

Using Streamwater Chemistry to Assess the Impacts of Acid Deposition at the Lye Brook Wilderness, Vermont

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Abstract

Streamwater chemistry was monitored in the Lye Brook Wilderness from May through October of 1996 as part of a surface water chemistry study that was initiated in 1994. Stream samples were collected once every three weeks at four sampling locations within the wilderness boundary. Samples were analyzed for pH, major cations and anions and total organic carbon (TOC). The low pH values of streams sampled indicates that many of the streams in this region are acidic. Sulfate appeared to be the dominant acid in stream water. However NO_3^- also contributed to the acidity of streams, particularly during the spring before vegetative uptake began. Wetland areas in the headwaters of some sampled streams were a source of TOC and associated organic acids. The presence of these organic compounds decreased the concentration of inorganic aluminum through the process of chelation. Therefore, although the pH of these waters may be low enough to cause mortality of some biota, Al toxicity does not appear to be a major threat.

Introduction

Much of northeastern United States is vulnerable to acid inputs because the region receives relatively large amounts of acid deposition and the streams generally have a low acid neutralizing capacity (Adams et al. 1991). Therefore, acid deposition caused by atmospheric pollution is a major threat to aquatic systems in the Lye Brook Wilderness. This research focuses on streamwater chemistry because there is very little existing data for streams and the effects of air pollution on streamwater chemistry have not been thoroughly established for this region of New England. The objectives of this study were to: 1) Investigate spatial and seasonal variability in stream chemistry as a function of site characteristics; 2) Determine factors that contribute to the acidity of streams in this region.

Methods

In 1994, nine streamwater sampling sites were established throughout the wilderness area by determining the major site dynamics of interest, such as geology, wetlands and elevation (Figure 1). Samples were collected from these sites once every two weeks until 1996. In 1996, the number of sampling sites was reduced to four (sites 2, 3, 8 and 9) and the sampling interval was changed to three weeks. These four sites were chosen because they had the lowest pH and acid neutralizing capacity values of the nine sites. Streamwater grab samples were collected at these locations from May 1996 through October 1996.

Determination of pH was made using a portable pH meter on the day the samples were collected. Cation values were obtained using direct current plasma spectroscopy. Anions, NH_4^+ and SiO_2 were measured on a continuous flow system (Autoanalyzer II). Speciated Al was also determined with an Autoanalyzer using pyrochatechol violet colorimetry (McAvoy et al. 1992). Total Al concentrations were calculated in $\mu\text{eq/L}$ using a charge of 3 if the $\text{pH} \leq 4.5$, 2.5 if the pH was 4.6 to 5.5 and 2 if the $\text{pH} \geq 5.5$. A Schimadzu 5000 organic carbon analyzer was used to measure TOC. The value of TOC in $\mu\text{eq/L}$ was calculated using a constant charge density approach similar to the one developed by Oliver et al. (1983).

Results and Discussion

Measurements of pH were used to determine the acidity of streams and to assess whether the streams in this region are susceptible to the affects of acid deposition. Sites 2, 3, 8 and 9 were sampled in 1996 because these sites were the most acidic of the nine original sites. Table 1 lists the streamwater chemistry for these four sites in mg/L and table 2 lists the streamwater chemistry in $\mu\text{eq/L}$. Streamwater ion values were converted from mg/L to $\mu\text{eq/L}$ for the purpose of making comparisons of ionic strength.

Based on the values in table 2, SO_4^{2-} was the dominant strong acid anion at all sites followed by Cl^- and NO_3^- . In addition, weak organic acids associated with TOC contributed substantially to the acidity of streamwater and was greater than Cl^- and NO_3^- acidity. The concentrations of base cations followed a general trend of $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ with the exception of site 2 which had slightly higher Mg^{2+} than Na^+ .

There are several factors that may affect the concentration of cations and anions and which consequently affect the acid-base status of streams. In the Lye Brook Wilderness watershed geology may influence the concentration of some ions in streamwater. The geologic substrates underlying the sampled streams consist of rock that is resistant to chemical weathering. Therefore weathering rates are generally not fast enough to completely buffer incoming acids. These rocks contain low concentrations of Ca^{2+} , Mg^{2+}

and K^+ and higher concentrations of Fe and Al resulting in leachates that are low in base cations and high in metals.

In addition, the soils in this area generally have a low cation exchange capacity. This causes a subsequent reduction of base cations in soil leachates and ultimately results in low concentrations of base cations in streamwater. Soils that are highly affected by acid deposition are characterized by the movement of NO_3^- and SO_4^{2-} in soil water. As these mobile anions are exported to streams they are balanced by mobile cations. Unless these cations are replaced by atmospheric deposition or weathering inputs, the base saturation of the soil will decrease and the soil will become acidified. In areas where base saturation is severely reduced, Al concentrations in soil water and streamwater increase.

In addition to factors associated with geology and soils, biological reactions can also increase or decrease acidity in surface waters. For example, factors such as uptake by vegetation and microbial decomposition can have a strong impact on inorganic elements, particularly NO_3^- which is biologically important. In Lye Brook streams NO_3^- concentrations were highest during May and early June. Concentrations of NO_3^- generally peak during spring because soil temperatures increase and mineralization and subsequent nitrification of N begins before vegetation initiates nutrient uptake (Likens et al. 1970; Galloway et al. 1987, Rascher et al. 1987). In the study streams, concentrations of NO_3^- were highest during spring which caused a subsequent reduction in pH. Despite this increase, SO_4^{2-} remained the dominant strong acid, unlike some other areas where NO_3^- acidity exceeds SO_4^{2-} (Stoddard and Murdoch 1991).

The presence of wetlands at the source of streams sampled resulted in high concentrations of TOC and organic acids. These naturally occurring, organic acids may partially explain the low pH of streamwater draining wetlands (McKnight et al. 1985). Site 8 is an exception because it does not have headwater wetlands and it had relatively high TOC concentrations compared to the nine original sample sites. The most likely reason for high TOC at this site is related to soil depth. Site 8 is located on an exposed ridge at a high elevation where soils are thin. Mineral soils absorb organic C; therefore streams draining thick soils generally have lower organic C concentrations (Lawrence et al. 1988; Cronan 1985). Factors regulating organic C concentrations are important because organic C may influence mineral weathering, cation leaching and trace metal speciation. Streams with high concentrations of TOC typically exhibit low pH values because of the contribution of organic acids associated with TOC.

In addition to contributing to stream acidity, organic acids can also increase weathering rates through chelation (Huang 1988). In this process, organic acids form complexes with Fe and Al, which subsequently affects the form and concentration of these elements in solution. When chelation occurs it causes a reduction in the concentration of inorganic Fe and Al because these metals are bound in non-labile, organic forms. In general, waters dominated by naturally occurring acids are less likely to cause damage to acid-sensitive biota because of the tendency of these waters to form Al complexes (Driscoll et al. 1980).

Therefore, the four sites that were sampled in 1996 had low inorganic Al concentrations despite low pH values.

Conclusion

This research indicates that the streams sampled in the Lye Brook Wilderness are acidic and have a low buffering capacity. Sulfate was the most abundant ion contributing to the acidity of streams, however NO_3^- was seasonally important, particularly during the spring. Increases in air pollution may increase streamwater concentrations of SO_4^{2-} and NO_3^- causing further reductions in pH. Although organic acidity contributed greatly to the low pH of sampled streams, it reduced concentrations of inorganic Al which is the form of Al that is most toxic to aquatic biota. Therefore although the pH of streams sampled was low enough to cause damage to acid-sensitive species, Al toxicity does not appear to be a major threat because of the complexation of inorganic Al with organic C compounds.

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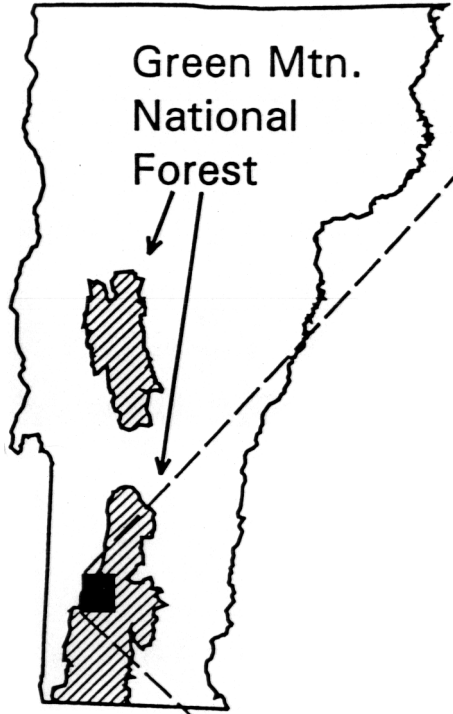
Table 1. 1996 chemistry of 4 study streams in the Lye Brook Wilderness.

DATE (yymmdd)	Site	pH	Cond. µeq/L	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	T-Al mg/L	O-Al mg/L	I-Al mg/L	Fe mg/L	NH4 mg/L	SO4 mg/L	NO3 mg/L	Cl mg/L	SiO2 mg/L	TOC mg/L
960515	2	4.1	26.8	0.65	0.22	0.30	0.13	0.33	0.27	0.06	0.19	0.28	4.97	0.09	0.70	1.71	12.11
960606	2	4.2	27.9	0.72	0.27	0.62	0.27	0.30	0.26	0.04	0.30	0.52	5.08	0.09	0.98	3.10	15.83
960627	2	4.2	31.0	0.81	0.27	0.59	0.29	0.32	0.28	0.04	0.65	0.67	7.14	0.00	0.88	4.14	17.40
960717	2	4.1	34.9	1.09	0.35	0.57	0.52	0.52	0.48	0.04	1.05	0.91	7.74	0.00	1.22	3.42	27.28
960809	2	4.3	28.0	0.98	0.36	0.65	1.03	0.59	0.59	0.00	2.48	1.94	7.29	0.00	1.45	3.80	25.36
960925	2	4.4	36.0	1.07	0.47	0.95	1.18	0.39	0.36	0.03	0.95	1.08	6.09	0.00	2.23	5.24	22.13
961018	2	4.6	27.3	0.94	0.40	0.72	0.84	0.41	0.35	0.06	0.72	0.79	6.02	0.00	1.34	5.78	19.81
960515	3	4.3	30.8	0.49	0.14	0.25	0.13	0.28	0.25	0.03	0.19	0.31	5.17	0.13	0.81	2.64	13.49
960606	3	4.1	32.5	0.77	0.23	0.59	0.29	0.34	0.31	0.04	0.26	0.49	6.29	0.13	1.25	4.92	19.50
960627	3	4.2	35.8	0.92	0.25	0.62	0.21	0.39	0.35	0.04	0.54	0.58	9.62	0.00	1.10	4.93	24.03
960717	3	4.1	37.1	0.82	0.21	0.51	0.19	0.46	0.46	0.00	0.54	0.73	9.24	0.00	1.48	4.45	27.36
960809	3	4.3	33.8	0.87	0.27	0.77	0.45	0.44	0.43	0.01	0.62	0.84	7.40	0.00	1.34	7.08	22.67
960925	3	4.0	62.4	1.20	0.35	0.67	0.19	0.50	0.43	0.07	0.52	0.52	8.88	0.00	1.51	5.63	24.66
961018	3	4.2	44.7	0.88	0.27	0.63	0.43	0.47	0.37	0.10	0.37	0.45	7.68	0.00	1.25	6.73	19.79
960515	8	4.2	37.9	0.31	0.10	0.14	0.32	0.32	0.27	0.04	0.66	0.41	6.49	0.09	1.21	2.41	18.23
960605	8	4.0	40.9	0.47	0.16	0.42	0.50	0.32	0.27	0.06	0.94	0.37	7.71	0.09	1.24	5.54	18.20
960627	8	4.1	44.8	0.60	0.20	0.53	0.50	0.35	0.29	0.06	1.34	0.35	10.21	0.00	1.11	6.71	19.96
960717	8	3.9	50.8	0.54	0.15	0.47	0.35	0.56	0.54	0.02	1.66	0.61	5.37	0.00	1.14	4.88	32.16
960809	8	4.2	40.1	0.56	0.23	0.87	0.78	0.33	0.30	0.03	1.31	0.24	4.90	0.22	1.68	10.31	12.77
960925	8	4.1	65.8	0.65	0.23	0.60	0.49	0.41	0.32	0.09	1.22	0.28	8.51	0.00	0.99	8.86	16.70
961018	8	4.0	57.7	0.58	0.21	0.50	0.50	0.46	0.33	0.13	1.06	0.27	8.02	0.00	0.91	8.22	19.55
960515	9	5.4	26.4	0.56	0.19	0.27	0.18	0.25	0.21	0.03	0.17	0.30	4.33	0.09	0.63	1.61	10.89
960605	9	4.2	20.9	0.66	0.24	0.61	0.35	0.25	0.23	0.03	0.25	0.62	4.88	0.13	0.85	2.48	12.63
960627	9	4.5	21.1	0.82	0.28	0.70	0.34	0.29	0.25	0.03	0.45	0.62	7.68	0.04	0.74	3.77	13.70
960717	9	4.2	25.2	0.90	0.26	0.50	0.12	0.37	0.35	0.02	0.54	0.73	9.73	0.00	0.83	3.02	19.31
960809	9	4.6	20.6	0.85	0.27	0.78	0.36	0.32	0.31	0.01	0.68	1.03	5.94	0.40	0.93	4.39	13.49
960925	9	4.4	36.9	1.17	0.43	0.87	0.45	0.31	0.25	0.06	0.40	0.48	6.14	0.00	0.94	5.03	14.85
961018	9	4.4	29.8	0.97	0.35	0.76	0.46	0.32	0.23	0.09	0.27	0.28	5.90	0.00	0.87	5.29	13.51

Table 2. Concentrations of major anions and cations in $\mu\text{eq/L}$ in 4 study streams in the Lye Brook Wilderness.

DATE (yymmdd)	Site	Ca $\mu\text{eq/L}$	Mg $\mu\text{eq/L}$	Na $\mu\text{eq/L}$	K $\mu\text{eq/L}$	T-Al $\mu\text{eq/L}$	NH4 $\mu\text{eq/L}$	SO4 $\mu\text{eq/L}$	NO3 $\mu\text{eq/L}$	Cl $\mu\text{eq/L}$	TOC $\mu\text{eq/L}$
960515	2	32.53	18.26	12.96	3.30	36.76	15.71	103.53	1.43	19.75	55.71
960606	2	35.78	22.54	26.84	6.88	33.47	28.56	105.82	1.43	27.65	72.82
960627	2	40.17	22.46	25.75	7.39	35.45	37.13	148.73	0.00	24.82	80.04
960717	2	54.39	28.54	24.75	13.22	57.82	50.69	161.22	0.00	34.42	125.49
960809	2	48.65	29.86	28.36	26.34	65.60	107.81	151.85	0.00	40.90	116.66
960925	2	53.39	38.66	41.37	30.17	43.36	59.97	126.85	0.00	62.91	101.80
961018	2	47.01	32.82	31.15	21.45	37.99	43.55	125.40	0.00	37.80	91.13
960515	3	24.40	11.76	10.79	3.27	31.41	17.14	107.69	2.14	22.85	62.05
960606	3	38.47	18.59	25.75	7.34	38.35	27.13	131.02	2.14	35.26	89.70
960627	3	45.86	20.89	27.06	5.42	43.64	32.13	200.38	0.00	31.03	10.54
960717	3	40.87	17.19	22.19	4.86	51.15	40.70	192.47	0.00	41.75	25.86
960809	3	43.61	21.80	33.58	11.58	48.92	46.41	154.14	0.00	37.80	04.28
960925	3	59.88	28.79	29.15	4.73	55.60	28.56	184.97	0.00	42.60	13.44
961018	3	44.11	22.21	27.19	11.02	52.26	24.99	159.97	0.00	35.26	91.03
960515	8	15.37	7.98	6.26	8.16	35.31	22.85	135.19	1.43	34.13	83.86
960605	8	23.65	13.08	18.44	12.79	35.94	20.71	160.60	1.43	34.98	83.72
960627	8	29.69	16.37	23.23	12.71	39.44	19.28	212.67	0.00	31.31	91.82
960717	8	26.70	12.42	20.62	9.03	62.27	33.56	111.86	0.00	32.16	47.94
960809	8	28.04	19.08	37.80	19.84	36.69	13.57	102.07	3.57	47.39	58.74
960925	8	32.24	19.17	26.14	12.61	45.59	15.71	177.26	0.00	27.93	76.82
961018	8	29.09	17.44	21.58	12.84	51.15	14.99	167.06	0.00	25.67	89.93
960515	9	27.99	15.38	11.66	4.53	22.72	16.42	90.19	1.43	17.77	50.09
960605	9	33.08	19.74	26.71	8.85	28.34	34.27	101.65	2.14	23.98	58.10
960627	9	41.02	23.12	30.32	8.67	31.84	34.27	159.97	0.71	20.88	63.02
960717	9	44.81	21.55	21.53	3.12	41.14	40.70	202.68	0.00	23.41	88.83
960809	9	42.42	22.46	33.97	9.21	29.65	57.12	123.73	6.43	26.24	62.05
960925	9	58.38	35.04	37.67	11.58	34.47	26.42	127.90	0.00	26.52	68.31
961018	9	48.35	29.04	33.06	11.79	35.58	15.71	122.90	0.00	24.54	62.15

Vermont



Lye Brook Wilderness

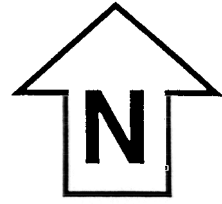
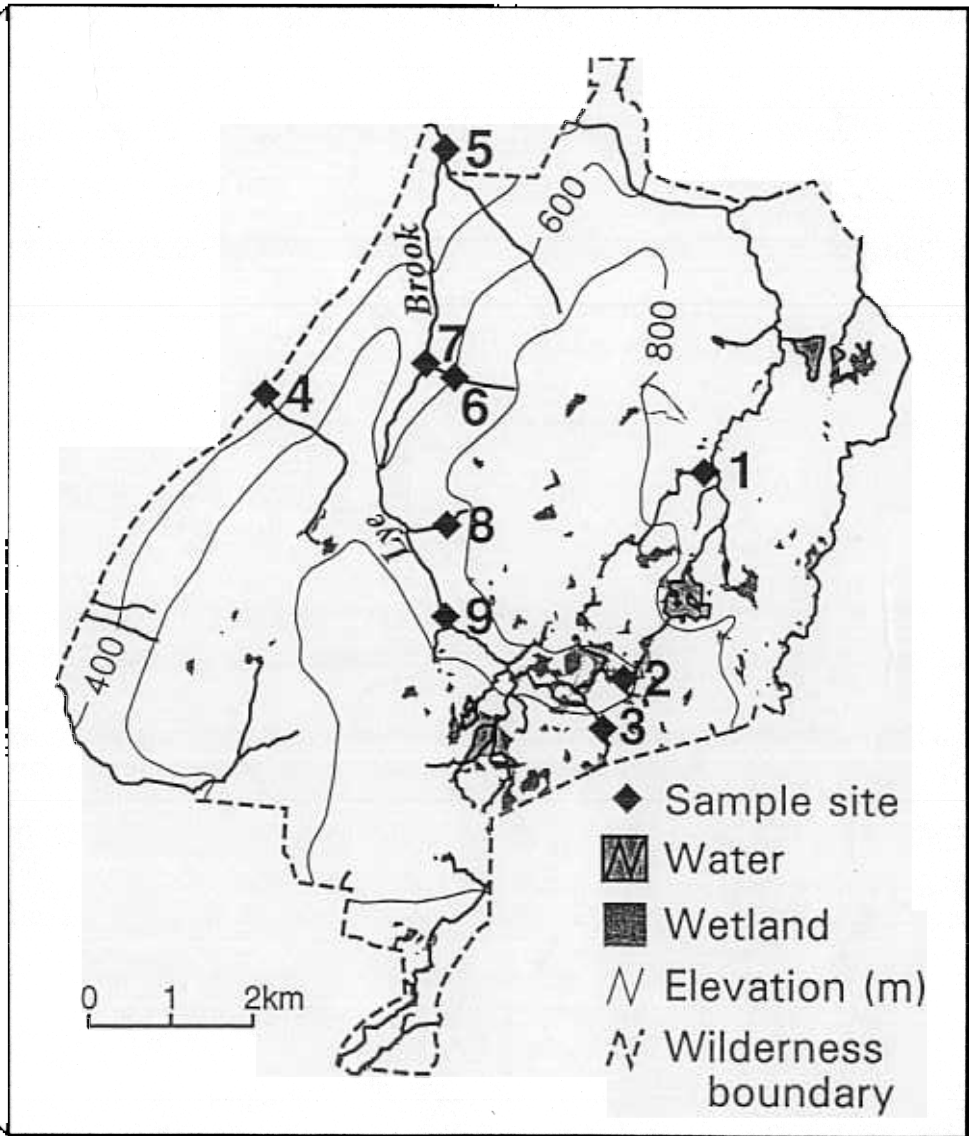


Figure 1. Study site and sample locations.