

Spatial relationships of aluminum chemistry in the streams of the Hubbard Brook Experimental Forest, New Hampshire

G. B. LAWRENCE, R. D. FULLER and C. T. DRISCOLL

Department of Civil Engineering, Hinds Hall, Syracuse University, Syracuse, New York 13210, U.S.A.

Key words: acidic deposition, aluminum, soil catena and stream chemistry

Abstract. Aluminum chemistry was evaluated in two headwater streams in the White Mountains of New Hampshire. Observed elevational trends in stream aluminum chemistry may be related to spatial variations of vegetation type and mineral soil depth within the watersheds. At the highest elevations maximum densities of spruce and fir vegetation occur and aluminum appears to be mobilized predominantly by transformations involving dissolved organic matter. At the mid-elevations hardwood vegetation predominates and the mechanism of aluminum mobilization shifts to dissolution by strong acids within the mineral soil. At the lowest elevations, relatively thick mineral soil seems to limit aluminum mobility, resulting in low concentrations in streamwater. Comparison of these results with an earlier study of an adjacent watershed, indicates that subtle differences in watershed characteristics such as tree species distribution and topography may cause significant variations in stream aluminum chemistry. Control of aluminum mobility by imogolite minerals was not indicated by the stream chemistry of these watersheds. To determine the relationship between acidic deposition and aluminum mobility, natural variations which occur in the aluminum cycle must be addressed.

Introduction

Concern over the impact of acidic deposition has recently focused attention on aluminum in the environment. High concentrations of aqueous aluminum in headwater systems have been related to atmospheric inputs of strong acids by numerous investigators (Dickson 1978, Cronan and Schofield 1979, Johnson 1979). However, studies have shown the aluminum cycle to be extremely complex, involving a number of biogeochemical and hydrologic processes which are not fully understood (Johnson et al. 1969, David and Driscoll 1984, Driscoll et al. 1985, Hooper and Shoemaker 1985).

Regions which are regarded as sensitive to strong acid inputs generally have soils undergoing the process of podzolization. The traditional concept of podzolization is based on the mobilization and transport of soil aluminum (and iron) through organic complexation. Naturally occurring organic compounds, originating from the forest floor or canopy drip, mobilize aluminum in the E horizon. Once in solution, organic aluminum complexes are transported deeper into the soil profile until oxidation of organic matter, increased availability of metals for complexation and/or increase in pH and

ionic strength result in precipitation of the aluminum (De Conink 1980, Ugolini et al. 1977).

Elevated concentrations of aluminum in surface waters have been attributed to changes in the podzolization process due to atmospheric deposition of strong acids (Cronan and Schofield 1979). Inputs of sulfuric acid are believed to facilitate the mobilization of aluminum from the lower B horizon to soil solution and surface waters. Johnson et al. (1981) expanded this hypothesis by suggesting that strong acids in precipitation were initially neutralized by the dissolution of alumina, creating a solution containing both aluminum and H^+ acidity. This secondary acidity was then neutralized by the dissolution of silicate minerals if the soil residence time of water was long enough to allow for mineral weathering.

Recent work has also expanded our understanding of the role of naturally occurring organic compounds in the aluminum cycle. In a study of an Adirondack Mountain Spodosol, David and Driscoll (1984) found that over 50% of aluminum in soil solution collected below the B horizon was associated with organic matter. They also observed substantial concentrations of aluminum in leachates draining the organic horizons of this soil. In fact, most aluminum appeared to be released to solution directly from the forest floor. This finding differs with the traditional concept of podzolization, which considers aluminum movement to be restricted to the mineral soil. Driscoll et al. (1985) also found that aluminum was predominantly bound to organic matter in soil solutions of both organic and mineral horizons, at three elevations in a Spodosol, at the Hubbard Brook Experimental Forest in the White Mountains of New Hampshire (HBEF).

These observations complicate previous concepts of soil development in Spodosols. Significant concentrations of aluminum in the forest floor suggest that aluminum is being assimilated from the mineral soil by vegetation since the forest floor is formed primarily by litter fall and root turnover. Organically bound aluminum in soil solutions draining the B horizons may also indicate that aluminum chemistry is biologically influenced below the zone of major root activity. Biocycling of aluminum in natural soils has been documented (Messenger 1975, Messenger et al. 1978), but its role in the chemistry and transport of aluminum in soils has not been assessed.

Past and current research on aluminum transport in podzolic soils has strongly emphasized the importance of organic complexation, however, an alternative hypothesis has recently been presented. Farmer et al. (1980) have proposed that aluminum moves through soils as a positively charged, hydroxy-aluminum silicate sol, termed proto-imogolite, rather than an organic complex. Proto-imogolite is thought to form in the upper mineral soil and remain in suspension until reaching the B horizon, where it is deposited as imogolite or proto-imogolite allophane. These workers argue that organic aluminum substances are formed within the B horizon by the sorption of organic matter to previously precipitated proto-imogolite. This

hypothesis presents a major challenge to the current understanding of podzolization processes and warrants further investigation.

In an effort to better understand the processes which control aluminum cycling, our study was conducted using the small watershed approach (Likens et al. 1977). This approach requires watertight bedrock and well defined watershed boundaries to insure that stream chemistry is strictly a function of meteoric inputs and biogeochemical processes operating upstream of a given location. Using this approach, stream chemistry, vegetation type and mineral soil depth were investigated in two adjacent watersheds to:

1. determine the pattern of spatial variability in streamwater aluminum chemistry at the HBEF,
2. establish factors which are related to these variations and
3. evaluate mechanisms which may control streamwater aluminum chemistry.

Experimental methods

Study site

This study was conducted from June 1982 through May 1983, in watersheds 5 (W5; area = 22.5 ha) and 6 (W6; area = 13.1 ha) at the HBEF, (43° 56'N, 71° 45'W). W5 and W6 are located adjacent to each other on steep slopes (20–30%) with a southerly aspect. Elevations range from 490 m to 775 m in W5, and 540 m to 800 m in W6. Soils in W5 and W6 are classified as Spodosols, comprised primarily of Haplorthods.

W5 and W6 are completely forested, predominantly with northern hardwood species (yellow birch, American beech and sugar maple; *Betula alleghaniensis*, *Fagus grandifolia* and *Acer saccharum*, respectively) at mid and lower elevations and small stands of balsam fir (*Abies balsamea*) and red spruce (*Picea rubens*) at upper elevations. A summary of spruce and fir distribution for both watersheds is given in Figure 1. These watersheds were logged in 1910–1919, but have not been disturbed since. Additional information on the watershed characteristics and instrumentation are available elsewhere (Likens et al. 1977, Bormann and Likens 1979).

Experimental design and procedures:

The streams in W5 and W6 were sampled at monthly intervals during the study period. All sites were sampled twelve times during the study with the exception of site one in watershed 6 (Figure 1), which was sampled nine times due to occasional dry periods. The data presented represent the mean observations from these sampling dates. This includes pH which was converted to H⁺ concentration before averaging.

Considerable seasonal variation, closely related to discharge, occurred in the stream chemistry of these watersheds, however, the elevational trends remained very consistent over time. Since this paper focuses on spatial rather

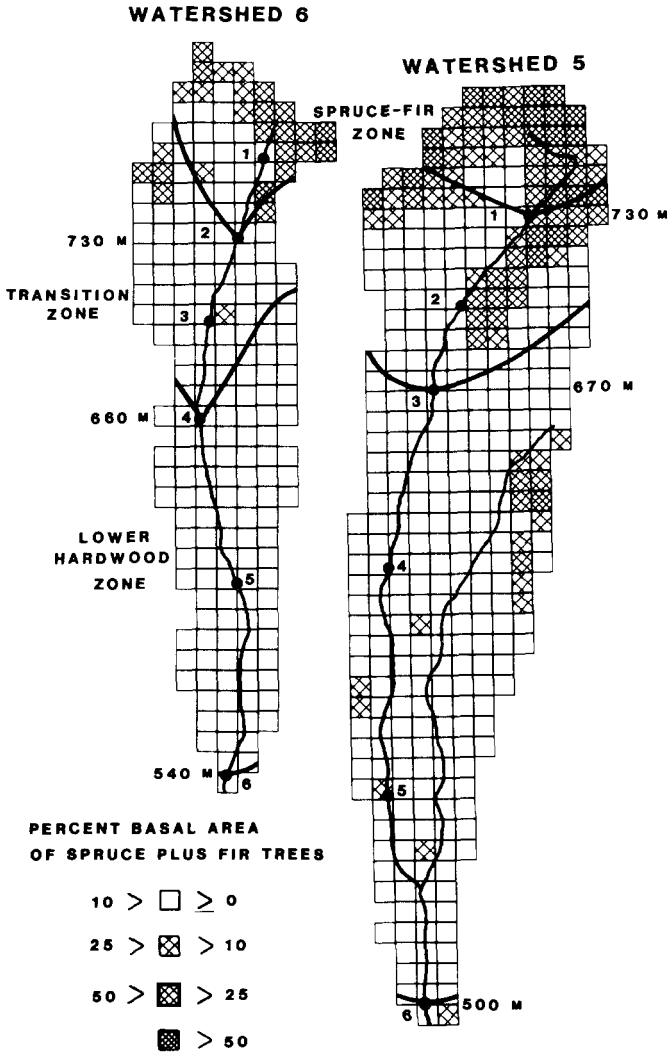


Figure 1. Streamwater sampling locations (circles), distribution of spruce and fir trees (cross hatching) and watershed divisions (thick lines) based on characteristic vegetation, stream sampling locations and drainage patterns in watersheds 5 and 6. Each square represents a 625 m² plot. Weirs at the bottom of each watershed are indicated by triangles.

than temporal relationships, mean concentrations were not weighted by discharge. Statistical significance of elevational trends was determined by one way analysis of variance. Note that seasonal variation was used as the error estimate for this analysis.

Sampling sites were located along an elevational gradient from a weir,

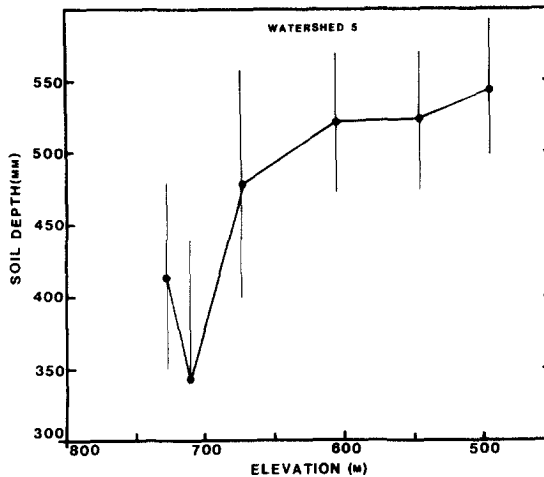


Figure 2. The elevational gradient of mean mineral soil depth (mm; not including the C horizon) in watershed 5. Watershed 5 was divided into the areas drained by each stream sampling location excluding the areas drained by upstream sites. Each point represents the mean depth of soil pits excavated within each area and is plotted vs. elevation of the corresponding stream sampling site. Standard errors are indicated by vertical bars.

installed at the base of each watershed, up to an elevation where the streams became intermittent (Figure 1). Spacing between sites was determined by estimates of the magnitude of changes in water chemistry occurring over the reaches. These estimates were based on a previous study in an adjacent watershed (Johnson et al. 1981).

To assess mineral soil depth W5 was divided into the areas drained by each stream sampling site, excluding areas drained by upstream sites (Figure 2). Mineral soil depth was estimated by averaging the depth of soil pits excavated within each area. A total of 60 pits was used for these estimates.

Water samples were collected and stored in 500 ml polyethylene bottles at 4°C. Aliquots were measured for pH, amputated for the analysis of dissolved organic carbon (DOC) and extracted for the analysis of monomeric aluminum, shortly after collection. Each sample was analyzed for all major solutes, including three forms of aluminum (total aluminum, total monomeric aluminum and non-labile monomeric aluminum), using analytical methods described in Table 1.

Total aluminum includes all colloidal and dissolved forms of aluminum. Total monomeric aluminum, estimated by complexation with 8-hydroxyquinoline followed by rapid extraction into methyl isobutyl ketone (MIBK) includes non-labile and labile monomeric forms (Barnes 1975, Driscoll 1984). The difference between total aluminum and total monomeric aluminum represents the less reactive colloidal and organically occluded species and is termed acid soluble aluminum. Non-labile monomeric aluminum estimates organically complexed monomeric aluminum species (Driscoll

Table 1. Procedures used in the analysis of streamwater samples from the HBEF. Precision represents combined analytical and sampling error of triplicate samples taken on each sampling date, expressed as average coefficients of variation

Parameter	Method	Precision	Reference
SO ₄ ²⁻	Ion chromatography (IC).	2.08	Tabatabai and Dick, 1983
NO ₃ ⁻	IC.	12.10	ibid
Cl ⁻	IC.	7.90	ibid
pH	Potentiometrically; glass electrode.	0.20	
Ca ²⁺	Atomic absorption spectrophotometry (AAS).	3.73	Slavin, 1978
Mg ²⁺	AAS.	2.50	ibid
Na ⁺	AAS.	2.60	ibid
K ⁺	AAS	3.24	ibid
Dissolved Organic Carbon (DOC)	Filtration, ampulation, persulfate oxidation, syringe stripping of CO ₂ and detection by gas chromatography.	5.81	Menzel and Vaccaro, 1964
Dissolved Si	Heteropoly blue complex colorimetry; autoanalyzer.	1.61	Std. Methods 1981
Total F	Potentiometrically with ion selective electrode after TISAB addition.	3.68	Orion, 1976
Free F	Same as total F without addition of TISAB.	7.33	ibid
Total Al	AAS; graphite furnace.	2.81	Slavin, 1968
Monomeric Al	Field extraction in MIBK, analysis by AAS; graphite furnace.	3.39	Barnes, 1975 Driscoll, 1984
Non-labile monomeric Al	Fractionation by ion exchange, analysis for monomeric Al.	7.42	Driscoll, 1984

1984). The difference between total monomeric aluminum and non-labile monomeric aluminum, termed labile monomeric aluminum, includes aquo aluminum (Al³⁺) as well as fluoride, sulfate and hydroxide complexes of monomeric aluminum. The limitations of this operational procedure are discussed in detail elsewhere (Driscoll 1984).

Chemical speciation of labile monomeric aluminum was calculated using an iterative computer program that accounts for the effect of ionic strength, temperature, pH, and the concentrations of labile monomeric aluminum, total fluoride, sulfate and dissolved silica. Thermochemical data used for this program were obtained from Johnson et al. (1981). Activity corrections were

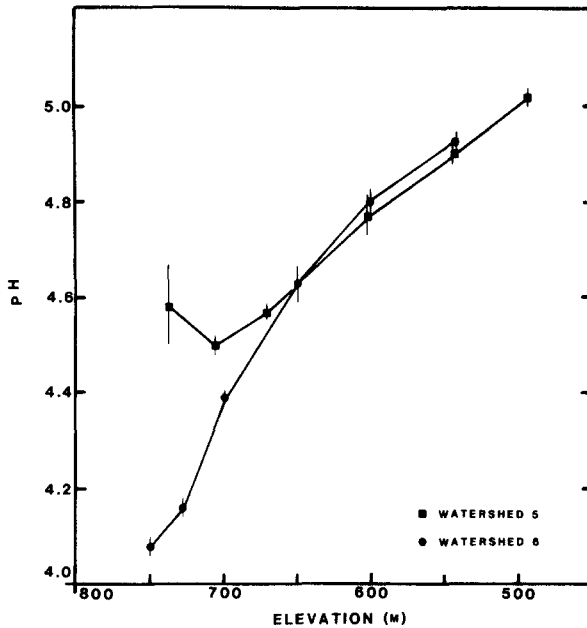


Figure 3. Annual mean pH along elevational gradients in the streams of watersheds 5 and 6. Standard errors are indicated by vertical bars.

made with the Debye-Huckel equation (Stumm and Morgan 1981). The proximity of HBEF solutions to the theoretical solubility of aluminum minerals was quantified by calculating mineral saturation indices (SI).

$$SI = \log \frac{Q_p}{K_p} \quad \text{Where } Q_p \text{ is the ion activity product,} \\ K_p \text{ is the equilibrium constant and} \\ SI \text{ is the saturation index.}$$

An SI value near zero suggests equilibrium with the mineral phase of interest, while an SI value greater than zero indicates oversaturation and less than zero, undersaturation. A basic assumption inherent in these calculations is that the activity of solutes did not change during the period from sampling to analysis.

Results

Mineral soil depth (not including the C horizon) of the subwatersheds in W5 generally increased with decreasing elevation (Figure 2), although this trend was not statistically significant ($p > 0.05$) due to the large amount of variation. A previous study (Bormann et al. 1980) in W6 showed that the depth of till (solum plus parent material) also increased moving downslope. Tree species were distributed similarly in both watersheds (Figure 1), with

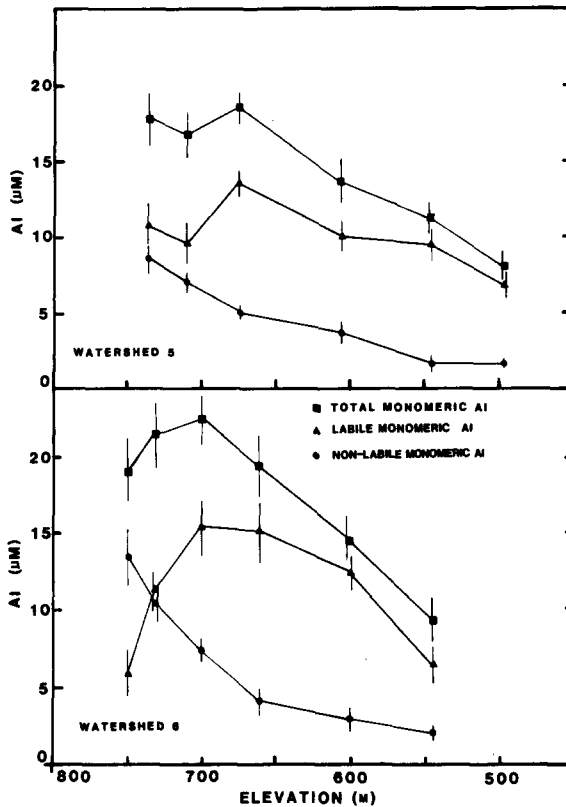


Figure 4. Annual mean concentrations of total monomeric aluminum, labile monomeric aluminum (an estimate of inorganic forms) and non-labile monomeric aluminum (an estimate of organic forms) along elevational gradients in streams of watersheds 5 and 6. Standard errors are indicated by vertical bars.

balsam fir and red spruce most prominent at the highest elevations and yellow birch, beech and sugar maple dominant at mid and low elevations.

As with soil and vegetation, stream chemistry in W5 and W6 showed pronounced spatial variation. In both watersheds, pH consistently increased (Figure 3; $p < 0.01$), while total aluminum (Figure 5; $p < 0.01$) total monomeric aluminum (Figure 4; $p < 0.01$) and acid soluble aluminum decreased (Figure 5) with decreasing elevation. A shift in aluminum speciation also occurred, with non-labile monomeric aluminum comprising over half of total monomeric aluminum at the highest sites, but decreasing to approximately one third at the lowest sites in each watershed (Figure 4). Sulfate was the dominant anion at all sites in both watersheds with highest concentrations at the uppermost sites (65 and $70 \mu\text{M}$, respectively, in W5 and W6) and a decreasing trend to minimum concentrations at the lowest sites (57 and $59 \mu\text{M}$, respectively, in W5 and W6). DOC concentrations also decreased with decreasing elevation (Figure 6; $p < 0.01$) and were positively correlated (Table 2) with non-labile monomeric aluminum.

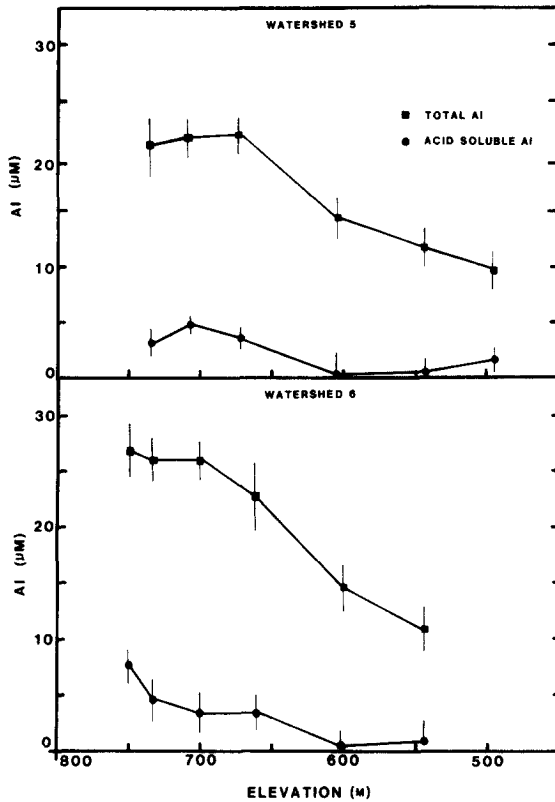


Figure 5. Annual mean concentrations of total aluminum and acid soluble aluminum (the difference between total aluminum and total monomeric aluminum) along elevational gradients in the streams of watersheds 5 and 6. Standard errors are indicated by vertical bars.

In addition to these trends, the ratio of DOC to total aluminum concentrations decreased to the mid-elevation sites, then increased slightly at the lowest sites (Figure 7). This pattern reflects the pronounced decline of DOC concentrations, coupled with a more moderate decline of total aluminum at upper elevations. Throughout the lower elevations (< 600 m) DOC concentrations remained fairly constant (Figure 6), while total aluminum concentrations continued to decrease (Figure 5), causing the slight upward shift in the ratio.

To investigate other factors which may be related to stream aluminum concentrations, SI values for eight mineral phases (natural gibbsite, microcrystalline gibbsite, synthetic gibbsite, amorphous aluminum tri-hydroxide, kaolinite, halloysite, jurbanite, and alunite) were calculated. As reported in the study of Johnson et al. (1981), stream water at the HBEF was closest to saturation with respect to the solubility of natural gibbsite (Figure 8).

Table 2. Empirical equations describing the concentrations of non-labile monomeric aluminum (ORGAL) as a function of dissolved organic carbon (DOC), in watersheds 5 and 6. ORGAL and DOC are expressed in mol/l.

Equation	n	r ²	p	S. E.	
				slope	intercept
Watershed 5 ORGAL = $0.0115 (\text{DOC}) + 9.05 \times 10^{-7}$	84	0.722	< 0.0001	7.84×10^{-4}	3.60×10^{-7}
Watershed 6 ORGAL = $0.0109 (\text{DOC}) + 1.57 \times 10^{-6}$	72	0.818	< 0.0001	6.12×10^{-4}	4.32×10^{-7}
Combined Watersheds ORGAL = $0.0111 (\text{DOC}) + 1.24 \times 10^{-6}$	156	0.796	< 0.0001	4.52×10^{-4}	1.24×10^{-7}

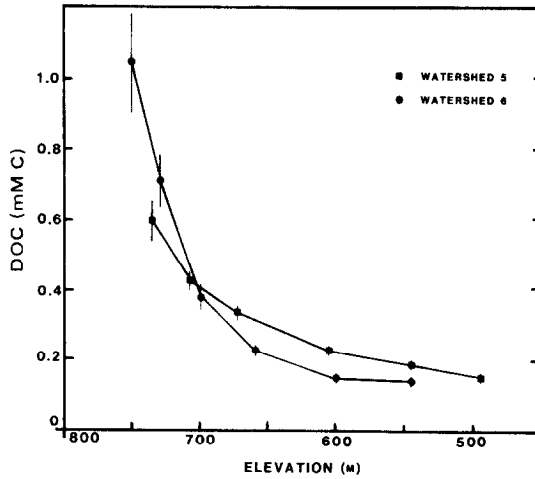


Figure 6. Annual mean DOC (dissolved organic carbon) concentrations along an elevational gradient in the streams of watersheds 5 and 6. Standard errors are indicated by vertical bars.

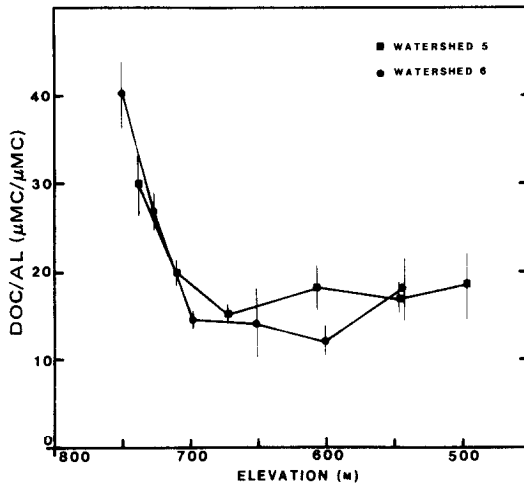


Figure 7. Elevational trends in the annual mean ratio of dissolved organic carbon (DOC) concentrations to total aluminum concentrations in the streams of watersheds 5 and 6. Standard errors are indicated by vertical bars.

However, at higher elevations solutions were undersaturated with respect to the solubility of natural gibbsite and SI increased with increasing drainage area (Figure 8). It should be noted that the highest labile monomeric aluminum concentrations occurred at the elevations where the SI approximated zero.

Shifts in the speciation of labile monomeric aluminum also occurred in

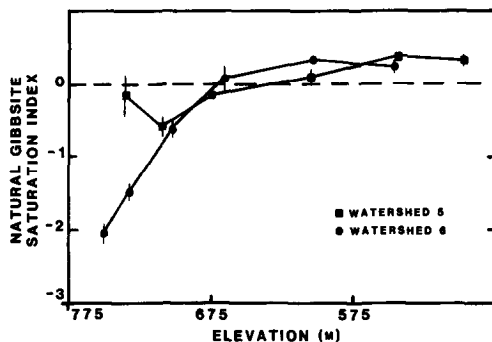


Figure 8. Elevational trends in annual mean saturation index with respect to the solubility of natural gibbsite in the streams of watersheds 5 and 6. Standard errors are indicated by vertical bars.

each watershed (Figure 9). Al^{3+} was the predominant inorganic form at all elevations, reaching maximum concentrations at mid-elevations followed by decreasing concentrations downslope. $AlOH^{2+}$ concentrations also reached a maximum at mid-elevation sites (although downslope of the Al^{3+} peak in W6), where $Al(OH)_2^+$ concentrations were greatest in the lower reaches of both watersheds. These trends are related to the pH gradient exhibited by the streams (Figure 3).

Fluoride bound aluminum concentrations increased moving downslope (Figure 9) corresponding to the trend of total fluoride concentrations (Figure 10; $p < 0.01$). Moving downslope free fluoride concentrations also increased to maximum concentrations at the lowest sites (Figure 10; $p > 0.05$ in W5; $p < 0.01$ in W6). Basic cation concentrations (the equivalent sum of calcium, magnesium, potassium and sodium) initially decreased to a minimum at the mid-elevations then increased with increasing drainage area (Figure 11). Basic cation concentrations showed a significant overall increasing trend moving downslope in W6 (Figure 11; $p < 0.01$).

Discussion

Results of this investigation indicate that consistent elevational trends in stream chemistry occur in W5 and W6. Tree species composition and soil depth also exhibit distinctive spatial variation which may influence the trends in stream chemistry. For the purpose of discussion, W5 and W6 were divided into 3 elevational zones (Figure 1), based on drainage area and characteristic vegetation: spruce-fir, upper elevation hardwood and lower elevation hardwood.

Spruce-Fir Zone:

The maximum density of coniferous tree species occurs at the highest elevations of both watersheds (Figure 1; above 730 m in both watersheds),

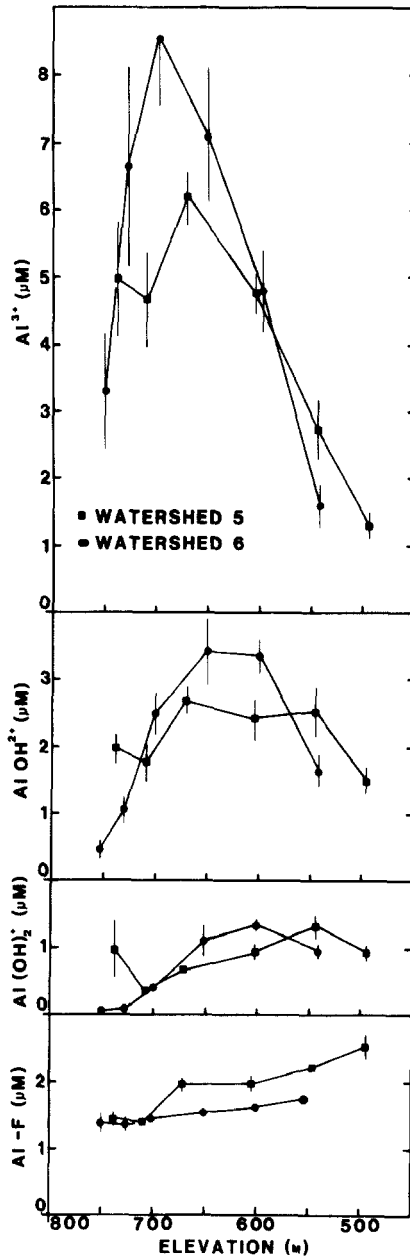


Figure 9. Annual mean concentrations of aquo aluminum (Al^{3+}), two forms of aluminum hydroxide complexes ($AlOH^{2+}$ and $Al(OH)_2^+$) and the sum of aluminum fluoride complexes ($Al-F$) along elevational gradients in the streams of watersheds 5 and 6. Standard errors are indicated by vertical bars.

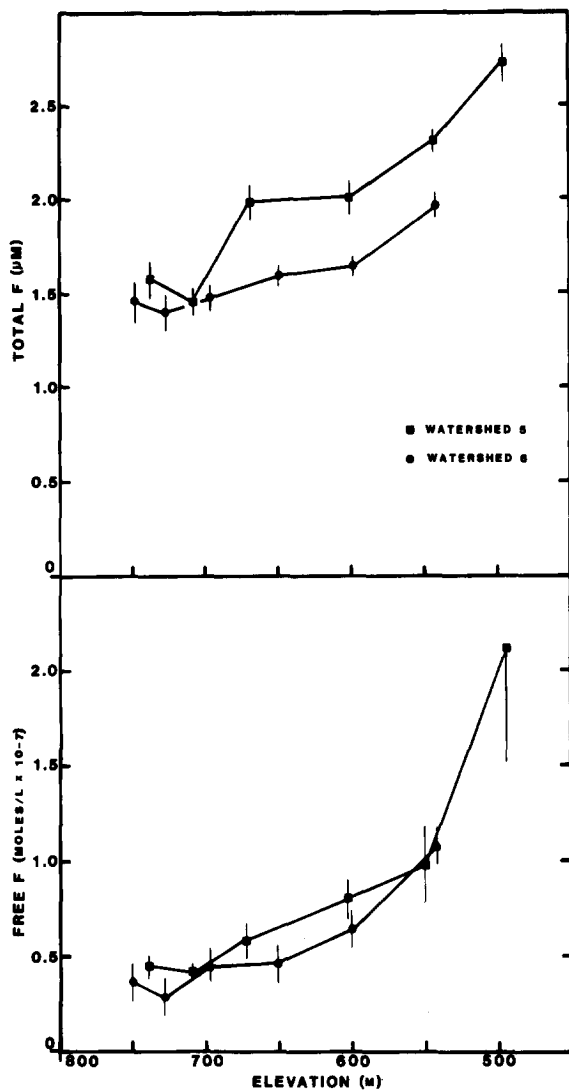


Figure 10. Annual mean concentrations of free (uncomplexed) fluoride (Free F) and total fluoride (Total F) along elevational gradients in the streams of watersheds 5 and 6. Standard errors are indicated by vertical bars.

the zone in which stream aluminum was largely in a non-labile monomeric or acid soluble form and DOC concentrations were highest. The acidic conditions observed in this zone were related to high concentrations of sulfate and organic anions relative to concentrations of basic cations. To maintain electroneutrality, acidic cation equivalence (H^+ and aluminum) was, therefore, elevated.

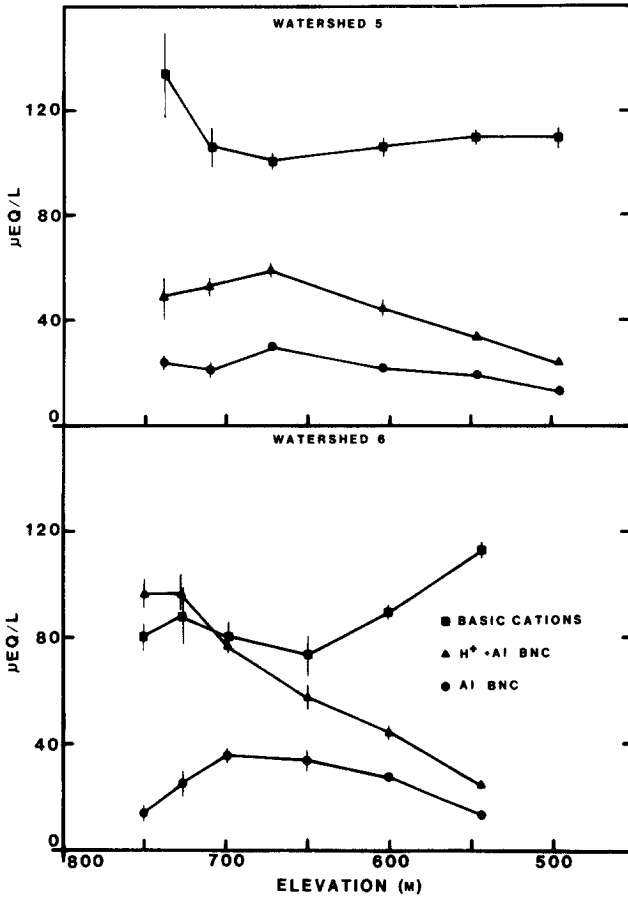


Figure 11. Annual means of the sum of basic cation equivalence (calcium, magnesium, sodium and potassium), aluminum base neutralizing capacity (Al BNC) and H^+ plus aluminum base neutralizing capacity (H^+ + Al BNC) along an elevational gradient in the streams of watersheds 5 and 6. Base neutralizing capacity is defined as the equivalent sum of all acids that can be titrated by strong base to pH 8.3. Standard errors are indicated by vertical bars.

The relationships of DOC to both total aluminum (Figure 7) and aluminum speciation (Figure 4) suggest that transformations regulating DOC influence aluminum concentrations within the spruce-fir zone. The apparent control of streamwater aluminum concentrations by processes regulating DOC in this zone may be linked to coniferous vegetation and shallow soils. Soils beneath coniferous stands have been shown to have higher concentrations of aluminum in the forest floor than soils beneath hardwood stands, presumably due to increased assimilation of aluminum from mineral soil by coniferous species (Messenger 1975). In addition, David and Driscoll (1984) observed higher concentrations of aluminum in leachates collected below O and E horizons of soil beneath a conifer site, than leachates of O and

E horizons of a hardwood site. In both horizons, solution aluminum was predominantly associated with organic matter, either as acid soluble or non-labile monomeric aluminum. An increased flux of organically bound aluminum in the upper solum of the spruce-fir zone in conjunction with shallow soils may result in the higher organic aluminum concentrations observed in the streams of this zone. This relationship depends, however, on aluminum immobilization processes within the lower solum and the flow-path soil solution takes to the stream channel.

Transition zone

The transition zone lies immediately downslope of the spruce-fir zone (Figure 1; between 730m and 670m in W5; 730m and 660m in W6) and is dominated by beech, yellow birch and sugar maple, although significant densities of spruce and fir vegetation occur. In this zone non-labile monomeric aluminum and DOC concentrations decreased with increasing drainage area, however, total monomeric aluminum concentrations remained high (Figure 4) due to an increase of labile monomeric aluminum. Stream pH increased somewhat from the spruce-fir zone (Figure 3) due to a decrease in the concentrations of sulfate and DOC.

In this zone trends in non-labile monomeric aluminum, DOC and mineral saturation indices suggest that control of streamwater aluminum has shifted from processes regulating DOC to control predominantly by mineral solubility. Dissolution of inorganic, solid phase aluminum was likely to be responsible for the relatively high concentrations of streamwater Al^{3+} in the transition zone. This form of aluminum exceeded the concentrations of all other aluminum species due to low concentrations of complexing ligands (DOC, fluoride and hydroxide). Concentrations of hydroxide and fluoride complexed aluminum did, however, increase relative to concentrations in the spruce-fir zone.

The higher concentrations of total monomeric aluminum with a shift in speciation again suggest the influence of vegetation and soil processes on the chemistry and transport of aluminum. Lower DOC concentrations in the stream solutions of W5 and W6 may be related to differences in the quality and quantity of organic acids derived from microbial processing of hardwood and coniferous litter. Sugar maple and beech, species of major importance in this zone, produce litter which is more rapidly decomposed than spruce and fir (Gosz et al., 1973). Furthermore, David and Driscoll (1984) observed that concentrations of DOC in forest floor leachates under hardwood vegetation were 40% less than in leachates from the forest floor under coniferous vegetation in the Adirondack Mountains of New York. Similar results were also shown in the Adirondack Mountains by Cronan and Aiken (1985). More rapid decomposition would potentially limit the mobility of DOC and associated aluminum, resulting in lower stream concentrations. It is also likely that the greater depth of mineral soil in this zone limits DOC

transport due to more opportunity for adsorption on free aluminum and iron surfaces (McDowell and Wood 1984, Fuller et al. 1985).

Lower elevation hardwood zone

The lower elevation hardwood zone comprises the lowest third of the watersheds (Figure 1; between 670 m and 500 m W5; 660 m and 540 m in W6) where yellow birch, beech and maple trees still dominate with little occurrence of spruce-fir vegetation. Average mineral soil depth reaches a maximum in this zone (Figure 2). Stream solutions in this zone differed markedly from both the spruce-fir and transition zones. Conditions of increased pH and decreased DOC concentrations, relative to the spruce-fir and transition zone, were primarily responsible for lower aluminum concentrations in the streams of the lower hardwood zone. The deeper soils in this zone may provide greater opportunity for the neutralization of H^+ and aluminum acidity through mineral weathering and exchange reactions as evidenced by the increase in basic cation concentrations. In addition, deep soils may facilitate sorption of DOC and associated aluminum. Aluminum plus H^+ base neutralizing capacity (the equivalent sum of all acid that can be titrated by strong base to a pH of 8.3; Stumm and Morgan 1981) show an inverse relationship to basic cation concentrations and soil depth over the elevational gradient (Figure 11; Figure 2).

Comparisons with the Falls Brook study

Several years prior to this study, aluminum chemistry was studied along an elevational gradient in Falls Brook, located in the HBEF adjacent to W6 (Johnson et al. 1981). Sampling in the Falls Brook study was conducted from the highest elevation of the stream to a point where the stream was classified as fifth order (812 m to 415 m). The stream reach studied, therefore, was much longer than in the present study of W5 and W6.

In general, elevational trends in the stream chemistry of Falls Brook were similar to those of W5 and W6. Concentrations of total aluminum and H^+ decreased with increasing drainage area, while basic cation concentrations increased. Similarity in these trends can be related to the similar topography, aspect, geology and vegetation of Falls Brook and W5 and W6.

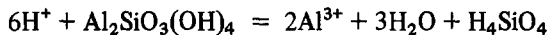
A noteworthy difference occurred, however, in the trends of DOC and non-labile monomeric aluminum concentrations in the streams of these watersheds. In Falls Brook, DOC and non-labile monomeric aluminum concentrations increased slightly with decreasing elevation, rather than the pronounced decrease we observed in W5 and W6. The difference in these trends may be related to differences in vegetation of high elevation sites. A detailed vegetation survey has not been conducted in the Falls Brook watershed, however, spruce and fir species do not appear to occur in high densities in any part of the watershed and are absent from the highest elevations.

When comparing first order reaches, an additional difference between

Falls Brook and W5 and W6 becomes evident. Higher pH values and basic cation concentrations and lower DOC and aluminum concentrations were observed in Falls Brook. This discrepancy is likely to be due in part to the lack of spruce and fir vegetation at the upper elevations of Falls Brook. However, the topography at the highest elevations of Falls Brook exhibits less relief than the upper regions of W5 and W6 suggesting that soils may be deeper than in W5 and W6.

The possible influence of imogolite structures

Dissolved silica concentrations reported in the study of Johnson et al. (1981) were used by Farmer and Fraser (1982) as evidence that imogolite type minerals may occur in the soils of the HBEF. These authors suggest that proto-imogolite buffers dissolved silica concentrations between 33 and 100 μM . Calculation of the saturation index of imogolite using a free energy value of -2929.7 kJ/mol , (Farmer and Fraser 1982), however, show the streams of W5 and W6 to be highly oversaturated with respect to the solubility of imogolite ($\text{SI} > 5.5$). The saturation index was determined by substituting the measured concentrations of Al^{3+} , H^+ and dissolved silica into the formula for congruent dissolution of imogolite, given below, to obtain the mineral ion activity product. Free energy values to calculate the equilibrium constant (K) were obtained from May et al. (1979) for Al^{3+} and H_2O , and from Wagman et al. (1968) for $\text{Si}(\text{OH})_4$.



Our observations of solution chemistry in the streams of W5 and W6 are inconsistent with the imogolite hypothesis. The predominant fraction of total aluminum in streamwater was in the monomeric form (Figure 4; Figure 5). It is, therefore, doubtful that proto-imogolite is an important form of aqueous aluminum, since the rapid extraction procedure for determining monomeric aluminum (Barnes 1976) would not recover the proto-imogolite sol. Farmer et al. (1980) also state that the presumption of migration of aluminum as an organic complex has arisen largely from the lack of an alternative mechanism. Estimation of organically complexed aluminum by the procedure of Driscoll (1984), however, refutes this. The high correlation of non-labile monomeric aluminum with DOC concentrations (Table 2) in streamwater strongly suggests that much of this aluminum is associated with organic matter.

Conclusion

The chemical composition of streamwater at any location in the watershed will be altered by water entering the stream channel from the soil adjacent to the reach. Stream chemistry at each sampling location, therefore, represents an integration of the biogeochemical processes occurring within

the upstream drainage area. In W5 and W6, these processes are regulated by spatial variation in topography, climate, vegetation and soil. When these variations are related to soil formation processes it becomes possible to apply the concept of soil catena (Glazovskaya 1968, Buol et al. 1980), defined in this case as a continuum of soils whose properties vary with their position on the hillslope. The trends in stream chemistry of W5 and W6 may be an expression of soil catenas which produce soil solution with a chemical composition that varies elevationally.

Comparison of stream chemistry in W5 and W6 to Falls Brook, indicates that significant variations can occur in adjacent watersheds. Care must be taken, therefore, if the results of this study are to be extrapolated to other streams. This study does, however, present variations of aluminum transport which may operate in other watersheds. Surface water quality in upper elevation watersheds is directly related to the mechanisms controlling aluminum transport. If, for example, the majority of a watershed is similar to the transition zone of W5 and W6, it could produce drainage waters high in inorganic aluminum, the form of aluminum toxic to aquatic organisms (Baker and Schofield, 1982, Hall et al. 1985).

Mechanisms of aluminum transport in a watershed are also significant when related to acidic deposition. The importance of strong acids to aluminum mobility in the transition zone of W5 and W6, suggests that this type of ecosystem may be impacted by acidic deposition. Alternatively, watersheds similar to the lower hardwood zone may be resistant to impact from acidic deposition. A more detailed understanding of the processes affected by acidic deposition is needed, however, before a direct link to aluminum in surface waters can be made. Future investigations into the relationship between acidic deposition and aluminum mobility must address the natural variations which occur in the aluminum cycle.

Acknowledgements

We are extremely grateful for the field assistance of Wayne Martin and Don Buso, which was essential to the successful completion of this study. We also thank Tom Siccama for supplying the data on tree species distribution and Art Johnson and Steve Hamburg for supplying the information on mineral soil depth. Mark David's review of the manuscript is also appreciated. Computer modeling of Al speciation was made possible through the programming efforts of Bill Schecher.

This work is a contribution to the Hubbard Brook Ecosystem Study and was supported by the National Science Foundation. The Hubbard Brook Experimental Forest is operated by the U.S.D.A. Forest Service, Broomall, Pennsylvania.

References

- Baker JP and Schofield CL (1982) Aluminum toxicity to fish in acidified waters. *Water Air and Soil Pollution* 18:289–309
- Barnes RB (1975) The determination of specific forms of aluminum in natural water. *Chemical Geology* 15:177–191
- Bormann FH and Likens GE (1979) *Pattern and Process in a Forested Ecosystem*. Springer-Verlag, New York, New York, USA
- Bormann FH, Siccama TG, Likens GE and Whittaker RH (1970) The Hubbard Brook Ecosystem Study: composition and dynamics of the tree stratum. *Ecological Monographs* 40:373–388
- Buol SW, Hole FD and McCracken RJ (1980) *Soil Genesis and Classification*, 2nd Ed. Iowa State University Press, Ames, Iowa, USA
- Cronan CS and Aiken GR (1985) Chemistry and transport of soluble humic substances in forested watersheds of the Adirondack Park, New York. *Geochimica et Cosmochimica Acta* 49:1697–1705
- Cronan CS and Schofield CL (1979) Aluminum leaching response to acid precipitation: effects on high-elevation watersheds in the Northeast. *Science* 204:304–306
- David MB and Driscoll CT (1984) Aluminum speciation and equilibria in soil solutions of a Haplorthod in the Adirondack Mountains (New York, USA). *Geoderma* 33:297–318
- De Conink F (1980) Major mechanisms in formation of spodic horizons. *Geoderma* 24:101–128
- Dickson W (1978) Some effects of acidification of Swedish lakes. *Internationale Vereinigung für theoretische und angewandte Limnologie, Verhandlungen* 20:851–856
- Driscoll CT (1984) A methodology to fractionate aluminum in natural aqueous solutions. *International Journal of Environmental and Analytical Chemistry* 16:267–283
- Driscoll CT, van Breemen N and Mulder J (1985) Chemistry and transport of aluminum in Spodosols (typic Fragiorthods) at the Hubbard Brook Experimental Forest. *Soil Science Society of America Journal* 49:437–444
- Farmer VC and Fraser AR (1982) Chemical and colloidal stability of soils in the Al_2O_3 - Fe_2O_3 - SiO_2 - H_2O system: their role in podzolization. *Journal of Soil Science* 33:737–742
- Farmer VC, Russell JD and Berror ML (1980) Imogolite and proto-imogolite allophane in spodic horizons: evidence for a mobile aluminum silicate complex in podzol formation. *Journal Soil Science* 31:673–684
- Glazovskaya MA (1968) Geochemical landscapes and types of geochemical soil sequences. *Transactions of the 9th International Congress of Soil Science* 4:303–310
- Fuller RD, David MD and Driscoll CT (1985) Sulfate adsorption relationships in forested Spodosols of the northeastern USA. *Soil Science Society of America Journal* 49:1034–1040
- Gosz JR, Likens GE and Bormann FH (1973) Nutrient release from decomposing leaf and branch litter in the Hubbard Brook Experimental Forest, New Hampshire. *Ecological Monographs* 43:173–191
- Hall RJ, Driscoll CT, Likens GE and Pratt JM (1985) Physical, chemical and biological consequences of episodic aluminum additions to a stream. *Limnology and Oceanography* 30:212–220
- Hooper RP and Shoemaker CA (1985) Aluminum mobilization in an acidic headwater stream: temporal variation and mineral dissolution disequilibria. *Science* 229:463–464
- Johnson NM (1979) Acid rain: neutralization within the Hubbard Brook ecosystem and regional implications. *Science* 204:497–499
- Johnson NM, Driscoll CT, Eaton JS, Likens GE and McDowell WH (1981) 'Acid rain', dissolved aluminum and weathering at the Hubbard Brook Experimental Forest, New Hampshire. *Geochimica et Cosmochimica Acta* 45:1421–1437
- Johnson NM, Likens GE, Bormann FH, Fisher DW and Pierce RS (1969) A working model for the variation in stream water chemistry at the Hubbard Brook Experi-

- mental Forest, New Hampshire. *Water Resources Research* 5:1353–1363
- Likens GE, Bormann FH, Pierce RS, Eaton JS and Johnson NM (1977) *Biogeochemistry of a Forested Ecosystem*. Springer-Verlag, New York, New York, USA
- May HM, Helmke PA and Jackson ML (1979) Gibbsite solubility and thermodynamic properties of hydroxy-aluminum ions in aqueous solution at 25°C. *Geochimica et Cosmochimica Acta* 43:861–868
- McDowell, WH, Wood T (1984) Podzolization: soil processes control dissolved organic carbon concentrations in stream water. *Soil Science* 137:23–32
- Menzel DW and Vaccaro RF (1964) The measurement of dissolved organic and particulate carbon in seawater. *Limnology and Oceanography* 9:138–142
- Messenger AS (1975) Climate, time and organisms in relation to podzol development in Michigan sands; II. relationships between chemical element concentrations in mature tree foliage and upper humic horizons. *Soil Science Society of America Journal* 39:698–702
- Messenger AS, Kline JR and Wildrotter D (1978) Aluminum biocycling as a factor in soil change. *Plant Soil* 49:703–709
- Orion, Instruction Manual (1976) Fluoride Electrodes, Orion Research, Inc., Cambridge, Massachusetts, USA
- Slavin W (1968) *Atomic Absorption Spectroscopy*. Wiley Interscience, New York, New York, USA
- Standard Methods for the Examinations of Water and Wastewater, 15th ed. 1981. American Public Health Association, Washington, D.C., USA.
- Stumm W and Morgan JJ (1981) *Aquatic Chemistry*. Wiley Interscience, New York, New York, USA
- Tabatabai MA and Dick WA (1983) Simultaneous determination of nitrate, chloride, sulfate and phosphate in natural waters by ion chromatography. *Journal of Environmental Quality* 12:209–213
- Ugolini FC, Dawson H and Zachara J (1977) An example of soil processes in the *Abies amabilis* zone of the central Cascades, Washington. *Soil Science* 124:291–302
- Wagman DD, Evans WH, Parker BV, Bailey SM and Schumm RH (1968) Selected values of chemical thermodynamic properties. National Bureau of Standards Tech. Notes 270-3 and -6, Washington, D.C., USA