

Chemical Changes Induced by pH Manipulations of Volcanic Ash-Influenced Soils

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Abstract

Data from volcanic ash-influenced soils indicates that soil pH may change by as much as 3 units during a year. The effects of these changes on soil chemical properties are not well understood. Our study examined soil chemical changes after artificially altering soil pH of ash-influenced soils in a laboratory. Soil from the surface (0-5 cm) and subsurface (10-15 cm) mineral horizons were collected from two National Forests in northern Idaho. Soil collections were made from two undisturbed forest stands, a partial cut, a natural bracken fern (*Pteridium aquilinum* [L.] Kuhn) glade, an approximately 30-year-old clearcut invaded with bracken fern, and a 21-year-old clearcut invaded with western coneflower (*Rudbeckia occidentalis* Nutt.). Either elemental sulfur (S) or calcium hydroxide ($\text{Ca}(\text{OH})_2$) were added to the soil to manipulate pH. After 90 days of incubation, pH ranged from 3.6 to 6.1 for both National Forests and all stand conditions. Total C, total N, and extractable base cations (Ca, Mg, and K) were generally unaffected by pH change. Available P increased as pH dropped below 4.5 for both depths and all soil types. Nitrate was highest at pH values greater than 5.0 and decreased as pH decreased indicating that nitrification is inhibited at lower pH. Contrary to nitrate, potentially mineralizable N increased as pH declined. Total acidity and exchangeable aluminum increased exponentially as pH decreased, especially in the uncut and partial cut stands. Data from this laboratory study provides information on the role of pH in determining the availability of nutrients in ash-cap soils.

Introduction

In north-central Idaho, some forests are characterized by conifer regeneration problems despite favorable climatic conditions (udic moisture and frigid soil temperature regimes). Forest stands at mid-elevations are most at risk after timber harvest or other disturbance because they are quickly invaded by bracken fern (*Pteridium aquilinum* [L.] Kuhn), western coneflower (*Rudbeckia occidentalis* Nutt.), and pocket gophers (*Thomomys talpoides*). These sites are collectively known as the Grand Fir Mosaic (GFM) and are named for the dominant conifer, grand fir (*Abies grandis* [Doug]. ex D. Don] Lindl.), that occurs in a mosaic pattern with shrub and forb communities (Ferguson 1991a; Ferguson and others, this proceedings).

Timber harvesting began in the GFM in the 1960s and it soon became evident that regeneration problems existed. Woody vegetation is still infrequent on many of these sites 30 years after clearcutting, even with repeated plantings (Ferguson and Adams 1994). Clearcut stands were quickly invaded by forbs (predominately bracken fern and western coneflower) and rodents. The allelopathic potential of both bracken fern and western coneflower has been well documented (Stewart 1975; Ferguson and Boyd 1988; Ferguson 1991b). In addition to invading forbs, pocket gophers also cause substantial seedling mortality (Ferguson and others 2005). Competition for light, moisture, and nutrients within the GFM is high. While the combination of competition, pocket gophers, and allelopathy contribute to the arrested state of secondary succession (Ferguson and Adams 1994), these factors do not appear to entirely explain reforestation failures.

Soils throughout the GFM are strongly influenced by volcanic ash in the surface horizons. The ash was deposited approximately 7,700 years ago when Mt. Mazama erupted (Zdanowicz 1999). Volcanic ash-influenced soils have unique parent materials and secondary mineral assemblages that, in general, are not as well understood as those in other mineral soils. Volcanic ash-influenced soils are classified as either *allophanic* or *nonallophanic*, depending on the relative abundance of organic matter and inorganic short-range-order minerals (Shoji and others 1993). Nonallophanic soils have more organic matter, lower pH, higher levels of KCl-extractable aluminum (Al), and lower levels of calcium (Ca) relative to allophanic soils (Shoji and others 1993). Low soil pH may increase concentrations of extractable (potentially plant available) Al, leading to Al toxicity to woody vegetation (Dahlgren and others 1991). Clearcutting and intensive utilization (whole tree harvesting) of forest biomass may accelerate soil acidification processes (Ulrich and others 1980; Nosko and Kershaw 1992). In addition to acidification from harvest activities, vegetation-induced acidification appears to occur under bracken fern and western coneflower plant communities (Johnson-Maynard and others 1997). These acidified volcanic ash-influenced soils, which are high in exchangeable Al, may release Al into soil solution at levels toxic to woody vegetation (Anderegg and Naylor 1988).

Two soil factors have become a concern in GFM forest openings. First, soil pH drops below 5.0 after harvest operations and the subsequent invasion of bracken fern and western coneflower (figs. 1 and 2). At this pH, Al can reach toxic levels and low soil pH can inhibit growth of some seedling species (Nosko and Kershaw 1992). Second, there are seasonal pH fluctuations of 2-3 pH units that are not typically found in bulk mineral soil unless heavily impacted by acid rain or, occasionally, harvest activities (Mroz and others 1985; Brais and others 1995; Alewell and others 1997). Winter pH values average around 6, but drop below 4 during the growing season. These seasonal pH fluxes could be correlated with inputs of acid litter from bracken fern and western coneflower, increasing root respiration during the growing season, or decreases in soil moisture content. In addition, these two species likely take up high amounts of nutrients from the soil, which may also contribute to acid conditions (Gilliam 1991). Many factors influence forest soil pH (for example, precipitation, nutrient exchange, and soil age), but harvest activity can particularly influence it (Staaf and Olsson 1991). Although forest harvesting can lower pH, subsequent invasion by bracken fern and western coneflower appears to contribute to and maintain low pH relative to undisturbed forest soils.

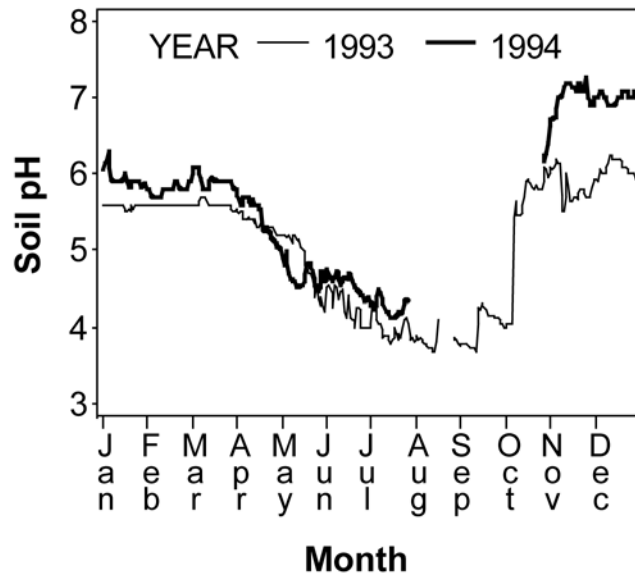


Figure 1—Average soil pH at 2.5 cm for the Nez Perce National Forest coneflower-invaded clearcut (from Ferguson and Byrne 2000). The bold line is 1994, which was a dry growing season. The thin line is 1993, which was a wet growing season. Discontinuous parts of the line are from removal of the pH probe during the driest part of the growing season. Soil pH at this site was assessed *in situ* using pH probes (model 613, IC controls Orangeville, Ontario, Canada) buried 2.5 cm below the mineral soil surface.

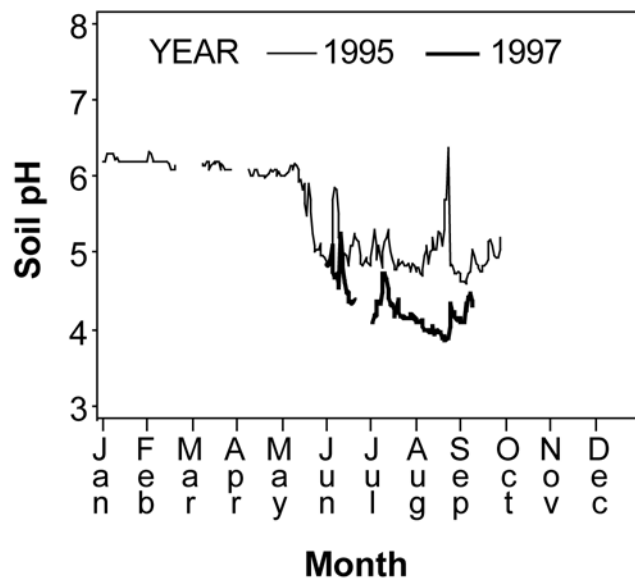


Figure 2—Average soil pH at 2.5 cm for the Clearwater National Forest fern-invaded clearcut (unpublished data collected as described in Ferguson and Byrne 2000). The bold line is 1997 and the thin line is 1995.

The slow forest regeneration process in the GFM has decreased management options for fuel reductions and biomass production, biodiversity of native flora and fauna, and aesthetic values in and near these areas. Low soil pH and its cyclic nature over a growing season may be altering soil chemistry, nutrient cycling processes, and preventing establishment of woody vegetation. Consequently, our objective was to artificially alter pH of ash-influenced forest soils from the GFM by additions of sulfur (S) or calcium hydroxide (Ca(OH)₂) to better evaluate potential *in situ* chemical changes within these soils.

Study Site Description

Two study sites, one on the Clearwater National Forest and one on the Nez Perce National Forest of north-central Idaho, were selected to provide a north/south range of plant community cover types for soil collection. There are thicker deposits of volcanic ash in the northern part of the GFM where these soils are classified as Andisols. Inceptisols dominate in the southern part of the GFM where ash deposits are thinner and more highly mixed. Bracken fern dominates forb communities in the northern part of the GFM and western coneflower dominates in the southern part, although both species occur together throughout the GFM. Table 1 lists study site locations, vegetation types, and soil classifications.

Clearwater National Forest soil samples were collected in 1994 near Eagle Point (elevation 1,400 m, eastern aspect, 20 percent slope, T40N, R7E, S35). The dominant soil feature of this study area is approximately 60 cm of Mt. Mazama volcanic ash underlain with colluvium or residuum derived from fine-grained igneous rock. To assess the importance of vegetation community structure, soil samples were collected from adjacent areas with similar slope, aspect, and parent material, but different vegetation cover. Soil samples were collected from the undisturbed forest (46 m² ha⁻¹ basal area of overstory), a partial cut (approximately 30 m² ha⁻¹ of overstory remaining), a naturally occurring bracken fern glade (present when the adjacent areas were harvested), and a ~30-year-old bracken fern-invaded clearcut (invaded by bracken fern and western coneflower after harvesting between 1965 and 1968).

Nez Perce National Forest soil samples were collected in 1994 at Dogleg (elevation 1,740 m, southern aspect, 5 percent slope, T31N, R6E, S34). The dominant soil feature is approximately 40 cm of Mt. Mazama volcanic ash underlain with deeply weathered mica schist (Sommer 1991). Vegetation types at this site were undisturbed forest (45 m² ha⁻¹ basal area of overstory) and a 21-year-old western

Table 1—Location, vegetation type, and soil classification of study sites.

National Forest	Vegetation type	Soil classification [‡]
Clearwater	Undisturbed forest	Typic Hapludand
Nez Perce	Undisturbed forest	Vitrandid Cryumbrept
Clearwater	Partial cut	Typic Hapludand
Clearwater	Natural bracken fern glade	Alic Fulvudand
Clearwater	30-year-old bracken fern-invaded clearcut	Alic Hapludand
Nez Perce	21-year-old western coneflower-invaded clearcut	Vitrandid Cryumbrept

[‡] Clearwater National Forest soil classifications from Johnson-Maynard and others (1997)
Nez Perce National Forest soil classifications from Sommer (1991).

coneflower-invaded clearcut (invaded by western coneflower and bracken fern after harvesting in 1973). Vegetation types were adjacent to each other, having similar slope, aspect, and parent material. There were no natural western coneflower glades dating to pre-harvest activities and no partial cut stands in the vicinity.

Methods

Field Collection Methods

In each forest and vegetation type, mineral soil was collected from the 0-5 cm and 10-15 cm depths. Soil samples were brought to the USDA Forest Service, Moscow Laboratory, air dried, and passed through a 2-mm sieve. Initial pH was measured electrometrically in a 2:1 water:soil suspension.

Laboratory Methods

Depending on initial soil pH, we chose five treatments to raise or lower soil pH in an attempt to establish a range of pH values from 3.5 to 6.0. For each vegetation type and depth, S at rates of 0.45, 0.90, 1.80, 2.70, or 3.6 g kg⁻¹ or Ca(OH)₂ at rates of 0.45, 0.90, or 1.80 g kg⁻¹ were added to provide a range of pH values. In addition, there was a control (no chemical added) for each vegetation type and soil depth. Each S or Ca(OH)₂ soil addition rate and the control from each vegetation type was replicated three times. Soil was placed in 655 cm³ plastic tubes with nylon screen over the bottom openings to prevent soil loss.

Soil water potential was brought to -0.033 MPa by the addition of deionized water. The tubes were randomly located on a greenhouse bench and incubated at a daytime temperature of 25 °C and a nighttime temperature of 18 to 20 °C until the pH stabilized (90 days). When soil water potential dropped below -0.10 MPa, additional deionized water was added until the soil reached field capacity. After pH stabilized (unchanged for 5 days), soil was air dried for chemical analyses. Final pH was measured as described above after the incubation period.

Total carbon (C) and nitrogen (N) were analyzed in a LECO induction furnace operated at 1050 °C (LECO Corp, St. Joseph, MI). Total acidity and exchangeable Al were extracted with 1N KCl (Bertsch and Bloom 1986). Exchangeable calcium (Ca), magnesium (Mg), and potassium (K) were extracted using 1N NH₄Cl (Palmer and others 2001). Calcium and Mg were analyzed by atomic absorption spectroscopy, and K was analyzed by flame emission. Nitrate-N (NO₃-N) was determined on moist samples using 1N KCl extract and an Alpkem Rapid Flow Analyzer (Mulvaney 1996). Potentially mineralizable N (PMN) was estimated using the 7-day anaerobic incubation technique on moist samples (Powers 1980). Extractable phosphorus (P) was determined using either the Bray 1 method (for samples with a pH < 6.0) or the Olsen method (for samples with a pH > 6.0) (Kuo 1996). Organic matter was determined by weight loss after combustion at 375 °C for 16 h (Ball 1964).

Statistical Analyses

Regression equations were developed using PROC MIXED in SAS (Littell and others 1996), at the 0.05 significance level, and LSMEANS was used to compare vegetation types within soil depths. When analyzing results for Ca, we excluded

treatments to raise soil pH because the $\text{Ca}(\text{OH})_2$ would have artificially elevated Ca levels. Transformations of variables were explored to achieve homogeneity of error variance, normality and independence of error and block effects, and to obtain additivity of effects (Littell and others 1996).

Results and Discussion

Soil pH Changes

Field studies in the GFM indicate that substantial pH fluxes occur throughout the year (figs. 1 and 2) (Ferguson and others, this proceedings). Results of our controlled study confirm our initial observation that changes in vegetation type influence forest soil pH (table 2). Before treatment with S or $\text{Ca}(\text{OH})_2$, the 0-5 cm soil pH was lowest in the natural bracken fern glade (5.0) and fern-invaded clearcut (4.7) on the Clearwater National Forest, intermediate on the Nez Perce National Forest undisturbed area (5.4) and coneflower-invaded clearcut (5.4), and highest on the Clearwater National Forest undisturbed forest (6.3) and partial cut (6.4) (table 2). Soil pH at the 10-15 cm depth followed the same trends. After treatment with S or $\text{Ca}(\text{OH})_2$ and 90 days of incubation, final pH values ranged from 3.6 to 6.1 (table 2). Most pH changes occurred within 45 days of starting the incubation period, but the lowest pH values were achieved after 85 days.

Interestingly, untreated soils from the Clearwater National Forest undisturbed and partial cut treatments exhibited a decline in soil pH during incubation in the greenhouse. For example, the initial average pH in the undisturbed forest was 6.3, but at the end of the incubation period, the highest pH value was 5.4. This "natural" decrease in the absence of vegetation and biotic processes is similar to the pH decreases shown in figures 1 and 2. In these two figures, winter pH values average around 6, but drop below 4 during the growing season. These seasonal pH fluxes may be driven by inputs of acid litter from bracken fern and western coneflower. In addition, these two species likely take up high rates of nutrients from

Table 2—Initial and final soil pH ranges after treatment with S or $\text{Ca}(\text{OH})_2$.

National Forest	Vegetation type	Initial pH	Final pH range
-----0-5 cm depth-----			
Clearwater	Undisturbed forest	6.3	3.7 - 5.4
Nez Perce	Undisturbed forest	5.4	3.8 - 5.3
Clearwater	Partial cut	6.4	3.6 - 5.0
Clearwater	Natural bracken fern glade	5.0	3.7 - 5.0
Clearwater	30-year-old bracken fern-invaded clearcut	4.7	3.7 - 5.6
Nez Perce	21-year-old coneflower-invaded clearcut	5.4	3.8 - 5.8
-----10-15 cm depth-----			
Clearwater	Undisturbed forest	5.8	3.6 - 5.3
Nez Perce	Undisturbed forest	5.3	3.8 - 5.5
Clearwater	Partial cut	6.2	3.8 - 5.2
Clearwater	Natural bracken fern glade	4.9	3.9 - 5.1
Clearwater	30-year-old bracken fern-invaded clearcut	4.3	3.7 - 5.1
Nez Perce	21-year-old coneflower-invaded clearcut	5.6	3.8 - 6.1

the soil, which may also contribute to acid conditions (Gilliam 1991). Although forest harvesting can lower pH, subsequent invasion by bracken fern or western coneflower appears to contribute to and maintain low pH relative to undisturbed forest soils. However, the laboratory data indicates that some pH changes within these soil types are possible even without vegetation facilitating the change.

Carbon and Nitrogen

There were significant differences in total C concentration among the vegetation types (table 3). Soil C concentration was highest under the fern-invaded clearcut at both depths (11.27 percent 0-5 cm depth; 10.00 percent 10-15 cm depth). Total C was lowest at the 10-15 cm depth where conifers were present (both undisturbed forests and partial cut). The soils that support the highest vegetation turnover rates (bracken fern and western coneflower) had similar C concentrations at both depths, while vegetation types with conifers present had about twice as much C in the surface soil compared to the 10-15 cm depth.

The fern-invaded clearcut has approximately 390 g/m² of bracken frond biomass added to the soil annually (Znerold 1979). On the Clearwater National Forest, rhizome and fine root biomass in the fern-invaded communities averaged 4000 g/m² (Jimenez 2005); in the natural glade, rhizome and fine root biomass averaged 3200 g/m². It is not surprising that this vegetation type has higher C concentrations. We expected that the natural bracken fern glade would have as much C as the fern-invaded clearcut, but this was not the case. The natural bracken fern glade soil appears to be at an intermediate point between the undisturbed forest and the fern-invaded clearcut. These results are similar to C and N data collected from nearby sites within the GFM (Johnson-Maynard and others 1997). One explanation may be that the natural bracken fern glade has reached a steady state.

Table 3—Mean C, N, Ca, Mg, and K in the control treatment, by vegetation type and depth. Each mean is an average of three replications.

National Forest	Vegetation type	Carbon	Nitrogen	Calcium	Magnesium	Potassium
		----- percent -----			--- mg/kg ---	
		0-5 cm depth				
Clearwater	Undisturbed forest	6.60 a‡	0.40 a	12.21 d	1.12 b	1.54 b
Nez Perce	Undisturbed forest	7.87 b	0.74 c	14.16 e	1.14 b	0.99 a
Clearwater	Partial cut	6.23 a	0.36 a	7.86 b	0.74 a	0.99 a
Clearwater	Natural bracken fern glade	7.93 b	0.61 b	6.88 a	3.29 d	2.77 c
Clearwater	Bracken fern-invaded clearcut	11.27 c	0.69 bc	6.70 a	2.34 c	2.89 c
Nez Perce	Coneflower-invaded clearcut	6.17 a	0.35 a	9.16 c	0.92 a	1.02 a
		10-15 cm depth				
Clearwater	Undisturbed forest	3.17 a	0.24 a	5.41 c	0.74 d	1.22 c
Nez Perce	Undisturbed forest	3.90 b	0.22 a	5.38 c	0.41 a	0.71 b
Clearwater	Partial cut	3.63 ab	0.25 a	3.79 b	0.49 c	0.71 b
Clearwater	Natural bracken fern glade	5.90 c	0.48 c	4.25 b	1.38 e	2.20 e
Clearwater	Bracken fern-invaded clearcut	10.00 d	0.67 d	2.72 a	0.77 d	1.30 d
Nez Perce	Coneflower-invaded clearcut	6.27 c	0.34 b	5.66 c	0.45 b	0.46 a

‡ Within soil depth, means followed by different letters are significantly different ($p = 0.05$) using LSMEANS.

Because bracken fern produces high levels of allelopathic chemicals (Ferguson and Boyd 1988), it is perhaps becoming autotoxic (Gliessman and Muller 1978), which results in less frond biomass (natural glade 678 g/m²; fern-invaded clearcut 916 g/m² (Jimenez 2005)) and less organic C incorporated into the soil. These two types of bracken fern stands (natural glade and invaded clearcut) may also be at different lifecycle stages (Atkinson 1986).

Higher soil C concentrations in the fern-invaded clearcut are consistent with the development of nonallophanic soil characteristics following invasion (Nanzoyo and others 1993; Johnson-Maynard and others 1997; Dahlgren and others 2004). Increased levels of C in the bracken fern sites, as compared to undisturbed soils, may increase the potential for preferential formation of Al-humus complexes (Dahlgren and others 1993).

Forest sites invaded by western coneflower maintained moderate levels of C throughout the sampling depths. At the 10-15 cm depth the coneflower-invaded clearcut had nearly twice as much C as the undisturbed forest soil (table 3). Carbon was distributed deeper in the soil profile in the coneflower-invaded clearcut than on the bracken fern sites. This may be because the coneflower-invaded site had greater surface and subsoil mixing caused by pocket gophers (Ferguson and Adams 1994) or because of slightly less surface volcanic ash deposition (Sommer 1991).

For each vegetation type, there was generally more N in the 0-5 cm depth than in the 10-15 cm depth, with two notable exceptions. Both the fern-invaded clearcut and the coneflower-invaded clearcut soils had as much N in the 10-15 cm depth as the surface soil. This is likely caused by the large annual inputs of forb biomass that usually occur in newly invaded clearcuts (Attiwill and others 1985).

Regression analyses showed that total C and N were unchanged after altering pH. This result was not unexpected since we did not add organic matter.

Base Cation Concentrations

Based on the control samples, vegetation type does influence soil Ca, Mg, and K concentrations in these volcanic ash soils (table 3). For both soil depths, the fern glade and the fern-invaded clearcut had significantly more K and Mg than soils from under the other vegetation types. In contrast, Ca content was greatest in soils under both undisturbed forests.

Regression analysis showed that base cation concentrations (Ca, Mg, and K) did not change as a result of pH changes (data not shown). Our results differ from those of Mohebbi and Mahler (1988) who found a strong correlation between pH and cation concentration after artificially changing pH in a loessal soil. In their study, as pH increased, both K and Mg decreased; however, Ca sharply increased from pH 5 to 7. It also increased after pH dropped below 3.5. It is unusual that soil consisting of volcanic-ash influenced materials, which have a variable charge, did not show a marked reduction in the retention of exchangeable bases with decreasing pH. This indicates there may be enough permanent charge minerals to maintain base concentrations. In the fern glade and the fern-invaded clearcut, soils may be developing properties typical of nonallophanic Andisols (Johnson-Maynard and others 1997).

Lack of pH-driven changes in cation concentration in our study may be related to high organic C content of the ash-influenced soil (Shoji and others 1993). Theoretically, once these sites are harvested, substantial losses of basic cations are

possible. Both loss of nutrients from aboveground pools (Boyle and others 1973; Federer and others 1989) and increased leaching losses have been reported after harvesting (Hendrickson and others 1989). However, cations may be redistributed into new, immediate regrowth of bracken fern or western coneflower after harvesting and not lost from the site (Johnson and others 1997).

Available Phosphorus

Phosphorus (P) amounts varied significantly among vegetation types and soil depths. The mean values for P in the control treatment are shown in table 4. The largest P means are in the 0-5 cm depth under the undisturbed forests (Nez Perce National Forest 3.17 $\mu\text{g/g}$ and Clearwater National Forest 3.03 $\mu\text{g/g}$). The fern glade (2.73 $\mu\text{g/g}$) and fern-invaded clearcut (2.20 $\mu\text{g/g}$) were intermediate in P, and the lowest means were in the coneflower-invaded clearcut (1.87 $\mu\text{g/g}$) and partial cut (1.70 $\mu\text{g/g}$).

Regression analyses showed that P increased with decreasing pH. Response of soil P was similar at both soil depths; therefore, regression equations are shown only for the 0-5 cm depth (table 5). The vegetation types had similar response

Table 4—Mean P, potentially mineralizable N (PMN), nitrate ($\text{NO}_3\text{-N}$), aluminum (Al), and total acidity in the control treatment, by vegetation type and soil depth. Each mean is the average of three replications.

National Forest	Vegetation type	P	PMN	$\text{NO}_3\text{-N}$	Al	Total acidity
		$\mu\text{g/g}$	----- mg/kg -----			----- cmol/kg -----
0-5 cm depth						
Clearwater	Undisturbed forest	3.03 c [‡]	100.41 b	87.73 a	0.17 a	0.28 a
Nez Perce	Undisturbed forest	3.17 c	60.16 ab	172.01 b	0.22 a	0.41 ab
Clearwater	Partial cut	1.70 a	14.96 a	105.18 a	0.34 ab	0.58 bc
Clearwater	Natural bracken fern glade	2.73 c	7.56 a	230.07 bc	0.54 b	0.78 c
Clearwater	Bracken fern-invaded clearcut	2.20 b	55.32 ab	246.99 c	1.14 c	1.77 d
Nez Perce	Coneflower-invaded clearcut	1.87 ab	2.14 a	97.51 a	0.23 a	0.34 ab
10-15 cm depth						
Clearwater	Undisturbed forest	1.80 c	6.55 a	24.03 a	0.18 a	0.31 a
Nez Perce	Undisturbed forest	2.10 d	38.85 a	36.51 a	0.81 ab	0.95 ab
Clearwater	Partial cut	1.40 b	28.04 a	51.68 ab	0.50 a	0.61 a
Clearwater	Natural bracken fern glade	1.50 b	3.97 a	136.94 c	1.38 b	1.70 b
Clearwater	Bracken fern-invaded clearcut	2.53 e	192.30 b	127.45 bc	3.55 c	4.22 c
Nez Perce	Coneflower-invaded clearcut	0.93 a	29.31 a	47.61 ab	0.21 a	0.31 a

[‡] Within each soil depth, means followed by different letters are significantly different ($p = 0.05$) using LSMEANS.

Table 5—Regression equations for 0-5 cm depth (bold lines on figs. 3, 5, and 6).

$Y = \exp(\beta_0 + \beta_1 \cdot \text{pH})$ and Y , β_0 , and β_1 take on the following values:

Definition	Dependent (Y)	β_0	β_1
P concentration	PHOS	2.6789	-0.3612
Potentially mineralizable N	PMN	10.4498	-1.4457
$\text{NO}_3\text{-N}$ concentration	$\text{NO}_3\text{-N}$	-7.1482	2.2212
KCl-extractable Al	ALUM	10.5408	-2.2514
Total acidity	ACID	9.9878	-2.0526

surfaces (fig. 3). Soil from the Clearwater National Forest undisturbed forest had the highest available P when pH dropped below 4.0. Both humus and allophane content in volcanic ash-influenced soils affect P availability and the high level of C in the fern-invaded clearcut soil may be sorbing P (Wada 1985). These results are quite different from the loessal soils that have a strong linear increase in available P as pH increases (Mohebbi and Mahler 1988). For volcanic ash-influenced soils, the pH dependency of phosphate sorption is highest between pH 3 and 4, and generally decreases with increasing pH (Nanzyo 1987). This is especially true for allophanic ash-influenced soils as compared to nonallophanic ash-influenced soils (Nanzyo and others 1993).

In soils consisting of weathered volcanic ash, P sorption is a major soil fertility problem (Andregg and Naylor 1988). In most mineral soils, organic matter is an important reservoir for P. However, in many volcanic ash-influenced soils, organic matter protects P from sorption (Moshi and others 1974). This appears to be the case for these soils as well.

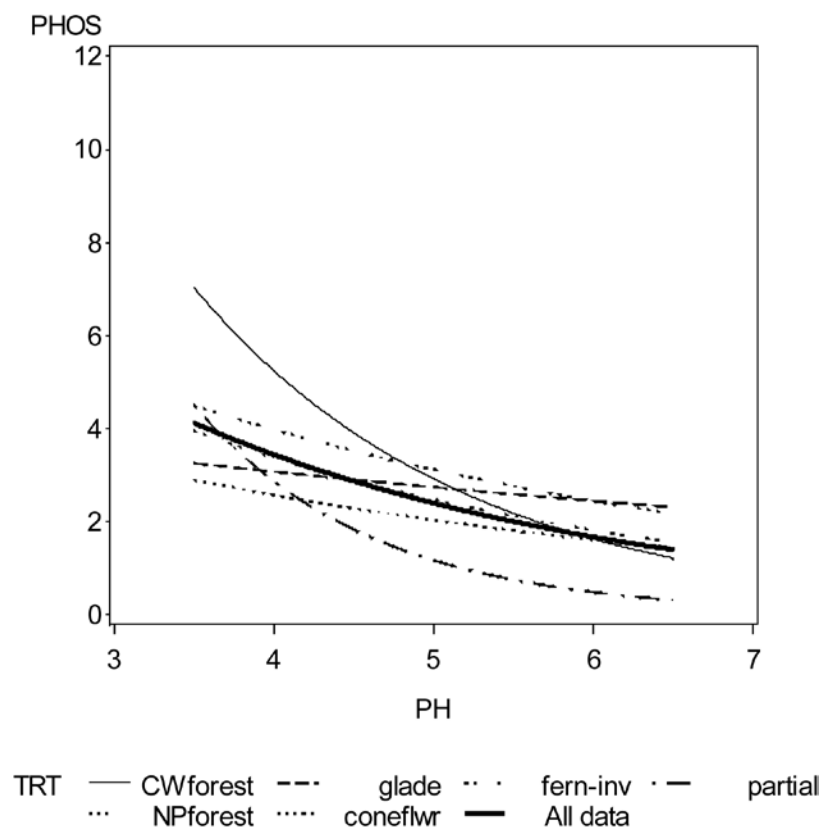


Figure 3—Regression equations for available P concentration (µg/g) of the 0-5 cm depth as affected by pH manipulation by vegetation type. The bold line is the regression for all vegetation types.

Potentially Mineralizable N and Nitrate-N

Potentially mineralizable N (PMN) concentrations varied widely among vegetation types and soil depths (table 4). For example, in the control soil for the 0-5 cm depth, PMN ranged from a low of 2.14 mg/kg in the coneflower-invaded clearcut to 100.41 mg/kg in the undisturbed forest on the Clearwater National Forest. Amounts of PMN at the 0-5 cm soil depth was low in the fern glade, but intermediate in the fern-invaded clearcut.

Nitrate-N ($\text{NO}_3\text{-N}$) also varied among vegetation and soil depths. The largest means at the 0-5 cm depth for the control soil (table 4) were in the fern-invaded clearcut (246.99 mg/kg) and fern glade (230.07 mg/kg), and the lowest mean was 87.73 mg/kg in the undisturbed forest soil from the Clearwater National Forest. Means for $\text{NO}_3\text{-N}$ at the 10-15 cm depth were lower than the 0-5 cm depth, but the trends were similar.

Analyses showed that PMN concentrations declined rapidly as soil pH increased above 5.0 and, in contrast, soil $\text{NO}_3\text{-N}$ concentration increased rapidly above pH 5.0, except in the fern glade and fern-invaded clearcut where this change in N form occurred below pH 4.5 (fig. 4a-f). While the soils in both undisturbed forests and the partial cut forests exhibited a threshold level of pH 5.0 for substantial changes in the quantity of available N, the two sites with bracken fern vegetation types and the coneflower-invaded clearcut had steady changes in N as pH increased. Both soil depths have similar regression curves for each vegetation type; therefore, only the 0-5 cm soil depth is shown (table 5).

The sharp decline in PMN from these ash-influenced sites is different from the northern Idaho loessal soils, which had a significant increase in PMN as pH increased from 3.0 to 7.0 (Mohebbi and Mahler 1988). This may indicate a difference in organic matter concentration from loess-grassland areas to ash-forested areas, and suggests that organic N in volcanic ash-influenced soils may be fairly resistant to microbial decomposition because of the Al-organic complexes that are formed (Shoji and others 1993).

While soil from most of the vegetation types show a crossover in relative abundance of PMN and $\text{NO}_3\text{-N}$ around pH 5.0, the bracken-fern dominated vegetation types change below pH 4.5. Increased $\text{NO}_3\text{-N}$ and decreased PMN at higher pH values is consistent with results of acid rain and soil nutrition studies (Schier 1986; Marx 1990). Nitrogen mineralization often increases when soil pH is raised (Montes and Christensen 1979), but occasionally has been shown to decrease (Adams and Cornforth 1973). Nitrification is also pH sensitive and generally increases as pH is raised from very acid to moderately acid (Robertson 1982). In this study, the clearcuts invaded with either bracken fern or western coneflower likely exhibit this N change each year as pH changes (Binkley and Richter 1987).

Aluminum and Total Acidity

KCl-extractable Al (which reflects exchangeable Al) and total acidity varied significantly among vegetation types and soil depths. Mean values in the control treatments are shown in table 4. Aluminum and total acidity are significantly higher in the fern glade and fern-invaded clearcut, for both depths. Mean Al and acid values are generally higher in the 10-15 cm depth soil as compared to the 0-5 cm depth.

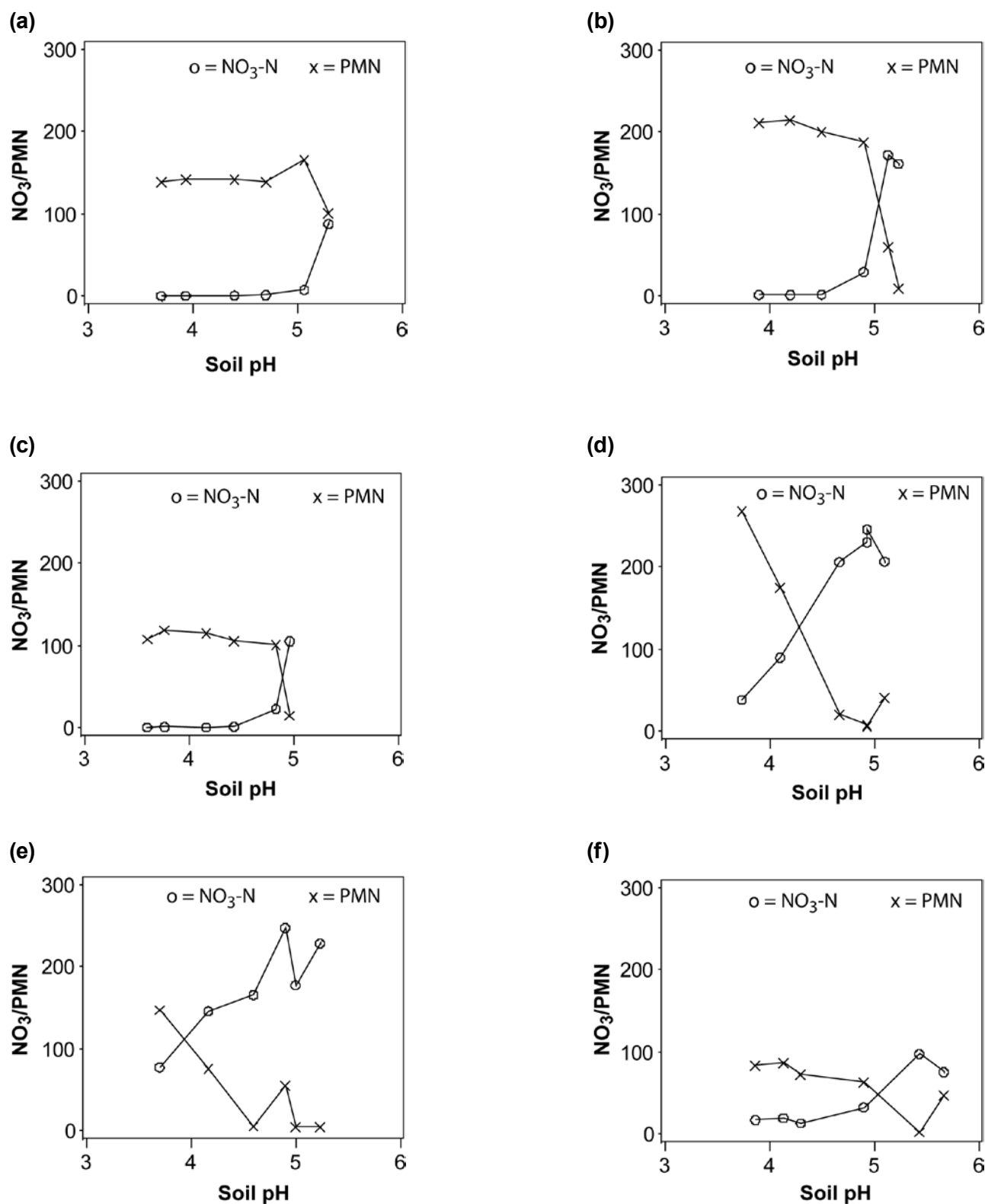


Figure 4—Soil $\text{NO}_3\text{-N}$ and PMN concentration (mg/kg) in the 0-5 cm depth as affected by pH manipulation, by vegetation type (a) Clearwater National Forest, undisturbed, (b) Nez Perce National Forest, undisturbed, (c) Clearwater National Forest, partial cut, (d) Clearwater National Forest, bracken fern glade, (e) Clearwater National Forest, bracken fern-invaded clearcut, (f) Nez Perce National Forest, coneflower-invaded clearcut.

Regression analyses showed that Al was highly correlated with changes in pH (table 5) in all vegetation types. Aluminum increased exponentially when the pH decreased below 4.5 (fig. 5). Both 0-5 cm and 10-15 cm depths had similar curves; therefore, only the 0-5 cm soil depth regression lines are shown. Volcanic ash-influenced soils contain high levels of Al-containing materials that can undergo dissolution under acidic (less than pH 5.0) conditions (Tisdale and others 1993). In these soils, very little exchangeable Al was detected above pH 5.0. Based on continuous soil measurements of pH (figs. 1 and 2), soils under bracken fern and coneflower vegetation have a pH below 5.0 each growing season. Soil pH 5.0 is generally considered to be the critical point for Al toxicity to woody vegetation (Wolt 1994).

In general, woody plant species appear to be more tolerant of Al than agriculture crops (McCormick and Steiner 1978; Ryan and others 1986), and there is considerable variation in Al tolerance among tree species (McCormick and Steiner 1978; Steiner and others 1984; Arp and Ouimet 1986; Hutchinson and others 1986; Schaedle and others 1989; Raynal and others 1990). Aluminum toxicity alters tree root anatomy, which first occurs in the roots (Hutchinson and others 1986; Schaedle and others 1989; McQuattie and Schier 1990; Nosko and Kershaw 1992; Schier 1996). The result of Al toxicity is impaired root development, resulting in reduced root length and formation of a shallow root system. At high

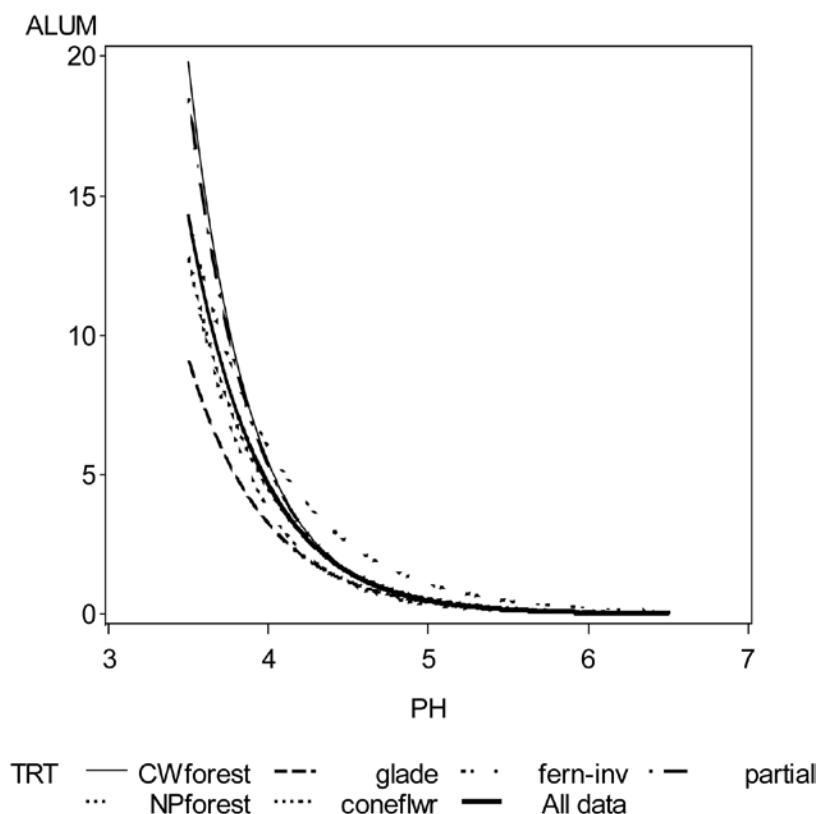


Figure 5—Exchangeable Al concentration (cmol/ kg) in the 0-5 cm depth as affected by pH, by vegetation type. The bold line is the regression for all vegetation types.

Al levels, mitosis is almost completely inhibited. Leamy (1988) noted that in volcanic ash-influenced soils, Al toxicity may occur at concentrations of 2 cmol/kg soil, and this value is used as a threshold in Soil Taxonomy for identifying those Andisols in which Al phytotoxicity may occur (Soil Survey Staff 2003). Aluminum levels found in this laboratory study are much higher than 2 cmol/kg when pH decreased below 5.0 and indicates a strong potential for Al toxicity in these ash-influenced soils as pH values decline.

The various studies on Al toxicity in tree species are difficult to compare because of different study methods, units of measure, growth media, length of experiments, and age of trees (Schaedle and others 1989; Nosko and Kershaw 1992). However, one important finding is that young seedlings are more sensitive to Al toxicity than older seedlings. For example, Schier (1996) found that Al concentrations of 0.32 mM/l inhibited root biomass in newly germinated red spruce (*Picea rubens*) seedlings, while the threshold was 2.1 mM/l in 1-year-old seedlings. It seems reasonable to assume that conifer seed germinating on GFM sites could be impacted by low concentrations of Al. Aluminum toxicity, allelopathic compounds, and competition could combine to eliminate the natural establishment of trees and other woody plant species on these sites.

Regression analyses for total acidity followed the same trend as extractable Al (fig. 6), and only the 0-5 cm soil regression lines are shown. The regression equation for total acidity is shown in table 5. Most of the acidity in these soils

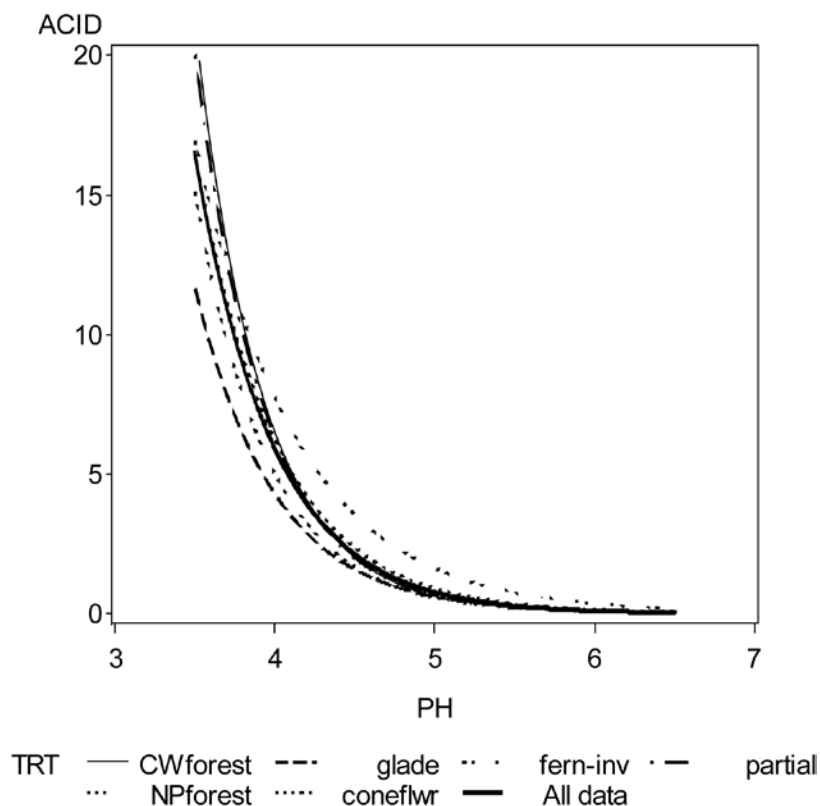


Figure 6—Total acidity (cmol/kg) in the 0-5 cm depth as affected by pH manipulation by, vegetation type. The bold line is the regression for all vegetation types.

occurs as Al. The relationship between exchangeable Al and total acidity is not unusual since most of the exchangeable acidity is derived from Al and H on the exchange sites (Binkley and Richter 1987). Changes in exchangeable acidity generally occur over a long period of time and are due to acidification through weathering, leaching, cation uptake, or atmospheric deposition (Richter 1986). Rapid changes in acidity occur occasionally by other H-ion inputs. In the GFM, both bracken fern and western coneflower vegetation have the potential to input H-ions via organic acid production or additions of high amounts of organic C through yearly vegetation cycles.

Summary

Analysis of unaltered soil samples supporting undisturbed grand fir forest and bracken fern/western coneflower plant communities suggests that chemical properties of GFM forest soil are altered through invasion of successional plant species after timber harvest or other disturbance. Changes in soil conditions are similar to a depth of 15 cm. Seasonal decreases in soil pH under bracken fern and western coneflower vegetation types most likely cause a release of exchangeable Al at levels toxic to woody vegetation. High levels of C, exchangeable Al, and total acidity under these two vegetation types may also be facilitating a localized conversion of these ash-influenced soils from allophanic to nonallophanic Andisols. Forested soils in the GFM are capable of exhibiting these same characteristics once disturbed.

Results of this study also provide insights into the chemical changes that may occur in volcanic ash-influenced soils as pH fluctuates. Mechanisms that contribute to forb-dominated secondary successional plant communities have been identified. For example, the apparent change in N between PMN and $\text{NO}_3\text{-N}$ has implications in determining which species can grow on these sites, as does the exponential increase of Al below pH 5.0. Clearly, this laboratory study points out the potential for Al toxicity that may accompany seasonal pH fluctuations. These laboratory study findings are consistent with *in situ* soil solution data, which indicate that soils invaded by bracken fern and western coneflower undergo conversion from allophanic to nonallophanic properties (Johnson-Maynard and others 1997). However, altering the pH of ash-influenced soils differed from altering loessal soils (Mohebbi and Mahler 1988). These soil-type differences are likely attributable to the unique physical, chemical, and biological properties of ash-influenced soils as compared to those derived from other parent materials (Dahlgren and others 2004).

This laboratory study highlights important characteristics of ash-influenced soils that may contribute to changes in vegetation. This type of study, combined with field work, will help in the development of practical management recommendations.

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