kearney, Nebraska	1931–1932	...	...	...	...	...	...	...	...	0.14	2.0	...	*Collins and Williams* [1933]
Drummond, Wisconsin	1977–1978	...	...	...	...	...	...	0.27	1.55	...	...	...	*Tabatabai et al.* [1981]
Brookings, South Dakota	1974–1978	...	...	3.28	2.02	1.00	1.51	1.21	0.82	...	...	...	*Tabatabai et al.* [1981]
Iowa	1971–1973	...	6.15	...	...	...	...	0.81	2.66	...	4.70	...	*Tabatabai and Laflen* [1975]
Hubbard Brook, New Hampshire	1963–1974	...	4.14	0.17	0.05	0.07	0.12	0.22	1.60	0.50	2.9	0.008	*Likens et al.* [1977]
Northeastern United States	1965–1966	...	4.38	0.60	0.11	0.16	...	0.22	0.34	...	4.30	0.04	*Pearson and Fisher* [1971]
inland		...	...	...	...	...	0.27	...	...	0.45	...	...	
coastal		...	...	...	...	...	1.13	...	...	2.10	...	...	
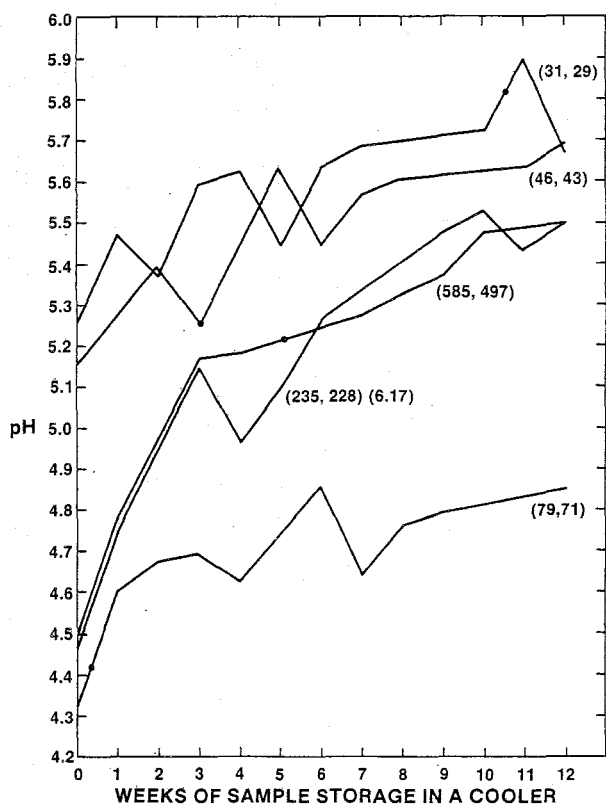
Fig. 1.   Change of field pH in stored samples. Numbers in parentheses are total anions, total cations in microequivalents per liter at the time of Central Analytic Laboratory (CAL) analyses. Dots or second parentheses represent CAL pH.

The completeness and average accuracy of ion determinations were determined by comparing total anions to total cations. Measured H^+ was included for pH values, and bicarbonate was estimated from corresponding OH^- values according to *Stensland* [1979].

RESULTS AND DISCUSSION

Concentrations

Concentration means with a 5% confidence interval and volume-weighted means for cations, anions, specific conductance, and pH are given for rain and snow events in each of the 2 years and for the total 2-year period (Table 1). Data taken earlier at the Marcell Experiment Forest and data taken from the literature are shown in Table 2. In all literature examples, bulk samples were used, and values are based on at least a 12-month volume-weighted average. *Alway et al.*'s [1937] data are referenced as deposition values, but were recalculated on a concentration basis using nearby (5 to 20 km) U.S. Weather Bureau precipitation amounts.

Mean pH measured at the field location was 4.30 as opposed to a mean pH of 4.91 measured at CAL (Table 1). In either case, these values are lower than the operationally defined normal pH of 5.65. The measured values represent a 22 and 5 times stronger hydrogen ion concentration for the field and CAL values, respectively.

Several mechanisms may be responsible for the rise in pH values from the field to CAL. Among these are errors in determination, changes in CO_2 equilibrium, biological changes, and the dissolution of mineral material. To check that changes in pH between the field and CAL were real, we stored 25-ml

aliquots in a cooler and remeasured pH each week for 12 weeks. Examples of measurements started in October and November of 1981 are shown in Figure 1. Indeed, pH change occurs. This information taken with the strict NADP quality control on pH standards and blind samples indicates that pH measurement is accurate at both the field and CAL locations. However, apparent chemical reactions shift pH readings with storage.

Mean sea level elevations at the Marcell Experimental Forest and CAL are similar; thus differences in CO_2 equilibrium should be minimal. I suspect that either biologic changes or dissolution of mineral matter are responsible for the pH change. It should be noted in Figure 1 that the samples showing the greatest change have high anion and cation loads compared to those showing less pH change. The changes in pH are real, but further studies are needed to identify the importance of biologic or mineral dissolution factors. The pH of 4.30 then is characteristic of hydrogen ion concentration occurring in north central Minnesota from July 1978 to July 1980. This should be kept in mind when published NADP pH maps are constructed using CAL measurements.

Concentrations of ions measured in bulk precipitation at the Marcell Experimental Forest in 1971–1973 are similar to those measured in wet precipitation in 1978–1980 (Table 2). Field measurements of pH are also similar to those measured in the northeastern United States, Ontario, and Scandinavia where serious problems with lake acidification exist [*Scheider et al.*, 1979; *Dovland et al.*, 1976; *Pfeiffer and Festa*, 1980]. For other ions it is important to point out some regional trends in mean concentrations. Nitrate levels at the Marcell Experimental Forest, southern Ontario, and the Midwest are higher than those reported in the Northeast and South Dakota, while sulfate levels are low at Marcell in comparison to other locations. Sulfate levels at Marcell (1.73 ± 0.36) are not different from those measured at Kearney, Nebraska, in 1931 (2.0) or those at Becida and Bemidji, Minnesota (2.1 and 2.4), in 1936 and 1937.

TABLE 3.   Equivalent Concentrations for Cations and Anions by Snow and Rain Periods, Marcell Experimental Forest, 1978–1980

	1978–1979		1979–1980		1978–1980, All Precipitation
	Snow	Rain	Snow	Rain	
Cations					
Ammonium	7.76	23.84	11.09	28.27	21.62
Sodium	8.70	10.44	30.02	20.88	15.22
Calcium	7.48	16.47	13.97	16.97	14.97
Hydrogen (CAL)	32.38	3.77	12.08	14.59	12.42
Magnesium	1.65	4.94	4.11	4.94	4.11
Potassium	1.02	2.05	1.53	1.53	1.79
Total cations	58.99	61.51	72.80	87.18	70.13
Anions					
Sulfate	23.53	33.73	27.48	49.34	36.02
Nitrate	24.68	18.39	24.52	27.58	22.74
Chloride	3.67	3.95	8.18	5.64	4.80
Phosphate	0.06	0.38	0.19	0.09	0.22
Total anions	51.94	56.45	60.37	82.65	63.78
Undetermined anion	7.05	5.06	12.43	4.53	6.35
All determined ions	110.93	117.96	133.17	169.83	133.91
Percent undetermined of determined ions	6.4	4.3	9.3	2.7	4.7

Except for last row, values are in microequivalents per liter. CAL is Central Analytic Laboratory.
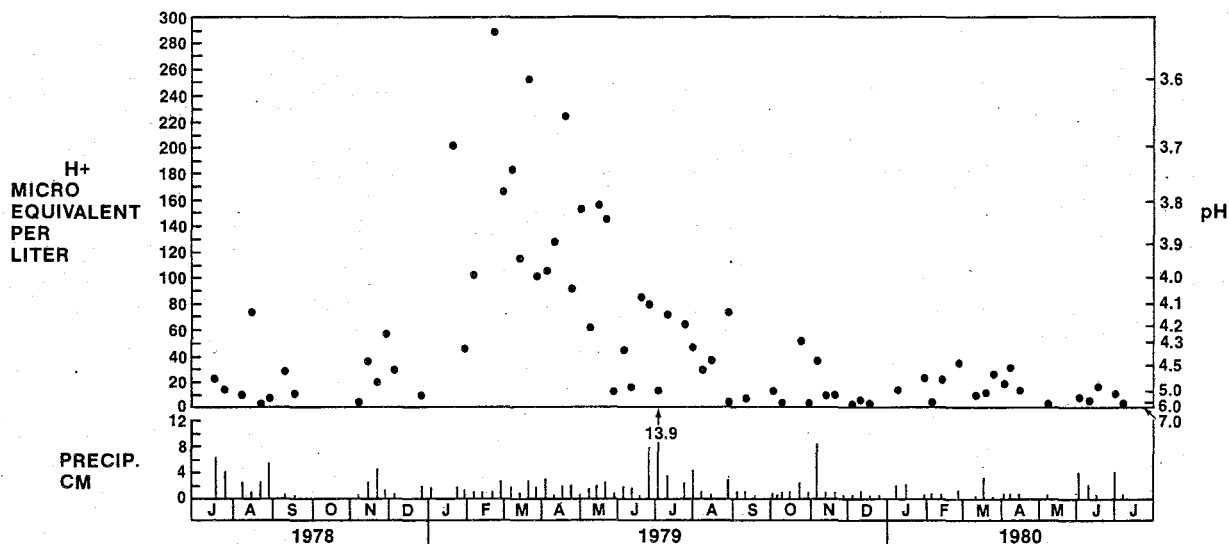
Fig. 2. Precipitation, hydrogen concentration, and field pH at the Marcell Experimental Forest, north central Minnesota, 1978–1980.

These data from the 1930's represent accurate determinations and should not be confused with other 1930's data, some from the same investigators, which utilized zinc-plated containers. In contrast all other locations show higher sulfate concentrations. Brookings, South Dakota, is particularly high in Ca, Mg, K, and Na.

Equivalent Weight Importance

Equivalent concentrations for the major anions and cations are given by years for rain and snow and for all precipitation during the 2-year period on a volume-weighted basis in Table 3. These values are all based on CAL analyses. Ammonium, sodium, calcium, and hydrogen are the major cations, and sulfate and nitrate are the major anions. Sulfate and nitrate are always the major anions regardless of the year or kind of precipitation.

Cation importance varies with year and kind of precipitation. Ammonium was most important for rain in both years, but was replaced by hydrogen as most important in the relatively high snow year of 1978–1979 (21.34 cm) and was replaced by sodium as the most important in the relatively low snow year of 1979–1980 (12.73 cm).

A snowpack was present on Great Plains and Midwest soils from mid-November 1978 to the spring of 1979. Thus windblown dust was not a source of basic cations. During this period, storms were sometimes associated with low-pressure cells originating in the Dakotas, Minnesota, or near Winnipeg and moving east or southeast. Most storms were associated with low-pressure cells originating in the southern and middle Great Plains and moving northeast through Iowa and Minnesota, Missouri, Illinois and Wisconsin, or through Illinois, Indiana, and lower Michigan. Occasionally, a low-pressure trough running from Winnipeg to Texas would move easterly with east winds preceding it. The breadth of low-pressure cells typically ranged from the Ohio River Valley to Minnesota (NOAA daily weather maps). In short, summertime storm tracks persisted throughout the winter and spring periods of 1978–1979. From mid-November 1979 to mid-July 1980, there was little snow cover (or rain), and thus basic cations were prevalent in precipitation. Storm tracks were either similar to those of the 1978–1979 period or followed low-pressure centers

originating in the northern Great Plains and southern Canada. The low pH values in the December 1978 to September 1979 period (Figure 2) appear to be derived from moisture-laden air in the Mississippi and Ohio River valleys, where hydrogen concentrations are consistently higher, during a period when basic cations were less available. In the later period (1979–1980), dust was more available, and storm tracks varied more in relation to the Marcell site, some from the west, some to the north, and some through the Mississippi and Ohio River valleys. Thus north central Minnesota may receive air masses whose precipitation varies widely in hydrogen concentration (pH 3.5 to 6.5 or 316 to 0.31 microequivalents per liter (μeq/l)).

An overall check on the accuracy and completeness of analyses was made by subtracting the sum of all measured anions from all measured cations (Table 3). The resulting difference is either analytical error or undetermined anions. This value

TABLE 4. Correlation (r) of Ion Species in Precipitation at the Marcell Experimental Forest

Species Combination	Correlation Coefficient	Species Combination	Correlation Coefficient
$NH_4 : SO_4$	0.60*	$H : SO_4$	−0.24
$NH_4 : NO_3$	0.68*	$H : NO_3$	0.12
$NH_4 : Cl$	0.12	$H : Cl$	−0.20
$NH_4 : PO_4$	0.12	$H : PO_4$	0.02
$NH_4 : ?†$	0.03	$H : ?†$	−0.20
$Ca : SO_4$	0.72*	$Mg : SO_4$	0.56*
$Ca : NO_3$	0.62*	$Mg : NO_3$	0.57*
$Ca : Cl$	0.57*	$Mg : Cl$	0.48*
$Ca : PO_4$	0.00	$Mg : PO_4$	−0.03
$Ca : ?†$	0.51*	$Mg : ?†$	0.37*
$Na : SO_4$	0.64*	$K : SO_4$	0.25
$Na : NO_3$	−0.03	$K : NO_3$	0.14
$Na : Cl$	0.63*	$K : Cl$	0.32*
$Na : PO_4$	−0.02	$K : PO_4$	0.20
$Na : ?†$	0.91*‡	$K : ?†$	0.22

There are 82 pairs in each species combination.

*Significant at 0.01 level.

†Differences between total measured cations and total measured anions.

‡Reduces to 0.75 when one large Na value (510 μeq/l) is deleted from the data.

TABLE 5. Correlation (r) of Ion Species in Precipitation and Storm Size With Excess Acidity or Net Alkalinity

Ionic Species	Net Acidity	Net Alkalinity
NO_3	+0.53*	
Cl	+0.15	
SO_4	+0.09	
storm size	−0.04	−0.17
Na		+0.91*†
Ca		+0.38‡
Mg		+0.24
NH_4		−0.13
K		+0.04

There are 81 pairs for storm size, 52 for excess acidity, and 30 for excess alkalinity.

*Significant at 0.01 level.

†Reduces to 0.67 when one large Na value (510 µeq/l) is deleted from the data.

‡Significant at 0.05 level.

averages 4.7% of all determined ions during the 2-year period. Calculated bicarbonate values for each weekly collection, weighted by precipitation volume, averaged 2.01 µeq/l for the 2-year period. This would reduce the amount of undetermined anion from 6.35 (Table 3) to 4.34 µeq/l and the overall analytical error from 4.7 to 3.2%.

Measured cations were correlated with measured anions and unmeasured anions (sum of all cations minus all anions) for all data (Table 4). The unmeasured anions may be bicarbonate, carbonate, organic anions, or analytical errors. Taken in mass, the constituents of precipitation occur primarily as metal or ammonium salts, with $H NO_3$ as the only acid showing a weak but positive correlation.

We could not measure specific molecular combinations in precipitation, but the ion species correlations taken together with the microequivalent weight of ion species indicate that ammonium nitrate, sodium sulfate, and calcium sulfate are the most abundant species combinations occurring in precipitation. The high correlation ($r^2 = 0.91$) for sodium and an unknown anion may be indicative of the occurrence of sodium carbonate minerals such as nahcolite ($Na HCO_3$) or trona ($Na_2 CO_3 \cdot Na HCO_3 \cdot 2H_2O$) [Donner and Lynn, 1977]. These minerals and similar ones associated with calcium may be responsible for the average increase of field pH from 4.3 to 4.9 measured later in the Central Analytic Laboratory, assuming mineral dissolution as the sample sits in transit or storage.

Predicting Hydrogen Ion Concentration

Hydrogen ion concentrations have been calculated from old data sets that did not have a measurement of pH, but did measure the other major anions and cations [Cogbill and Likens, 1974; Stensland, 1979]. As a check on the accuracy of such methods, the volume-weighted 2-year means for the current Marcell data set were used to calculate mean pH after Stensland [1979]. Calculated mean pH was 5.2 compared to a measured mean pH done at CAL at the time of analysis of 4.9. The calculated pH is a reasonable estimate of the measured value with a difference of 0.3 pH units or 6.17 µeq/l of hydrogen; but in areas where pH changes rapidly in storage, it overestimates field-measured pH (4.3) by 0.9 pH units or 43.85 µeq/l of hydrogen.

Calculating pH from microequivalent data does not help explain what is causing high or low pH values. As a first step to do this, we entered all measured ions (in microequivalents per liter) into a multiple regression to predict hydrogen ion activity
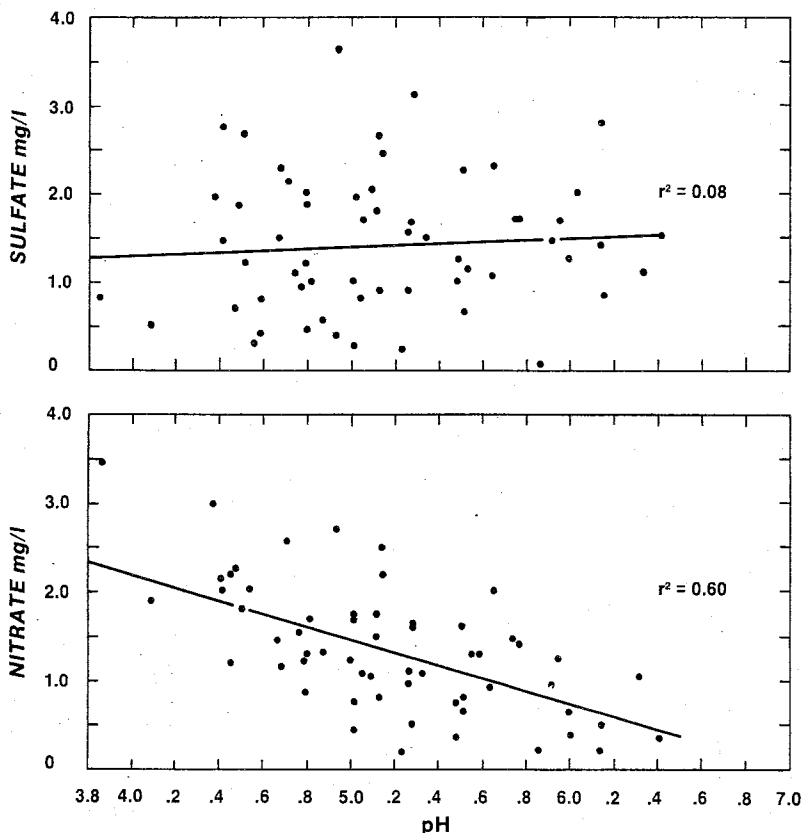

Fig. 3. Sulfate or nitrate concentrations as a function of pH for samples with total ionic concentrations less than 100 µeq/l.

Fig. 4. Volume-weighted pH in 1980 for the NADP/Canadian Network for Sampling Air Pollution networks. Prepared by J. H. Gibson and C. V. Baker. Reproduced by permission of the National Atmospheric Deposition Program. March, 1982. X marks the Marcell Experimental Forest site.

as measured at CAL. Only coefficients for Ca^{2+}, NH_4^+, and NO_3^- were significant. When these three variables are regressed with hydrogen ion activity, the resulting equation (values in microequivalents per liter) is

$$H^+ = 10.65 - 0.33(Ca^{2+}) - 0.17(NH_4^+) + 0.4(NO_3^-) \qquad (1)$$

Equation (1) is significant, and all coefficients are significant ($\alpha = 0.01$); but it can explain only 35% of the variation in hydrogen ion activity. It has a standard error of estimate of ± 10.91, which translates to a range about the mean pH (4.9 in Table 1) of 4.6–6.0. Equation (1) is not a good predictor of H^+, but it is important in showing that Ca^{2+} and NH_4^+ tend to reduce H^+ while NO_3^- tends to increase H^+. Conspicuous by its absence is SO_4^{2-}, which does not relate to H^+ (a result similar to that of *White and Kramer* [1980] for a site 120 km to the southeast). *Galloway and Likens* [1981] have also demonstrated the importance of NO_3^- in causing acid precipitation. They report for the eastern United States that NO_3^- was less than 1 mg/l until 1945 and now ranges between 2.5 and 3.0 mg/l. On the other hand, sulfate in the eastern United States was approximately 6 mg/l prior to 1950 and has now decreased to 4 mg/l. Northern Minnesota had similar SO_4^{2-} concentrations near 2 mg/l in 1936 and 1979. There is limited evidence that NO_3^- is increasing. Junge's data reported by *Stensland* [1979] show nitrate at 0.90 mg/l for International Falls, Minnesota, in 1955–1956; we measured 1.30 in 1971–1973 and 1.41 in 1978–1980 at the Marcell Experimental Forest. Emissions of NO_x relative to SO_2 in the United States have also increased from 1940 to 1976 from 0.25 to 0.60 [*Environmental Protection Agency (EPA)*, 1978]. This trend may be similar near the Marcell site also because of the construction of a large coal-fired power plant and natural gas–burning taconite-processing plants in the 1960's.

Ion Correlations With Excess Acidity or Excess Alkalinity

Further insight into possible acidic or basic inputs to ecosystems can be gained by correlating ions with excess acidity or excess alkalinity after the method of *Reuss* [1975]. When these values for each weekly collection are calculated, nitrate is the major ion associated with acidic inputs, and sodium is the major ion associated with basic inputs (Table 5). Calcium and magnesium also contribute to basic inputs. Storm size (weekly collection) is not well correlated with either net acidity or net alkalinity, and neither are the other ions including sulfate.

Nitrogen oxides originate for the most part from the combustion of coal and petroleum [*Gorham*, 1975]. Sodium originates from sodium minerals. Soils high in sodium are common in North and South Dakota where it accumulates at the top of B horizons. Such horizons may be exposed to the wind on hillsides and by plowing or in mining spoils and thus lifted in the air as dust.

Hydrogen Control in Precipitation

Together, the excess alkalinity and acidity correlations, the multiple regression for H^+, and microequivalent per liter concentrations (Table 3) suggest that pH is controlled in its midrange (4.5–5.5) by a mixture of ions including Ca^{2+}, NH_4^+, Na^+, SO_4^{2-}, and NO_3^+. When pH (and excess alkalinity) is higher, Na^+ dominates the cations. When pH is lower, nitrate dominates the anions (rising as high as 5.85 mg/l) but only when Ca^{2+} and NH_4^+ are low.

Since sulfate and nitrate are consistently the major anions, they must rise in concentration whenever cations in several combinations (principally calcium, ammonium, and sodium) rise. Because of this, it is not possible to see direct correlations of sulfate and nitrate with pH when the entire data set is

examined. However, when total cation concentrations (excluding hydrogen) above 100 μeq/l are dropped from the data set, the relationships of nitrate and sulfate to pH are clearly displayed (Figure 3).

Sulfate has no correlation with pH, a result which confirms nonsignificance in the multiple regression analysis including all data. Nitrate concentrations are positively correlated ($r^2 = 0.60$) with low pH, a result which strengthens the significant positive coefficient for nitrate in the multiple regression analysis and the weak all-data correlation ($r = 0.12$) between hydrogen and nitrate (Table 4).

CONCLUSIONS

The NADP data sampled at the Marcell Experimental Forest show that low pH values occur in north central Minnesota, but high values also occur. Total ion concentrations range from samples of 17 total μeq/l to 834, and field pH from 3.5 to 6.5.

Stensland [1979], reporting EPA emissions data, shows that the eastern United States contributed 80% of the total nitrogen oxide emissions in 1972. Six states, New York, Pennsylvania, Ohio, Michigan, Indiana, and Illinois, contributed 45% of the total. Half of the total sulfur oxide emissions in the United States came from the northeastern sector in 1972. These emission estimates together with the correlation of high nitrate and low pH suggest that part of the nitrate in north central Minnesota comes from relatively near midwestern sources, while high sulfate emissions concentrated in the northeastern United States do not travel this far. The Marcell site is on the western fringe of low pH occurrence. It should be remembered that the gradient to consistently lower pH values steepens sharply to the near east beginning in central Wisconsin (Figure 4). In contrast the transect data of *Munger* [1981] indicate increasing calcium, sodium, and ammonium values from northeastern Minnesota west to North Dakota (Table 2). Thus precipitation pH in north central Minnesota fluctuates as high nitrate and high or low cation concentrations interact.

If low pH precipitation continues, we can expect lowered pH values in lakes with hard-rock watersheds unable to add bases to runoff waters (*Henriksen* [1980] suggests a precipitation of 4.6 or lower will affect bedrock lakes). The extent to which lake pH may be lowered must be demonstrated by lake surveys (past and present) and continued precipitation monitoring. A recent survey [*Verry*, 1981] indicates that glacial till basin lakes near the Marcell site have sufficient buffering capacity to handle current acid inputs, but some hard-rock basin lakes further east can be expected to show the loss of bicarbonate (acidification) if precipitation pH consistently averages near 4.6. Other concerns regarding the impact of acid rain on forests relate to disease interactions on leaf or needle surfaces and increased base leaching from soils.

Emission control is a means of reducing acid deposition, but the method for calculating sulfate deposition in northern Europe that deletes the amount of ocean-derived sulfate will need expansion if the concept is applied across the North American continent. A general case for high ionic concentrations should be developed to handle both ocean salts and dust from dry and wind-blown soils. Recognition of high equivalent concentrations would remove a portion of sample events and accompanying variation from data sets relating hydrogen to sulfate, nitrate, or their equivalent sum. At the Marcell site, 27% of the sample events (12% of precipitation) were considered dominated by dust. The first step is regressing sulfate

and/or nitrate with hydrogen in low-ionic concentration samples at many locations. Second, these regressions can be matched to regional emissions, and fair recommendations for emission limits proposed where real impacts on aquatic and terrestrial resources are known.

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