Lime Effects on Soil Acidity, Crop Yield, and Aluminum Chemistry in Direct-Seeded Cropping Systems

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Soil acidification threatens dryland crop production in the inland Pacific Northwest (IPNW). Our objective was to assess the efficacy of lime to lower soil acidity, alter Al chemistry, and increase crop yield in a direct-seeded system. Treatments of subsurface banded fertilizer (120–168 kg N ha^{-1} yr^{-1}) alone or with subsurface banded lime (224 kg ha^{-1} yr^{-1}), or a one-time broadcast application of lime (7000 kg ha^{-1}) or elemental S (1000 kg ha^{-1}) were initiated in spring 2002. Grain yield was measured annually from 2002 to 2005 in a spring barley (*Hordeum vulgare* L.)–spring wheat (*Triticum aestivum* L.)–winter wheat rotation. Soil was sampled in spring 2004 to assess pH and model Al speciation. Low pH was evident at the depth of fertilizer placement (5–10 cm). Broadcast lime increased pH in the surface 15 cm, although reductions in Al^{3+} activity [(Al^{3+})] occurred only in the 0- to 5-cm layer. Relative to banded N, there was no increase in pH at the 5- to 10-cm depth where banded lime was placed. At the 0- to 5-cm depth, lower pHs were observed with broadcast S (4.6) compared with the banded N control (5.1) or banded lime (5.0). There was no effect of treatment on yield. Modeling suggests that soluble Al is dominated by organic matter–Al complexes (fulvic acid, FA; FA$_2$Al$^+$ and FA$_2$AlOH^0). Solid- and solution-phase organic complexes may control (Al^{3+}) at pH <5.5. Although acidification is a concern in the IPNW, the high organic matter content in direct-seeded soils may buffer against Al phytotoxicity.

Abbreviations: CT, conventionally tilled; DS, direct seeded; FA, fulvic acid; IPNW, inland Pacific Northwest; NT, no-till.

<div style="writing-mode: vertical">**SOIL FERTILITY & PLANT NUTRITION**</div>

Soil acidity influences many chemical and biological reactions that control plant nutrient availability and element toxicity (Sumner et al., 1991; Lavelle et al., 1995). Worldwide, soil acidification affects an estimated 30% of the total topsoil (Sumner and Noble, 2003). Furthermore, 75% of acid topsoils are also affected by subsoil acidity, and failure to address topsoil acidity may result in subsoil acidification of even neutral to alkaline soils (Sumner and Noble, 2003).

The rate of acidification in agricultural soils is influenced by the form and amount of N fertilizer applied (Mahler and Harder, 1984; Bezdicek et al., 1998). Ammonium-based N forms are major contributors to soil acidification and are applied at relatively high annual rates (>100 kg N ha^{-1} yr^{-1}) for cereal grains in high-yielding areas of eastern Washington and northern Idaho (Mahler et al., 1985). Following the introduction of ammoniacal N fertilizers in the 1960s, the average pH in the surface 30 cm of agricultural soils in the region declined from a near-neutral native pH (6.5–7.2) to <5.7 by 1984 (Mahler and Harder, 1984) and <5.2 in 1995 on 21% of fields surveyed (Mahler, 2002). These soils are at or below critical pH levels for optimum yield of winter and spring cereals (pH 5.2–5.4) and grain legumes (pH 5.4–5.6) grown in the region (Mahler et al., 1985; Mahler and McDole, 1987).

The distribution of acidity in the soil profile differs with tillage and N placement practices (Mahler and Harder, 1984; Robbins and Voss, 1989). Soil acidity develops more rapidly at the depth of N fertilizer placement in direct-seeded (DS; no tillage, subsurface band placement of fertilizer) compared with conventionally tilled (CT) soils due to the absence of mechanical mixing and repeated N fertilizer application in the same zone (Mahler and Harder, 1984; Robbins and Voss, 1989). Soil pH as low as 4.9 in the fertilizer band of DS cropping systems has been reported in eastern Washington (Bezdicek et al., 1998; Wildey, 2003), with concomitant increases in extractable Al (Wildey, 2003). Ultimately, the accelerated development of

an acidic surface layer of soil may be an important constraint of DS systems (Mahler and Harder, 1984; McCool et al., 2001).

Aluminum phytotoxicity is a major concern in agricultural areas with low soil pH (Foy, 1984). These concerns are exacerbated by the sensitivity of many crops to micromolar concentrations of Al in solution and variation in Al tolerance among plant species (Delhaize and Ryan, 1995; Reddy et al., 1995). The occurrence of Al phytotoxicity in acid soils depends on the solution activity of toxic forms of Al, which is a function of Al complexation, solid-phase control of Al solubility, and the edaphic environment (Kinraide, 1997). Most Al in the soil solution is complexed with inorganic and organic ligands, altering the proportion and activity of phytotoxic forms of Al (Berggren and Mulder, 1995; Kinraide, 1997). Overall, the activity of Al^{3+} [(Al^{3+})], rather than measures of total soluble or exchangeable forms, is a better indicator of potential phytotoxicity in acid soils, even though it may not be the sole toxic form of Al (Shann and Bertsch, 1993).

Lime increases soil pH, improves crop growth (Moschler et al., 1973; Arshad and Gill, 1996), and decreases extractable Al^{3+} (Moschler et al., 1973; Wildey, 2003) as well as (Al^{3+}) in DS systems. In the IPNW, lime is rarely used because of its relatively high cost and studies showing little or no yield response (Jackson and Reisenauer, 1984; Mahler and McDole, 1985; Bezdicek et al., 2003; Wildey, 2003). Alternative application strategies such as placement of lime in a band beneath the row at seeding may allow lower rates of lime to be used and thereby offset economic constraints posed by high application rates; however, the effects of this practice on soil pH and crop yield have not been extensively studied. In 1 yr of research, subsurface banded lime at a rate of 220 kg ha^{-1} was shown to effectively reduce soil acidity in the surface 10 cm at an eastern Washington location, but no grain yield response was observed (Wildey, 2003).

The objectives of this study were to: (i) assess the distribution with depth of soil acidity created by banded fertilizer and subsurface banded or broadcast lime or elemental S applications; (ii) determine yield responses to lime and S amendments; and (iii) model Al speciation in these systems to evaluate the potential for Al phytotoxicity.

MATERIALS AND METHODS
Study Site, Treatments, and Sampling

A long-term study was initiated in the spring of 2002 at the Palouse Conservation Field Station (PCFS) located near Pullman, WA. Agricultural soils in this area are predominately silt loam texture Mollisols with slopes ranging from 7 to 25% (Soil Survey Staff, 1980; McCool et al., 2001). Rainfall ranges from 460 to 580 mm yr^{-1}, with 60% occurring during the period November through March (Soil

Survey Staff 1980; McCool et al., 2001). Mean air temperature is 8.3°C, with a frost-free period of 100 to 160 d (Soil Survey Staff, 1980). The elevation at the PCFS is approximately 800 m (Soil Survey Staff, 1980). The study site is in a 3-yr rotation of spring barley (cv. Baronesse)–hard red spring wheat (cv. Hank)–hard red winter wheat (cv. Falcon) and had been managed using DS and conventional pest control practices since 1996. A Cross-Slot seed and fertilizer applicator (Baker No-Tillage Ltd., Feilding, New Zealand) was used to place urea–NH_4NO_3 solution in a band 7 cm below the soil surface at rates of 120, 134, 168, and 145 kg N ha^{-1} in the spring of 2002, spring of 2003, fall of 2003, and spring of 2005, respectively. Subsurface-banded N fertilizer was placed 1.25 cm to the side of the seed. Additional N in the form of dry urea was broadcast at rates of 90 and 45 kg N ha^{-1} for hard red wheat production in the fall of 2002 and spring of 2004, respectively.

Treatments were subsurface-banded N fertilizer using methods and rates described above (control), banded fertilizer with a one-time broadcast application of pelleted lime (Calpril, Pacific Calcium, Tonasket, WA; 91% $CaCO_3$ equivalent) spread by hand at a rate of 7000 kg ha^{-1}, banded fertilizer with annual subsurface-banded lime placed with the fertilizer at a rate of 224 kg ha^{-1}, or banded fertilizer with a one-time broadcast application of pelletized elemental S (90% S) spread by hand at a rate of 1000 kg ha^{-1}. Lime and S treatments were initiated in March 2002. Individual plots were 3 m wide by 24 m long in a randomized complete block design with three replications. Each replicate of the treatments was established in a separate field on the PCFS. Soil types in each field were Thatuna (fine-silty, mixed, superactive, mesic, Oxyaquic Argixeroll), Latah (fine, mixed, superactive, mesic Xeric Argialboll), and Palouse (fine-silty, mixed, superactive, mesic Pachic Ultic Haploxeroll).

Winter wheat was growing in all three replicate fields at the time of soil sampling in May 2004. One vertical soil face was exposed in each treatment of each field by excavating a pit 30 cm deep by 60 cm wide. Soil was collected vertically and horizontally at 5-cm intervals using a 3.8-cm-diameter core inserted 7.6 cm into the soil face (72 cores per excavation, 862 cores total). A 4-m^2 area from the center of each plot was sampled each year for grain yield determination.

Sample Analysis and Speciation Modeling

Soil samples were passed through a 2-mm sieve and air dried for 24 h at room temperature. Soil pH and electrical conductivity (EC) were determined on a 1:1 soil/water extract shaken for 24 h, centrifuged at 14,500 rpm for 30 min, and then passed through a 0.1-μm filter to remove colloidal Al fractions (Table 1). Soil pH was determined with a 6-cm-long MI-414 pH microelectrode (Microelectrodes, Bedford, NH); EC was measured with a 1056 Digital Conductivity Meter (Amber Science, Eugene, OR).

Cross-variogram analysis indicated that soil pH was more similar horizontally than vertically, meaning an analysis by depth increment

Table 1. Soil chemical properties for the banded N fertilizer control treatments sampled in 2004. Each value is the mean of three replicates ± standard deviation.

Depth	pH	Electrical conductivity	log (Al^{3+})	KCl-extractable Al	Total concentration in water extracts					
					Al†	Ca	PO_4	SO_4	F	STOC‡
cm		mS cm^{-1}		mg kg^{-1}	———————————————mg L^{-1}———————————————					
0–5	5.11 ± 0.78	0.59 ± 0.17	−7.77 ± 1.91	28.3 ± 27.0	0.30 ± 0.32	33.84 ± 13.37	1.12 ± 0.43	10.45 ± 2.59	0.00	24.54 ± 8.24
5–10	4.73 ± 0.48	0.36 ± 0.27	−6.56 ± 0.49	54.7 ± 48.4	0.36 ± 0.13	27.51 ± 16.85	0.39 ± 0.21	20.25 ± 16.15	0.06 ± 0.13	15.80 ± 3.16
10–15	5.48 ± 0.28	0.17 ± 0.06	−8.66 ± 1.33	7.1 ± 4.8	0.29 ± 0.33	9.89 ± 2.43	0.24 ± 0.16	6.55 ± 6.32	0.00	17.37 ± 3.42
15–20	5.94 ± 0.85	0.14 ± 0.04	−9.83 ± 6.58	4.5 ± 3.5	0.02 ± 0.02	13.94 ± 5.14	0.16 ± 0.13	7.63 ± 4.49	0.00	13.00 ± 4.98
20–30	6.30 ± 0.33	0.13 ± 0.02	−9.81 ± 6.98	3.4 ± 3.4	0.23 ± 0.37	12.66 ± 2.69	0.22 ± 0.02	6.70 ± 4.05	0.05 ± 0.10	14.91 ± 3.46

† Total Al concentration determined by inductively coupled argon plasma–atomic emission spectroscopy on 1:1 water extracts.

‡ Soluble total organic C, determined by a Phoenix 8000 UV-Persulfate analyzer (Tekmar-Dohrman, Cincinnati, OH) on 1:1 water extracts.

Table 2. Aqueous input parameters and predicted output components for Al speciation using visual MINTEQ version 2.32.

Component	Input (concentration)†	Output (activity)‡
Cations	Al, Ca, Fe, K, Mg, Mn, Na	Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$(aq), $Al(OH)_4^-$, $AlSO_4^+$, AlF^{2+}, AlF_2^+, $AlHPO_4^+$, FA_2Al^+, FA_2AlOH
Anions	F, Cl, NO_3–N, NO_2–N, PO_4, SO_4	F^-, SO_4^{2-}, PO_4^{3-}, $Al(OH)_4^-$, $Al(SO_4)_2^-$, AlF_4^-
Other	Dissolved organic C pH	pH

† Data from 1:1 soil/water extracts.

‡ Predicted using the multiproblem sweep feature in Visual MINTEQ.

was appropriate for these data. Four samples were randomly selected from the three replicates at each depth (0–5, 5–10, 10–15, 15–20, and 20–30 cm) for each treatment (80 samples total) for complete analysis and Al speciation modeling. The 1:1 soil/water extracts, described above, were divided and those for cation analysis preserved with one drop of concentrated HNO_3. Samples were analyzed for Al, Ca, Mg, Na, and K by inductively coupled argon plasma–atomic emission spectroscopy (ICP–AES; Jarrell-Ash, Thermo Fisher Scientific, Waltham, MA) and SO_4, Cl, F, NO_3, and PO_4 by ion chromatography (Dionex Corp., Sunnyvale, CA) (Table 1). Soluble total organic carbon (TOC) was also determined on the 1:1 extract using a Phoenix 8000 UV-Persulfate TOC Analyzer (Tekmar-Dohrman, Cincinnati, OH).

Aqueous ion and TOC concentrations (Table 2) were entered into the geochemical speciation model Visual MINTEQ Version 2.32 using the Stockholm Humic Model default parameters to estimate the aqueous activity of Al^{3+} and Al complexes. Solid phases were not specified or allowed to precipitate. The program predicts the equilibrium composition of dilute aqueous solutions using a combination of nonlinear mass action expressions and linear mass balance relationships from a thermodynamic database and input parameters (Allison et al., 1991). Activity coefficients were calculated by MINTEQ using the Davies equation and an iterative approach to improve estimates of the ionic strength and species concentrations (Allison et al., 1991). Aluminum complexation with humic acid was not considered in this study due to the default parameters of MINTEQ that exclude complexation with humic acids in aqueous solutions and assume that only fulvic acid (FA) may be dissolved (Gustafsson and VanSchaik, 2003). The aqueous concentration of total dissolved FA is estimated by the measured value of total dissolved organic C and aver-

aged parameters from 25 FAs fitted to the model (Gustafsson and van Schaik, 2003). See Allison et al. (1991) for additional details.

Statistics

Analysis of variance was performed using the Statistical Analysis System (SAS) software Version 9.1 (SAS Institute, 2000). Mean comparisons for pH and (Al^{3+}) by depth were separated using Tukey's pairwise comparison in the PROC GLM procedure ($P \leq 0.05$). A negative inverse log transformation was required on the (Al^{3+}) data to satisfy model assumptions. Grain yield data were analyzed using the PROC MIXED procedure ($P \leq 0.05$).

RESULTS AND DISCUSSION
Soil pH

There was a significant ($P \leq 0.05$) treatment × depth interaction for soil pH (Fig. 1). The average 0- to 5-cm soil pH was 5.11 in the banded N fertilizer (control) treatment. This low pH could be due in part to decomposition of accumulated organic matter (Haynes and Mokolobate, 2001) and broadcast urea used to supplement subsurface-band application for the hard red wheat crops. Upward migration of N fertilizer in channels created by the fertilizer applicator may also occur (Robbins and Voss, 1989). Horizontal and vertical spreading of acidic zones, centered at the depth of fertilizer placement, with repeated NH_3 fertilizer application has been observed in soils under conservation tillage systems (Robbins and Voss, 1989).

Subsurface-band placement of N fertilizer resulted in an average soil pH of 4.73 at the 5- to 10-cm depth. Previous studies in the IPNW documented soil pH values of 5.1 (Mahler and Harder, 1984), 4.9 (Bezdicek et al., 2003; Wildey, 2003), and 4.6 (Bezdicek et al., 1998) at the depth of fertilizer placement in reduced tillage systems. Blevins et al. (1983) reported average soil pH values of 5.2 and 4.7 with annual rates of broadcast NH_4NO_3 at 168 and 336 kg N ha^{-1} compared with 5.95 with a 0 N control treatment in the surface 0 to 15 cm of a no-till (NT) soil in Kentucky after 10 yr. Persistent acidic zones with a 0.9 to 1.8 unit lower pH than the bulk soil were reported by Robbins and Voss (1989) in an Iowa soil under NT management where NH_3 was injected below the surface.

Two years after lime was broadcast, a statistically significant increase in soil pH relative to the control was detected to a depth of 15 cm (Fig. 1). Soil pH was increased by 1.9, 0.5, and 0.3 units with broadcast lime at the 0- to 5-, 5- to 10-, and 10- to 15-cm depths, respectively. The influence of broadcast lime on subsurface soil pH may be due to greater pore continuity or enhanced earthworm activity in DS systems (Blevins et al., 1983; Bezdicek et al., 1998). Broadcast lime applications in DS systems have been found to increase soil pH in the surface 10 cm in as little as 3 (Malhi et al., 1998) to 8 (Moschler et al., 1973) yr. Caires et al. (2005) observed a 0.7 to 1.7 unit increase in pH in the surface 0 to 10 cm of soil
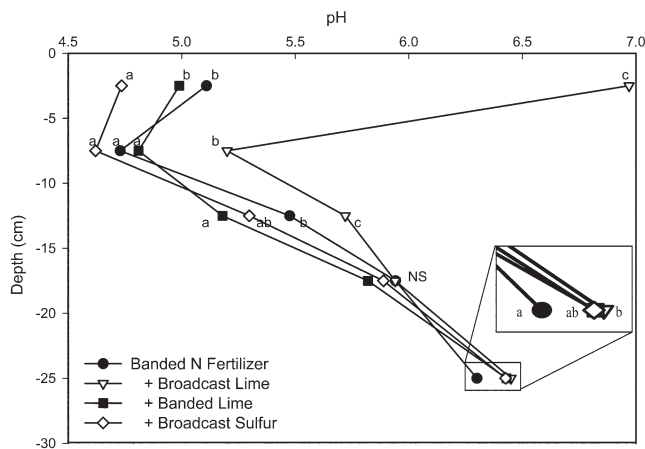

Fig. 1. The effect of lime and S treatments on the distribution of soil pH in a 30-cm profile 2 yr after application. Because there was a significant treatment × depth interaction, all treatment comparisons were made within depth increments. Within depths, data points followed by the same letter(s) are not significantly different using Tukey's pairwise comparisons ($P \leq 0.05$).

after 1 yr, and a 0.2 to 0.4 unit increase in pH at the 10- to 20-cm depth 2.5 yr after broadcast application of 6.7 Mg ha^{-1} of dolomitic limestone to a NT Brazilian soil. Lower rates of lime (1.7 Mg ha^{-1}) increased soil pH by 0.35 at the 5- to 10-cm depth in a NT Australian soil 2 to 4 yr after surface application (Conyers et al., 2003).

There was no difference in pH between the control and subsurface banded lime treatment in the surface 10 cm of soil (Fig. 1). This may be due to the relatively low annual application rate of lime (224 kg ha^{-1}) or uneven distribution of lime pellets in the row. Pelleted lime placed with the seed at a rate of 224 kg ha^{-1} increased soil pH by 0.17 units at the 5- to 7.5-cm depth in a Palouse, WA, study (Wildey, 2003); however, soil pH at that depth of lime placement (5.44) was higher than at the 5- to 10-cm depth of placement in the present study (4.73).

Elemental S was included in this study to accelerate surface soil acidification. Two years after application, broadcast S significantly reduced pH at the 0- to 5-cm depth compared with the control treatment (Fig. 1). Sulfur residue was still evident in the 0- to 5-cm-depth soil samples, indicating incomplete oxidation of S even after 2 yr. Mahler et al. (1985) hypothesized that soils in the IPNW would buffer against pH declines below pH 4.8 based on pH surveys of northern Idaho and eastern Washington soils. The pH of 4.62 in the surface 5 cm of the broadcast S treatment in this study indicates that some portions of the profile are near the lowest values predicted by Mahler et al. (1985) and further declines may be possible if inputs of acidic materials continue. When pH declined below 6, it was estimated that the typical N rates used for cereal crop production in the IPNW may decrease soil pH by 0.5 to 1 pH unit within 7 yr (Jackson and Reisenauer, 1984). Mahler and McDole (1985) similarly predicted that soil pH declines were occurring at a rate of 0.5 pH units every 10 yr in northern Idaho and eastern Washington. Acidity produced by NH$_4$–based fertilizer is initially confined to the surface 30 cm of the soil but could impact seedling emergence (Voight and Mosjidis, 2002), disease pressure, and root growth (McColl et al., 1991; Delhaize et al., 1993) during early stages of growth, and may reduce nutrient and water acquisition (Ritchey et al., 1988; Delhaize et al., 1993), leading to reduced crop vigor (Voight and Mosjidis, 2002) and yield (McColl et al., 1991).

Grain Yield

There was no effect of lime or S treatments on cereal grain yield (Table 3). Variability among replicate treatments was high for spring barley in 2005; however, results suggest trends may be emerging wherein the S treatment is beginning to limit yields. Considering the low soil pH measured in this study (Fig. 1), yield responses were expected. Mahler and McDole (1987) estimated the critical surface 30-cm soil pH for maximum lentil (*Lens culinaris* L.), spring pea (*Pisium sativum* L.), spring barley, and spring and winter wheat yields to be 5.65, 5.52, 5.23, and 5.19 to 5.37, respectively, in northern Idaho CT systems. Lime broadcast at a rate of 4400 kg ha^{-1} and incorporated to a depth of 15 cm using CT increased winter wheat, spring barley, and pea yields by 383 to 636, 212, and 433 kg ha^{-1}, respectively, in northern Idaho (Mahler and McDole, 1985). Corresponding pHs in the surface 45 cm were as low as 4.54

Table 3. Effect of lime and S treatments on grain yield at the Palouse Conservation Field Station, Pullman, WA.

| Treatment | Grain yield | | | |
	2002 spring barley	2003 spring wheat	2004 winter wheat	2005 spring barley
	——————————— kg ha^{-1} ———————————			
Banded N fertilizer	4881 ± 694 a†	3236 ± 828 a	5138 ± 1180 a	3835 ± 375 a
+ broadcast lime	5617 ± 103 a	3182 ± 363 a	4937 ± 525 a	4243 ± 655 a
+ banded lime	5536 ± 137 a	3421 ± 851 a	5100 ± 1072 a	3299 ± 677 a
+ broadcast S	5226 ± 986 a	3191 ± 638 a	5161 ± 509 a	2525 ± 770 a

† The uncertainties for each value are standard deviations calculated using the n − 1 method. Within columns (year and crop), data followed by the same letter are not significantly different using the PROC Mixed procedure in SAS ($P \leq 0.05$).

for untreated controls to as high as 5.15 for the 4400 kg ha^{-1} lime treatment. An average 199 kg ha^{-1} winter wheat grain yield increase was observed in eastern Washington, with broadcast lime applications of 2680 kg ha^{-1} incorporated using CT or subsoil ridge tillage, but no pea yield increase was observed (Bezdicek et al., 2003). Corresponding pH in the surface 20 cm was 4.92 for the untreated control and 5.34 for the lime treatment, which is still below the optimum for pea. There was no wheat or pea yield response to lime at a second site in northern Idaho with initial soil pH from 5.50 to 5.76, above the critical level for these crops. The lack of a yield response to broadcast lime in the present study, despite pHs near or below the critical value for maximum yield, suggests that soil pH alone is not a reliable indicator of lime response potential in DS systems. The difference in soil properties of NT compared with CT systems (Ismail et al., 1994) could contribute to varied crop response to pH and lime between these tillage systems.

Solution Aluminum Chemistry

Aluminum activity is considered to be a more reliable indicator of potential Al phytotoxicity than Al concentration ([Al]), extractable Al, or pH (Shann and Bertsch, 1993; Delhaize and Ryan, 1995). There was a significant ($P \leq 0.05$) treatment × depth interaction for (Al^{3+}) (Fig. 2). In the surface 0- to 5-cm
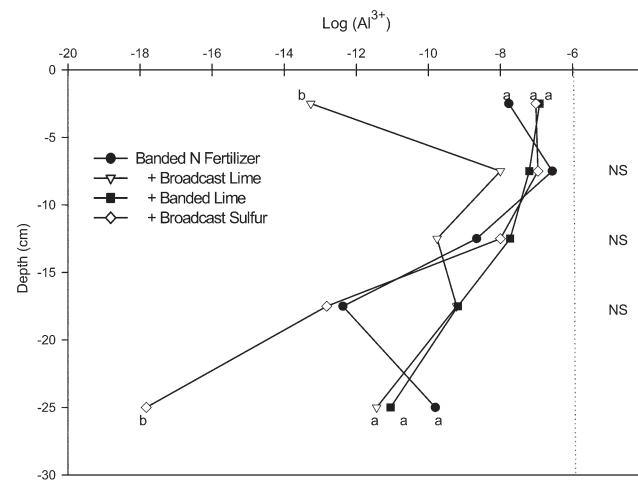

Fig. 2. The effect of lime and S treatments on Al^{3+} activity [(Al^{3+})] in a 30-cm soil profile. Because there was a significant treatment × depth interaction, all treatment comparisons were made within depth increments. Within depths, data points followed by the same letter(s) are not significantly different using Tukey's pairwise comparisons ($P \leq 0.05$). A log (Al^{3+}) of approximately −6 corresponds to the level where Al phytotoxicity has been expressed by many crops (dotted line).
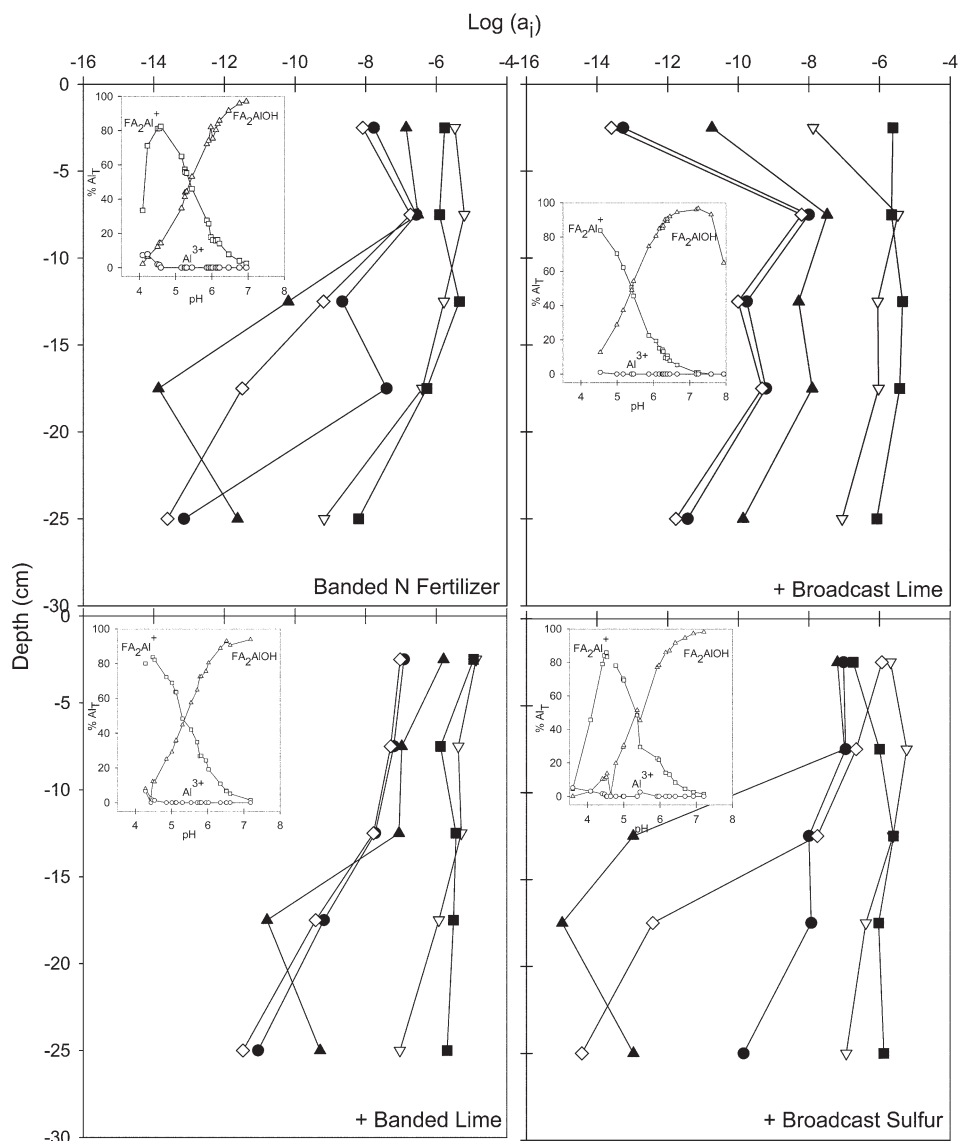
Fig. 3. Predicted activity of Al^{3+} and Al complexes (a_i) as a function of depth in soil extracts. Activities were modeled using data from water extracts input into Visual MINTEQ. The insert graphs show the percentage of total Al (Al$_T$) present as Al^{3+} or organically complexed Al as a function of pH for each treatment; ● = Al^{3+}, ▽ = fulvic acid (FA) as FA$_2$Al$^+$, ■ = FA$_2$AlOH, ◇ = AlSO$_4^+$, ▲ = AlHPO$_4^+$. Note: The 20- to 30-cm depth interval of the broadcast S treatment values are based on one sample. Concentrations of Al$_T$ were below the detection limit of the inductively coupled argon plasma–atomic emission spectroscopy for the other replicates.

was approximately 0.5 units higher than at the 15- to 20-cm depth. This higher pH may result in greater Al precipitation and, hence, reduced (Al^{3+}); however, this would still not explain the difference among treatments, since higher pH at the 20- to 30-cm depth was found for all treatments (Fig. 1). Aluminum activity did not exceed 10^{-6}, the level near which Al phytotoxicity is expressed in many crops (Shann and Bertsch, 1993; Kinraide, 1997), for any treatment or depth (Fig. 2).

Predicting the activity and distribution of Al species in the soil solution under different management strategies is desirable because differential absorption and phytotoxicity exists for different Al species (Lindsay, 1979; Anderson and Bertsch, 1988). The organic FA complexes FA$_2$Al$^+$ and FA$_2$AlOH^0 dominated the predicted Al speciation among treatments at the depths sampled (Fig. 3). In the majority of samples, the predicted activity of FA–Al species was at least one order of magnitude greater than other Al complexes or Al^{3+}. Activities of the Al^{3+}, FA$_2$Al$^+$, and FA$_2$AlOH^0 species were quite similar among treatments at a given pH, and FA$_2$Al$^+$, and FA$_2$AlOH^0 were predicted to dominate total solution Al (Al$_T$) at pH 4.0 to 5.5 and 5.5 to 8.0, respectively (Fig. 3 inserts).

The relatively high proportion of Al$_T$ predicted to be present as FA$_2$Al$^+$ and FA$_2$AlOH^0 complexes in the pH range of these soils has important implications for Al phytotoxicity because they are considered less toxic or nontoxic com-

layer, broadcast lime significantly lowered predicted (Al^{3+}) compared with the other treatments as a result of the large increase in soil pH at this depth (Fig. 1). The (Al^{3+}) was highest at the 5- to 10-cm depth for all treatments, corresponding to the layer most acidified by banded N fertilizer applications. Consistent with effects on pH, subsurface banded lime did not significantly reduce (Al^{3+}) compared with the control at the 5- to 10-cm placement depth.

We are unable to explain the extremely low predicted (Al^{3+}) at the 20- to 30-cm depth in the S treatment (Fig. 2). Three of the four total [Al] data points at this depth were below the detection limit of the ICP–AES for this treatment. Although the SO$_4^{2-}$ activity was slightly higher than the other treatments at this depth (data not shown), the predicted activity of the dominant Al–sulfate complex (AlSO$_4^+$) was less than the other species (Fig. 3) due to low total [Al]. At the 20- to 30-cm depth, the pH

pared with Al^{3+} (Reddy et al., 1995; Haynes and Mokolobate, 2001). Improved crop growth through Al complexation with humic and low molecular weight aliphatic organic acids has been observed in soils amended with organic residues (Haynes and Mokolobate, 2001). Increased pH and decreased monomeric Al, as a proportion of Al$_T$, was observed in a study by Mokolobate and Haynes (2002) using organic residues of grass, household compost, sugar mill waste, and poultry manure as potential liming materials. Reductions in exchangeable Al and (Al^{3+}) have also been reported in acid soils amended with organic material or containing greater soil organic matter (Zysset et al., 1999; Muhrizal et al., 2003). The characteristically high organic matter content of NT surface soils (Bezdicek et al., 1998) may play an important role in complexing Al solubilized under acid soil conditions (Ismail et al., 1994).

Other inorganic Al complexes predicted to occur in these soils included $AlSO_4^+$ and $AlHPO_4^+$. As expected, the elemental S treatment generally resulted in higher ($AlSO_4^+$) than other treatments at depths of 0 to 15 cm (Fig. 3); however, predicted values of FA–Al complexes were generally higher than $AlSO_4^+$. This could result from the chelation effect of bidentate FA, which is more stable and less dependent on concentration than Al complexation with SO_4^{2-} ligands (Driscoll, 1989; Tipping, 2002). At the 0- to 5-cm depth in the S treatment, predicted ($AlSO_4^+$) exceeded the predicted (FA_2AlOH^0). Formation of $AlSO_4^+$ and $AlHPO_4^+$ complexes in acid soils amended with phosphogypsum (Alva and Sumner, 1989), $CaSO_4$ (Noble et al., 1988), and banded P fertilizer (Sloan et al., 1995) decreases (Al^{3+}) and, presumably, reduces Al phytotoxicity in acid soils (Sloan et al., 1995). While the effect of these amendments on (Al^{3+}) may be short lived (Sloan et al., 1995), they may reduce the potential for Al toxicity in emerging seedlings.

Solid-Phase Control of Aluminum Ion Activity

Solid-phase dissolution of Al-bearing minerals can be an important control of soil solution levels of Al_T, and their solubility is primarily dependent on pH (Lindsay, 1979; Sumner et al., 1991). The relationship between (Al^{3+}) in a soil solution and the equilibrium solubility of known solid phases containing Al^{3+} can help identify which solid phases control (Al^{3+}) in a particular soil system (Sumner et al., 1991; Xu, 1991). At pH >5.5, data points from this study cluster along the solubility line for amorphous $Al(OH)_3(s)$ (Fig. 4), suggesting that an Al hydroxide phase controls (Al^{3+}) in this pH range. The (Al^{3+}) at pH <5.5 was below the predicted values for amorphous $Al(OH)_3$, suggesting that another solid phase or process other than dissolution of $Al(OH)_3(s)$ controls (Al^{3+}) at pH <5.5 in these soils. Other Al-bearing solid phases would also be expected to result in an increase in (Al^{3+}) with decreasing pH for equilibrium dissolution, but the slope of (Al^{3+}) vs. pH is near zero below pH 5.5 (Fig. 4). The behavior observed at low pH is representative of that expected for Al controlled by complexation with soil organic matter (Berggren and Mulder, 1995; Zysset et al., 1999). Another possibility is that nonequilibrium conditions existed due to kinetic constraints of $Al(OH)_3$ and other mineral dissolution during the relatively short (24-h) equilibration time; however, it is unlikely that Al dissolution would be less rapid at pH <5.5 than at pH >5.5 because dissolution rates of Al hydroxide minerals generally increase with decreasing pH (Stumm and Wollast, 1990). Interestingly, (Al^{3+}) appears to be buffered near 10^{-6} at pH <5.5 (Fig. 4), which is near the (Al^{3+}) where phytotoxicity has been observed (Delhaize and Ryan, 1995; Reddy et al., 1995).

Undersaturation with respect to $Al(OH)_3(s)$ by approximately 1 to 2 log (Al^{3+}) units between pH 4 and 5 (Fig. 4), coupled with the high proportion of Al_T predicted to be complexed by FA in solution (Fig. 3), suggests that Al–organic matter complexes exert control over (Al^{3+}) at pH <5.5 in the surface horizons of this DS system. Undersaturation by 0.6 to 0.7 log (Al^{3+}) units with respect to gibbsite was reported by Wong and Swift (1995) on addition of humic acid to soil of pH 3.2 to 4.6. Complexation of Al by humic and low molecular weight organic acids was also shown to lower solution (Al^{3+}) and
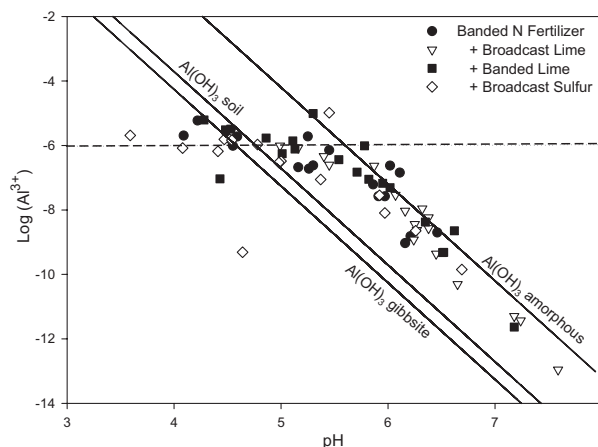

Fig. 4. A comparison of equilibrium values of Al^{3+} activity [(Al^{3+})] from 1:1 water extracts (data points) with theoretical values predicted from $Al(OH)_3$–controlled (Al^{3+}) (lines). Equilibrium expressions were derived from Visual MINTEQ Version 2.32 thermodynamic database. Points falling above the equilibrium line are supersaturated with respect to the mineral while points falling below the equilibrium line are considered undersaturated with respect to the mineral. A log (Al^{3+}) of approximately −6 corresponds to the level where Al phytotoxicity has been expressed by many crops (dashed line).

extractable Al, with concomitant increases in root growth in acid soils amended with organic materials (Mokolobate and Haynes, 2002; Muhrizal et al., 2003). The relatively high organic matter content in the surface of DS soils could provide solid-phase and dissolved organic matter for complexation with Al and offers a reasonable explanation for the departure of (Al^{3+}) from the $Al(OH)_3(s)$ solubility line at pH <5.5 in this study.

CONCLUSIONS

Although measured soil pH is below previously established critical levels for barley and wheat in the IPNW, liming DS systems may not result in crop yield responses at this time. There is evidence that solution- and solid-phase complexation of Al with organic matter may limit solution (Al^{3+}) near the activity at which phytotoxicity is expressed by many plants. In this regard, the higher soil organic matter levels in DS systems could provide a natural buffer against low pH and Al toxicity. Nevertheless, the continued use of NH_4–based fertilizers and concomitant decline in soil pH suggests some form of pH control may be needed in the future.

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