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Carl F. Aten^a; John B. Bourke^b; John C. Walton^b

^a Department of Chemistry, Hobart and William Smith Colleges, Geneva, NY, USA ^b Department of Food Science and Technology, New York State Agricultural Experiment Station, Geneva, NY, USA

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ION-CONTENT OF STREAMS IN THE COLD R. AND CHUBB R. WATERSHEDS; 1983-5

CARL F. ATEN

*Department of Chemistry, Hobart and William Smith Colleges, Geneva, NY 14456
USA*

JOHN B. BOURKE and JOHN C. WALTON

*Department of Food Science and Technology, New York State Agricultural
Experiment Station, Geneva NY 14456 USA*

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Two adjacent watersheds in the Adirondack Mountains (New York, USA) were sampled in late summer in the years 1983 to 1985. Measurements were made of pH, specific conductance; and concentrations of 19 elements by plasma emission spectroscopy. Concentrations of Cl^- , NO_3^- , and SO_4^{2-} were measured by HPLC in the samples taken in 1985. The results showed that the streams were less acidic than rainfall, and that they contained substantial, but not unusual, concentrations of Ca and Mg, probably from reaction with limestone. Small concentrations of Al and Fe were found but the other elements "measured" were not present in concentrations greater than the detection limits. The ionic content of the streams may be described nearly completely in terms of H^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , and SO_4^{2-} .

KEY WORDS: Natural waters, streams, acid rain, ions, heavy metals, calcium ions, magnesium ions, neutralizing capacity, pH measurement, inductively coupled plasma emission spectroscopy.

INTRODUCTION

Streams and lakes in the eastern United States have often been cited as susceptible to the effects of acidic precipitation. A survey of streams in the mid-Atlantic and southeastern United States (National Stream Survey, NSS) has found that nearly one-half of the streams surveyed have acid neutralizing capacities less than 200 microequivalents per liter.¹ General reviews of the history and sources of acidic atmospheric precipitation, and of the aqueous chemistry associated with acidic precipitation have been written.^{2,3}

Three principal components of interest in acidic precipitation are the ions H^+ , NO_3^- , and SO_4^{2-} which arise from the combustion of fossil fuels.⁴ However, many other substances are found, too, for example, NH_4^+ , Ca^{2+} and K^+ deposition have been reported in a forest in Tennessee, and heavy metals in rainfall have been surveyed.⁵⁻⁷

Studies of natural waters (streams and lakes) in forested areas have attributed several effects to acidic precipitation:

1. decreased pH in regions with low buffer capacity^{8,9}

2. increased mobility of nutrient and of toxic metal elements¹⁰⁻¹⁴
3. increased concentrations of NO_3^- and SO_4^{2-} ⁽¹⁵⁾

A feature of water in forests that has attracted attention is the presence of humic acids. These substances may act as complexing agents for metal ions and contribute to the total acidity of the water, but since they are weak acids, they do not lower the pH appreciably.¹⁶⁻¹⁸

Studies of natural water systems are difficult, slow, and incomplete because of the remote locations of many interesting sites, the poor reproducibility of conditions, the seasonal aspect of weather patterns, and the fact that measurement capabilities are necessarily limited. Three experimental approaches have been used. First, many investigators have selected one or more natural sites and have observed or probed them in specific ways for limited times.^{1,8,10} Second, some investigators have simulated natural water systems in the laboratory.^{19,20} Last, the first two techniques have been combined by adding spikes of pollutants to natural systems in order to observe the effect.²¹⁻²³

In this study water samples were taken from sites in two adjacent watersheds in the Adirondack Mountains (New York, USA) during three successive years at approximately the same time of year, late July. The pH and metal ion concentrations of the samples were determined and in one set of samples the anion concentrations of the samples were determined, also. The intent was to compare the watersheds with each other, and to see if any changes with time were apparent. The principal advantage of the study is the continuity of sampling the same sites under similar conditions for three consecutive years. The principal disadvantage is that samples were not taken continuously over the three years. In particular the spring thaw of the winter snowfall has been shown to be important in natural waters, but our samples were taken after this annual event.^{24,25}

EXPERIMENTAL

The samples for this work were taken in the time periods:

- 29 July to 4 August 1983,
- 27 July to 1 August 1984 and 8 September to 13 September 1984,
- 22 July to 27 July 1985.

Samples were taken in both the Cold River watershed and in the Chubb River watershed (except in 1983). These watersheds lie along the 30 mile section of the Northville-Lake Placid trail between Long Lake and Lake Placid. The sampling sites are shown in U.S. Geological Survey maps for the Long Lake quadrangle and the Santanoni quadrangle, covering the region 74°00' to 74°30'W and 44°00' to 44°15'N. Both the main streams and smaller tributaries were sampled. Samples were taken from the Cold River from about two miles upstream of its junction with the Raquette River (about one-half mile downstream from Long Lake) to its sources in Moose Creek and Moose Pond, Roaring Brook, and Preston Ponds. The Chubb River was sampled between Wanika Falls, where there is already a

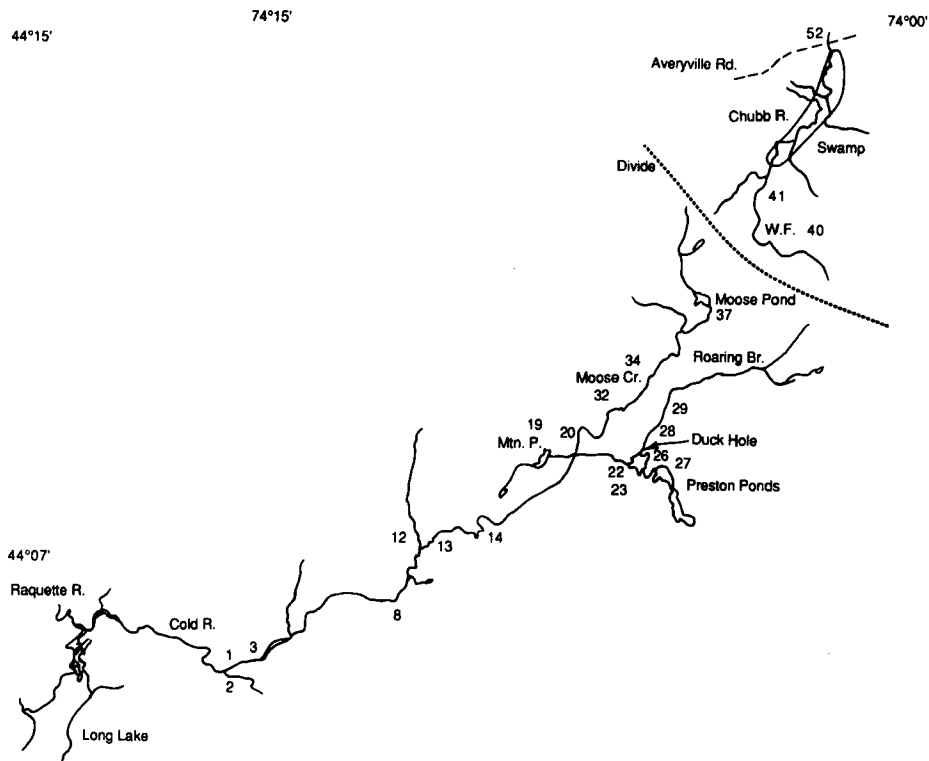


Figure 1 Map of the Cold River and Chubb River watersheds showing principal site numbers where samples were taken. Samples were numbered consecutively. Missing numbers are for tributary streams between the sites shown.

substantial flow, and the Averyville Road, approximately five miles farther downstream and four miles above its end in Lake Placid. Between the Falls and the road, the river flows through a swamp. Figure 1 is a sketch of these watersheds and indicates the points where samples were taken; Table 1 is a complete list of sample sites.

The pH at each site was measured both *in situ* and later in the laboratory. Some experimental difficulty was encountered in the field measurements. In 1983 a Markson Model 74 portable meter with a gel-filled combination electrode calibrated at pH 4.0 and 7.0 was used. Although its response was slow, it functioned well. In 1984 a Corning pH/Temp Meter 4 with a glass combination electrode (solution filled) calibrated at pH 4.0 and 7.0 was used. The early readings in July were good, but as the trip progressed the readings drifted to lower values until they were simply absurd (pH2). In several cases we drank the water, and it was not a pH 2 solution. Presumably the problem with the meter was some combination of moisture in its circuitry and the low conductivity of the samples. In 1985 the field readings were taken with indicator paper, EM Reagents No. 9656. Two different indicators were used with ranges 0.5 to 5.0 and 5.5 to 9.0,

Table 1 Sampling sites in the Cold River and Chubb River watersheds (cf. Figure 1)

<i>Id</i>	<i>Sample No.</i>	<i>Sample source</i>
<i>Cold River watershed</i>		
<i>Principal sources of Cold River</i>		
A	20, 32, 34, 37	Moose Pond and Moose Creek
B	30, 31, 33, 35, 36, 38, 39	Small tributaries of Moose Creek
C	28, 29	Roaring Brook
D	26, 27	Preston Ponds
E	22, 23	Duck Hole
F	19	Mountain Pond
<i>Downstream from junction of principal sources</i>		
G	1, 3, 8, 13, 14	Cold River
H	12	Seymour Brook
I	2, 4-7, 9-12, 15-18	Small tributaries of Cold River
<i>Chubb River watershed</i>		
J	40	Chubb River at Wanika Falls
K	41	Chubb River 1 mile below Wanika Falls
L	42-47	Small tributaries of Chubb River
M	48-51	Small tributaries in swamp
N	52	Chubb River at Averyville Road

calibrated in 0.5 pH units. When the pH was measured in the laboratory, two drops of 0.08 M KNO_3 were added to 8 mL of sample in order to raise the conductivity of the sample. The pH was then read with a glass, solution-filled combination electrode.

For laboratory analyses, duplicate samples were collected in 60 mL polyethylene bottles. The samples were stored at 1 °C. Specific conductance and pH of each sample was measured within a few days of returning the samples to the laboratory.

The samples were examined for the concentrations of 19 elements by inductively coupled plasma emission spectroscopy (ICP) (Plasma 100: Instrumentation Laboratory Inc. now Thermo Jarrell Ash Corp.) Element concentrations were determined by the emission intensity from one line for each element except cadmium, for which three lines were used. All water samples were analyzed directly by ICP with no special preparation.

The samples taken in 1985 were analyzed for anions by high-pressure liquid chromatography (LDC Milton Ray Constametric III pump and Conductomonitor III detector with Ionphase-10 anion exchange column). The carrier was 2 mM sodium salicylate and 0.2 mM sodium borate at pH7.

RESULTS AND DISCUSSION

The analytical results are summarized in Table 2 and will be discussed individually below. For comparison, certain average results from the National Stream Survey

Table 2 Summary of analyses over sites and times. Entries are either mean values with standard deviations or the observed range of values

<i>Id</i> ^a	<i>pH range</i>	<i>Ca</i> ^b	<i>Mg</i> ^b	<i>Al</i> ^b	<i>Fe</i> ^b	<i>Cl</i> ^{-b,c}	<i>NO₃</i> ^{-b,c}	<i>SO₄</i> ^{2-b,c}
A	5.0–6.6	2.4 ± 0.3	19.7 ± 2.4	4.9 ± 4.1	4.3 ± 23	12.6 ± 1.3	8.6 ± 1	55.9 ± 10
B	4.5–7.7	41 to 82	9 to 33	0 to 14	0 to 11	8 to 51	0 to 64	52 to 76
C	4.5–6.2	56.4 ± 9.2	13.4 ± 1.3	5.5 ± 2.5	0 ± 0.23	10.8 ± 6.5	7.4 ± 4	64.4 ± 3
D	4.8–5.8	51.4 ± 1.5	12.9 ± 1.0	3.0 ± 2.1	0.11 ± 0.25	15.8	45.2	68.7
E	5.0–6.0	51.9 ± 2.3	12.8 ± 1.0	1.7 ± 1.8	0.41 ± 0.45	12.7	23.0	64.8
F	5.4–6.7	82.3 ± 6.2	20.8 ± 0.9	2.8 ± 0.6	0.56 ± 0.46	27.7	48.3	54.9
G	5.9–7.2	85 ± 22	23.7 ± 5.0	2.2 ± 1.5	1.50 ± 0.90	18.0 ± 6.8	17.6 ± 1	62.4 ± 5
H	5.5–7.0	74.1 ± 4.5	18.8 ± 1.5	2.4 ± 1.3	0.04 ± 0.09	11.4	42.6	62.1
I	5.0–7.0	90 to 190	12 to 62	0 to 10	0 to 3.6	10 to 89	23 to 71	50 to 83
J	4.2–5.3	54.9 ± 7.2	13.3 ± 2.3	10 ± 5	0.09 ± 0.12	12.4	42.3	72.6
K	4.5–5.7	43.2 ± 11.7	20.2 ± 6.6	4.8 ± 3.3	0 to 0.25	0 to 23	70.6	69.9
L	4.0–6.3	62 to 160	21 to 60	0 to 10	0 to 21	12 to 100	9 to 99	26 to 88
M	4.5–7.0	232 to 357	50 to 119	0 to 2	0 to 0.54	24 to 104	22 to 75	26 to 96
N	5.0–7.0	138 ± 9.0	58.4 ± 4.6	2.8 ± 2.0	7.5 ± 2.4	50.3	35.9	60.8
NSS ¹	7.2	223	101	3.3	0.46	132	38	113
ELS ⁸	6.7	72	27	2.5	0.73	11	0.6	60
ELS ²⁷		195 ± 194	67 ± 70			44 ± 122	2.3 ± 4	60 ± 13

^aSee Table 1 and Figure 1 for site identification.^bUnits mole/L.^cResults for 1985 samples only.

—Phase 1 (NSS) are included in Table 2.¹ The numbers listed are the average, drainage-area values given for streams in the three northern regions Poconos/Catskills, Northern Appalachians, and Valley and Ridge. Although these regions lie south of the Adirondacks where our samples were taken they are part of the same mountain range. In addition, median values for Adirondack lakes from a survey of northeastern lakes are included.^{8,27}

pH

For the various sites the pH range observed is listed. No trends with time were found. In general, the pH range observed was 4 to 7 which with the rather high concentrations of Ca and Mg found implies that the streams flow over substantial beds of limestone. Although, the accuracy of the field readings is not high, as noted above, the readings at each site agree within 1.5 units over the three years (disregarding the 1984 field readings entirely). The 1985 field readings (pH paper) were 0.5 to 1.5 units lower than the laboratory readings. However, a comparison of the paper No. 9565 with known buffers showed that we read the paper 0.5 unit too low in daylight. Thus, the two sets of data taken in 1985 agreed within one unit. Also, the 1983 field and laboratory readings agreed within one unit. The source regions for the Cold River were somewhat more acidic than the downstream part of the river; Moose Creek 5.0–6.4; Roaring Brook 4.5–6.2; and Preston 4.8–5.8 whereas the lowest part of the river was pH 6 to 7. The pH range for the Chubb River was 4.5 to 6.8 with the same range for the tributary streams and the

Table 3 Mean Ca^{2+} concentrations at Cold River sites, averaged over the four sample sets

Site no. ^a	Ca ^b	σ^c
14	62	8.5
13	70	0.2
8	82	5.0
3	84	6.5
1	123	6.7

^aSee Table 1 and Figure 1 for site identification.

^bCa concentrations in μM .

^cStandard deviation in μM .

streams in the swamp. Again, the downstream pH, 6–7, was slightly higher than that upstream. In 1983 while at site 13, about two inches of rain fell. The pH of the rain was 4.7. This was apparent in the streams since samples taken earlier were mostly near pH7 while those taken after the rainfall were nearer 5.5.

Ca and Mg

These elements gave the highest cation concentrations and are well correlated, with the Mg concentration being about $\frac{1}{4}$ that of calcium on a mole basis. As shown in Table 2, most Ca concentrations were in the range 50 to 80 μM except for the Chubb River streams in the swamp where these metal concentrations rose about five-times higher. In the Cold River system, there was a gradual increase from source concentrations of Ca of about 50 μM to downstream values near 130 μM (Table 3). The concentrations found at particular sites were constant within about 10% over the three year sampling period; the large standard deviation in Table 3 for samples (1, 3, 8, 13, 14) in the Cold River is associated with the fact that different sites are included in the average.

Aluminum

The Al determinations are marginal being near the ICP sensitivity limit, 0.7 μM . In the Cold River system the highest values were found in the source streams at mean concentrations of 3.5 to 5.0 μM , and generally lower values farther downstream, typically 0.7 to 1.0 μM . Similarly, in the Chubb River the upstream concentration at Wanika Falls, 104 μM , was higher than the downstream concentration at the Averyville Road, 3.0 μM . Within the swamp streams, the Al concentrations were lowest, <2 μM .

Iron

Concentrations of Fe were generally low and variable. The Moose Creek system had the highest concentrations, 20 μM , but values of 0.3 to 3.0 were observed in

Table 4 Elements not found in Cold River and Chubb River

<i>Element</i>	<i>Detection limit^a</i>
Ba	0.001
Mn	0.001
Ti	0.002
V	0.002
Cu	0.002
Zn	0.006
Cd	0.007
Ni	0.012
Co	0.013
Cr	0.017
Pb	0.061
Sn	0.12
P	0.17
As	0.22

^aDetection limits in mg/L. See reference 6a.

most samples. No trends in time or place were apparent in the Cold River. In the Chubb River the downstream concentration was highest, $7\mu\text{M}$, whereas the upstream values were very low. A few tributary streams had concentrations near $20\mu\text{M}$ and apparently are the source of the downstream concentration. The streams in the swamp showed very low concentrations.

Other metallic elements

Low concentrations of Sr were observed in the range 0 to $0.5\mu\text{M}$ with most values in the range 0.1 to $0.2\mu\text{M}$. Other elements which were included in the ICP analysis and their practical detection limits are listed in Table 4. These elements were not found in the samples. The absence of Ti is of some interest since there is a mine a few miles southeast of Duck Hole.

Anions

Concentrations of Cl^- , NO_3^- , and SO_4^{2-} were determined in the 1985 samples by HPLC anion exchange chromatography. Although the Cl^- and SO_4^{2-} peaks were well resolved, the NO_3^- signal was superposed on variable amounts of unresolved signal of unknown origin (possibly a mixture of "humic acids"). The anion concentrations for 44 of the 1985 samples are summarized in Table 2.

Two checks on the overall consistency and completeness of the data are possible:

1. The measured cation normality for the ions H^+ , Ca^{2+} and Mg^{2+} may be

compared with the measured anion normality for the ions Cl^- , NO_3^- , and SO_4^{2-} . For 34 samples, the mean absolute error and its standard deviation was:

$$(\overline{\text{abs. error}}) = -2.2 \pm 32.4 \mu\text{N}$$

and the mean relative error with its standard deviation was:

$$\overline{\text{rel. error}} = \frac{1}{34} \sum \frac{(\text{abs. error})_i}{(\text{total cation})_i} = -0.036 \pm 0.185.$$

Thus, the overall absolute uncertainty in the measurements is approximately $30 \mu\text{N}$ which is the standard deviation of the absolute error, and the mean relative uncertainty is about 20% which is the standard deviation of the relative error. In each case the mean error is enough smaller than its standard deviation to suggest that the errors are random, and that no large systematic error occurred.

2. The specific conductance of the samples was calculated from the element and anion determinations and was compared with the measured specific conductance. The mean absolute error with its standard deviation was:

$$\overline{\text{abs. error}} = \overline{K_{\text{calc}} - K_{\text{obs}}} = 1 \pm 3 \mu\text{ohm}^{-1} \text{cm}^{-1}$$

and the mean relative error with its standard deviation was:

$$\frac{\overline{K_{\text{calc}} - K_{\text{obs}}}}{\overline{K_{\text{obs}}}} = 0.05 \pm 0.12.$$

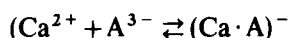
Again, the small mean values relative to their standard deviations suggest random errors, and the apparent relative error of 12% is small enough to suggest that no important element or ion was overlooked. For example, Na^+ , K^+ and NH_4^+ were almost certainly present, but apparently not in high concentrations. For 147 Adirondack Park lake samples, the following mean concentrations and standard deviations have been reported for Na^+ , K^+ and NH_4^+ ; 62 ± 97 , 9 ± 6 and $2 \pm 2 \mu\text{M}$, respectively.²⁷

The specific conductance values at particular sites agreed within 10% over the three years. The 1985 samples will be discussed particularly below since the anion concentrations were measured in these samples.

The observed range of specific conductance (1985) was 17 to $66 \mu\text{ohm}^{-1} \text{cm}^{-1}$, with four of the five highest values ($K > 52$) from streams in the swamp along the Chubb River. The other high value is from a small stream that feeds directly into the Cold River. Of the remaining samples, 24 were in the range 17 to $24 \mu\text{ohm}^{-1} \text{cm}^{-1}$, and 17 samples were in the range 25 to $44 \mu\text{ohm}^{-1} \text{cm}^{-1}$. These specific conductivities are lower than the median values found in NSS; 50 , 109 and $112 \mu\text{ohm} \text{cm}^{-1}$ for the three northern regions (1).

The largest errors between cation and anion normalities occurred in five small streams that empty directly into the Cold River, three small streams that empty directly into the Chubb River, the downstream value for the Chubb River itself,

and especially the streams in the swamp (which empty into the Chubb River above its downstream sampling point). In each case the apparent anion normality (Cl^- , NO_3^- , SO_4^{2-}) was lower than the apparent cation normality, but the error in the calculated specific conductance was not unusual. Similar anion deficits have been reported for lakes in Norway²⁸ and in NSS.¹ To some extent these results can be accounted for by the presence of complexing anions, which may be represented as A^{3-} , so that reactions like the following might take place:



The ICP measurements would not yield any information about such complexes since only the total metal ion concentrations are determined by the method. The apparent cation normality would be larger than the apparent anion normality since the ions A^{3-} would neither be detected nor be included in the anion count. Although the HPLC analysis could not have detected A^{3-} since the retention volume would have been too large for the instrumental conditions used, single-charged complex ions $(\text{Ca} \cdot \text{A})^-$ might possibly have been the interference observed with NO_3^- . It is not obvious why the observed specific conductivity and that calculated without any consideration of complex formation should agree. The largest discrepancies between cation and anion normalities were observed at sites 48, 49 and 51 in the swamp. If we assume that the entire difference between cation and anion normalities is some complexing anion, A^{3-} , and that this anion is completely bound with Ca^{2+} to form $\text{Ca} \cdot \text{A}^-$, then the observed and calculated conductances would agree if the equivalent conductance of $\text{Ca} \cdot \text{A}^-$ were about 130, that is, slightly more than twice the value for Ca^{2+} . Although this value is not impossibly large it is unlikely since most anions have equivalent conductances less than 100. This view of these solutions may be partly correct, but is apparently incomplete.

Our results do not show an appreciable mobilization of metals except for calcium and magnesium, perhaps because the residence time of the stream water on the rocks of the stream was too brief to reach equilibrium or perhaps because the equilibrium concentrations were below our detection limits. For example, in Dart's Lake in the Adirondacks, monitoring during 1982 showed a pH range of 4.8 to 5.6, similar to values we observed, but soluble lead concentrations only up to $15 \times 10^{-9} \text{ M}$, which is well below our detection limit for lead of $300 \times 10^{-9} \text{ M}$.²⁹

In summary, the Cold river and Chubb River watersheds are rather well buffered by limestone and their ionic composition is largely described by the concentrations of Ca^{2+} , Mg^{2+} , SO_4^{2-} , Cl^- and NO_3^- . The buffering appears to be somewhat less than that found in both the NSS and lake survey results (Table 2) since the Cold and Chubb Rivers were acidic in the upstream regions whereas the survey averages were neutral. Also, the lower nitrate and sulfate concentrations imply a lower influx of acid from the atmosphere to the Cold and Chubb Rivers than to the area sampled by NSS. However, this effect may be due to the difference in time of year the samples were taken since NSS sampling was in spring. The Adirondack Lake survey found sulfate values comparable to ours but lower nitrate concentrations.^{8,27}

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