Aluminum Mobilization in an Acidic Headwater Stream: Temporal Variation and Mineral Dissolution Disequilibria

Abstract. *Intensive sampling was performed along an elevational gradient in a headwater stream during snowmelt and storm events to study the chemical response of the stream to acidic inputs. Aluminum is an important constituent because of its toxicity to some fish species. The results indicate that aluminum concentrations during this period were not in equilibrium with a readily formed mineral phase, as has been assumed, and that the increase in aluminum concentration due to episodic depressions in* pH *lessened during the snowmelt. It is hypothesized that this temporal variation is caused by the depletion of a slowly forming, labile pool of aluminum in the soil.*

Richard P. Hooper
Christine A. Shoemaker
Department of Environmental Engineering, Cornell University, Ithaca, New York 14853

Several mathematical models have been developed to estimate the impact of acid deposition on surface water chemistry. Three of the more process-oriented models (*1–3*) have included aluminum chemical species since aluminum is an important buffer in dilute acidic waters and since the elevated concentration of aluminum that accompanies decreases in the *p*H of stream water has been found to be toxic to important fish species (*4*). Reliable prediction of the timing and magnitude of aluminum mobilization is necessary for the assessment of biological impacts of acid precipitation because all life stages are not equally sensitive and sensitive life stages are present only at certain times of the year. All the models are based on the assumption that aluminum mobilization can be characterized as an equilibrium reaction between an aluminum trihydroxide ($Al(OH)_3$) mineral and free (aquo) aluminum (Al^{3+}) activity. The authors of one of these models (*2*) acknowledged the possibility of a kinetic constraint in very acidic soil horizons and included a first-order kinetic representation of the reaction as an option.

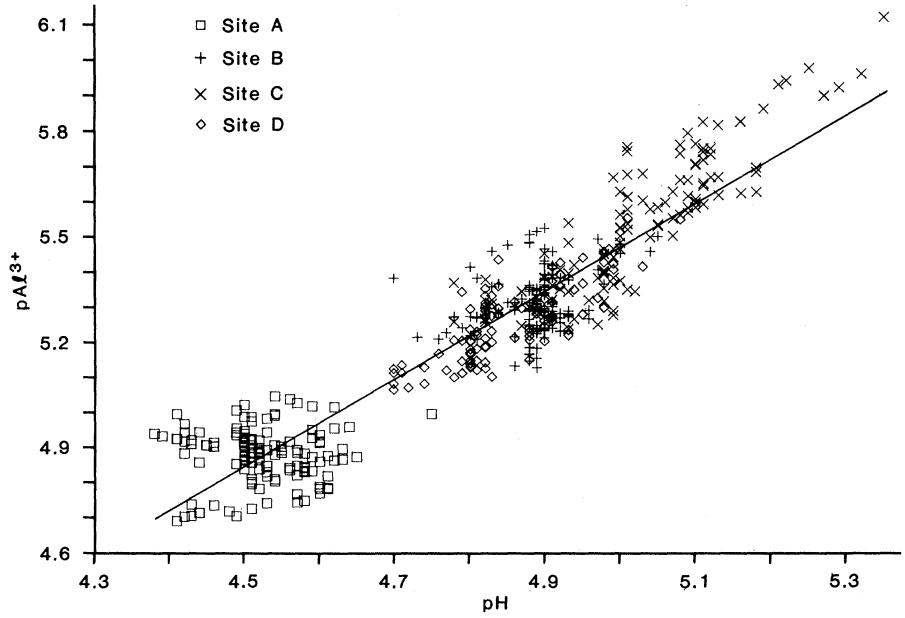
This equilibrium dissolution mechanism was supported by the findings of Johnson *et al.* (*5*) in an important early study of acid rain neutralization and aluminum chemistry in Falls Brook, a stream in the Hubbard Brook Experimental Forest, New Hampshire. Part of their effort was the collection of samples along an elevational gradient for the analysis of aluminum speciation. Four suites of samples were taken, three at nine sites in the spring and one at seven sites under drought conditions in the autumn. The results indicated that aquo aluminum activity varied stoichiometrically with *p*H (that is, three hydrogen ions were consumed for every aluminum ion released, for a slope of 3 on a graph of *p*Al versus *p*H). The calculated $Al(OH)_3$ solubility was similar to that reported for readily formed $Al(OH)_3$ minerals.

As part of an integrated field and modeling study, we undertook a more extensive sampling effort on an instrumented watershed at the Hubbard Brook Experimental Forest near Falls Brook to examine the chemical response of a stream to snowmelt and storm events during the spring of 1984. Our results indicate a much more complicated aluminum mobilization mechanism than that suggested by the Falls Brook results. There is evidence of both disequilibrium from mineral dissolution and temporal variation in the response of aluminum concentration to acidic events.

Four sampling sites were established on experimental watershed 3, which has an area of 42.4 ha (*6*). Site A, at the top of the watershed, was 10 m downstream of a small perennial seep. Site B was approximately halfway down the watershed, 366 m downstream from site A, immediately above the confluence of the first major tributary to the stream. Site C, 497 m downstream of site A, was located below the confluence of the major surface tributaries with the main stream. Site D was located immediately above a weir, 732 m downstream of site A. The stream width ranges from less than 100 cm at site A to over 2 m at site D.

A total of 484 samples of stream water were collected from late January to early May 1984. Sampling frequency was determined by the hydrologic status of the watershed. The most intense sampling was performed during the rising limb of the hydrograph and at peak flows, with the frequency of sampling decreasing on the falling limb. During the snowmelt, the maximum rate of sampling was one sample at each site every 3 hours; during storms, the peak rate was one sample per hour. Samples were taken on a weekly basis under conditions of low flow.

Stream water was sampled during three distinct periods: a midwinter thaw (13 February to 21 February), the spring thaw (20 March to 18 April), and an early spring period after the melting of the snowpack but before the leaves of the deciduous canopy trees had opened (20 April to 13 May), during which there were two storms (30 April to 1 May and 4 to 6 May). The hydrograph was dominated by a peak flow of 0.71 m^3/sec on 5 April 1984 after a rainstorm of more than 6 cm on a saturated snowpack; typical baseline flows for this watershed under



wet spring conditions are on the order of 0.015 m^3/sec.

The aluminum analysis was performed with methods developed by Driscoll (7). This technique yields a measure of labile, inorganic species of monomeric aluminum and has a precision of ±1 μmol/liter. The concentrations of inorganic monomeric aluminum ranged from 7 to 25 μmol/liter. Thermodynamic calculations were performed to determine the activity of aquo aluminum in equilibrium with competing complexes of hydroxide, fluoride, and sulfate ligands. Temperature and activity corrections were made; thermodynamic constants were the same as those used in the Falls Brook study (5).

The observed relation between *p*H and Al^{3+} activity for all samples collected is depicted in Fig. 1. The slope of the best-fit line to these data is 1.25 ± 0.04 (95 percent confidence level), significantly different from the stoichiometric ratio of 3 found in the Falls Brook study and required for equilibrium with an $Al(OH)_3$ mineral.

The disequilibrium index, defined by Paces (8) as the logarithm of the ratio of the mineral activity product to the equilibrium constant of a given mineral, was calculated for three $Al(OH)_3$ minerals (Table 1). Values greater than zero indicate oversaturation; less than zero, undersaturation; and zero, equilibrium with the mineral under consideration. Although the Falls Brook data are not significantly different from zero for any of these minerals, the watershed 3 data are different from zero for all the minerals. The watershed 3 and Falls Brook indices are significantly different ($P = 0.07$) (9).

Table 1. Mean disequilibrium index (±95 percent confidence interval).

Mineral	Watershed 3 (n = 484)	Falls Brook (n = 32)
Microcrystalline gibbsite	−0.157 ± 0.034	−0.69 ± 0.71
Natural gibbsite	0.423 ± 0.034	−0.11 ± 0.71
Synthetic gibbsite	1.183 ± 0.034	0.55 ± 0.71

Table 2. Statistics for best-fit line for pAl^{3+} versus *p*H, watershed 3.

Sampling period	Slope	95 percent confidence interval	R^2	n
		Site A		
Overall	0.05	±0.21	0.04	139
Midwinter	0.71	±0.15	0.76	32
Early melt	0.57	±0.27	0.29	46
Late melt	−0.08	±0.28	0.02	28
After melt	0.53	±0.34	0.24	33
		All sites		
Overall	1.25	±0.04	0.88	484
Midwinter	1.42	±0.03	0.96	107
Early melt	1.43	±0.03	0.96	135
Late melt	0.92	±0.04	0.87	102
After melt	1.17	±0.04	0.86	140

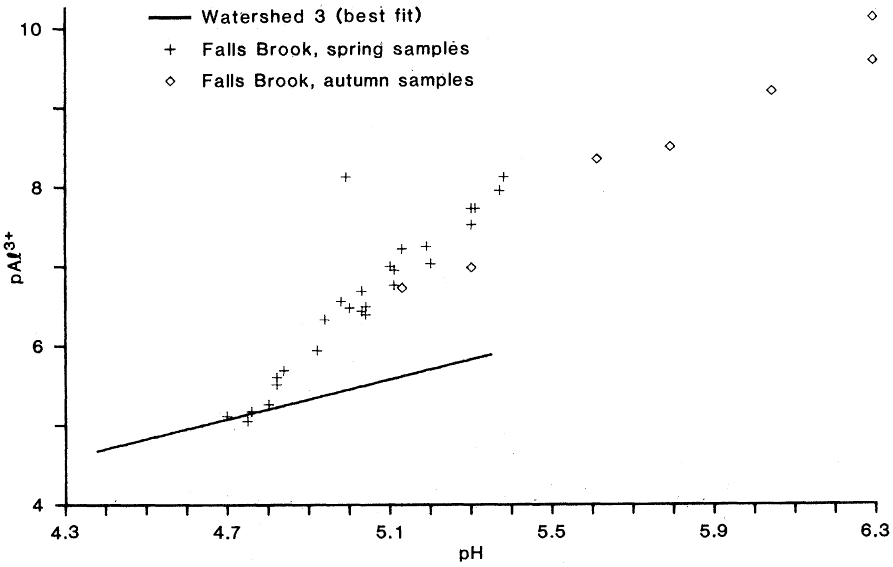


Fig. 2. Comparison of the Falls Brook and watershed 3 data.

This difference is surprising in light of the proximity of Falls Brook and watershed 3; they drain the same ridge and are approximately 3 km apart. In Fig. 2 the data for watershed 3 are compared with the results of the Falls Brook study (5). At the lowest *p*H recorded in the Falls Brook data, the aluminum concentrations found in the two streams agree. As the *p*H increases, the aluminum concentration in the Falls Brook samples decreases much more rapidly than that in the watershed 3 samples. For example, at a *p*H of 5.3, the concentration of Al^{3+} is 10 to 100 times higher in watershed 3 than in Falls Brook.

One explanation for the higher aluminum concentrations in our samples is a kinetic constraint in the precipitation of an aluminum mineral. Since our sampling effort focused on high-flow events, the higher aluminum concentrations at the higher *p*H's found downstream at sites C and D (watershed 3) could have been due to transport of aluminum that did not have time to precipitate out of solution. To examine this possibility, we separated our data into two subsets: those samples taken when the flow at the weir was less than 1 ft^3/sec (0.028 m^3/sec) and those taken at higher flows. This division, double typical base-flow conditions, was chosen because flows greater than 0.028 m^3/sec occur in watershed 3 only when forced by rainstorms or large melt events. If there is a kinetic limitation, the slope of the line should be greater (the concentration of aluminum falls more rapidly) under low-flow conditions. The results support this explanation: the slope for the samples taken under low-flow conditions is 1.41 ± 0.06, significantly different from the slope for the high-flow samples. Both values, however, are still quite different from the Falls Brook findings.

The data for site A (Fig. 1) show no significant slope, unlike the data for other sites. However, when the data are separated temporally into the early melt prior to the peak flow on 5 April, the late melt period from 5 April to the disappearance of the snowpack, and the period after the snowmelt (Table 2), the slope of the line for pH versus $p\mathrm{Al}^{3+}$ is significantly different from zero in all periods except late melt (*10*).

When the data for all sites are separated temporally in a similar manner (Table 2), there is a significant decrease in the slope during late melt, although the change is not so dramatic as when the site A data are considered alone. The Falls Brook data (Fig. 2) also exhibit a temporal variation in the pH versus $p\mathrm{Al}^{3+}$ relation. The slope of the best-fit line for the spring samples is 4.40 ± 0.76, and that for the autumn samples is 2.74 ± 0.59.

This temporal variation in the aluminum response to pH depressions also indicates a more complicated aluminum mobilization mechanism than a mineral dissolution equilibrium. One explanation for this phenomenon is that aluminum is slowly converted into a labile form from the weathering of primary minerals and is accumulated in the soil. The first major flush (the midwinter thaw, in this case) following an extended period of low flow would mobilize this more soluble form of aluminum. If this labile pool is leached out of the soil in the early stages of the melt by a large volume of water flowing through the watershed over a short period, there would be no elevation in aluminum above baseline levels during later acidic events. In watershed 3, especially at site A, the aluminum concentration did not increase as much in response to lower pH in the late melt period (following the large melt and rain event of 5 April) as it did in earlier events. The interval between the disappearance of the snowpack and the storms may have permitted the formation of labile aluminum, thereby accounting for the increase in the slope during the spring period. Laboratory studies of aluminum mobilization kinetics have found that exchangeable aluminum is depleted with increased leaching (*11*).

These findings are important to much of the ongoing acid rain research, especially that focusing on predictive mathematical models or biological effects. The observed disequilibrium between aluminum concentrations in stream water and a readily formed $\mathrm{Al(OH)_3}$ mineral phase reduce our confidence in predictions of short-term temporal changes in stream chemistry made by investigators using models based on an equilibrium.

Our findings also indicate that the temporal pattern of the snowmelt is important in the mobilization of aluminum. We observed the highest aluminum concentrations in the midwinter thaw, not during the main spring melt. Because sensitive life stages of fish species are present only at certain times of the year, such patterns are important in the assessment of the biological impacts of acid precipitation.

In a broader context, these results emphasize the importance of temporally intensive event sampling to identify the mechanisms controlling stream water chemistry and hence to establish the relationship between the acidity of precipitation and the resultant surface water chemistry.

References and Notes

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4. C. T. Driscoll *et al.*, *Nature (London)* **284**, 161 (1980).
5. N. M. Johnson, C. T. Driscoll, J. S. Eaton, G. E. Likens, W. H. McDowell, *Geochim. Cosmochim. Acta* **45**, 1421 (1981).
6. The Hubbard Brook Experimental Forest has been described extensively by G. E. Likens *et al.* [*Biogeochemistry of a Forested Ecosystem* (Springer-Verlag, New York, 1977)]. The area was subjected to heavy glaciation. Its bedrock is composed of granite and highly metamorphosed schist; this is overlain with glacial till of local origin. The soils are thin, well-drained spodosols (haplorthods). The vegetation, undisturbed for over 60 years, is northern hardwood forest, with some conifers along ridge crests.
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9. Because there are a large number of samples, the normal approximation, which assumes the population variance is known, can be used. In this way, the difference between the means can be tested independent of the variance, unlike the usual *t*-test for sample means, which assumes that the samples are drawn from populations with equal variances. The null hypothesis of equal means would also be rejected by the *t*-test.
10. A similar temporal variation is found when total monomeric aluminum concentration (which is measured directly) is plotted against pH. This finding is not dependent on the assumption of equilibrium conditions among the solution complexes of aluminum.
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12. We thank H. G. Rosenthal and T. Rourke for their assistance in sampling and chemical analyses; G. Likens and C. Driscoll for the direction they provided, particularly during the initial phases of the study, and for their review of the manuscript; W. Martin and D. Buso for valuable support and guidance during fieldwork and for critiquing the manuscript; J. Hornbeck for the digitized and edited weir data; and K. Bencala, J. Bisogni, F. H. Bormann, W. Bowden, C. Hall, N. Johnson, L. Lion, R. Pierce, S. Riha, and C. Schofield for their thoughtful reviews of the manuscript. Funded as part of the National Acid Precipitation Assessment Program by the Environmental Protection Agency/North Carolina State University Acid Precipitation Program and by funds from the Andrew W. Mellon Foundation awarded to G. Likens. This is a contribution to the Hubbard Brook Ecosystem Study. The Hubbard Brook Experimental Forest is operated by the U.S. Forest Service, Broomall, Pa.

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Smoke Production from Multiple Nuclear Explosions in Nonurban Areas

Abstract. *The amount of smoke that may be produced by wildland or rural fires as a consequence of a large-scale nuclear exchange is estimated. The calculation is based on a compilation of rural military facilities, identified from a wide variety of unclassified sources, together with data on their geographic positions, surrounding vegetation (fuel), and weather conditions. The ignition area (corrected for fuel moisture) and the amount of fire spread are used to calculate the smoke production. The results show a substantially lower estimated smoke production (from wildland fires) than in earlier "nuclear winter" studies. The amount varies seasonally and at its peak is less by an order of magnitude than the estimated threshold level necessary for a major attenuation of solar radiation.*

R. D. Small, B. W. Bush
Pacific-Sierra Research Corporation,
Los Angeles, California 90025

Several estimates in scientific journals (*1–3*) have attributed approximately half the global smoke production resulting from a general nuclear exchange to wildland fires; a National Academy of Sciences (NAS) study (*4*) estimated a smaller fraction from wildland fires. The estimates of the smoke fraction due to nonurban fires are scenario-dependent and vary from nil for city-only exchanges to 100 percent for city-avoidance attacks. In general, the baseline scenarios of these earlier studies have projected a wildland smoke production of roughly 10^{14} g—an amount sufficient to initiate a prolonged and possibly catastrophic cooling of the earth's surface.

Although many facets of these estimates warrant attention, we focus here on the source function—the nonurban area burned and the amount of smoke produced. We do not consider the mechanics of smoke injection, the scavenging of smoke particles, the transport and distribution of smoke, the composition and optics of the particulate cloud, or the earth energy balance. Our calculation of the global smoke production suggests a much smaller atmospheric loading than that estimated previously.