

# Phosphorus in Soils of Temperate Forests: Linkages to Acidity and Aluminum

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We used P fractionation techniques to study the accumulation, mobilization, and availability of soil P in six watersheds of the eastern United States and Europe, two of which included paired long-term acidification experiments. Although total soil P concentrations varied widely among these watersheds, the proportions of P fractions were relatively uniform. The mean for the P fraction operationally defined as being associated with Al in the reference watersheds was 71% of total extractable P ( $SE \leq 1\%$ ). Experimental whole-watershed acidification resulted in significant depletion of Al-P concentrations from the upper mineral soil in treated watersheds due to the dissolution of Al hydroxide by acidic solutions traveling along shallow flow paths. Acidic soil solutions mobilize both Al and P, leading to P depletion from the Al-P fraction in the mineral soils. Across this suite of watersheds, lower pH appears to decrease Al/P ratios in the Al-P fraction of these mineral soils through changes in Al solubility. Biocycling in these forests can play a critical role in linking subsurface mineral soil P to surface O horizon available P. In this study, sites with the lowest mineral subsoil Al/P ratios generally had the lowest mineral soil pH values and the highest O horizon available P concentrations. The net effect was to leave subsoil P more bioavailable at the lower pH values because of a lower Al/P ratio in the mineral subsoil at the pH range of 3.1 to 4.6 found in this study. These results suggest that changes in soil acidity due to management, air pollutants, or pedogenesis could shift P availability by altering acidity and the Al/P balance.

**Abbreviations:** BBWM, Bear Brook Watershed in Maine; EB, East Bear; FEF, Fernow Experimental Forest; HB, Hadlock Brook; LP, Lesni Potok; MP, Mud Pond; SB, Strengbach; WB, West Bear.

Phosphorus inputs to unfertilized forest lands are largely limited to those derived from soil parent materials, with minimal inputs from precipitation (Walker and Syers, 1976; Newman, 1995). In most parent materials, P occurs predominantly in apatite [ $Ca_5(PO_4)_3(OH,F,Cl)$ ] (Walker and Syers, 1976). Geochemical weathering in soils results in the dissolution of primary minerals, and in the case of apatite, weathering releases P into the soil environment to be utilized by biota, adsorbed to Al and Fe secondary phases, precipitated as a secondary Ca phase, or leached from the ecosystem (Smeck, 1973; Crews et al., 1995). In temperate, humid forests occurring on pedogenically young, acidic soils, the majority of the P is associated with Al and Fe hydroxides (Wood et al., 1984; Fox et al., 1990; Darke and Walbridge, 2000; Kana and Kopáček, 2005; Norton et al., 2006; Sherman et al., 2006). In a study of 11 Maine lakes, Amirbahman et al. (2003) suggested that in eutrophic lakes, Fe dominated the internal P cycling in sediments, while in mesotrophic and oligotrophic lakes, other mechanisms including the adsorption of P by Al hydroxide probably dominated the internal P cycling. Kopáček et al. (2005) demonstrated that, in lake sediments with high Al concentrations, P sorption by Al can be sufficient to prevent P release even during periods of anoxia and that under these conditions Al will limit lake P cycling. The high concentrations of secondary Al in soils derived from the weathering of aluminosilicate parent materials should lead to Al domination of P retention mechanisms in soils as well (Walker and Syers, 1976; Likelema, 1980; Wood et al., 1984; Richardson, 1985; Schoenau et al., 1989; Beck

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and Elsenbeer, 1999; Darke and Walbridge, 2000; Richardson et al., 2004; Norton et al., 2006; Sherman et al., 2006).

Both the eastern United States and Europe have been influenced by atmospheric deposition of S and N that have contributed to soil acidification during the past century (Likens et al., 1996; Fernandez et al., 2003; Watmough et al., 2005). Acidification of soils results in base cation depletion as a result of base cation exchange buffering processes (Fernandez et al., 2003). As acidification progresses, base cation exchange buffering is depleted and Al buffering becomes increasingly important, resulting in the mobilization of soil Al (Driscoll, 1985; David et al., 1991; Norton et al., 2004). We hypothesized that if Al exhibits strong controls on the accumulation of P, the mobilization of Al due to acidification could alter soil P dynamics. This occurred at the Bear Brook Watershed in Maine (BBWM), where whole-watershed experimental acidification resulted in increased stream export of Al, Fe, and P during high-discharge events (Roy et al., 1999; Reinhardt et al., 2004). These hydrologic events were associated with precipitation and snowmelt, leading to soil solutions moving through shallow, relatively acidic soil flow paths, dissolving Al hydroxide and mobilizing the associated P.

While S deposition has declined in the United States and Europe, N deposition is predicted to increase globally (Galloway et al., 2004; Kopáček and Veselý, 2005). Besides contributing to soil acidification, atmospheric deposition of N can influence P cycling by reducing N nutrient limitations on forest vegetation and increasing the potential for P limitation (Aber et al., 1998; Gradowski and Thomas, 2006).

Evidence suggests that soil acidification can result in the mobilization and potential export of Al, Fe, and P from soils. Although we recognize that Al is important in soil P sorption, we have limited knowledge of the relative distribution of various chemical forms of P in acidic, forested mineral soils. Furthermore, we do not know which chemical forms of soil P are most likely to contribute to P mobilization and export during episodic or chronic acidification. Understanding these mechanisms is important to define the trajectory of change in N and P stoichiometry in soils and associated surface waters.

One approach to characterizing the phases of elements in soils is through chemical fractionation techniques. There is a large literature on the utilization of P fractionation techniques in soils, such as those originally developed by Chang and Jackson (1957), which provided the foundation for later modifications such as those of Hedley (1982) and Psenner et al. (1988). These techniques characterize the distribution of P into operationally defined, yet chemically meaningful fractions. The objectives of this study were to use P fractionation techniques on soils from a suite of acidic, forested watersheds to determine (i) if there was a predictability in the distributions of P, Al, and Fe among chemical fractions under ambient conditions in temperate forest soils, (ii) what the consequences of acidification would be for soil P, Al, and Fe fractions, and (iii) if there was evidence of spatial patterns of P, Al, and Fe fractions relative to soil depth and distance from the stream within these watersheds.

## MATERIALS AND METHODS

### Watershed Research Sites

This study was conducted at six humid, temperate watershed research sites in the eastern United States and Europe (Fig. 1). The study sites represented cool, temperate forested watersheds on acidic soils, each with a history of research on the biogeochemistry of watershed acidification. The watersheds were first-order stream watersheds with relatively thin soils, often <1 m, and minimal presence of a riparian zone.

#### The Bear Brook Watershed in Maine

Located in eastern Maine, the BBWM is a long-term, paired watershed acidification experiment. East Bear (EB) comprises 11.0 ha and serves as the reference watershed while West Bear (WB) is 10.3 ha, and has been treated bimonthly with  $(\text{NH}_4)_2\text{SO}_4$  at the rate of 28.8 kg S  $\text{ha}^{-1} \text{yr}^{-1}$  and 25.2 kg N  $\text{ha}^{-1} \text{yr}^{-1}$  since November 1989. The mean annual temperature is 4.9°C, ranging from -30 to 35°C. Mean annual precipitation has been 140 cm. Soils in both watersheds are typically coarse-loamy, isotic, frigid Typic Haplorthods formed from till. The bedrock is primarily quartzite and gneiss with granitic intrusions (Fernandez et al., 2003). Vegetation was similar in both watersheds, with higher elevations dominated by red spruce (*Picea rubens* Sarg.) and balsam fir (*Abies balsamea* L.); lower elevations were dominated by northern hardwoods, predominately American beech (*Fagus grandifolia* Ehrh.), sugar maple (*Acer saccharum* Marsh.), and red maple (*Acer rubrum* L.) (Norton et al., 1999).

#### The Fernow Experimental Forest

The Fernow Experimental Forest (FEF) is a long-term, paired watershed acidification experiment located in the Appalachian Mountains of north-central West Virginia. Watershed 4 (F4) is 34 ha and is a reference, while Watershed 3 (F3) is 39 ha and has been treated three times per year with  $(\text{NH}_4)_2\text{SO}_4$  at a rate of 40.6 kg S  $\text{ha}^{-1} \text{yr}^{-1}$  and 35.4 kg N  $\text{ha}^{-1} \text{yr}^{-1}$  since January 1989. Mean annual temperature was 8.8°C and mean annual precipitation was 147 cm (U.S. Forest Service, 2008). Soils in both watersheds were loamy-skeletal, mixed, active, mesic Typic Dystrachrepts formed in colluvium and residuum overlying quartzose sandstone and shale (Kochenderfer, 2006). The watershed was not glaciated during the Wisconsinan. The dominant overstory vegetation consisted of American beech, black cherry (*Prunus serotina* Ehrh.), red maple, and red oak (*Quercus rubra* L.) (Edwards et al., 2002).

#### Hadlock Brook

The Hadlock Brook (HB) watershed is 47.2 ha and is located in Acadia National Park (ANP) in eastern Maine. The mean annual temperature for nearby Bar Harbor, ME, was 7.5°C and mean annual precipitation was 141 cm (Nelson, 2002). Soils developed from till and were predominately coarse-loamy, mixed, frigid Aquic Haplorthods (Parker et al., 2002). Vegetation in the lower watershed was dominated by red spruce and balsam fir with areas of gray birch (*Betula populifolia* Marsh.) (Sheehan et al., 2006).

#### Mud Pond

The Mud Pond (MP) watershed is located in eastern Maine. The mean annual precipitation was 111 cm and the mean annual tempera-

ture was 6°C. Soils were loamy, mixed, isotic Lithic Haplorthods and coarse loamy-skeletal, mixed, isotic Typic Haplorthods formed from till (Rustad and Cronan, 1995). The canopy was dominated by red spruce (*Picea rubens* Sarg.).

### Lesni Potok

The 76-ha Lesni Potok (LP) watershed is approximately 30 km east-southeast of Prague in the Czech Republic. The mean annual temperature was 7°C and mean annual precipitation was 60 cm (Navrátil, 2003). The soils are classified as Dystrochrepts (Dystric Cambisols). The bedrock is granite. The watershed was not glaciated during the Wisconsinan. Vegetation was predominately European beech (*Fagus sylvatica* L.) and Norway spruce (*Picea abies* L.).

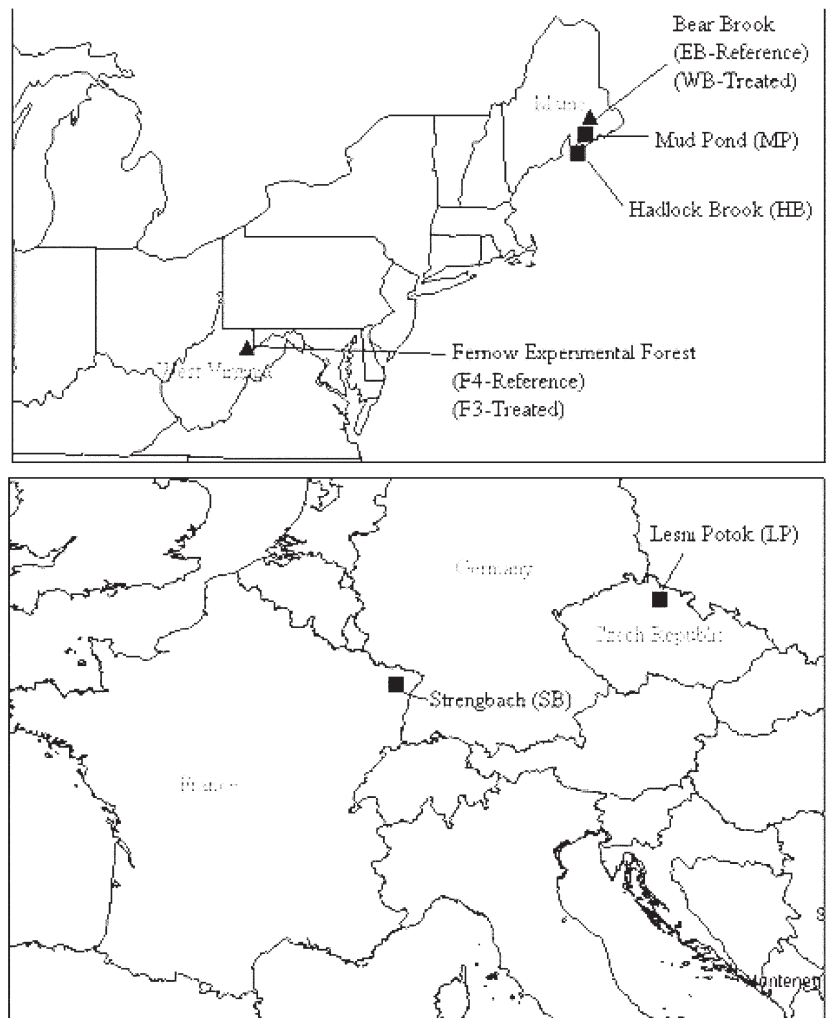
### Strengbach

The 80-ha Strengbach (SB) watershed is in the Vosges Mountains of northeastern France. The mean annual temperature was 6°C with 140 cm of annual precipitation. The soils were classified as Dystrochrepts and Haplorthods (Fichter et al., 1998a). The bedrock is hydrothermally altered granite (Fichter et al., 1998b). The watershed was not glaciated during the Wisconsinan. Vegetation in the catchment was dominated by Norway spruce, with stands of European beech.

### Soil Sampling

Soil sampling was conducted during the summers of 2005 and 2006. Four of the watersheds (HB, MP, F3, and F4) were sampled using a balanced paired transect design (Fig. 1). Within each watershed, two transects were established, originating at the stream and extending upslope to the watershed boundary perpendicular to the stream. Transects were located in areas of the watershed representative of the dominant watershed characteristics with respect to the vegetation, slope, and soils. This resulted in all samples being collected under a hardwood canopy at the FEF and under a softwood canopy at HB and MP. Sampling locations were along transects at (i) 0.1, 1, and 3 m from the stream, and then (ii) at four additional locations distributed evenly along the remaining extent of the transect. This resulted in a total of seven sample pedons per transect.

At the European sites (SB and LP), a similar paired transect design was used; however, one transect was more intensively sampled than the other. At SB, sampling locations along the intensive transect were located under a softwood canopy at 0.1, 1, and 3 m, with five additional pedons distributed along the transect. The second transect at SB was established to study the substantial area of the watershed dominated by a hardwood canopy. This transect consisted of four sampling locations distributed along the hillslope and the transect did not intersect the stream channel. At LP, sampling locations along the intensive transect were at 0.1, 1, 3, and 10 m from the stream, and then every 10 m to a



**Fig. 1.** Location of study sites in the eastern United States and western Europe. Paired, whole-watershed acidification experiments are designated by triangles, others by squares.

distance of 80 m. The second transect was sampled at 1, 40, and 80 m from the stream. Both transects at LP were under hardwood canopies.

In all watersheds, a single pedon was excavated at each sampling point. The O horizons were quantitatively sampled from within a 30- by 30-cm frame. The O horizons in this study represent the whole surface horizon made up of organic soil materials and are equivalent to the sum of Oa, Oe, and Oi horizons, sometimes referred to as L, F, and H. The E horizons were not sampled for analysis because of their thin and inconsistent presence and limited chemical reactivity. Two depth increments of the underlying mineral soil were sampled to include (i) an uppermost sample that best represented the dominant pedogenic processes at the site and the mineral soil increment most vulnerable to the effects of acid deposition, and (ii) a deeper sample that represented soils that had undergone limited development. The upper sample was standardized as the 0- to 10-cm depth increment of the B horizon. Because several sites have C horizons consisting of dense basal till, the deeper increment was standardized to be the 10-cm increment immediately above the C horizon. Upper mineral soils were sampled by inserting a bulb corer to a depth of 10 cm and removing the soil. Deep samples were collected by excavating the pedon to the C horizon and sampling the 10 cm above the C horizon. At F3 and F4, deeper soils made collection of the 10 cm above the C horizon impractical and the deep increment was standardized as the

40- to 50-cm depth increment representing the lower B horizon below the zone of maximum illuviation. In ~10% of pedons, collecting the 10 cm above the C horizon was impossible or impractical because the soils were too shallow due to bedrock or obstructions. In those cases, the deepest possible 10-cm increment was collected. The mean depth for all deep mineral soil samples was 40.05 cm, consistent with the ~40- to 50-cm depth interval used at the FEF.

At the BBWM, a total of 12 pedons were distributed among four compartments representing two forest types on two watersheds (i.e., EB softwoods, EB hardwoods, WB softwoods, and WB hardwoods). The O horizons were sampled quantitatively by removing all the organic soil within a 30- by 30-cm frame. Mineral soil depth increments sampled at the BBWM included 0 to 5, 5 to 25, and 25 cm to the top of the C horizon (i.e., the 25-C horizon) for consistency with the time series of BBWM soil studies. A grab sample of the upper C horizon was obtained from all pedons where possible. All other aspects of the sampling procedures at the BBWM were identical to those used at the other watersheds in this study. In this discussion, the 0- to 5-cm increments from the BBWM and the 0- to 10-cm increments from the other watersheds are referred to as the upper B, and the 25-C increment at the BBWM and the 10 cm above the C horizon from the other watersheds are referred to as the lower B.

## Soil Analysis

Soil samples were secured in double plastic bags in the field, placed immediately in coolers on ice, and transported to the laboratory the same day. The soil samples were air dried, sieved (2-mm sieve for mineral horizons, 6-mm sieve for organic horizons), and homogenized before being subsampled for chemical analyses. The subsamples were oven dried at 105°C (mineral) or 70°C (organic) to determine the air-dried moisture content, to allow data to be expressed on an oven-dried basis. Soils from all sites were air dried and characterized for pH, organic matter, and exchangeable cations in the O horizon and mineral soils as described by SanClements (2009).

## Phosphorus Fractionation

Soil samples were analyzed using a modified version of the sequential P fractionation method developed by Psenner et al. (1988). In our study, modifications included extracting with 1 mol L<sup>-1</sup> NH<sub>4</sub>Cl in the first fraction rather than H<sub>2</sub>O, and using 0.1 mol L<sup>-1</sup> instead of 1 mol L<sup>-1</sup> NaOH solution in the third fraction (Likelema, 1980; Wilson, 2008). One-gram soil samples were sequentially extracted into the following P fractions: (i) 1 mol L<sup>-1</sup> NH<sub>4</sub>Cl, pH 7, moderately shaken at 25°C for 1 h, considered the exchangeable fraction (P<sub>NH4Cl</sub>); (ii) 0.11 mol L<sup>-1</sup> NaHCO<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (BD) moderately shaken at 40°C for 30 min, considered P adsorbed by reducible metal hydroxide (P<sub>BD</sub>) and thought to be primarily Fe-bound P; (iii) 0.1 mol L<sup>-1</sup> NaOH moderately shaken at 25°C for 16 h, considered P predominately associated with Al hydroxide and organic P phases, as well as some Fe hydroxide P (P<sub>NaOH-25</sub>); (iv) 0.5 mol L<sup>-1</sup> HCl moderately shaken at 25°C for 16 h, considered to be acid-soluble primary mineral P as apatite P (P<sub>HCl</sub>); (v) 1 mol L<sup>-1</sup> NaOH moderately shaken at 85°C for 24 h, considered to be the refractory and residual P (P<sub>NaOH-85</sub>). Moderate shaking was achieved by placing samples in centrifuge tubes on racks in a Thermo Scientific Precision

Dubnoff shaking water bath (Thermo Scientific, Waltham, MA) and shaking at medium speed for the times noted. The P<sub>NaOH-25</sub> extract was split and an aliquot was analyzed for PO<sub>4</sub> defined by Psenner et al. (1988) as “reactive P” (P<sub>NaOH25r</sub>), using the molybdate-blue spectrophotometric method (Murphy and Riley, 1962). The difference between total P<sub>NaOH-25</sub> and P<sub>NaOH25r</sub> was termed P<sub>NaOH25nr</sub> nonreactive P, which is thought to represent primarily organic P (Psenner et al., 1988; Psenner and Pucsko, 1988). All extractions were centrifuged at 3000 × *g* for 15 min and filtered through Whatman no. 42 filter paper (Whatman Inc., Clifton, NJ). Extractions were then repeated with an agitation time of 1 min to rinse the samples. All fractionation runs contained reagent blanks and sample replication to assure data quality. The symbols used and fractions they represent are summarized in the Appendix. All extracts were analyzed for P, Al, Fe, and Ca by inductively coupled plasma atomic emission spectrometry.

## Exposed and Occluded Apatite

A subset of samples from the BBWM, MP, FEF, LP, and SB were analyzed a second time using a further modification of the Psenner fractionation. This modification sought to gain additional insight into the amount of apatite occluded by the mineral matrix. The initial P<sub>HCl</sub> extraction was followed by drying and pulverization of the sample with mortar and pestle until the entire sample passed through a 250-μm sieve, and then re-extracted with 0.5 mol L<sup>-1</sup> HCl and moderately shaken at 25°C for 16 h (P<sub>HCl-pulv</sub>). All extracts were analyzed for P, Al, and Fe as described above.

## Total Digestions

A subset of 15 soil samples was randomly selected from BBWM, MP, and HB and analyzed to evaluate the efficacy of recovery in the Psenner fractionation by comparing the sum of the sequential Psenner fractions (P<sub>Sum</sub>) to the results of total sample digests (P<sub>HF</sub>). Digestions were performed on 0.25-g samples of air-dry soil using 8 mL of HNO<sub>3</sub> and 2 mL of HF, which were added to the soil in a 20-mL Teflon screw-cap vial. Samples were then gently heated (below boiling) for 8 h and evaporated to near dryness. The same digestion steps were repeated until complete dissolution was achieved. Following dissolution, 5 mL of 8 mol L<sup>-1</sup> HNO<sub>3</sub> was added and evaporated to dryness to drive off any remaining HF. The remaining residue was dissolved in 10 mL of concentrated HNO<sub>3</sub> over gentle heat, cooled, and diluted to 50 mL for analysis (Eaton et al., 1995). Samples were analyzed for total P, Al, and Fe as described above.

## Statistical Analysis

Data were logarithmically transformed to meet the assumptions of normality and constant variance. In instances where logarithmic transformations failed to result in constant variance, weighted least squares (1/variance) was used before ANOVA. Post-hoc pairwise comparisons were made using Tukey's honestly significant difference. Then P<sub>NH4Cl</sub> and P<sub>BD</sub> data required nonparametric analysis by the Kruskal-Wallis test. Comparisons between treated and reference watersheds were calculated using two-sample *t*-tests. Grand mean comparisons between upper and lower B horizons were conducted using two-sample *t*-tests. Regressions between P<sub>Sum</sub> and P<sub>HF</sub> were conducted using a general

linear model; data conformed to the assumptions of normality and variance. Statistical significance was designated at an  $\alpha$  level of 0.05. Statistical analyses were conducted using SYSTAT version 12.0 (Systat Software, Chicago).

## RESULTS AND DISCUSSION

Table 1 shows the means for measures of organic matter (as loss-on-ignition) and the acid–base status of the soils in this study. Mean O horizon pH in  $\text{CaCl}_2$  ranged from 3.02 to 3.42. Upper B horizon pH in  $\text{CaCl}_2$  ranged from 3.35 to 3.79 and increased with depth to a range of 3.77 to 4.33 in the lower B horizon. The loss-on-ignition decreased dramatically from the O horizon to the mineral soil and decreased with depth in the B horizon. The low base saturation in the mineral soil reflects the prevalence of Al on the exchange complex. The narrow range in pH and base saturation in both the forest floor and mineral soils across sites suggests a relatively narrow range in soil acidity common to these cool, temperate forest soils.

The upper B horizon typically best represents the dominant pedogenic processes in these soils. To study soil P fractions in the most pedogenically developed part of the solum, the upper B horizon increment was sampled across all sites to compare fractionation results among watersheds. Mean P, Al, and Fe concentrations from the fractionation analyses for the upper B horizons from all watersheds, excluding the experimentally acidified watersheds (i.e., WB and F3), are given in Table 2. The concentrations of P, Al, and Fe in all fractions were commonly significantly different among the upper B horizons. The  $P_{\text{Sum}}$  concentrations represent the sum of all sequential fractions and should be nearly equivalent to the total soil P. The  $P_{\text{Sum}}$  concentrations ranged fourfold among the six watersheds, from 6  $\text{mmol kg}^{-1}$  at MP to 26  $\text{mmol kg}^{-1}$  at SB. Comparing these differences in  $P_{\text{Sum}}$  to the results in Table 2 for  $P_{\text{HCl}}$ , operationally defined as a measure of primary mineral apatite P, leads us to conclude that the range in  $P_{\text{Sum}}$  was strongly linked to the concentrations of apatite in the parent material. That is, the sites with high  $P_{\text{Sum}}$  tend to have high values of  $P_{\text{HCl}}$  (Table 2). Although deep C horizon materials were not collected at all sites, a few C horizon samples were collected at the BBWM ( $n = 12$ ), LP ( $n = 1$ ), and SB ( $n = 1$ ). The  $P_{\text{HCl}}$  data from SB imply high parent material P concentrations (349  $\text{mmol kg}^{-1}$ ) compared with the BBWM (86  $\text{mmol kg}^{-1}$ ) and LP (38  $\text{mmol kg}^{-1}$ ). These concentrations were reflected in the greater B horizon  $P_{\text{HCl}}$  concentrations at SB and EB relative to LP.

Although there were notable differences in total P concentrations (Table 2) among the six watersheds, the relative distribution of the soil P fractions for any given watershed were remarkably similar. Figure 2 shows the grand mean (all pedons) relative distribution of P, by fraction, for the upper B horizons of all untreated watersheds, which was also relatively the same for any one of the individual sites. The available  $P_{\text{NH}_4\text{Cl}}$  fraction was the lowest concentration, with a mean across all upper B horizons of 0.12  $\text{mmol kg}^{-1}$ . The  $P_{\text{NH}_4\text{Cl}}$  fraction is considered the most biologically available fraction, and low concentrations of

**Table 1. Grand means (all pedons) for selected soil characteristics for the O and upper and lower B horizons. Data from SanClements (2009).**

Watershed	pH( $\text{CaCl}_2$ )	Base saturation	
		%	
O horizon			
East Bear Brook	3.13	87	49
West Bear Brook	3.15	79	33
Hadlock Brook	3.07	83	42
Mud Pond	3.03	88	33
Fernow 3	3.42	65	61
Fernow 4	3.02	84	41
Strengbach	3.31	52	38
Upper B horizon			
East Bear Brook	3.77	17	11
West Bear Brook	3.79	20	7
Hadlock Brook	4.14	13	15
Mud Pond	3.90	7	5
Fenow 3	3.84	6	6
Fernow 4	3.99	8	10
Lesni Potok	3.39	3	16
Strengbach	3.35	7	6
Lower B horizon			
East Bear Brook	4.20	10	7
West Bear Brook	4.31	13	7
Hadlock Brook	4.41	10	19
Mud Pond	4.33	6	7
Fernow 3	3.96	3	4
Fernow 4	4.02	7	8
Lesni Potok	3.77	2	47
Strengbach	3.98	5	4

available P are consistent with the reported low P bioavailability commonly found in the B horizons of acid, Al- and Fe-rich soils of humid temperate forests (Wood et al., 1984; Fernandez and Struchtemeyer, 1985; Yanai, 1992; Sherman et al., 2006). On a percentage basis, the  $P_{\text{NH}_4\text{Cl}}$  fraction contributed only 1% of the  $P_{\text{Sum}}$  in the upper B horizons of these soils, compared with 72% for the largest fraction, which was  $P_{\text{NaOH-25}}$ . The dominance of the  $P_{\text{NaOH-25}}$  fraction (which also contains a large amount of organic P and some Fe-P) relative to the other fractions underscores the importance of Al in P retention. The concentrations of Al and P paralleled each other in their distribution by fraction, following the sequence  $\text{NaOH-25} > \text{NaOH-85} > \text{HCl} > \text{BD} > \text{NH}_4\text{Cl}$ . The distribution of Fe among fractions did not follow the same general pattern as P and Al but occurred in the order  $\text{BD} > \text{NaOH-25} > \text{HCl} > \text{NaOH-85} > \text{NH}_4\text{Cl}$ . The dominance of Fe in the BD fraction demonstrates the ability of the reducing agent to isolate reducible Fe from the metal-hydroxide matrix in the mineral soil and is further reflected in the low  $\text{Al}_{\text{BD}}/\text{Fe}_{\text{BD}}$  ratios, which ranged from 0.023 to 0.11. The operationally defined Al-P fraction, designated here as NaOH-25, contained the second highest molar concentrations of Fe, with  $\text{Al}_{\text{NaOH-25}}/\text{Fe}_{\text{NaOH-25}}$  molar ratios ranging from 3 to 7. This suggests that, although Al concentrations dominate in the NaOH-25 fraction, Fe is an important component of this fraction. Therefore, the

**Table 2. Distribution of P, Al, and Fe by fraction (NH<sub>4</sub>Cl, labile P; BD, reducible Fe P; NaOH-25, Al- and some Fe-P; HCl, exposed apatite P; NaOH-85, refractory and residual P; Sum, sum of sequential Psenner fractions; NaOH-25r, reactive Al-P; NaOH-25nr, nonreactive Al-P) and watershed for upper B horizon samples. The Al and Fe values represent the concentrations of Al and Fe extracted along with P in each fraction.**

Watershed	NH <sub>4</sub> Cl	BD	NaOH-25	HCl	NaOH-85	Sum	NaOH-25r	NaOH-25nr
mmol kg <sup>-1</sup>								
<u>Phosphorus</u>								
Hadlock Brook	0.165abcd†	0.04abcd	8.9abcd	1.72	2.3	13.2a	0.98a	7.96abc
Mud Pond	0.04aef	0.07efgh	4.3aefg	0.55	1.3	6.3bcd	1.01bcd	3.30adefg
Fernow 4	0.04bgh	0.09aeijk	8.6ehij	0.22a	2.1a	11.1befg	1.73ce	6.89dhi
Strengbach	0.29cegij	2.75bfilm	19.7bfhk	1.68a	1.7b	26.2aceh	10.12abefg	9.55ej
Lesni Potok	0.09i	0.63cgjl	4.2cikl	0.58	1.1ab	6.7fhi	2.37df	1.89bfhjk
East Bear	0.06dfhj	0.70dhkm	15.7dgjl	0.79	1.8	19.1dgi	1.60g	14.11cgik
Mean	0.12	0.72	10.2	0.92	1.7	13.8	2.98	7.29
<u>Aluminum</u>								
Hadlock Brook	0.20ab	8.1abc	506abcd	265abc	120a	901ab		
Mud Pond	0.05acd	6.6de	207aef	98	110b	423		
Fernow 4	0.28e	3.9af	190bgh	38a	241abcde	475cd		
Strengbach	2.28f	4.6gh	102ci	37bd	157c	304ace		
Lesni Potok	0.09bcefg	1.3bdgi	66degk	41ce	151d	260bdf		
East Bear	0.44dg	20.8cephi	456fhik	83de	100e	661ef		
Mean	0.56	7.6	255	94	147	505		
<u>Iron</u>								
Hadlock Brook	0.07a	111abc	85abcd	81abc	0.22a	278abcd		
Mud Pond	0.05b	61e	39aef	46	0.20b	147ae		
Fernow 4	0.09c	64afg	28bghi	23ad	0.19c	117bfg		
Strengbach	2.50abcde	40bfh	14cgj	18be	0.78d	77cfh		
Lesni Potok	0.29d	60ci	9dehk	42cef	1.60abcde	115di		
East Bear	0.23e	205eghi	143fijk	67df	0.34e	416eghi		
Mean	0.54	91	53	46	0.6	192		

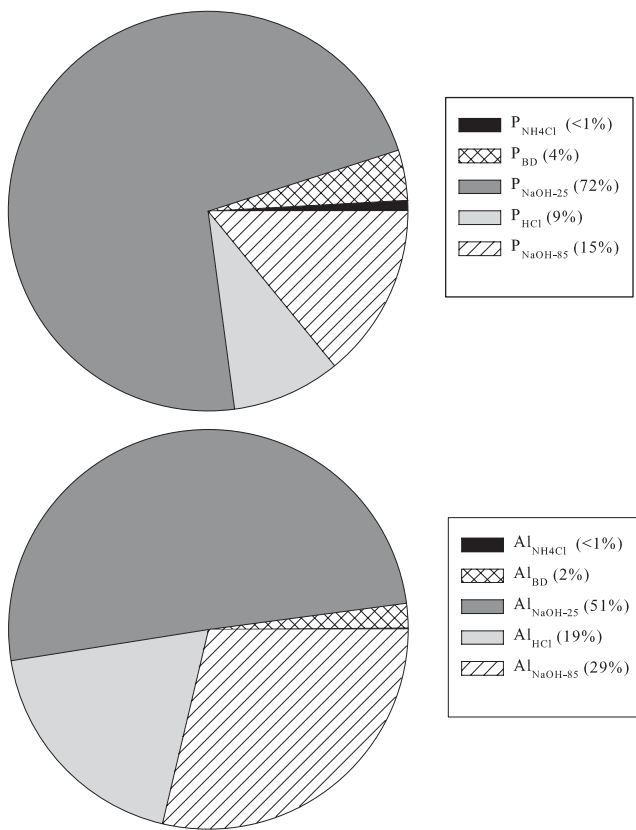
† Data followed by the same letter are significantly different among watersheds.

results must be carefully considered given the operational nature of the fractionation methods. Organic P is the dominant form of P in the NaOH-25 fraction within soils from all watersheds except LP. Upper B horizon grand mean molar ratios of Al<sub>Sum</sub>/P<sub>Sum</sub> and Fe<sub>Sum</sub>/P<sub>Sum</sub> ranged from 11 to 69 and 3 to 23, respectively. The molar ratio Al<sub>Sum</sub>/Fe<sub>Sum</sub> ranged from 1.6 to 4.1 for the upper B horizon mineral soils. The higher Al concentrations magnify the importance of Al in P sorption in these soils. Correlations between P, Al, and Fe for the upper B horizons were consistent with the evidence for a stronger correlation for P<sub>Sum</sub> with Al<sub>Sum</sub> ( $r = 0.55$ ) than with Fe<sub>Sum</sub> ( $r = 0.16$ ) in the soils.

The transect design and depth sampling used in this research allowed us to study spatial patterns of P fractionation. Evidence of consistent or incremental spatial patterns with distance from the stream were inconclusive and spatial patterns in the fractionation results varied widely among watersheds, and sometimes between transects within a single watershed. Therefore, there seems to be no evidence for patterns of P fractions in soils with distance upslope from the streams. Despite this overall variability, generalizations can be made about chemical associations among elements. There was a clear spatial association between P and Al, with a lesser but still evident association between Fe and P, and there were dramatic increases in variability in the data with proximity to the stream for the B horizon P, Al, and Fe fraction concentrations along nearly all transects.

Primary apatite is the original source of soil P that, once released, typically is retained in soils by sorption on secondary Al and Fe hydroxides or is biologically immobilized. The initial HCl extraction in this fractionation scheme is thought to extract exposed apatite P. In this study, we added an additional step to the fractionation scheme that included pulverization of the mineral grains after the initial HCl extraction, followed by an additional soil extraction with HCl. The additional P recovered derived from apatite that was occluded inside mineral grains (Syers et al., 1967; Nezat et al., 2007). This protected fraction accounted for the  $59 \pm 3.6\%$  of the total apatite P ( $P_{\text{HCl}} + P_{\text{HCl-pulv}}$ ) in the soils from the BBWM, MP, F4, LP, and SB. SanClements et al. (2009) similarly found that  $49 \pm 7.0\%$  of the total apatite P was in the occluded phase in the lower B horizon of the HB watershed. The occluded apatite P pool is probably important for long-term ecosystem P supply and represents a significant pool of P that persists in these soils for some time beyond that of the exposed apatite P. The literature also suggests that some of the occluded apatite P could be more immediately available to forest vegetation through extraction and uptake by ectomycorrhizal fungi (Wallander, 1999; van Schöll et al., 2008). Understanding the  $P_{\text{HCl-pulv}}$  pool is important to understanding P cycling and supply in these forests.

We compared the sum of the Psenner sequential fractions with a total soil digestion procedure ( $P_{\text{HF}}$ ) to evaluate P recov-

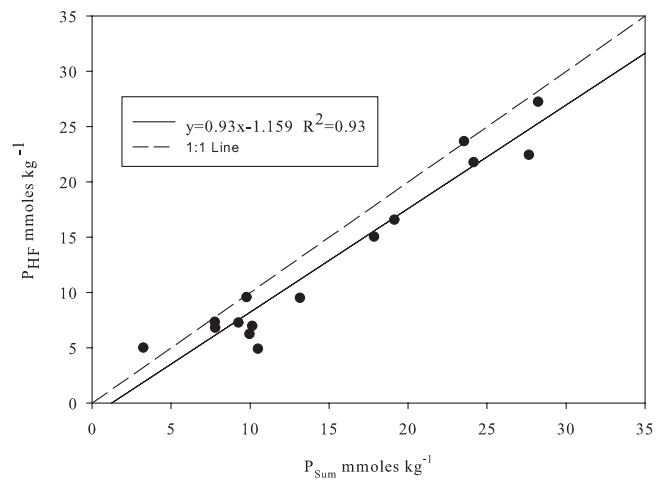


**Fig. 2.** Distribution of P and Al by fraction on a percentage basis ( $P_{\text{NH}_4\text{Cl}}$ , labile P;  $P_{\text{BD}}$ , reducible Fe P;  $P_{\text{NaOH-25}}$ , Al- and some Fe-P;  $P_{\text{HCl}}$ , exposed apatite P;  $P_{\text{NaOH-85}}$ , refractory and residual P). These data are upper B horizon grand means on a mass basis for all watersheds in this study excluding the treated watersheds at West Bear Brook Watershed (WB) and Fernow Experimental Forest (F3).

ery. Figure 3 shows the relationship between these two measures of total P and how they compared with the 1:1 line. The mean recovery of  $P_{\text{Sum}}$  was 123% of  $P_{\text{HF}}$  yet there was a considerable range in recovery from 64 to 212%. Despite this variation between measures of total soil P, regression analysis between  $P_{\text{Sum}}$  and  $P_{\text{HF}}$  showed that these two measures of total soil P were highly correlated (Fig. 3). The significant positive correlation between the sum of the sequential fractionations and the total digestion procedure suggests that P is conserved through the fractionation and  $P_{\text{Sum}}$  is a reasonable measure of total soil P.

### Effects of Experimental Acidification

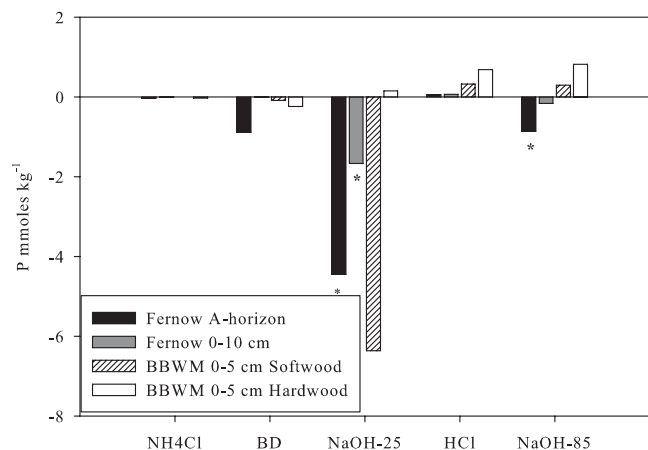
Two of the study sites (BBWM and FEF) included paired, whole-watershed acidification experiments with a 20-yr history of treatments at the time of this writing. Experimental acidification at both sites has led to increased export of soil base cations (Fernandez et al., 2003; Edwards et al., 2002). At BBWM, it was demonstrated that as base cationic buffering was depleted in the soils, Al buffering became the dominant acid buffering mechanism, with consequent mobilization and export of soil Al to the stream (Fernandez et al., 2003; Norton et al., 2004). Declining stream base cation concentrations at the BBWM have been accompanied by increased concentrations of dissolved Al in the treated WB from approximately  $5 \mu\text{mol L}^{-1}$  in 1989 to concen-



**Fig. 3.** The relationship between the sum of the sequential Psenner fractions ( $P_{\text{Sum}}$ ) and the results of total sample digests ( $P_{\text{HF}}$ ) from replicates in a subsample of soils from this study.

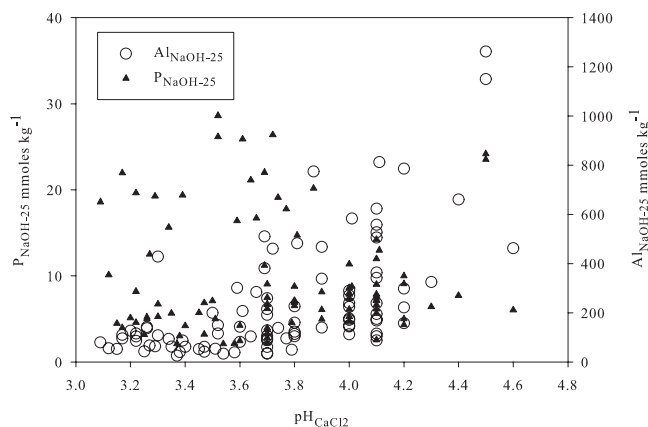
trations commonly exceeding  $40 \mu\text{mol L}^{-1}$  after two decades of treatment. During the same period, increases in episodic stream exports of particulate acid-soluble Al were even greater, ranging up to  $520 \mu\text{mol L}^{-1}$  Al in WB compared with  $185 \mu\text{mol L}^{-1}$  in the reference EB (Norton et al., 2004). Subsequent increases in total P (mostly as acid-soluble particulate) occurred in the WB stream during high-discharge events, with increases of up to  $100 \mu\text{g L}^{-1}$  (Norton et al., 2004; Reinhardt et al., 2004) despite base-flow P concentrations commonly being below analytical detection ( $<0.5 \mu\text{g L}^{-1}$ ). Stream water concentrations of particulate Fe increased during high flow in both the treated and reference watersheds at the BBWM, suggesting that Fe has not responded as quickly as Al to long-term experimental acidification. Similar evidence for chemical response during high flow has been seen in the treated watershed at FEF (Laird, 2006).

Evidence of Al mobilization with chronic experimental acidification at BBWM led to the hypothesis that P associated with these secondary Al phases might also be mobilized, potentially leading to a transient period of increased P availability and ultimately net P depletion in the soil. To examine the evidence for this hypothesis, we compared soil P, Al, and Fe fractions from the reference and experimentally acidified watersheds at BBWM and FEF. Figure 4 depicts differences in soil P concentrations by fraction between the treated and reference watersheds at BBWM and FEF. The  $P_{\text{NaOH-25}}$  fraction, which is predominately P associated with secondary soil Al and organic phases, dominated the pool of P in these soils at both sites and appeared most susceptible to mobilization by acidity. As acidification mobilized secondary Al, it appears that P associated with this Al was simultaneously mobilized and concentrations decreased with time. Both the A horizon and 0- to 10-cm increment of the B horizon in F3 had significantly lower concentrations of  $P_{\text{NaOH-25}}$  relative to the reference watershed F4 (Fig. 4). Experimental acidification on F3 at FEF was associated with a 30% lower concentration of  $P_{\text{NaOH-25}}$  in the A horizon and a 20% lower concentration of  $P_{\text{NaOH-25}}$  in the 0- to 10-cm increment of the B horizon (Fig. 4). In both instances, where significantly lower concentrations of



**Fig. 4.** Differences (treated minus reference) between P fraction concentrations ( $\text{NH}_4\text{Cl}$ , labile P; BD, reducible Fe P; NaOH-25, Al- and some Fe-P; HCl, exposed apatite P; NaOH-85, refractory and residual P) by site (Fernow Experimental Forest), and by site and forest type (The Bear Brook Watershed in Maine [BBWM]). Values below the line suggest decreased concentrations associated with the experimental treatments. Asterisks indicate significant differences between treated and reference watersheds at  $\alpha = 0.05$ . The difference shown for BBWM softwoods was significant at  $\alpha = 0.20$ .

$\text{P}_{\text{NaOH-25}}$  occurred, they were accompanied by significantly lower concentrations of  $\text{Al}_{\text{NaOH-25}}$  in the treated watersheds. The  $\text{Fe}_{\text{NaOH-25}}$  decreased by 10% in the A horizon with treatment, and increased by 17% in the 0- to 10-cm increment of the B horizon. The A horizon in F3 also exhibited a significant decrease in the  $\text{P}_{\text{NaOH-85}}$  fraction. This fraction is thought to contain more highly crystalline Al hydroxide and associated P. The persistence of this fraction through previous steps, and the characteristics of the extract, indicate the presence of recalcitrant Al hydroxide. The mean concentrations in the  $\text{P}_{\text{NaOH-85}}$  extract were 151 and 0.5  $\text{mmol kg}^{-1}$  for Al and Fe, respectively, demonstrating that the majority of the P was associated with Al. The 0- to 10-cm increment of the B horizon in F3 was not significantly different in  $\text{P}_{\text{NaOH-85}}$  (Fig. 4), which may reflect the limited exposure of the upper B horizons to the treatment relative to A horizons (Bache, 1984; Pellerin et al., 2002; Norton et al., 2006). The  $\text{P}_{\text{NaOH-25}}$  fraction from the 0- to 5-cm increment in WB softwoods was 45% lower than the  $\text{P}_{\text{NaOH-25}}$  fraction in the EB ( $P = 0.20$ ) (Fig. 4). The concentrations of  $\text{Al}_{\text{NaOH-25}}$  and  $\text{Fe}_{\text{NaOH-25}}$  were numerically lower, but not significantly, in the treated watershed by 22 and 28%, respectively. The similar increases in stream Fe concentrations during high flow in both the EB and WB (Reinhardt et al., 2004) suggest that export of Fe-associated P would be similar in both watersheds but undetectable in these experimental data. As in-stream concentrations of Fe did not change with treatment but did increase at high flow, the difference in  $\text{Fe}_{\text{NaOH-25}}$  could reflect a preexisting difference between the EB and WB. Alternatively, Fe mobilization could be more controlled by redox (and thus flow) than by small changes in pH. Furthermore, the small amount of  $\text{P}_{\text{BD}}$  relative to  $\text{P}_{\text{NaOH-25}}$  in the soils of the reference watershed indicates that little of the mobilized P was probably associated with Fe hydroxide.



**Fig. 5.** The Al/P ratio from the NaOH-25 fraction ( $\text{Al}_{\text{NaOH-25}}/\text{P}_{\text{NaOH-25}}$ ) plotted against pH from all upper B horizon increments analyzed (HB, Hadlock Brook; MP, Mud Pond; F3, Fernow Experimental forest, treated; F4, Fernow Experimental Forest, reference; SB, Strengbach; LP, EB, East Bear Brook Watershed; WB, West Bear Brook Watershed). The Al and P from the NaOH-25 fraction are considered to be extracted from Al hydroxide or P associated with Al hydroxide and organic P phases, as well as some Fe hydroxide P.

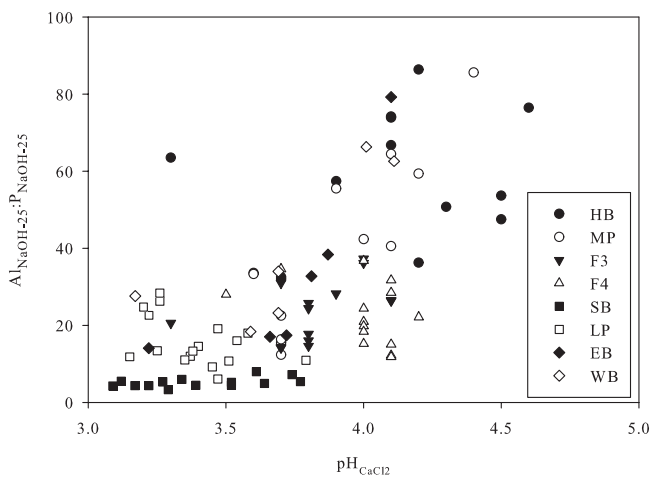
Experimental acidification did not result in lower  $\text{P}_{\text{NaOH-25}}$  (Fig. 4) or  $\text{Al}_{\text{NaOH-25}}$  in the soils from the 0-a to 5-cm increment of the B horizons under the hardwood canopy at BBWM. Although differences in the mean pH were not sufficient to explain the mobilization of  $\text{P}_{\text{NaOH-25}}$  and  $\text{Al}_{\text{NaOH-25}}$  from soils under hardwoods in the treated watersheds at FEF but not BBWM (Table 1), the soils from FEF (i.e., F3) appear to have exhibited a greater and more uniform difference in pH with treatment compared with BBWM (i.e., the WB) (Fig. 5). This greater apparent decrease in pH with treatment at FEF could reasonably result in the increased mobilization of Al under the F4 hardwoods, while the more variable and less evident pH effects under the WB hardwoods might not have been sufficient to mobilize  $\text{Al}_{\text{NaOH-25}}$  and  $\text{P}_{\text{NaOH-25}}$  from those soils.

Despite differences in forest type response by site, these data lend support to the hypothesis that chronic acidification can mobilize P due to acidified solutions moving through shallow soil flow paths where Al hydroxide is dissolved, thereby mobilizing the associated P.

### Linkages between Soil Phosphorus and Phosphorus Availability to Biota

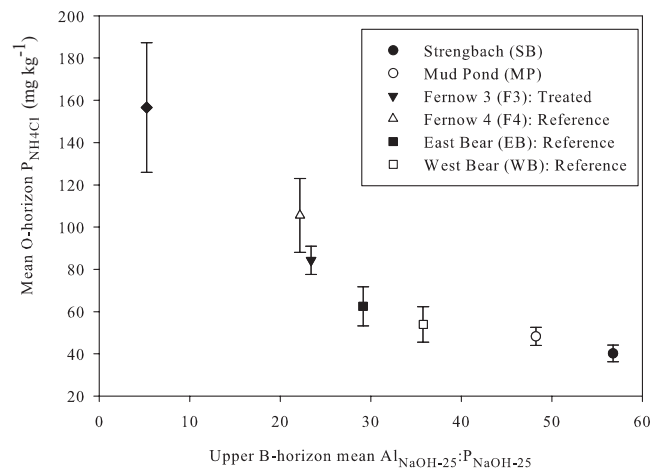
Kopáček et al. (2005) investigated geochemical controls on water column P concentrations in lakes in the Czech Republic and demonstrated the dominance of Al in controlling water column P availability and sediment P sorption. They used similar chemical fractionation methods as used in this study, except that in the first extraction for available P they used water rather than  $\text{NH}_4\text{Cl}$ , and  $1 \text{ mol L}^{-1}$  NaOH, instead of  $0.1 \text{ mol L}^{-1}$  NaOH in the third extraction. They used the proportions of sediment Al, Fe, and P as predictors of water column P concentrations because Al and Fe exert such strong controls on P mobility in sediments. Their results showed that in sediments with a molar ratio of  $\text{Al}_{(\text{H}_2\text{O}+\text{BD}+\text{NaOH-25})}/\text{Fe}_{(\text{H}_2\text{O}+\text{BD}+\text{NaOH-25})} > 3$  and  $\text{Al}_{\text{NaOH-25}}/\text{P}_{(\text{H}_2\text{O}+\text{BD})} > 25$ , anox-





**Fig. 6.** The P and Al from the NaOH-25 fractions ( $P_{\text{NaOH-25}}$  and  $Al_{\text{NaOH-25}}$ , respectively) as a function of pH for all upper B horizon samples in this study. The NaOH-25 fraction is considered to be extracted from Al hydroxide or P associated with Al hydroxide and organic P phases, as well as some Fe hydroxide P.

ia no longer resulted in P release from sediments. They interpreted this to mean that Al will dominate the P chemistry in lake sediments when sediment Al concentrations significantly exceed Fe or P concentrations. This is particularly important during periods of anoxia when Fe-bound P would otherwise be released to the water column but is irreversibly adsorbed by Al in the sediments (Norton et al., 2006). In this study of soil P fractions, we applied a similar approach to evaluating the interaction of Al and Fe with P, but substituted the  $\text{NH}_4\text{Cl}$  fraction for the  $\text{H}_2\text{O}$  fraction used by Kopáček et al. (2005), as described above. The mean  $Al_{(\text{NH}_4\text{Cl}+\text{BD}+\text{NaOH-25})}/Fe_{(\text{NH}_4\text{Cl}+\text{BD}+\text{NaOH-25})}$  ratios for the upper B horizons in this study ranged from 1.0 at LP to 2.6 at HB. These were all below the threshold of 3 proposed by Kopáček et al. (2005) for conditions that would abiotically immobilize P in lake sediments. By itself, this could suggest a greater potential for P mobility if these soils were exposed to reducing conditions. It is also important to note that these ratios may have been influenced by our choice of  $0.1 \text{ mol L}^{-1}$  NaOH as opposed to  $1 \text{ mol L}^{-1}$  NaOH. The ratio of  $Al_{\text{NaOH-25}}/P_{(\text{NH}_4\text{Cl}+\text{BD})}$  ranged from 34 to 2483 in our soils data, however, greatly exceeding Kopáček's threshold of 25 for P retention by Al in sediments. The somewhat lower  $Al_{(\text{H}_2\text{O}+\text{BD}+\text{NaOH-25})}/Fe_{(\text{NH}_4\text{Cl}+\text{BD}+\text{NaOH-25})}$  ratio tells us that these soils have significant illuvial accumulations of both Al and Fe, consistent with Spodosol development. The metal ratio tells us nothing about P concentrations, however, and it is evident from the ratios of Al to P (i.e.,  $Al_{\text{NaOH-25}}/P_{(\text{NH}_4\text{Cl}+\text{BD})}$ ), which ranged from 34 to 2483, and Fe to P (i.e.,  $Fe_{\text{NaOH-25}}/P_{(\text{NH}_4\text{Cl}+\text{BD})}$ ), which ranged from 24 to 338, that these soils have low available P relative to the concentrations of Al and Fe available for P retention. If these soils are subject to periods of anoxia during wet seasons, we expect some Fe reduction that would potentially mobilize Fe-fixed P. We hypothesize that P mobilized from Fe phases under reducing conditions would probably be irreversibly adsorbed by secondary Al phases because of the relatively high Al concentrations in these soils. This is consistent with evidence from soil solution and stream studies showing that little P escapes from



**Fig. 7.** The relationship between mineral soil mean Al/P ratio from the NaOH-25 fraction ( $Al_{\text{NaOH-25}}/P_{\text{NaOH-25}}$ ) and mean O horizon labile P ( $P_{\text{NH}_4\text{Cl}}$ ) for all watersheds excluding Lesni Potok, which did not have an O horizon. The NaOH-25 fraction is considered to be extracted from Al hydroxide or P associated with Al hydroxide and organic P phases, as well as some Fe hydroxide P.

these acid, forested watersheds through leaching or stream flow, even after harvest (Wood et al., 1984; Yanai, 1992, 1998; Reinhardt et al., 2004; Norton et al., 2006), and P availability is limited (Wood et al., 1984; Yanai, 1992).

Results for sites that were experimentally acidified showed evidence of Al mobilization, with subsequent changes in soil P. Therefore, we explored the relationships between soil acidity and Al or P accumulations in the suite of watersheds from this study. Because the NaOH-25 fraction appeared to be the primary chemical phase that responded to experimental acidification, we used the ratio  $Al_{\text{NaOH-25}}/P_{\text{NaOH-25}}$  to test this hypothesis.

The mobilization of P in soils by acid solutions appears to be driven largely by the mobilization of Al rather than Fe, the latter of which has a lower solubility under acidic conditions (Drever, 1997). Figure 6 shows the relationship between the soil pH in  $\text{CaCl}_2$  and the  $Al_{\text{NaOH-25}}/P_{\text{NaOH-25}}$  ratio for the upper B horizons from all pedons in this study, including the experimentally acidified watersheds. The results show that as the pH increased from 3.1 to 4.6, the  $Al_{\text{NaOH-25}}/P_{\text{NaOH-25}}$  ratio increased from approximately 3 to 86. Figure 6 shows the actual  $Al_{\text{NaOH-25}}$  and  $P_{\text{NaOH-25}}$  concentrations in these soils, with the trends in the data indicating that the relationship between the pH and  $Al_{\text{NaOH-25}}/P_{\text{NaOH-25}}$  ratio was driven more by decreasing  $Al_{\text{NaOH-25}}$  concentrations than by increasing  $P_{\text{NaOH-25}}$  concentrations as the pH decreased. We hypothesize that the pattern of Al and P chemistry across this pH range results from lower rates of illuvial Al hydroxide accumulation in the B horizons at lower pH due to conditions favoring higher Al solubility (Drever, 1997; Norton et al., 2006). The higher anion adsorption capacity of Al hydroxide at the lower pH, however, would increase the P retention through an increased anion adsorption capacity due to greater protonation of Al hydroxide (Mattingly, 1975; Kana and Kopáček, 2005; Navrátil et al., 2008). This effect would be consistent with the lower  $Al_{\text{NaOH-25}}/P_{\text{NaOH-25}}$  ratio at lower pH values (Fig. 6) and the tendency for higher  $P_{\text{NaOH-25}}$  at low-

er pH values (Fig. 5). These data suggest that, across this population of forest soils, pH controls the precipitation of Al hydroxide and the ability of these soils to adsorb P.

Although this study was not designed to investigate P dynamics in both abiotic and biotic ecosystem compartments, the results offer insights into possible linkages between soil chemical properties and the biocycling of P. Figure 7 shows the relationship between the mean upper B horizon  $Al_{NaOH-25}/P_{NaOH-25}$  ratio and the mean O horizon  $P_{NH_4Cl}$  for all watersheds in this study, including the experimentally acidified watersheds, but excluding LP where there was no O horizon. We used  $1 \text{ mol L}^{-1} NH_4Cl$  extractable P in the O horizon as an operationally defined measure of labile or loosely bound P (Chang and Jackson, 1957; Hieltjes and Liklema, 1980). Means are presented in Fig. 7 because subsoil fine root P uptake can involve a large volume of mineral soil that would transfer P to the forest canopy, to be returned to the soil surface through litterfall via biocycling. This mechanism of transfer from subsoils to surface O horizons can uncouple the linkage between surface horizons and the mineral soil immediately below in the individual pedon data.

Mean O horizon  $P_{NH_4Cl}$  decreased from  $156.6 \text{ mg kg}^{-1}$  at an  $Al_{NaOH-25}/P_{NaOH-25}$  ratio of 5.0 to  $40.2 \text{ mg kg}^{-1}$  at an  $Al_{NaOH-25}/P_{NaOH-25}$  ratio of 56 (Fig. 7). There was some indication that P was increasingly labile below an  $Al_{NaOH-25}/P_{NaOH-25}$  ratio of approximately 35. The highest concentrations of O horizon P occurred at sites with the lowest  $Al_{NaOH-25}/P_{NaOH-25}$  ratios (Fig. 6 and 7), consistent with the hypothesis that mineral soil  $Al_{NaOH-25}/P_{NaOH-25}$  reflects Al controls on P availability to roots, which is ultimately expressed in O horizon  $P_{NH_4Cl}$  concentrations through biocycling. Figure 6 shows that many of the lowest  $Al_{NaOH-25}/P_{NaOH-25}$  ratios in the upper B horizons occurred at lower pH values. Figure 7 also shows evidence for greater O horizon available-P concentrations at lower  $Al_{NaOH-25}/P_{NaOH-25}$  ratios, suggesting that lower mineral soil pH values in these ecosystems may result in greater P availability.

Foliar chemistry evidence from the whole-watershed acidification experiment at BBWM suggests that acidification could lead to transient increases in P availability. Elvir et al. (2005) demonstrated significant but annually inconsistent increases in foliar P concentrations in American beech and sugar maple on the treated watershed compared with the reference watershed at BBWM. These changes in foliar P concentrations could also have resulted from increased litterfall and P mineralization due to an ice storm in 1998. Similarly, Rustad (unpublished data, 2007) studied fine root dynamics at the BBWM and found evidence for increased P concentrations in live roots of <1 and 1 to 6 mm in diameter on the treated watershed. The evidence from soil and tree tissue chemistries supports the idea that experimental acidification of the mineral soils increases the bioavailability of P, in association with increased Al mobilization, that persists for an undetermined period of time.

## CONCLUSIONS

This study highlights the importance of Al in controlling P chemistry across a suite of acidic soils under humid, temperate forests. The results suggest that Al controls P accumulation, and that Al dynamics govern P mobility and biological availability. There is evidence that there are definable stoichiometries between Al and P that can be used to evaluate the status of P cycling in these forested ecosystems and that this evidence appears to be robust across both reference and experimentally acidified soils in these watersheds. Soils in the reference watersheds might be expected to persist in their current dynamic equilibrium for long time periods. Soils from the experimentally acidified watersheds could show initial responses such as P mobilization and a transient increase in P bioavailability. It is expected that this increase would not persist because chronic experimental acidification depletes more labile P-containing phases with time to achieve a new dynamic equilibrium. We would expect, however, that a legacy of this period of P mobilization would persist for some time after the geochemical sources of labile P are depleted due to biocycling in the ecosystem.

The fractionation scheme described in this research was useful in evaluating the operationally defined phases of soil P and produced surprisingly similar relative distributions among the fractions at all of the study watersheds. Absolute concentrations of the P fractions varied considerably among the watersheds, with absolute concentration differences attributable to differences in parent material (till or bedrock) P concentrations. The chemical fraction of P associated primarily with secondary Al and organic phases was the dominant fraction of P and also appeared to be the most responsive to experimental acidification. These results provide insight into mechanisms of P retention in these forest soils, the importance of pH in defining the manner in which Al governs P dynamics, and insight into the complexity of P cycling in response to environmental change.

## APPENDIX

### Symbols and Generic Names for Phosphorus Fractions

$NH_4Cl$	labile P
BD	reducible Fe P
NaOH-25	Al- and some Fe-P
NaOH-25r	reactive Al-P
NaOH-25nr	nonreactive Al-P
HCl	exposed apatite P
HCl-pulv	occluded apatite P
NaOH-85	refractory and residual P

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