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SOILALUMINUM, IRON, AND PHOSPHORUS DYNAMICS IN RESPONSE TO LONG-TERM EXPERIMENTAL NITROGEN AND SULFUR ADDITIONS AT THE BEAR BROOK WATERSHED IN MAINE, USA

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Abstract. Atmospheric deposition of nitrogen (N) and sulfur (S) containing compounds affects soil chemistry in forested ecosystems through (1) acidification and the depletion of base cations, (2) metal mobilization, particularly aluminum (Al), and iron (Fe), (3) phosphorus (P) mobilization, and (4) N accumulation. The Bear Brook Watershed in Maine (BBWM) is a long-term paired whole-watershed experimental acidification study demonstrating evidence of each of these acidification characteristics in a northeastern U.S. forested ecosystem. In 2003, BBWM soils were studied using the Hedley fractionation procedure to better understand mechanisms of response in soil Al, Fe, and P chemistry. Soil P fractionation showed that recalcitrant P was the dominant fraction in these watersheds (49%), followed by Al and Fe associated P (24%), indicating that a majority of the soil P was biologically unavailable. Acidification induced mobilization of Al and Fe in these soils holds the potential for significant P mobilization. Forest type appears to exert important influences on metal and P dynamics. Soils supporting softwoods showed evidence of lower Al and Fe in the treated watershed, accompanied by lower soil P. Hardwood soils had higher P concentrations in surface soils as a result of increased biocycling in response to N additions in treatments. Accelerated P uptake and return in litterfall overshadowed acidification induced P mobilization and depletion mechanisms in hardwoods.

Keywords: forest soils, acidity, aluminum, iron, phosphorus

1. Introduction

The deleterious effects of atmospheric nitrogen (N) and sulfur (S) deposition on terrestrial ecosystems have been widely studied (Adams, 2003; Burns, 2004; Driscoll *et al.*, 2003; Shannon, 1999). Ecosystem changes include the acidification of soils and surface waters (Driscoll *et al.*, 2001, 2003), the loss of base cations (Adams *et al.*, 2000; Fernandez and Rustad, 1990), N saturation (Aber, 1992; Peterjohn *et al.*, 1996) and metal mobilization (Johnson and Fernandez, 1992; Larssen *et al.*, 1999). Chronic acid deposition can lead to base cation depletion, decreasing soil pH, aluminium (Al) mobilization, and iron (Fe) mobilization as sequential acid neutralization mechanisms are activated in soils (Norton *et al.*, 2004). Changes in the form and distribution of Al and Fe in soils may directly affect biota, and indirectly affect soil phosphorus (P) availability.

Experimentally increased N and S deposition to forests in the eastern U.S. has simulated the effects of air pollutants in more heavily polluted regions, and accelerated acidification processes (Edwards *et al.*, 2002; Fernandez *et al.*, 2003). One of these sites is the Bear Brook Watershed in Maine (BBWM) where one of two adjacent watersheds has been treated bimonthly with N and S since November 1989. Quantitative soil studies at BBWM showed treatments had resulted in lower exchangeable calcium (Ca) and magnesium (Mg) concentrations, and higher exchangeable Al, in the treated watershed compared to the reference (Fernandez *et al.*, 2003). The majority of base cation losses in the first decade of treatments came from soil exchange sites, as Al buffering became increasingly important over time. These results are consistent with a progression of acid neutralization mechanisms leading to the mobilization of soil secondary Al, and eventually Fe phases. The objective of this study was to determine if fractionation techniques could be used to identify acidification-induced changes in soil P, Al and Fe.

2. Materials and Methods

2.1. STUDY SITE

The BBWM is located approximately 60 km from the Gulf of Maine, on the southeast slope of Lead Mountain (44°52′N., 68°06′W.). The BBWM includes two adjacent watersheds, East Bear and West Bear (Norton *et al.*, 1999). Each watershed is drained by a first order stream with comparable hydrology. Soils are loamy, mixed, frigid Typic Haplorthods with well-developed spodic horizons. Higher elevations in each watershed are dominated by softwood stands >100 years old, primarily composed of red spruce (*Picea rubens* Sarg.) and balsam fir (*Abies balsamea* L. Mill.). Lower elevations are dominated by hardwood stands $\sim$55 years old composed of declining American beech (*Fagus grandiofolia* Ehrh.), yellow birch (*Betula alleghaniensis* Britt.), red maple (*Acer rubrum* L.) and sugar maple (*Acer saccharum* Marsh.) (Norton *et al.*, 1999).

In November 1989, bimonthly helicopter applications of dry $(NH_4)_2SO_4$ to the West Bear watershed began and have continued to the present. Treatment rates are 1800 eq ha^{-1} yr^{-1} (25.2 and 28.8 kg ha^{-1} yr^{-1}) N and S, respectively. The East Bear watershed is the adjacent untreated reference site.

2.2. SAMPLE COLLECTION

Soils for this study were collected from BBWM in May and June of 2003. Sixteen locations were selected by a stratified random sampling procedure. This resulted in 8 sites per watershed, 4 each in the hardwood and softwood areas. Mineral soils were excavated from the upper 5 cm beneath the O horizon, 5–25 cm and 25 cm to the top of the C horizon from the face of each pedon.

2.3. LABORATORY ANALYSIS

Samples were dried, sieved (2 mm) and homogenized for chemical analyses. Air-dry moisture content was determined on the fine earth fraction by oven drying at 105 °C. The Hedley sequential fractionation procedure for P was used (Hedley *et al.*, 1982). The fractions extracted are operationally defined as: (1) anion exchange resin (Ionics Inc., AR204SZRA membrane) extracts labile forms of P(P_{resin}); (2) 0.5 M $NaHCO_3$ extracts biologically-available, labile P(P_{NaHCO_3}); (3) 0.1 M NaOH removes P associated with Al and Fe hydroxides, carbonates, and humic materials (P_{NaOH}); (4) 0.1 M NaOH coupled with ultra sonification (75 W using a Branson^{TM} 450 probe type sonifier) liberates P adsorbed to the inner surfaces of Al and Fe hydroxides and soil aggregates ($P_{NaOH\text{-}S}$); (5) 1 M HCl releases P associated with Ca (P_{HCl}), and (6) the sample is digested in H_2O_2/H_2SO_4 to free occluded or highly stable organic P(P_{digest}). We measured Al and Fe concentrations in these extracts to investigate relationships between P and these metals. All extracts were stored at 8 °C until analyzed by ICP-AES. We present here the inorganic P fraction results. At two points in the Hedley procedure, organic P is measured, but we do not present those results due to incomplete recovery from these acidic forest soils. Data quality was assured using extraction reagent blanks, sample replicates, and the in-house secondary standards of bulk BBWM mineral soils (Fernandez *et al.*, 2003).

2.4. STATISTICAL ANALYSIS

Differences among means for treatment and forest types were tested using ANOVA. Data were analyzed for equality of variance and normality. Data that did not meet these assumptions were rank transformed. Interactions among main effects were evaluated using Tukey's HSD for mean separations. Statistical analyses were performed using the Statistical Analysis System (SAS, 1999), $\alpha = 0.05$.

3. Results and Discussion

3.1. INORGANIC P AT BBWM

Table I shows the means by watershed and forest type for inorganic P fraction concentrations. Figure 1 shows the overall mean distribution of inorganic P fractions in the reference East Bear watershed. Approximately half of the inorganic P occurred as residual P in the final digestion step of the Hedley procedure. Next

TABLE I

Mean Inorganic P, AI and Fe fraction concentrations for the Hedley fractionation procedure for each watershed and forest type; statistical significance at alpha = 0.05[1]

Watershed	Forest type	Depth	Resin	$NaHCO_3$	NaOH	NaOH-S	HCl	Digest
					mg kg^{-1}			
					P			
West Bear	Hardwood	0–5 cm	28	12	43	3	19	82
West Bear	Hardwood	5–25 cm	9	7	77‡	9†	28	82
West Bear	Hardwood	25–C hor	10	5	83	5	55	66
East Bear	Hardwood	0–5 cm	14	13	40	2	13	88
East Bear	Hardwood	5–25 cm	10†	7	38‡	6	16	78†
East Bear	Hardwood	25–C hor	12	2	45†	4	45	67
West Bear	Softwood	0–5 cm	18	16	50	3	14	88
West Bear	Softwood	5–25 cm	11‡	18	46	2†	17	83
West Bear	Softwood	25–C hor	10	11	32‡	4‡	34	75
East Bear	Softwood	0–5 cm	11	14	48	7	22	118
East Bear	Softwood	5–25 cm	14†‡	15	51	10	19	112†
East Bear	Softwood	25–C hor	13	20	73†‡	24‡	22	130
					A1			
West Bear	Hardwood	0–5 cm	173	208	2448	145	1540†‡	2025
West Bear	Hardwood	5–25 cm	90	133	3875	465	2282	2604
West Bear	Hardwood	25–C hor	146	101	2916	256	1952	2133
East Bear	Hardwood	0–5 cm	52	271	2722	170	2255‡	3726
East Bear	Hardwood	5–25 cm	37	168	2499	376	2421	3463
East Bear	Hardwood	25–C hor	34	119	2571	267	2188†	2699
West Bear	Softwood	0–5 cm	27	170	1748	144	2140†	3793
West Bear	Softwood	5–25 cm	50	242	2354	213	2110	3630
West Bear	Softwood	25–C hor	50	218	1687	165	1608‡	2545
East Bear	Softwood	0–5 cm	60	227	1892	269	3027	4200
East Bear	Softwood	5–25 cm	38	207	2245	282	2803	3766
East Bear	Softwood	25–C hor	50	376	3327	400	2550†‡	3438
					Fe			
West Bear	Hardwood	0–5 cm	216	127	128	11	11031	4332
West Bear	Hardwood	5–25 cm	58	67	106	22	10617	4509
West Bear	Hardwood	25–C hor	87	39	60	16	6796	4076
East Bear	Hardwood	0–5 cm	80	177	199	3	16146	9609
East Bear	Hardwood	5–25 cm	36	53	99	21	11357	6942
East Bear	Hardwood	25–C hor	78	49	133‡	14	7045	4553
West Bear	Softwood	0–5 cm	52	128	71	12	16195	6655
West Bear	Softwood	5–25 cm	65	89	56	17	14438	6308
West Bear	Softwood	25–C hor	53	88	61	21	9793	5138
East Bear	Softwood	0–5 cm	117	399	133	13	34877	18398
East Bear	Softwood	5–25 cm	125	256	49	16	33044	15250
East Bear	Softwood	25–C hor	121	282	38†	19	39615	12213

[a,†] Statistically significant difference between forest types within a watershed.

[‡] Statistically significant difference between watersheds within a forest type.

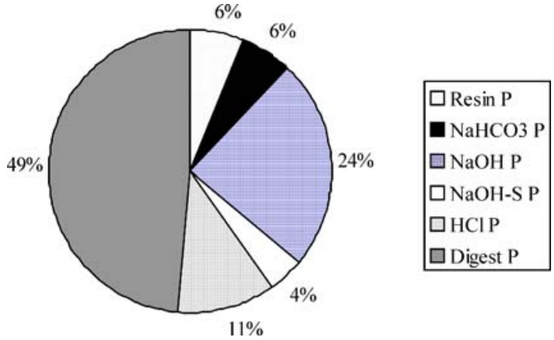
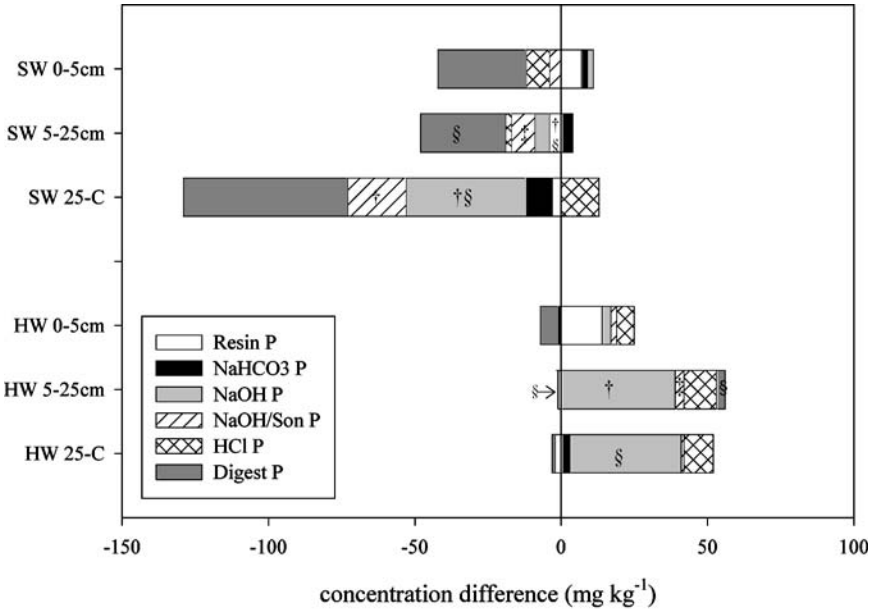


Figure 1. Mean area-weighted % of inorganic P in mineral soils at BBWM.

in importance is NaOH-extractable P,thought to represent P adsorbed to Fe and Al sesquioxides, and humic material, prevalent in these soils. Next in abundance is inorganic P extracted with HCl (~11%) associated with Ca, as in the mineral apatite ($Ca_5(PO_4)_3OH$), the primary source of most soil P, and a more recalcitrant fraction than P_{NaOH}. The smallest portion of the inorganic P occurred in the most labile resin or $NaHCO_3$-extractable fractions, presumably because this fraction is either biologically immobilized or depleted in these highly acidic (pH generally <5.0) forest soils.

The numerical means for P concentrations in most fractions (Table I) were lower in West Bear than East Bear for softwoods, with few statistically significant differences. For hardwoods, the treated West Bear soils had numerically higher mean concentrations of P in most fractions. Only P_{NaOH} in the 5–25 cm depth was significantly different between watersheds (Figure 2) with hardwoods higher in the treated watershed compared to the reference. In softwoods, the treated watershed had significantly lower P_{resin} in the 5–25 cm increment, and significantly lower P_{NaOH} and $P_{NaOH\text{-}S}$ in the 25-C horizon increment, compared to the reference. The possibility of opposing trends in the response of P fractions to acidification between hardwoods and softwoods could reflect differences in both soil and tree processes. If the data are representative of whole-ecosystem processes, we speculate that accelerated acidification in West Bear softwoods mobilizes Al and Fe along with the associated P, resulting in a depletion of P from the larger inorganic P pools for these soils. Stream chemistry in West Bear for high discharge events has similar ratios of Al/P to the ratios of $(Al/P)_{NaOH}$ in soils, suggesting mobilization of these fractions and translocation into surface waters during high discharge (Reinhardt *et al.*, 2004). Biological uptake of P by softwoods is not as efficient as hardwoods. Hardwoods, mostly maple, beech, and birch, are typically more nutrient-demanding than softwoods (White *et al.*, 1999) and more effective at taking up mobilized soil P and biocycling P through foliage and litterfall back into the soil. This is consistent with the evidence that the added N at BBWM is moving West Bear towards more rapid nutrient turnover and N saturation



[1]† = differences between watersheds within a forest type
‡ = differences between forest types within the treated site
§ = differences between forest types within the reference site

Figure 2. Hedley P fraction mean concentration differences (West Bear – East Bear) between watersheds by forest type. Differences between watersheds at $\alpha = 0.05^1$ (negative numbers represent lower concentrations in the treated (West Bear) site than the reference (East Bear) site, SW = softwoods, HW = hardwoods).

(Jefts *et al.*, 2004). The development of N saturation may reduce P availability by increasing N as well as P demand (Carreira *et al.*, 2000). If biocycling were more efficient in hardwoods, we would expect higher rates of P uptake along with higher P concentrations in foliage and litterfall. In agreement, Elvir *et al.* (2003) reported evidence of positive growth response to treatments in the West Bear hardwoods. Rustad and Fernandez (unpublished data) found significantly higher foliar P concentrations in hardwoods in West Bear, particularly in sugar maple, but no such consistent foliar P concentration increase for red spruce. In softwoods, lower foliar and litter P concentrations and slower rates of P mineralization do not result in a treatment-induced surface enrichment of labile P even though there may be subsoil mobilization of labile P into soil solutions due to acidification. At the BBWM, net N mineralization and net nitrification are greater in the treated West Bear watershed compared to East Bear, and greater in hardwood O horizons compared to softwoods (Jefts *et al.*, 2004). Higher rates of N cycling in the treated watershed and in hardwoods would support the idea that treatments have also increased P biocycling as evidenced in these data.

3.2. ALUMINUM AND IRON

We explored the utility of the Hedley extractions for gaining insights on Al and Fe relationships with P. The patterns of Al and Fe distribution found using the Hedley procedure closely paralleled the results using traditional pedological procedures (Sherman, 2005). There were few significant differences between forest types or watersheds for the Hedley fractions for the metals, although the numerical trends generally supported patterns and mechanisms discussed for the P data. In many instances there were numerically lower concentrations for Al and Fe in the treated West Bear compared to East Bear that supported earlier suggestions of an acidification-induced depletion of these metals, with significantly lower Al_{HCl} in the 0–5 cm increment for hardwoods and 25-C horizon increment for softwoods. Lower concentrations of amorphous and crystalline Al_{HCl} may result in lower concentrations of adsorbed P_{NaOH}. Hardwood stands in West Bear that had significantly lower concentrations of amorphous Al_{HCl} did not however have the expected lower concentration of associated P_{NaOH}. These soils contain significantly greater concentrations of P_{NaOH} in West Bear at the 5–25 cm increment, which may mean that the organic amorphous Al not reported in this study was responsible rather than inorganic forms of Al.

The abundance of crystalline Fe_{HCl} secondary mineral phases in these soils is noteworthy in discussing P availability. These mineral fractions are not thought to readily sorb P due to low porosity and a high degree of crystallinity, and have been considered to be unimportant in P retention despite their abundance. If these Fe_{HCl} phases become mobilized and form reactive secondary Fe hydrous oxides, or become associated with humic substances, we would expect a large potential increase in P immobilization and sequestration in these soils.

4. Conclusions

Soil chemistry at BBWM presents evidence that long-term elevated N and S deposition results in increased Al, Fe, and P mobilization, and increased rates of biocycling associated with N saturation processes. Softwood and hardwood forest types were notably different in their soil responses to watershed acidification, with softwoods showing the greatest indication of soil Al and Fe mobilization. Lower concentrations in some soil Al and Fe fractions in the treated watershed (e.g. amorphous and crystalline Al_{HCl}) were associated with similar differences in P, suggesting a coupled release of P that was bound in these Al and Fe fractions. While geochemical processes may explain the results for Al, Fe, and P in softwoods, hardwoods yielded different results. Higher available P in the upper soil horizons of hardwoods in the treated watershed is interpreted as a response to mobilization of soil P through acidification and accelerated vegetative uptake.This P is subsequently returned to the forest floor as litterfall. The naturally higher quality of litter in hardwoods compared to softwoods, further magnified by the N treatments, resulted in a more rapid rate of nutrient supply from litter decomposition in this forest type to upper soil horizons. Although forest soils are notoriously heterogeneous, and chemical fractionation methods provide data on operationally defined soil element phases only, the Hedley fractionation data appear useful in suggesting complex and evolving ecosystem responses to long-term acidification.

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