SOIL ALUMINUM DISTRIBUTION IN THE NEAR-STREAM ZONE AT THE BEAR BROOK WATERSHED IN MAINE

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Abstract. Near-stream and upslope soil chemical properties were analyzed to infer linkages between soil and surface water chemistry at the Bear Brook Watershed in Maine [BBWM]. Organic and mineral soil samples were collected along six 20 m transects perpendicular to the stream and one 200 m transect parallel to the stream. O horizon soils immediately adjacent to the stream had a significantly higher pH (4.20) and lower soil organic matter percentage (54%) than upslope O horizons (3.84 and 76%, respectively). Additionally, near-stream O horizon soils had significantly higher concentrations of water-soluble Al (2.7 ×), exchangeable Al (2.3 ×), and organically-bound Al (3.9 ×) and significantly lower concentrations of exchangeable Ca (0.4 ×) than O horizons upslope. These results suggest that Al can accumulate in non-hydric near-stream zone soils at this site. Mobilization of labile Al from near-stream zone soils during hydrologic events could play a key role in explaining controls on Al in stream water at BBWM.

Keywords: aluminum, cations, near-stream, riparian, soil chemistry, stream chemistry

1. Introduction

An important consequence of acidic deposition is the mobilization of aluminum [Al] in soils and the resulting increase in soil solution and surface water Al concentrations (Postek *et al.*, 1995). High Al concentrations may have potentially harmful effects on aquatic organisms (Baker and Schofield, 1982), forest vegetation (Minocha *et al.*, 1997; Shortle and Smith, 1988), and soil quality (Lawrence *et al.*, 1995; Mulder *et al.*, 1989). Elevated Al is particularly a concern in the northeastern United States and Europe.

The concentration and speciation of aqueous and particulate Al is regulated by a number of interrelated processes such as inorganic and organic complexation, surface adsorption, and mineral dissolution (Berggren and Mulder, 1995; Walker *et al.*, 1990; Dahlgren *et al.*, 1989). Water movement through soils is the mechanism of Al transport to surface water (Lawrence *et al.*, 1988).

Water flow paths and variations in source areas control the chemistry of drainage water in forested catchments (Ross *et al.*, 1994; Lawrence *et al.*, 1988). During baseflow, chemical equilibria can be approached as weathering reactions con-

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sume hydrogen [H] from the upper soil horizons, releasing alkali and alkaline earth metals (Neal *et al.*, 1989). Longer water residence time associated with micropore flow typically results in higher alkalinity (Peters and Murdoch, 1985), lower dissolved organic carbon [DOC] (McGlynn *et al.*, 1999), and lower inorganic Al concentrations in drainage waters (Neal *et al.*, 1989). During high discharge events, a large component of total streamflow is composed of water rapidly flowing along shallow flowpaths in the soil. This water may be enriched in both Al and H due to interactions with organic matter (Luxmoore *et al.*, 1990) and flow through more acidic and Al-bearing upper mineral soils (Neal *et al.*, 1989). Therefore, peak discharge during hydrologic events is of particular concern because it often corresponds to adverse biological effects in acidified streams (Vogt and Muniz, 1997).

Lawrence *et al.* (1995) hypothesized that Al, mobilized by acidification in mineral soils, can be transported into the forest floor from a rising water table or upward capillary movement of water through rapid drying of the forest floor by evapotranspiration. The downward movement of water into the soil profile, followed by an upward movement and renewed contact with organic-rich soils in return flow areas, has important consequences for Al concentrations in the forest floor and surface waters (Mulder *et al.*, 1991; Nilsson and Bergkvist, 1983).

Studies in forested catchments in Norway (Vogt and Muniz, 1997; Mulder *et al.*, 1995; Mulder *et al.*, 1991) reported accumulations of exchangeable Al in peat soils immediately adjacent to the stream. Vogt and Muniz (1997) hypothesized that Al is transported by a process similar to podzolization in these soils, but downslope by lateral flow rather than by vertical illuviation. In northern Sweden, Bishop *et al.* (1990) found that stream acidity was higher during storm events as a result of water flow through a thin layer of organic surface material along the banks. At a catchment in northern Vermont, McGlynn *et al.* (1999) found no evidence supporting the upward movement and discharge of deep groundwater through surficial organic soils near the stream. Another study in Vermont by Ross *et al.* (1994) noted that, without areas of peat or wetland near the stream bank, it was unlikely that lateral flow water chemistry was altered by the riparian zone.

The objective of this study was to determine if Al accumulates in non-hydric near-stream zone soils at the Bear Brook Watershed in Maine (BBWM). We consider non-hydric soils to be those without indications of saturated and anaerobic conditions under present or recent hydrologic regimes. This study was undertaken to better understand changes in soil chemistry that occur as soil water passes through the near-stream zone en route to the stream channel in a forested catchment. The results may also help interpret the influence of near-stream zone soils on stream water Al chemistry.

2. Methods

2.1. Site description

The Bear Brook Watershed in Maine (BBWM) is located in eastern Maine (44°52′ N, 68°06′ W), approximately 50 km from the Gulf of Maine. The site lies on the southeast slope of Lead Mountain, with a maximum elevation of 475 m and a total relief of 210 m. BBWM is the location of a long-term paired catchment study (Norton *et al.*, 1999b). The site for this study was the untreated East Bear Brook watershed, a 10.7 ha watershed drained by a perennial, low DOC (100–300 μmol C L^{-1}), low ANC (0–4 μeq L^{-1}) stream (Norton *et al.*, 1999b). The average slope of the watershed from the summit to the weirs is 31%. Bedrock is mainly quartzite and gneiss with granitic intrusions. Soils are primarily coarse-loamy, mixed, frigid Typic Haplorthods formed from compact Wisconsinin age basal till (Norton *et al.*, 1999b). Both the parent material and bedrock have a low to moderately low weathering potential due to the dominance of silicate minerals (Lawrence *et al.*, 1997). Soils are typically 0–1 m in thickness and are characterized as acidic with low base saturation, low cation exchange capacity, and low sulphate adsorption capacity (Norton *et al.*, 1999b). Vegetation is predominately northern hardwood with stands of softwood on steep slopes and higher elevations. Hardwoods are dominated by American beech (*Fagus grandifolia* Ehrb.), with interspersed yellow birch (*Betula alleghaniensis* Britt.), sugar maple (*Acer saccharum* Marsh.) and red maple (*Acer rubrum* L.). Softwoods are red spruce (*Picea rubens* Sarg.) with a minor component of balsam fir (*Abies balsamea* (L.) Mill.). Average air temperature is 4.9 °C and annual precipitation is approximately 1.3 m. Additional site information is in Norton and Fernandez (1999).

2.2. Soil sampling

2.2.1. *Perpendicular Transects*

Organic (O) and upper mineral (UB) horizon samples were collected from six transects perpendicular to East Bear Brook stream (Figure 1). One transect was sampled in September 1998 with the remaining five transects sampled during the summer of 1999. Transect locations ranged in elevation from approximately 275 to 375 m above sea level. The 1998 transect was sampled at 1, 2, 3, 5, 7, 9, 13, and 17 m from the stream edge. The 1999 transects were sampled at 0.5, 1, 2, 3, 5, 10, 15, and 20 m from the stream edge. At each sampling point, the O horizon was removed quantitatively inside a 12 × 12 cm frame. Bulk upper mineral soil samples were collected from the upper 10 cm of the B horizon. E horizons were present at many upslope locations but were not analyzed because of their relatively minor contribution to solum chemical pools, and due to limited resources. Soils were sampled from areas of hardwood or mixed vegetation (50–100% hardwood) that had no obvious indicators of surface water (i.e. water-stained leaves, drainage

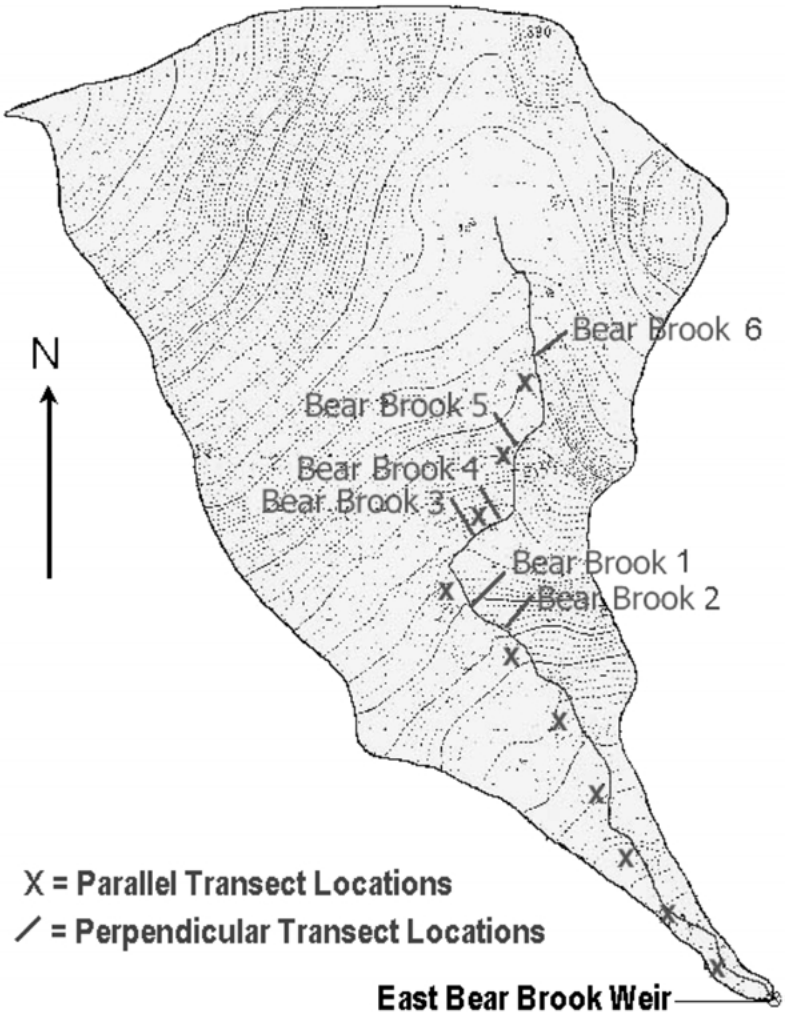

Figure 1. Sampling locations along East Bear Brook at the Bear Brook Watershed in Maine.

channels, scoured or bare areas). Soils were collected in clean plastic bags and returned to the laboratory for air-drying. Upslope soils were characteristic Spodosols, whereas near-stream soils had little Spodosol development but had distinct O and B horizons. Near-stream O horizons had a greater mineral component than upslope O horizons (Table I). Depth to bedrock or basal till averaged 26 cm immediately adjacent to the stream and 78 cm at the deepest upslope sampling locations. Near-stream B horizons were wetter than upslope B horizons, but were not hydric soils based on the absence of redoximorphic features (i.e. Fe and Mn concentrations and/or depletions). Slope in the sampling areas ranged from 19–34

TABLE I

Mean soil chemical and physical properties in the O horizon and upper mineral (UB) soils 0.5 m and 5 m from East Bear Brook stream, Bear Brook Watershed in Maine

Location	pH	SOM	AIS	BS	DI Al	Ex. Al	Org-Al	Org-Al/C
		%			$cmol_c\ kg^{-1}$			
0.5 m O	4.20 a	53.68 a	40.43 a	42.32 a	0.48 a	6.80 a	30.55 a	0.14 a
0.5 m UB	4.48 b	17.41 b	68.79 b	21.95 b	0.17 b	4.59 b	29.58 a	0.34 b
5 m O	3.84 c	75.50 c	13.41 c	61.95 c	0.18 bc	2.95 c	7.91 b	0.02 c
5 m UB	4.39 ab	15.41 b	72.60 b	17.25 b	0.24 c	5.42 ab	28.20 a	0.34 b

Location	Ca	Mg	Na	K	Fe	Mn	H	CEC
	$cmol_c\ kg^{-1}$							
0.5 m O	6.00 a	1.43 a	0.23 a	0.83 a	0.48 a	0.33 a	3.42 a	18.71 a
0.5 m UB	0.78 b	0.18 b	0.11 b	0.18 b	0.23 ab	0.08 b	0.66 b	6.62 b
5 m O	14.39 c	2.83 c	0.23 a	1.10 c	0.38 a	0.46 a	6.69 c	28.54 c
5 m UB	0.92 b	0.17 b	0.07 c	0.13 d	0.37 a	0.01 c	0.80 b	7.50 b

The same leter for the Mann-Whitney two-tailed test between soil types indicates no difference at the 95% confidence level. DI-Al is water-soluble Al, Org-Al is organically-bound Al, and Org-Al/C is organicallly-bound Al normalized to carbon (see text for further explanations).
N = 15 for O horizons and 10 for UB (upper mineral) soils.

A 10 m perpendicular transect was also sampled in 1998 at the Halfmile Stream Watershed as part of a separate study. Results from this single transect at a different watershed were included to see if there was evidence that patterns from BBWM might be found elsewhere. At the Halfmile Stream Watershed site, which is located approximately 20 km west of BBWM, comparable techniques were used to sample soils but sampling intervals along that perpendicular transect were at 0.1, 1, 4, and 10 m from the stream edge.

2.2.2. *Parallel Transect*

O horizon and upper B soils were collected from ten locations along a 200 m transect parallel to East Bear Brook during the summer of 1999 (Figure 1). Samples were collected at 20 m intervals starting from the East Bear Brook weir. At each location, samples were taken from points located at 0.5 and 5 m from the edge of the stream. The parallel transect provided a more intensive evaluation of near-stream (0.5 m) and upslope (5 m) soil properties. Sampling methods used were the same as for the perpendicular transects.

2.3. Sample analyses

Air-dried soil samples were sieved (through 6 mm for the organic horizon, 2 mm for the mineral horizon) and homogenized. pH was determined using a Corning® 340 pH meter and 1 g organic soil or 5 g mineral soil to 10 mL de-ionized water. Exchangeable base cations and Al were extracted with 1 *M* NH_4Cl (Blume *et al.*, 1990) at a ratio of 2 g of organic soil or 5 g of mineral soil to 100 ml extraction solution. Samples were shaken for 1 hr. Water-soluble [DI-Al] and organically-bound Al [Org.-Al] were extracted with de-ionized water and 0.5 *M* $CuCl_2$, respectively. Both Al phases were extracted at the same solution:soil ratios used in the NH_4Cl extraction. Water-soluble Al samples were shaken for 1 hr. The $CuCl_2$ procedure was modified from Hargrove and Thomas (1984) and Juo and Kamprath (1979) to include shaking for 6 hr. All extracts were vacuum filtered through Whatman 42 filter paper and analyzed by flame emission (K and Na) or plasma emission spectroscopy (Ca, Mg, Fe, Mn, exchangeable Al, water-soluble Al, and organically-bound Al). Exchangeable acidity was determined by extraction with 1 *M* KCl (Blume *et al.*, 1990) with titration to the phenolphthalein endpoint. Percent soil organic matter [SOM] was determined on oven-dried samples by loss-on-ignition over 12 hr at 450 °C using a Thermolyne 48000 Muffle Furnace. Cation exchange capacity [CEC] was calculated as the sum of the exchangeable base cations Ca, Mg, K, and Na plus exchangeable acidity. Base saturation [BS] was calculated as the percentage of the CEC occupied by exchangeable bases, whereas Al saturation [AlS] was the percentage of the CEC occupied by exchangeable Al. Exchangeable Al was operationally defined in this study as the NH_4Cl-exchangeable Al minus the water-soluble Al concentrations. Organically-bound Al was defined as the concentration of $CuCl_2$-extractable Al minus both NH_4Cl-exchangeable and water-soluble Al concentrations.

A subset of six O horizon samples and six upper B horizon samples (0.5 and 5 m samples from three perpendicular transect locations) were analyzed for water-soluble sulphate [SO_4^{-2}] and nitrate [NO_3^-] by ion chromatography (EPA method 600/R-93-100, 1993).

2.4. Statistical analyses

Since the data were generally not normally distributed, the nonparametric Mann-Whitney procedure was applied to test for statistically significant differences between soils at the 0.5 and 5 m locations. Additionally, Pearson's correlation coefficients were calculated with uncorrected probabilities to test for statistically significant relationships among Al phases, pH, and SOM. All comparisons were made at the 95% confidence level using SYSTAT version 8.0.

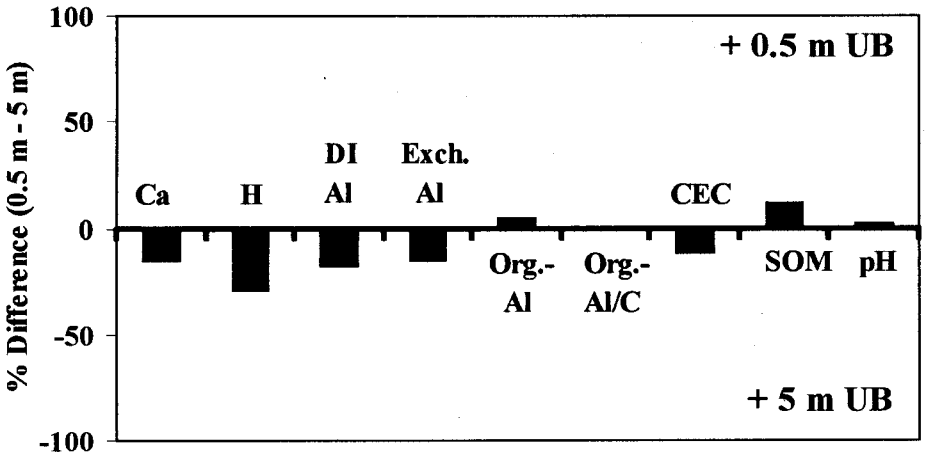

Figure 2. Percent difference between 0.5 m upper B horizon and 5 m upper B horizon based on means presented in Table I (see Table I and text for explanations). A positive percentage indicates higher values in the near-stream zone, a negative percentage indicates higher values in the upslope soils.

3. Results and Discussion

3.1. Influence of Flow Paths in Al Chemistry

Table I shows mean chemical and physical properties in the O horizon and upper B horizon soils at 0.5 and 5 m from the edge of East Bear Brook. These results include samples from both the parallel and perpendicular transects. Since our data showed that the 5 m samples were generally representative of all upslope (> 0.5 m) locations, results will be referred to as near-stream (0.5 m) and upslope (5 m) in this discussion. There were no significant differences in pH, exchangeable Al, and organically-bound Al concentrations between the near-stream O horizon and the upper B soils on the hillslope (Table I). Additionally, there were no significant differences in pH, exchangeable Al, and organically-bound Al concentrations between the upper B horizon soils in the near-stream zone and upper B horizon soils on the hillslope (Table I, Figure 2). The upslope O horizon had significantly lower concentrations of exchangeable Al, organically-bound Al, and pH than the near-stream O horizons (Table I, Figure 3) and upper B horizon soils in the near-stream zone and upslope. These similarities suggest a lateral extension of the upper B horizon flow path on the hillslope through the near-stream O horizon and upper B soils (Mulder *et al.*, 1991).

The perpendicular transect sampling, which consisted of six 20 m transects perpendicular to the stream, provides additional information on spatial patterns with distance from the stream channel at BBWM. Five out of six transects followed the general pattern of higher exchangeable Al and lower exchangeable Ca near the

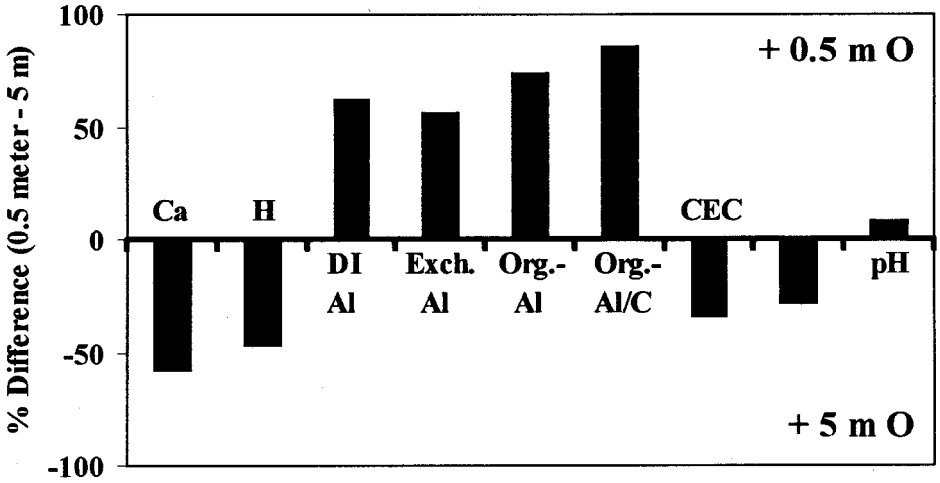

Figure 3. Percent difference between 0.5 m O horizon and 5 m O horizon based on means presented in Table I (see Table I and text for explanations). A positive percentage indicates higher values in the near-stream zone, a negative percentage indicates higher values in the upslope soils.

stream (Figure 4). The transect highest in the watershed (transect 6) did not follow this pattern and will be addressed below in the discussion.

The Halfmile Stream Watershed site included only one perpendicular transect with limited sampling intervals. The data from this site were included to see if the results from BBWM might be representative of other watersheds. Figure 5 shows similar patterns as reported for BBWM, with higher exchangeable Al and lower exchangeable Ca concentrations in the near-stream zone O horizon. This suggests the patterns described here are not limited to the BBWM site.

Chen and Betscha (1999) modeled flow paths at BBWM for a storm event in 1990 and suggested that during this event 44% was macropore flow, 38% was surface flow, and 18% was subsurface flow. Subsurface or baseflow had little effect on stream hydrograph peaks, while surface flow dominated the rising limb and macropore flow dominated the descending limb (Chen and Betscha, 1999). Deep groundwater flow through bedrock fractures at BBWM is believed to be a minor component of stream flow as this was a criterion during the original site selection process. Therefore, we assume that most water entering the stream passes through the shallow soils in the near-stream zone.

During baseflow periods, stream chemistry at East Bear Brook is determined by subsurface water moving slowly through deeper mineral soils in the watershed (Chen and Betscha, 1999). Soil water during baseflow reflects the hydrolysis of primary aluminosilicate minerals in the parent material and will therefore be enriched in base cations and silica [Si], and have a relatively high pH and low DOC concentrations. As it passes through the near-stream zone, this water is likely forced towards the soil surface by shallow bedrock. Figure 6 is a conceptual dia-

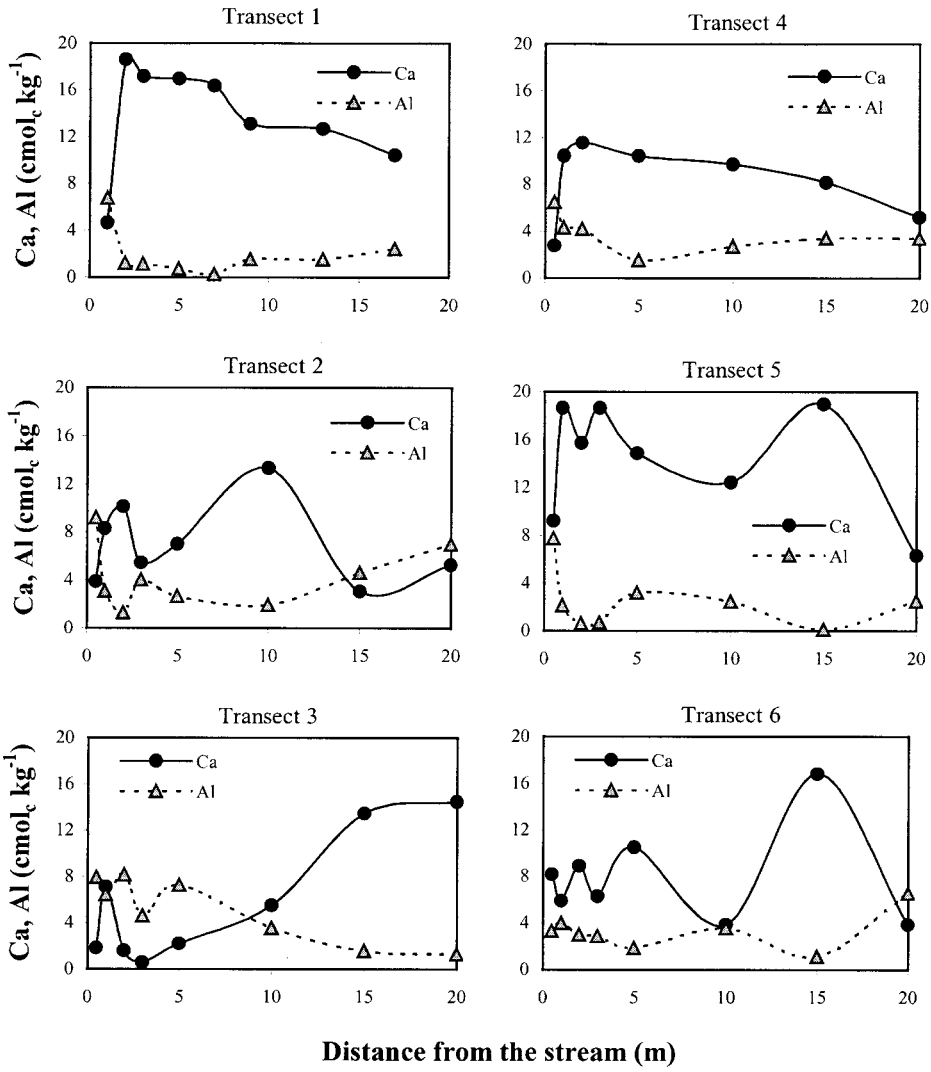

Figure 4. Exchangeable Ca and Al in the O horizon with distance from the stream at the six transects sampled perpendicular to East Bear Brook stream, Bear Brook Watershed in Maine.

gram that illustrates the upward movement of soil water in the near-stream zone as hydrologic flow paths approach East Bear Brook stream. However, during base-flow, water will likely remain as shallow subsurface flow at BBWM due to a combination of regolith thickness (mean = 26 cm at 0.5 m from the stream edge) and a smaller volume of water being discharged from the mineral soils during drier periods.

During high discharge events, the thickness of the saturated zone increases, resulting in macropore flow along shallow flow paths. Water passing quickly through

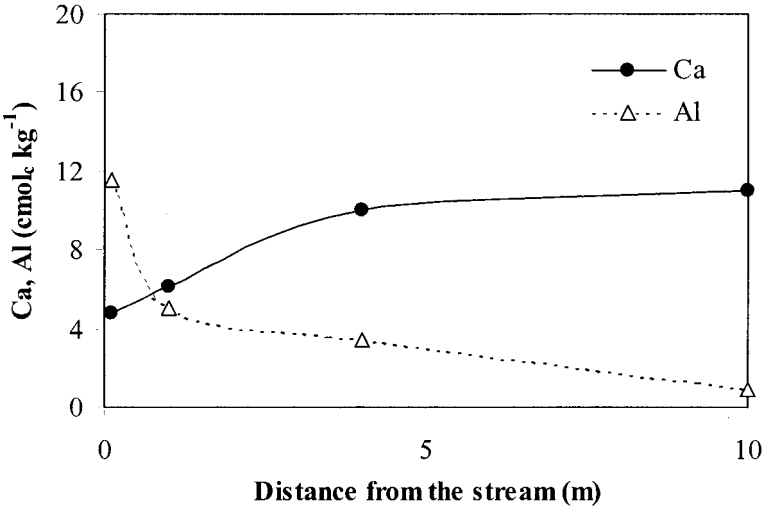

Figure 5. Exchangeable Ca and Al in the O horizon with distance from the stream at transect sampled perpendicular to Halfmile Stream, Halfmile Stream Watershed.

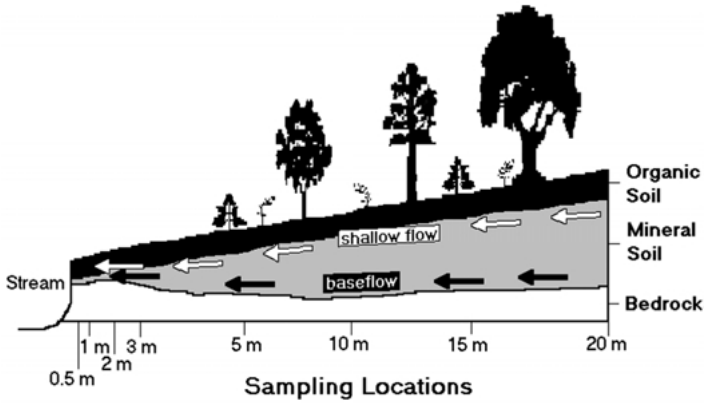

Figure 6. Flow paths and characteristics of water as it approaches the stream at the Bear Brook Watershed in Maine.

the uppermost mineral soils during storm events is generally enriched in both Al and H compared to baseflow waters (Luxmoore *et al.*, 1990; Neal *et al.*, 1989). In a study at nearby Tunk Mountain, Rustad and Cronan (1995) noted that highly acidic solutions from the O horizon can mobilize Al from the upper mineral soil, allowing it to then move laterally to the streams through macropore flow. Several studies have attributed higher Al concentrations in streamwater during high flow events at East Bear Brook to travel along these shallow flow paths (Norton *et al.*, 1999a; Postek *et al.*, 1995).

There were no clear elevational trends in near-stream soil chemistry in the perpendicular transect sampling. Transect 3 organic soils appeared to have been

disturbed and were well-mixed to 10 m from the stream edge. The 3 m sample from transect 4 was compromised during processing and is omitted from Figure 4. The transect highest in the watershed (transect 6) did not follow the pattern of higher exchangeable Al and lower exchangeable Ca near the stream (Figure 4). The near-stream zone of transect 6 was approximately twice as deep as the other five locations and had significant E and B horizon development. Therefore, it is unlikely that there would be any physical mixing of acidic, Al-rich shallow water and deeper soil water at this site.

A similar pattern was observed in the parallel transect sampling. All locations except the uppermost location had higher Al concentrations (all forms measured) and lower concentrations of exchangeable Ca and Mg in the O horizon immediately adjacent to the stream than upslope O horizon soils. In addition, all near-stream soils with the exception of the highest site lacked E horizon development. The 0.5 and 5 m samples from all locations were included as part of the data in Table I, however, and explain some of the variability in those data.

Stream water samples were collected between 286 and 374 m above sea level at East Bear Brook to evaluate changes in stream chemistry with elevation in the watershed. Samples collected from 1990 to 1995 showed increased Al concentrations with increased elevation. This pattern suggests greater contributions of mineral soil water and less inorganic Al-O horizon interaction with elevation. This is consistent with the soils data that suggest less water flow through the near-stream O horizon at the uppermost sampling locations because of greater soil depth. Additional near-stream soils data from the upper region of the watershed are not available so that the relationship between patterns in stream water Al and soil Al concentrations with elevation can not be confirmed.

3.2. AL CHEMISTRY IN THE NEAR-STREAM ZONE

Significant differences in several parameters occurred between the near-stream and upslope O horizons. The near-stream zone had higher pH, higher water-soluble, exchangeable and organically-bound Al, and lower exchangeable Ca concentrations (Table I, Figure 3). This relationship is in contrast to the more common inverse relationship in mineral soil materials between exchangeable Al and pH or exchangeable base cations. Skyllberg (1999), Skyllberg and Borggaard (1998), and Ross *et al*. (1996) suggested that increasing the Al saturation of organic exchange sites can increase soil pH. This occurs because organic Al complexes are a weaker form of acidity than the protonated form of the corresponding organic acid (Skyllberg, 1999). Significantly higher concentrations of organically-bound Al (Table I, Figure 3) and a significant positive correlation ($r = 0.81$, $P = 0.005$) between pH and organically-bound Al occurred in the near-stream O horizon. This relationship could indicate that higher Al saturation was contributing to the higher pH found in the near-stream zone as compared to upslope O horizon soils at BBWM. Mobiliz-

ation of Al is pH dependent, and a higher pH in the near-stream zone O horizon could result in decreased Al solubility.

Additionally, water approaching the stream along upper soil flow paths will likely encounter shallow, saturated soils in the near-stream zone during hydrologic events (Figure 6). The mixing of acidic, Al-rich shallow flow path water with higher pH baseflow water in the near-stream zone would neutralize soil solution acidity and decrease Al solubility (Neal *et al.*, 1989; Lawrence *et al.*, 1988).

Other factors may contribute to increased Al near the stream, but were not investigated as part of this study. For example, deposition of Al mobilized from the streambed during episodic acidification events could contribute Al to the near-stream soils (Norton *et al.*, 1992). However, we do not believe that this is a major source of near-stream soil Al because stream volume is rarely high enough to flood the near-stream zone.

Decreased Al solubility due to retention of strong acid anions from biological reduction in saturated soils could also cause accumulations of Al in the near-stream zone. However, the sub-sample of water-soluble soil extracts analyzed for SO_4^{-2} and NO_3^- showed no consistent trends with distance from the stream. CO_2 degassing as water emerges at the soil surface near the stream is more likely to have an impact on Al chemistry at these sites (Roy *et al.*, 1999). Dahlgren and Walker (1993) reported that water in contact with Spodosol Bs horizons at BBWM can quickly approach equilibrium with solid phase Al pools. As CO_2- enriched mineral soil water is forced to the surface in the shallow near-stream zone, CO_2 degases, increasing pH (Norton and Henriksen, 1983) and potentially immobilizing or precipitating Al in the near-stream zone.

3.3. Influence on Stream Chemistry by Near-Stream Zone Soils

Surface water acidification models such as MAGIC (Cosby *et al.*, 1985) and IL-WAS (Gherini *et al.*, 1985) have often assumed general equilibrium with an $Al(OH)_3$ mineral phase (de Wit *et al.*, 1999; Dahlgren and Walker, 1993). However, several studies have reported that equilibrium with a single $Al(OH)_3$ mineral cannot describe Al concentrations in many soil solutions and surface waters (de Wit *et al.*, 1999; Seip *et al.*, 1990; Dahlgren *et al.*, 1989; Cronan *et al.*, 1986). If water is in contact with lower mineral soils for extended periods of time, equilibrium with respect to $Al(OH)_3$ mineral solubility could be attained (Dahlgren *et al.*, 1989). Macropore water travelling along shallow flowpaths during hydrologic events, however, will generally be undersaturated with respect to $Al(OH)_3$ due to kinetic constraints (Franken *et al.*, 1995) or complexation by solid phase organics (de Wit *et al.*, 1999; Mulder and Stein, 1994).

In Norway, Mulder *et al.* (1990) and Sullivan *et al.* (1986) found increased stream water concentrations of organic Al and H, but decreased inorganic Al, during rain events as a result of increased flow through upper soil horizons. In contrast, several studies at BBWM have reported increased inorganic Al concentrations and

decreased pH in stream water during rain events (Roy *et al*., 1999; Postek *et al*., 1995). Postek *et al*. (1995) found that the relationship between inorganic Al and pH was more consistent with $Al(OH)_3$ mineral solubility control despite the influence of shallower flow path water. The authors suggested that increased inorganic Al in the stream during hydrological events may be the result of dissolution and mobilization of Al stored between the mineral soil and the stream channel. If low-pH water from shallow macropore flow mobilizes labile Al from near-stream zone soils, the stream could appear to follow an $Al(OH)_3$ mineral solubility model during hydrologic events. However, this study did not evaluate the mobilization of Al from the streambed during pH depressions, which has been shown to contribute Al to stream water during events (Norton *et al*., 1992).

4. Conclusions

O horizon soils immediately adjacent to the stream at the Bear Brook Watershed in Maine had significantly higher concentrations of water-soluble, exchangeable, and organically-bound Al and significantly lower exchangeable Ca and Mg than O horizons upslope. Due to an increasingly shallow water table and shallow depth to bedrock as we approach the stream, shallow flow path water likely mixes with deeper mineral water in the near-stream zone during hydrologic events. This mixing of higher pH baseflow water with acidic, Al-rich macropore water from shallow flowpaths would provide an opportunity to neutralize soil solution acidity and decrease Al solubility (Neal *et al*., 1989; Lawrence *et al*., 1988).

The accumulation of Al in the near-stream zone may also be dependent on organic complexation in a process similar to podzolization, but by a lateral flow path downslope rather than by vertical illuviation (Vogt and Muniz, 1997; Mulder *et al*., 1995). As Al-rich soil water passes through the shallow near-stream O horizon, organic surfaces may become saturated with Al. Increased Al saturation of organic exchange sites in the near-stream zone could result in a pH increase (Skyllberg, 1999; Skyllberg and Borggaard, 1998; Ross *et al*., 1996). Mobilization of Al is pH dependent, and this increase in pH could result in decreased Al solubility and subsequent Al accumulation in the near-stream zone O horizon.

The mobilization of labile Al from near-stream O horizon soils may complicate attempts to identify controls on Al solubility in stream water at BBWM. Additionally, the higher retention of organically-bound and exchangeable Al in near-stream soils could represent an important source of potentially toxic Al in stream waters if exposed to increased inputs of strong mineral acids.

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