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Vertical distribution of biological and geochemical phosphorus subcycles in two southern Appalachian forest soils

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Abstract. We measured Al, Fe, and P fractions by horizon in two southern Appalachian forest soil profiles, and compared solution PO_4^{3-} removal in chloroform-sterilized and non-sterilized soils, to determine whether biological and geochemical P subcycles were vertically stratified in these soils. Because organic matter can inhibit Al and Fe oxide crystallization, we hypothesized that concentrations of non-crystalline (oxalate-extractable) Al (Al_o) and Fe (Fe_o), and concomitantly P sorption, would be greatest in near-surface mineral (A) horizons of these soils.

Al_o and Fe_o reached maximum concentrations in forest floor and near-surface mineral horizons, declined significantly with depth in the mineral soil, and were highly correlated with P sorption capacity. Small pools of readily acid-soluble (AF-extractable) and readily-desorbable P suggested that PO_4^{3-} was tightly bound to Al and Fe hydroxide surfaces. P sorption in $CHCl_3$-sterilized mineral soils did not differ significantly from P sorption in non-sterilized soils, but $CHCl_3$-sterilization reduced P sorption 40–80% in the forest floor. $CHCl_3$-labile (microbial) P also reached maximum concentrations in forest floor and near-surface mineral horizons, comprising 31–35% of forest floor organic P. Combined with previous estimates of plant root distributions, data suggest that biological and geochemical P subcycles are not distinctly vertically stratified in these soils. Plant roots, soil microorganisms, and P sorbing minerals all reach maximum relative concentrations in near-surface mineral horizons, where they are likely to compete strongly for PO_4^{3-} available in solution.

Introduction

Complex processes control the cycling and availability of phosphorus (P) in forest soils. These processes can be grouped into relatively distinct biological and geochemical subcycles. Inorganic phosphate (P_i) in solution is the primary form of P taken up by plants (Stevenson 1986). Solution phosphate concentrations are low in most natural soils, but are buffered through equilibrium relationships with labile (readily-soluble) P_i and relatively insoluble secondary mineral (adsorbed) P_i. In combination with PO_4^{3-} released by the weathering of primary minerals, these relationships comprise an intrasystem geochemical subcycle (Fig. 1). Soil microorganisms can also influence solution phosphate concentrations through the opposing processes of mineralization and immobilization (Stevenson 1986), and in combination with plant uptake, leaching, and organic matter turnover, comprise an intrasystem biological subcycle (Fig. 1).

In attempting to determine the relative importance of biological (indexed by the distributions of plant roots and soil microorganisms) and geochemical (indexed by the distributions of HCl-extractable Al and Fe and P sorption capacity) processes in controlling phosphorus retention in a northern hardwoods forest Spodosol in New Hampshire, Wood et al. (1984) found that biological and geochemical subcycles were vertically stratified within the soil profile — biological processes (decomposition and plant uptake) controlled P cycling in forest floor and near-surface mineral horizons, while geochemical processes (sorption by Fe and Al sesquioxides) regulated P retention at depth (below 20 cm). The idea of 'vertical stratification' of biological and geochemical control has subsequently been raised in discussions of P cycling in a wide variety of forest soils (e.g., Binkley 1986; Attiwill & Leeper 1987).

Many forest soils in the southern Appalachians are Inceptisols or Ultisols that develop from parent materials rich in readily-weatherable Al and Fe (Hatcher 1988; Velbel 1988). Weathering causes the formation of free Al and Fe oxides and hydroxides that range from poorly-ordered, fine-textured non-crystalline (amorphous) compounds to highly-structured, coarse-textured crystalline forms. In acid soils, gibbsite (Al) and goethite (Fe) are the most stable crystalline oxides, but a number of soil constituents can inhibit crystallization, favoring the persistence of non-crystalline forms. Both types of compounds sorb PO_4^{3-} by the same mechanism, but non-crystalline forms tend to dominate soil sorption reactions because of their larger surface area/mass ratios (Hsu 1977; Schwertmann & Taylor 1977; Parfitt & Smart 1978).

At the Coweeta Hydrologic Laboratory, North Carolina, three components of the bedrock are both weatherable and sufficiently abundant to influence dissolved mineral concentrations — biotite mica, almandine garnet, and plagioclase feldspar (Velbel 1988). All are potential sources of Al; biotite and garnet are also potential sources of Fe. Velbel (1984) found that almandine garnet in A and B horizons of Coweeta soils did not develop the gibbsite-goethite crust characteristic of weathered garnet particles in saprolite (C horizons), and suggested that biochemical or biological processes in the soil prevented the formation of the crystalline Al and Fe layer.

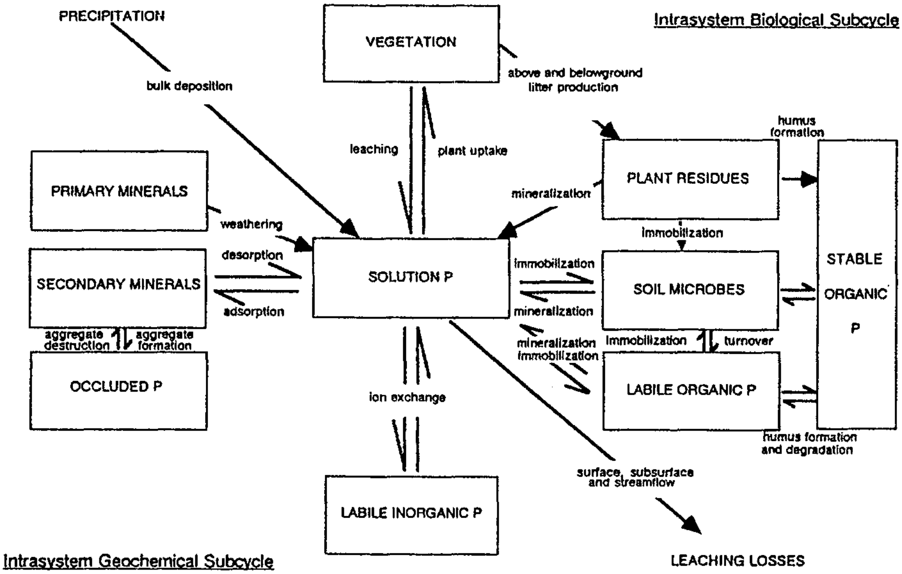

Fig. 1. Conceptual model of the phosphorus cycle of a forest ecosystem (adapted from Chauhan et al. 1981; Wood et al. 1984; Monk & Day 1988). The model indicates major ecosystem inputs (precipitation) and outputs (leaching losses) and delineates intrasystem biological and geochemical subcycles. Boxes represent phosphorus pools; labeled arrows indicate important P transfers. (From 'Phosphorus availability in acid organic soils of the lower North Carolina coastal plain' by M. R. Walbridge, *Ecology*, 72, 1991. © 1991 by the Ecological Society of America. Reprinted by permission.)

Because organic matter can also inhibit Al and Fe oxide crystallization (Schwertmann 1966; Hsu 1977; Kodama & Schnitzer 1977, 1980; Schwertmann & Taylor 1977), we hypothesized that concentrations of non-crystalline Al and Fe, and concomitantly P sorption, would be greatest in near-surface mineral horizons of Coweeta soils having well developed forest floors, and would decline with depth. This contrasts with the Spodosol profile examined by Wood et al. (1984), where P sorption was minimal in surface horizons.

To test this hypothesis we measured changes in Al, Fe, and P fractions with depth, and compared solution PO_4^{3-} removal in $CHCl_3$-sterilized and non-sterilized soils, in two southern Appalachian forest soil profiles. Our objective was to determine whether biological and geochemical P subcycles were vertically stratified in these soils.

Methods

Study sites

Our study was conducted at the Coweeta Hydrologic Laboratory, Otto, NC. The Coweeta Basin (latitude 35°03'N, longitude 83°25'W) is part of the Nantahala Mountain Range, in the Blue Ridge Physiographic Province of the southern Appalachians (Swank & Crossley 1988). Mean annual temperature is 13 °C. Mean annual precipitation is 1810 mm and is evenly distributed throughout the year (Swift et al. 1988).

The study sites were located in two watersheds. Watershed 18 (WS18) is a 12.5-ha north-facing catchment dominated by mixed, mature hardwoods. Watershed 1 (WS1) is a 16.2-ha south-facing catchment that was clearcut in 1956 and planted with white pine (*Pinus strobus* L.) in 1957 (Swank & Douglass 1977). The Tallulah Falls Formation, common throughout the eastern Blue Ridge, is the underlying parent material in both watersheds, consisting of feldspar- and biotite-rich metasandstones interlayered with mafic volcanic rocks and aluminous schists (Hatcher 1988). Study sites were located on mid-slope positions of moderate to steep southwest- or southeast-facing slopes, on soils identified *in situ* as Chandler (micaceous, mesic, Typic Dystrochrept) or Fannin (micaceous, mesic, Typic Hapludult) series soils in WS18 and WS1, respectively (S. Browning, USFS-Asheville). Although both soil types are common in each watershed, in this paper 'WS1 soils' will refer specifically to Fannin (Typic Hapludult) soils, and 'WS18' soils will refer specifically to Chandler (Typic Dystrochrept) soils. Some basic characteristics of each soil type are given in Table 1.

Soil and forest floor collection and general analysis

Soil samples were collected on October 15 and December 6, 1985, and October 7, 1986, from a 0.1-ha (20 × 50-m) plot in each watershed. Each plot was divided into 5 10 × 20-m subplots and a 20-m transect was randomly located within each subplot. Two soil cores were collected along each transect, at random locations within the 0—10 and 10—20-m segment of each transect. Each core consisted of 1 forest floor (Oi + Oe + Oa) and 4 mineral soil horizon samples. Collection depths followed Swank et al. (1984) and Strickland et al. (1984) for WS18 and WS1, respectively (Table 1).

Forest floor samples were collected intact by cutting around a 10 × 10-cm metal template with a serrated knife, after removing surface litter. Mineral soils were collected with a 6-cm diameter hand corer (A horizon) or a 7-cm diameter closed bucket soil auger. Samples from each horizon were composited by transect (n=2/transect) into 5 replicate samples horizon^{-1} plot^{-1}, placed in individual polyethylene bags, and kept cool until returning to the laboratory where they were stored field-moist at 4 °C. Prior to chemical analysis, each sample (n = 5 horizon^{-1} site^{-1}) was

Table 1. General properties of Coweeta soils. Data are means with standard errors in parentheses.

Horizon	Depth (cm)	Loss on ignition[1] (%)	Sand[1] (%)	Silt[1] (%)	Clay[1] (%)	Soil pH[2] (water)	Bulk density[3] (g/cm^3)
Watershed 1 (Typic Hapludult)							
O	0—4	52.1 (3.0)	74.1 (0.1)	22.3 (1.1)	3.6 (1.1)	ND	0.059
A	4—13	10.0 (0.3)	55.0 (1.1)	22.6 (1.0)	22.3 (0.1)	4.56	0.62
BA	13—32	7.9 (0.1)	49.2 (0.5)	24.3 (0.9)	26.5 (1.4)	4.58	0.68
Bt	32—66	7.5 (0.1)	45.8 (2.0)	20.3 (2.1)	33.8 (0.1)	4.63	0.64
Bc	66—95	7.2 (0.0)	46.5 (1.5)	19.3 (0.5)	34.2 (1.0)	4.76	0.72
Watershed 18 (Typic Dystrochrept)							
O	0—4	43.8 (2.2)	59.9 (1.1)	32.1 (0.5)	8.0 (0.6)	ND	0.063
A	4—14	9.5 (0.0)	63.1 (4.3)	14.8 (5.6)	22.2 (1.2)	4.30	0.85
AB	14—29	7.3 (0.0)	53.3 (1.4)	20.4 (0.4)	26.3 (0.9)	4.42	0.86
Bw	29—69	6.0 (0.1)	58.8 (1.3)	18.3 (1.4)	22.9 (0.1)	4.66	0.92
Cr	99—104	5.6 (0.1)	60.9 (1.0)	20.2 (0.9)	18.9 (0.1)	4.84	1.11

[1] (n = 2).

[2] (n = 5)

[3] Bulk densities estimated by undisturbed core method (Swank, unpublished data).

thoroughly mixed by hand to a homogeneous mixture, removing gravel and coarse root material.

Soil pH was determined by pH electrode in a 1:2 slurry of soil: deionized water. Soil organic matter was estimated by mass loss on ignition in a muffle furnace at 500 °C for 4 hrs. Soil texture was determined by the Bouyoucos method (Day 1965).

Free soil Al and Fe fractions

We used selective dissolution to estimate concentrations of non-crystalline and crystalline Al and Fe in these soils. Replicate 0.4-g dry weight equivalent (dwe) subsamples (n=2) of soils collected in 1985 were extracted with 40 ml of either 0.1 *M* sodium pyrophosphate, or 0.2 *M* acid ammonium oxalate adjusted to pH 3 (USDA 1972; Johnson & Todd 1983). Replicate 0.4-g dwe subsamples (n=2) of soils collected in 1986 were sequentially extracted with sodium pyrophosphate, acid ammonium oxalate, and dithionite-citrate-bicarbonate (DCB) (Wieder & Lang 1986).

Oxalate dissolves both non-crystalline and organically-bound forms of Al and Fe, but with the exception of magnetite, does not attack crystalline forms (McKeague & Day 1966; Baril & Bitton 1969; Blume & Schwertmann 1969; McKeague et al. 1971; Borggaard 1982; Schwertmann et al. 1982; Fordham et al. 1984). DCB dissolves crystalline Fe, liberating Al substituted for Fe in crystalline Fe minerals, as well as non-crystalline and organically-bound forms of both Fe and Al. However DCB does not dissolve highly crystalline Al minerals such as gibbsite (McKeague et al. 1971; Fordham et al. 1984; Parfitt & Childs 1988). Pyrophosphate has been used to selectively dissolve organically-bound Fe and Al (Aleksandrova 1960; McKeague 1967; Bascomb 1968; Loveland & Digby 1984; McKeague & Schuppli 1985), but can dissolve significant amounts of both non-crystalline ferrihydrite and crystalline goethite in some soils (Borggaard 1988; Parfitt & Childs 1988).

All three procedures provide only empirical estimates of the relative proportions of organically-bound, non-crystalline and crystalline Al and Fe in soils (Schwertmann 1973). They are not 100% efficient, and are not capable of identifying specific soil minerals unless used in conjunction with other methods such as Mossbauer spectroscopy or X-ray diffraction (McKeague et al. 1971; Schwertmann & Taylor 1977; Ericsson et al. 1984; Borggaard 1988; Parfitt & Childs 1988). They are, however, routinely and generally successfully used to identify relative proportions of non-crystalline and crystalline Al and Fe in a wide range of soils (Aleksandrova 1960; McKeague & Day 1966; McKeague 1967; Bascomb 1968; Blume & Schwertmann 1969; McKeague et al. 1971; USDA 1972;

Schwertmann et al. 1982; Johnson & Todd 1983; Loveland & Digby 1984; McKeague & Schuppli 1985; Johnson et al. 1986; Wieder & Lang 1986).

P sorption

Soil sorption and desorption capacities were determined by equilibrating replicate 2.70-g dwe subsamples of mineral soil, or 1.35-g dwe subsamples of forest floor, with 25 or 12.5 ml, respectively, of 0.01 *M* $CaCl_2$ containing 0.00, 0.01, 0.10, 1.00, or 10.00 mM/L KH_2PO_4 (n=4 sample^{-1} treatment^{-1}). To inhibit microbial uptake, half of the replicates (n=2 sample^{-1} treatment^{-1}) were sterilized by adding 0.5 ml of liquid $CHCl_3$ prior to PO_4^{3-} and/or $CaCl_2$ addition; the other half received no $CHCl_3$ prior to $PO_4^{3-}/CaCl_2$ addition. Samples were shaken on a mechanical shaker for three 30-min priods at 0, 12, and 23.5 hrs after $PO_4^{3-}/CaCl_2$ addition, and then centrifuged to clarity at 3000 rpm for 10 minutes and the PO_4^{3-} concentrations of the supernatants determined (Nair et al. 1984; Richardson 1985). $CHCl_3$ was not evaporated from fumigated samples prior to subsequent treatment since we did not intend to re-inoculate treated soils with active microbial cultures.

Adding $CHCl_3$ to soils lyses microbial cells releasing both PO_4^{3-} and labile organic P (P_o) to the soil solution (Brookes et al. 1982; Hedley & Stewart 1982). Since 'P sorbed' is usually calculated as (PO_4-P added minus PO_4-P remaining in solution), additional PO_4^{3-} released by $CHCl_3$ treatment should be included with 'PO_4-P added' when calculating P sorbed by $CHCl_3$-sterilized soils. Though difficult to measure, we estimated this additional potentially sorbable PO_4^{3-} by extracting another set (n=2 sample^{-1} treatment^{-1}) of $CHCl_3$-treated forest floor and mineral soil subsamples with 25 or 12.5 ml, respectively, of 0.01 *M* $CaCl_2$ immediately after $CHCl_3$ addition. The PO_4-P measured in these extracts was included as 'P added' when calculating P sorbed in $CHCl_3$-sterilized soils. Our estimate of the PO_4^{3-} released by $CHCl_3$ treatment probably underestimates the actual amount since some PO_4^{3-} may have been sorbed immediately after adding $CHCl_3$, while additional PO_4^{3-} may have been liberated by the hydrolysis of labile microbial P_o during the 24-h equilibration period of the P sorption procedure.

PO_4^{3-} removed from solution in sterilized soils was used to estimate P sorption by soil minerals (geochemical sorption), assuming that no microbial immobilization occurred in $CHCl_3$-sterilized soils during the 24-h equilibration period. PO_4^{3-} removed from solution in non-sterilized soils was used to estimate the sum of P sorption plus microbial immobilization. Sorption data from the 10 mM/L KH_2PO_4 addition (287 mgP/100 g soil) were used to develop a P sorption index for each soil horizon using the formula x/log c (Bache & Williams 1971; Richardson 1985), where x = P sorbed (mg P/100 g soil) and c = the equilibrium P concentration (μM/L). Bache & Williams (1971) suggested using 150 mg P/100 g soil to determine the P sorption index because 100 mg P/100 g soil was too low and there were potential analytical problems at 200 mg P/100g or greater. Of the levels of addition used in our sorption studies, 10 mM KH_2PO_4 was the only level suitable for developing the P sorption index (1 mM KH_2PO_4, or 28.7 mg P/100g soil, would be too low), and the only level that indicated saturation of P sorption capacity across all soil horizons. No problems of analytical precision were observed in our P analyses.

Soil P fractions

We estimated readily acid-soluble (available) P by dilute acid-fluoride (AF) extraction of replicate 5-g subsamples of each soil sample (Olsen & Sommers 1982). Microbial biomass P was estimated by the net increase in AF-extractable PO_4-P (not total P) in samples treated with 0.5 ml of liquid $CHCl_3$ and then incubated for 18 hrs in capped 50 ml polypropylene centrifuge tubes. All extractions were made within 24 hours of soil collection.

In estimating microbial P in these acid soils, we used AF as an alternative to the 0.5 *M* $NaHCO_3$ extraction (pH 8.5) used by Brookes et al. (1982) and Hedley & Stewart (1982) (Walbridge & Vitousek 1987). Due to the much shorter extraction time (1 min vs. 16 hrs), we did not use a PO_4^{3-} spike to estimate P sorbed during soil extraction (Brookes et al. 1982). We assumed that 40% of microbial biomass P was extracted by $CHCl_3$/AF. This value has been found to closely approximate microbial P extracted by $CHCl_3/NaHCO_3$ in soils ranging from pH 6.2 to 8.2 (Brookes et al. 1982; Hedley & Stewart 1982), and represents the average percentage (range 37—46%) of microbial P extracted by $CHCl_3$/AF from 14 acidic NC coastal plain forest and wetland soils of pH 3.6 to 4.2 (Walbridge 1991).

Total soil P (P_T) and N (N_T) were determined by H_2SO_4-H_2O_2 digestion (Schoenau & Bettany 1987). This procedure does not recover some tightly-bound forms of mineral P (Williams et al. 1970), and may have caused us to underestimate soil P_T in mineral horizons. Soil P_o was estimated by the net increase in P extracted by 25 ml of 1 *M* H_2SO_4 from replicate 0.5-g subsamples at 400 °C for 1 hr, vs. non-ashed samples (Olsen & Sommers 1982; Schimel et al. 1985). As such, P_o estimates include PO_4^{3-} complexed with organic matter and/or associated with humic and fulvic acids, and possibly some tightly-bound mineral P.

Chemical and statistical analyses

Orthophosphate concentrations of soil extracts and P and N concentrations of soil digests were analyzed by standard methods of autoanalysis (Orion Scientific Instruments Corporation 1984). Al and Fe concentrations of pyrophosphate, oxalate, and DCB extracts were determined with a Perkin-Elmer Model 2380 atomic absorption spectrophotometer (Perkin-Elmer 1982). For each watershed, significant differences in Al, Fe, P, and N concentrations among soil horizons were determined by ANOVA (n=5/horizon), and by Fisher's LSD when the overall ANOVA was significant at P=0.95. Statistical analyses were made using SAS ANOVA and GLM procedures (SAS Institute Incorporated 1985).

Results

Free soil Al and Fe fractions

In both soil profiles, oxalate-extractable Al (Al_o) and Fe (Fe_o) reached maximum concentrations in forest floor (O) and/or near-surface mineral (A) horizons, and declined significantly with depth in the mineral soil (Table 2). Al_o and Fe_o concentrations in soils previously extracted with sodium pyrophosphate (sequential extraction) were lower than those determined by separate extraction, but showed similar trends. Changes in pyrophosphate-extractable Al (Al_p) and Fe (Fe_p) with depth were less consistent, varying significantly in 1985 vs. 1986 soils, while DCB-extractable (Al_d, Fe_d) and total free (Al_T, Fe_T) Al and Fe showed little significant variation with depth in either soil. Al_T concentrations were similar in both soils, but Fe_T concentrations were about 1.5 times higher in the WSl profile.

When oxalate and DCB extractions are performed on separate samples, Fe_o/Fe_d ratios can be used as an index of the degree of crystallinity of free Fe in soils (Blume & Schwertmann 1969). Al_o/Al_d ratios are less well defined since DCB does not extract gibbsite (Parfitt & Childs 1988). We used Fe_T and Al_T from the sequential extractions to estimate total DCB-extractable Fe and Al (DCB dissolves all species of free Fe and Al that are extracted by both pyrophosphate and oxalate) and calculated Fe_o/Fe_d and Al_o/Al_d ratios using Fe_o and Al_o from the separate extraction of 1985 soils. Fe_o/Fe_d ratios declined with depth in both soils, suggesting an increase in free Fe crystallinity with depth, and were greater in surface horizons of the WS18 profile (Fig. 2). Al_o/Al_d ratios also declined with depth in both soil profiles.

Table 2. Concentrations of pyrophosphate-extractable (Al$_p$, Fe$_p$), oxalate-extractable (Al$_o$, Fe$_o$), dithionite-extractable (Al$_{,d}$, Fe$_d$), and total free (Al$_T$, Fe$_T$) Al and Fe determined by separate extractions of soils collected in October/December 1985 and sequential extraction of soils collected in October 1986. Values are means of five replicates, with standard errors in parentheses.

Horizon	Al$_p$	Al$_o$	Al$_d$	Al$_T$ (mmol/kg)	Fe$_p$	Fe$_o$	Fe$_d$	Fe$_T$
1985 collection (separate extraction)								
WS1 O	120 (15)	68 (6) bc[1]	ND[2]	ND	38 (4) c	24 (2) c	ND	ND
A	201 (19)	124 (12) a	ND	ND	66 (4) b	49 (3) a	ND	ND
BA	220 (19)	88 (9) b	ND	ND	78 (3) ab	32 (2) bc	ND	ND
Bt	259 (28)	54 (6) c	ND	ND	100 (6) a	26 (4) c	ND	ND
BC	194 (57)	49 (5) c	ND	ND	65 (16) b	36 (4) b	ND	ND
WS18 O	213 (10) a	135 (11) a	ND	ND	70 (4)	47 (3) a	ND	ND
A	227 (2) a	126 (4) a	ND	ND	76 (1)	47 (2) a	ND	ND
AB	223 (9) a	94 (6) b	ND	ND	76 (3)	30 (1) b	ND	ND
Bw	202 (14) a	40 (3) c	ND	ND	72 (5)	22 (2) c	ND	ND
Cr	139 (20) b	38 (4) c	ND	ND	61 (16)	21 (3) c	ND	ND
1986 collection (sequential extraction)[3]								
WS1 O	105 (10) c	*40 (3) b	68 (11) b	212 (23) b	36 (6) b	*16 (2) b	155 (22) b	207 (24) b
A	239 (16) b	*72 (9) a	134 (12) a	446 (31) a	*110 (5) a	*24 (1) a	327 (29) a	460 (33) a
BA	*333 (20) a	68 (9) a	120 (3) a	521 (24) a	*107 (8) a	*23 (3) a	296 (16) a	426 (12) a
Bt	366 (55) a	45 (5) b	130 (5) a	542 (60) a	124 (10) a	*16 (2) b	309 (16) a	449 (23) a
BC	325 (33) ab	37 (2) b	132 (4) a	495 (33) a	*126 (9) a	*24 (1) a	341 (32) a	493 (32) a
WS18 O	*297 (26) a	*42 (1) b	66 (9) b	405 (34) b	*106 (11) b	*16 (1) a	99 (11) b	221 (16) c
A	*332 (15) a	*44 (1) ab	95 (3) a	471 (14) ab	*136 (3) a	*17 (1) a	140 (10) ab	292 (11) ab
AB	*372 (5) a	*49 (2) a	112 (6) a	532 (6) a	*114 (6) b	*16 (0) a	163 (13) a	294 (19) ab
Bw	*332 (46) a	33 (3) c	104 (6) a	469 (48) ab	*107 (9) b	*11 (1) b	184 (10) a	302 (14) a
Cr	182 (55) b	*23 (3) d	93 (17) ab	298 (65) bc	55 (3) c	12 (2) b	173 (31) a	240 (33) bc

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[1] Lower case letters indicate significant differences between horizons by soil/extraction, based on ANOVA and Fisher's LSD ($P \geqslant 0.95$).

[2] ND = not determined.

[3] Asterisks (*) indicate significant differences in 1986 vs. 1985 extracts ($P \geqslant 0.95$).

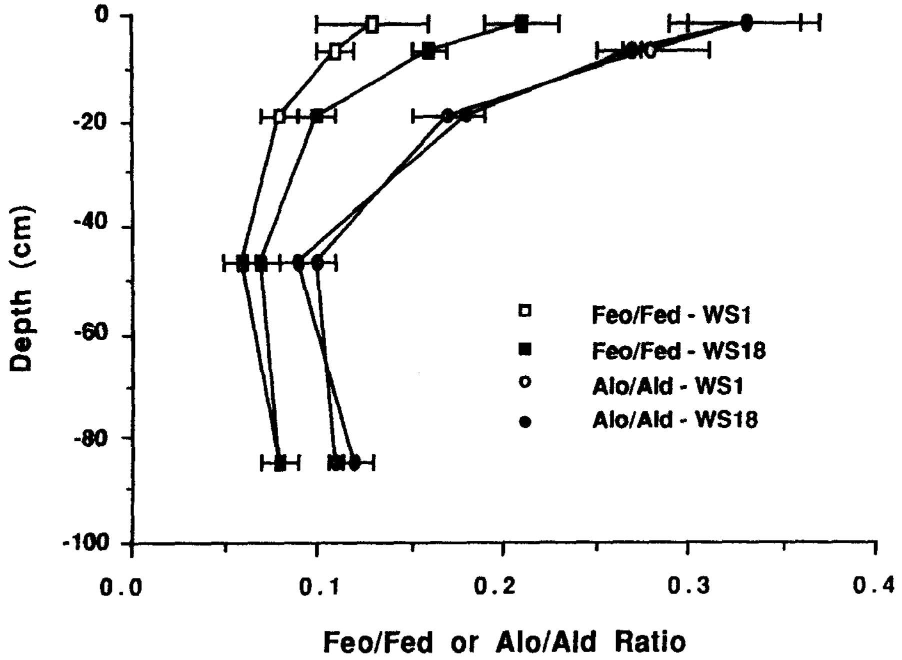

Fig. 2. Changes in the ratio of oxalate-extractable (non-crystalline) Fe or Al (Fe_o, Al_o) to dithionite-citrate-bicarbonate-extractable Fe or Al (Fe_d, Al_d), as estimated by the sum of pyrophosphate-extractable + oxalate-extractable + dithionite-citrate-bicarbonate-extractable Fe or Al, with depth in two Coweeta soil profiles. Watershed 1 (WS1) is a 31-year old white pine (*Pinus strobus* L.) plantation; Watershed 18 (WS18) is a mature mixed hardwoods forest. Study sites were located on Fannin (Typic Hapludult) and Chandler (Typic Dystrochrept) soils in WS1 and WS18, respectively. Fe_o/Fe_d can be used as an index of the relative crystallinity of free Fe in soil, with crystallinity increasing as the value approaches zero. Al_o/Al_d is less well defined (see text for further explanation). Error bars indicate ± 1 SE.

P sorption

When soils were equilibrated with 0.01 *M* $CaCl_2$, P desorbed and resulting equilibrium P concentrations were low and did not differ significantly among mineral horizons (Table 3). Equilibrium P concentrations were greater in the forest floor, but P desorbed per unit soil volume did not differ significantly between forest floor and mineral horizons.

When soils were equilibrated with 0.01 *M* $CaCl_2$ solutions of varying PO_4^{3-} concentration, nearly all PO_4^{3-} was removed from solutions of 1 mM/L KH_2PO_4 or less (Fig. 3). Biocidal treatment with $CHCl_3$ had little effect on P sorption in mineral horizons, but significantly reduced P sorption in forest floor (O) horizons. At the lowest level of P addition,

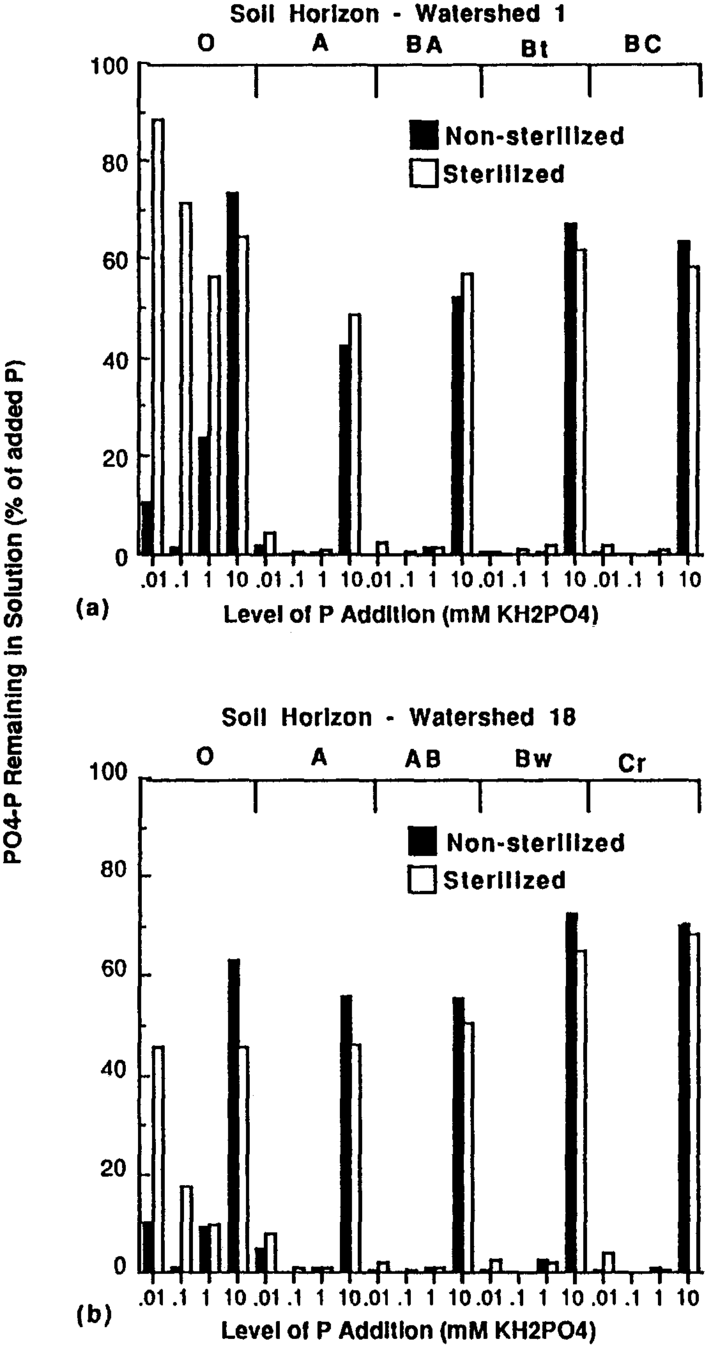

Fig. 3. P sorption, as indicated by the % of added PO_4^{3-} -P remaining in solution, at 4 levels of KH_2PO_4 addition in $CHCl_3$-sterilized (open symbols) and non-sterilized (closed symbols) soils from five horizons in WS1 (a) and WS18 (b) at Coweeta. Values are means of five replicates.

Table 3. P desorbed per unit soil mass and volume, and resulting equilibrium P concentrations, for soils equilibrated with 0.01 M $CaCl_2$ solutions. Values are means with standard errors in parentheses.

Horizon WS1	WS18	Equilibrium P Concentration (ug/1) WS1	WS18	P desorbed by soil (ug/g soil) WS1	WS18	(ug/cm^3 soil) WS1	WS18
O	O	41.7 (14.8)	37.0 (6.2)	0.590 (0.232)	0.502 (0.093)	0.035 (0.014)	0.032 (0.006)
A	A	6.7 (1.0)	5.2 (0.8)	0.063 (0.010)	0.050 (0.008)	0.039 (0.006)	0.043 (0.007)
BA	AB	2.2 (0.3)	3.0 (0.5)	0.020 (0.003)	0.029 (0.005)	0.014 (0.002)	0.025 (0.004)
Bt	Bw	3.3 (0.5)	2.2 (0.5)	0.031 (0.005)	0.021 (0.005)	0.020 (0.003)	0.019 (0.005)
BC	Cr	3.0 (0.5)	1.7 (1.2)	0.028 (0.005)	0.016 (0.012)	0.020 (0.004)	0.018 (0.013)

Table 4. Pearson correlation coefficients for the relationship between concentrations of pyrophosphate-extractable, oxalate-extractable, and pyrophosphate + oxalate extractable Al and Fe, and an index of P sorption capacity (x/logc), for 5 soil horizons in two watersheds at Coweeta, NC.

	Pyrophosphate		Oxalate		Dithionite		Total Free	
Collection Date	Al	Fe	Al	Fe	Al	Fe	Al	Fe
1985 (separate extraction)	0.302	0.037	0.969*	0.856*	ND[1]	ND	ND	ND
1986 (sequential extraction)	0.106	0.294	0.688*	0.468	−0.078	−0.117	0.163	0.009

* Indicates probability of a significant relationship ($P \geqslant 0.95$).

[1] Not determined.

$CHCl_3$ treatment reduced solution PO_4^{3-} removal in the forest floor by 40 and 80% in WS18 and WS1, respectively.

As indexed by x/log c, P sorption was highly correlated with Al_o and Fe_o, but not with pyrophosphate, DCB, or total free Al and Fe (Table 4). Correlations between P sorption and Al_o or Fe_o by sequential extraction were lower than correlations between P sorption and Al_o or Fe_o by separate extraction. Among mineral horizons, maximum P sorption potentials occurred in near-surface (A) horizons and declined with depth, consistent with the decline in Al_o concentration (Fig. 4).

Soil P fractions

AF-extractable P concentrations were low in both soils, ranging from 0.9—2.9 μg/g in mineral horizons, and 3.7—5.4 μg/g in the forest floor. AF-extractable P comprised a small portion (0.16—0.64%) of soil P_T, as estimated by H_2SO_4 — H_2O_2 digestion (Table 5). Extractable P content per unit soil volume was an order of magnitude lower in the forest floor than in the mineral soil. In both soils, a much larger pool of P_i was extracted with 1 *M* H_2SO_4 than with AF.

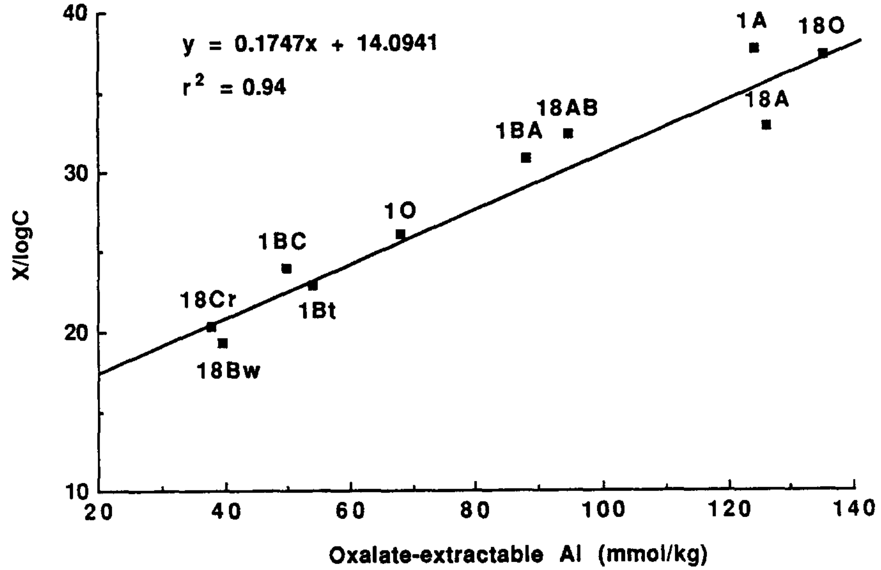

Fig. 4. The relationship between soil oxalate-extractable Al concentration and P sorption, as indexed by x/log c at 10 mM KH_2PO_4 addition (Bache & Williams 1971; Richardson 1985), in 10 soil horizons from two forested Coweeta watersheds. Points are labeled to indicate watershed number and soil horizon.

Table 5. Phosphorus fractions and total P and N contents of soils from two forested watersheds at Coweeta, North Carolina. Values are means of five samples; each sample is a mean of two replicates.

Horizon	Depth (cm)	[1]P_{ext}	[2]P_{mic}	[3]P_{acid}	[4]P_0	[5]P_T	[5]N_T
				(kg ha^{-1} cm^{-1})			
Watershed 1							
(Typic Hapludult)							
O	0—4	0.031 d[6]	1.17 a	1.1 c	3.95 c	4.84 c	65.2 b
A	4—13	0.134 a	0.76 b	6.5 b	30.6 a	38.7 b	80.1 a
BA	13—32	0.110 b	0.36 c	6.4 b	26.2 a	41.5 ab	43.6 c
Bt	32—66	0.060 c	0.06 d	5.2 b	18.2 b	36.5 b	23.6 d
Bc	66—95	0.075 c	0.02 d	8.3 a	24.3 ab	48.1 a	20.2 d
Watershed 18							
(Typic Dystrochrept)							
O	0—4	0.023 b	1.08 b	0.9 d	3.61 c	5.98 c	59.2 b
A	4—14	0.163 ab	1.61 a	9.6 b	22.7 b	46.7 b	117.1 a
AB	14—29	0.153 b	0.52 c	7.6 c	25.0 b	43.1 b	60.6 b
Bw	29—69	0.146 b	0.03 d	8.6 bc	27.1 ab	58.1 ab	15.8 c
Cr	99—104	0.326 a	0.07 d	13.2 a	31.2 a	73.5 a	10.6 c

[1] P extracted by dilute acid-fluoride (AF) solution.

[2] Increase in AF-extractable PO_4^{3-}-P following 18 h $CHCl_3$ fumigation.

[3] P extracted by 1 *M* H_2SO_4.

[4] Increase in P extracted by 1 *M* H_2SO_4 following combustion at 400 °C for 1 h.

[5] P extracted by H_2SO_4-H_2O_2 digest.

[6] Lower case letters indicate significant differences among horizons (n=5/horizon) within a watershed for each variable ($P \geqslant 0.95$, ANOVA and Fisher's LSD).

$CHCl_3$-labile (microbial) P reached maximum concentrations in O and A horizons in both soils and declined significantly with depth in the mineral soil (Table 5). Microbial P also comprised a small portion (0.04—3.45%) of soil P_T in mineral horizons, but represented 18—24% of P_T in the forest floor and 31—35% of soil P_o (Table 5). Microbial P was much greater than extractable P in all near-surface horizons (O, A, and AB/BA) and was the only soil P fraction that did not exhibit an order-of-magnitude decline in the forest floor relative to the mineral soil.

A large portion (40 to 80%) of soil P_T appeared to be present as P_o throughout each soil profile (Table 5). This fraction would include P complexed with organic matter and P associated with humic and fulvic acids in addition to true organic P compounds, and could also include some tightly-bound mineral P (Olsen & Sommers 1982).

Discussion

Free soil Al and Fe fractions and P sorption capacity

We hypothesized that concentrations of non-crystalline Al and Fe, and concomitantly P sorption, would be greatest in near-surface mineral horizons of these Coweeta soils because of the inhibitory effect of organic matter on the crystallization of Al and Fe oxides and hydroxides and because non-crystalline Al and Fe hydroxides tend to dominate soil sorption reactions due to their comparatively large surface area/mass ratios (Schwertmann 1966; Hsu 1977; Kodama & Schnitzer 1977, 1980; Schwertmann & Taylor 1977). We found maximum Al_o and Fe_o concentrations in near-surface O or A horizons (Table 2), an increase in free Fe crystallinity with depth (Fig. 2), and a strong correlative relationship between P sorption and Al_o and Fe_o (Table 4, Fig. 4). These findings support our hypothesis and contrast with Wood et al. (1984), who observed minimal HCl-extractable Al and Fe concentrations and P sorption in near-surface mineral horizons of a Spodosol profile in New Hampshire.

Al_o concentrations in our Coweeta profiles were intermediate between those observed by Johnson et al. (1986) in two Pacific NW Inceptisol profiles and two Tennessee Ultisol profiles. The vertical distribution of Al_o, however, was similar (Fig. 5). The concentrations and vertical distribution of Al_o in the Spodosol profile studied by Wood et al. (1984) were more similar to those of Spodosol profiles studied by Wang et al. (1987). Similar trends were observed when bulk density differences among horizons were considered (Fig. 5).

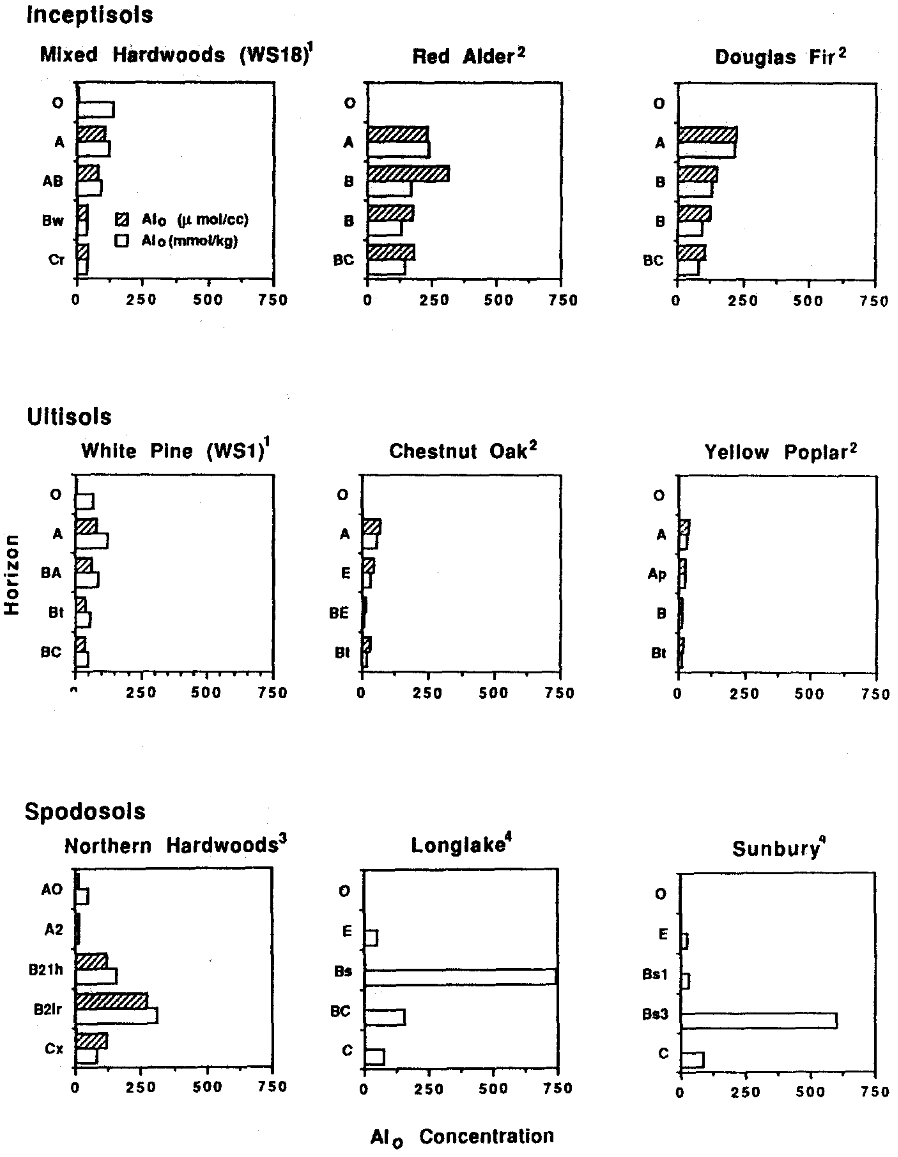

Fig. 5. A comparison of oxalate-extractable Al (Al$_0$) concentrations by horizon in nine forest soil profiles. Shaded bars denote concentrations corrected for bulk density differences among horizons for profiles where bulk density data were available. Labels indicate predominant vegetation, or soil series when vegetation data were not available. [1]Our study; [2]Johnson et al. (1986) — the Inceptisols are from the Pacific Northwest, the Ultisols are from Walker Branch, TN; [3]Wood (1980) — Hubbard Brook, NH; [4]Wang et al. (1987) — Canada (Note: Johnson et al. (1986) and Wang et al. (1987) did not analyze forest floor Al$_0$ content).

Higher concentrations of Al_o vs. Fe_o (Table 2), and the stronger correlation between Al_0 and P sorption capacity (Table 4), suggest that Al may be more important than Fe in controlling solution PO_4^{3-} dynamics in these soils. Weathering equations for the three major soil-forming minerals at Coweeta suggest a greater potential for Al vs. Fe weathering (Velbel 1988). In particular, plagioclase feldspar produces only Al and weathers by a two-stage process in which all Al initially formed is amorphous (non-crystalline). The feldspar-rich Tallulah Falls Formation was the underlying parent material in both study areas (Hatcher 1988).

Al_p and Fe_p varied significantly between 1985 and 1986 soils. In addition to organically-bound Fe and Al, sodium pyrophosphate can dissolve both non-crystalline and crystalline Al and Fe minerals in some soils (Schuppli et al. 1983; Kassim et al. 1984). The fact that Al_p and Fe_p concentrations were often greater than separate Al_o and Fe_o concentrations (Table 2) suggests that pyrophosphate did extract some non-crystalline and/or crystalline Al and Fe from these soils, and therefore does not provide a reliable estimate of organically-bound Al and Fe.

Vertical distribution of biological and geochemical P subcycles

For their NH Spodosol profile, Wood et al. (1984) graphed concentrations of plant roots and soil microorganisms (biological agents) and HCl-extractable Al and Fe (geochemical agents) vs. depth, demonstrating that biological and geochemical subcycles were vertically stratified. We constructed a similar diagram for WS18 using the vertical distributions of plant roots (McGinty 1976), microbial P (Table 5), and Al_0 (Table 2).

The most significant difference between these two soil profiles occurs in the A horizon (Fig. 6). In the A2 horizon at Hubbard Brook (9—15 cm), relative concentrations of both biological and geochemical agents are low; in the A horizon of WS18 (4—13 cm), biological and geochemical agents reach maximum concentrations. Although root distribution data for WS1 are less detailed (McGinty 1976), vertical distributions of plant roots, microbial P, and Al_0 appear to follow a pattern similar to WS18 (Tables 2, 5). Biological and geochemical soil P subcycles do not appear to be vertically stratified in these Coweeta soil profiles.

Based on the observed differences in P sorption between $CHCl_3$-sterilized and non-sterilized forest floors and mineral soils (Fig. 3), and on the vertical distributions of plant roots (McGinty 1976), microbial P (Table 5), and Al_0 and Fe_0 (Table 2), it seems logical that biological processes regulate solution PO_4^{3-} concentrations in the Coweeta forest floors we examined, while geochemical processes most likely regulate solution PO_4^{3-} concentrations below 30 cm. However we can not eliminate

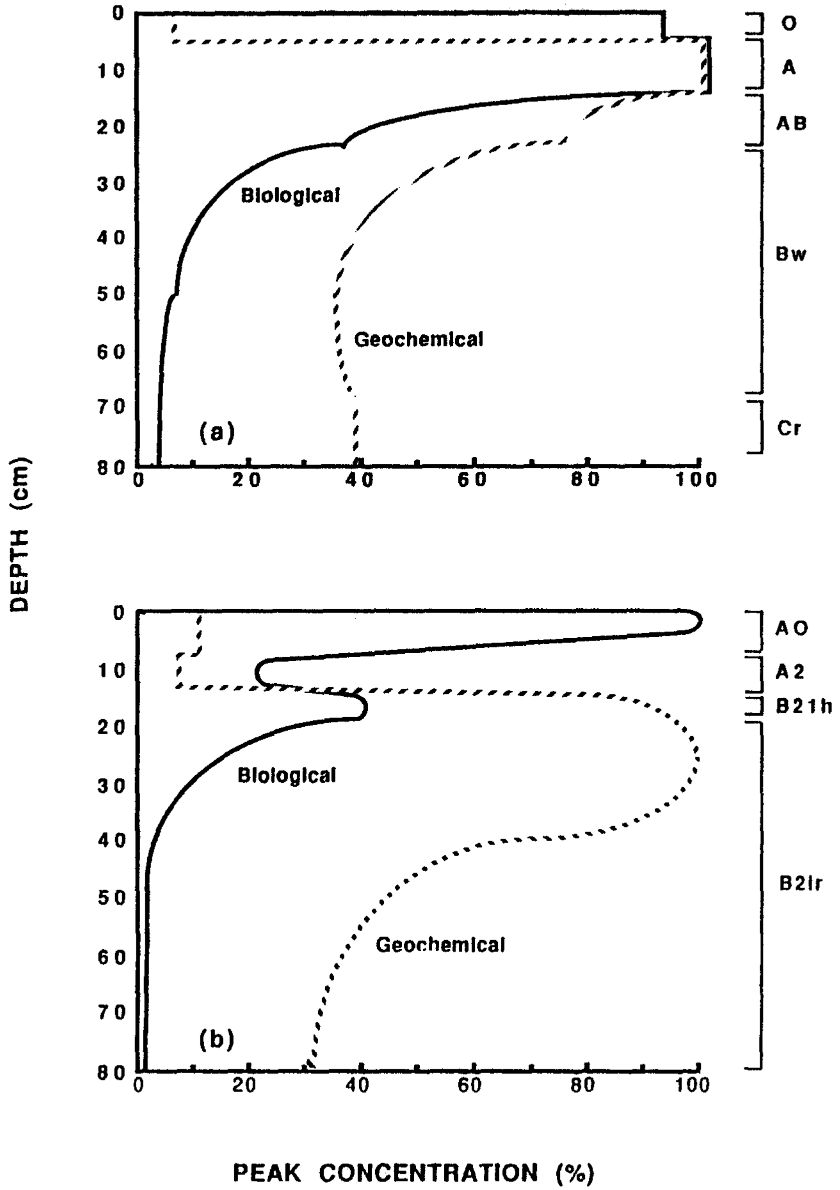

Fig. 6. A comparison of (a) the vertical distribution of biological (plant roots and microbial biomass P) and geochemical (oxalate-extractable Al) agents that contribute to phosphorus retention in an Inceptisol profile (WS18) at the Coweeta Hydrologic Laboratory, NC, with (b) the vertical distribution of biological (plant roots and soil microorganisms) and geochemical (HCl-extractable Al and Fe) agents that contribute to phosphorus retention in a Spodosol profile at the Hubbard Brook Experimental Forest, NH (adapted from Wood et al. 1984; © 1984 by the AAAS). Concentrations are expressed as a percentage of peak (maximum) concentration (after Wood et al. 1984). Approximate horizon depths are indicated at the right of the figure.

the importance of either biological or geochemical processes in controlling solution PO_4^{3-} dynamics in near-surface mineral horizons. Maximum concentrations of plant roots, microbial P, Al_o, and Fe_o co-occur in these horizons, particularly between 4 and 14 cm (Fig. 6; Table 2). Our sorption experiments in sterilized soils indicate that P sorption capacity in near-surface mineral horizons is sufficient to remove virtually all PO_4^{3-} likely to be added to solution under ambient conditions (Fig. 3), but without using radioisotopes it is not possible to determine the relative importance of microbial uptake vs. P sorption in non-sterilized soils. Plant roots, soil microorganisms, and/or P-sorbing minerals could all be important in controlling solution PO_4^{3-} dynamics *in situ* in these near surface mineral horizons (Fig. 6).

Although we also observed high concentrations of Al_o and Fe_o (Table 2) and high P sorption capacity (Fig. 4) in the WS18 forest floor, bulk density differences would reduce both factors by an order of magnitude relative to mineral horizons (Table 1). Competition between PO_4^{3-} and organic anions for binding sites would also inhibit P sorption in forest floor horizons at ambient PO_4^{3-} concentrations despite significant Al_o content (Struthers & Sieling 1950; Larsen et al. 1959; Hingston et al. 1968; Guar 1969; Nagarajah et al. 1970; Johnson & Todd 1983; Singh 1984; Johnson et al. 1986; Nesterenkova et al. 1986). At higher loading rates the increased concentration of PO_4^{3-} ions coupled with their stronger affinity for binding sites should overcome this competitive effect, consistent with the relatively high P sorption observed in sterilized WS18 forest floors at solution PO_4^{3-} concentrations of 10 mM/L KH_2PO_4 (Fig. 3, 4).

Although geochemical processes probably regulate solution PO_4^{3-} dynamics below 30 cm, significant amounts of soil P_o (including P complexed with organic matter, P associated with humic and fulvic acids, and some tightly-bound mineral P) were also observed at these depths (Table 5). Schoenau & Bettany (1987) suggested that fulvic acids, produced in biologically active surface horizons, were important agents of C, N, P, and S transport in Alfisols and Mollisols in Canada, and that P appeared to be the element most susceptible to deep leaching in organic form. Much of the 'organic P' found at depth in these Coweeta soils could be the result of a similar process. Although high, our observed P_o/P_T ratios (Table 5) are within the range of literature estimates for forest soils (Stevenson 1986).

Conclusions

1) In the Coweeta soil profiles we examined, maximum Al_o and Fe_o

concentrations and P sorption capacity occur in near-surface mineral horizons, probably because high concentrations of organic matter inhibit Al and Fe crystallization. The strong correlation between P sorption and soil Al_o and Fe_o content suggests that non-crystalline Al and Fe oxides and hydroxides dominate P sorption reactions in these soils.

2) Although solution PO_4^{3-} dynamics in Coweeta forest floors appear to be controlled largely by biological processes, both biological and geochemical factors may be important in controlling solution PO_4^{3-} dynamics in near-surface mineral horizons. Biological and geochemical P subcycles are not vertically stratified in these soils.

3) While geochemical processes probably regulate solution PO_4^{3-} dynamics in deeper mineral horizons, organic P, including P complexed with organic matter and/or associated with humic or fulvic acids, comprises a large portion of the soil P_T at depth in these soils. Much of this 'P_o' may have been formed in biologically active surface horizons and subsequently transported to depth by percolating water.

4) While both biological and geochemical processes are likely to be important in controlling P cycling in a wide variety of forest soils, vertical stratification of biological and geochemical P subcycles may only develop under certain conditions. Vertical stratification might be expected to occur in Spodosols or soils exhibiting podzolic properties because of the characteristic leaching of Fe and Al from surface horizons and subsequent precipitation at depth. Conversely, soils with well-developed forest floors that develop from parent materials rich in readily-weatherable Fe and Al might exhibit vertical distributions more similar to those of our Coweeta soils. Factors such as soil age, climate, and relief might also affect the degree of stratification of biological and geochemical subcycles within a soil profile, and care should be taken in applying the idea of vertical stratification without consideration of soil type and/or major soil-forming processes.

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