

Phosphorus forms and related soil chemistry of Podzolic soils on northern Vancouver Island. I. A comparison of two forest types

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Abstract: When cedar–hemlock (CH) and hemlock – amabilis fir (HA) forests of northern Vancouver Island are clearcut and replanted, growth of replanted trees is often poor on CH clearcuts but not adjacent HA clearcuts. This poor growth can be overcome with nitrogen (N) and phosphorus (P) fertilization, which suggests differences in nutrient cycling between CH and HA forests. The objective of this study was to investigate soil P in mature, uncut stands of CH and HA forests. The results suggest that there are no inherent differences in soil P concentration between the CH and HA forests. The diversity of P forms as revealed by ^{31}P -NMR spectroscopy was typical of cool, moist acidic forests with high P immobilization. Diester phosphates were found throughout the soil profile, albeit at very low levels in the mineral horizons. Phosphorus forms and cycling were vertically stratified down the profile. Most of the P in the LF horizon was in organic forms typical of litterfall. In the more humified H horizon the P forms were more typical of soil organisms. The high C/N and C/P ratios in the LF and H horizons at the CH site are consistent with microbial immobilization. In the upper Bhf horizon, inorganic P was predominantly nonoccluded. Organic P was present, mainly as orthophosphate monoesters, which were probably adsorbed on soil colloids. In the lower Bhf horizon, most P was occluded in amorphous sesquioxides, with low levels of organic P, mainly as orthophosphate monoesters.

Résumé : Quand les forêts de cèdre et de pruche (CP) et de pruche et de sapin gracieux (PS) du Nord de l'île de Vancouver sont coupées à blanc et reboisées, la croissance des arbres plantés est souvent pauvre sur les sites CP coupés à blanc mais non sur les sites PS adjacents aussi coupés à blanc. On peut remédier à cette croissance réduite avec une fertilisation azotée (N) et phosphatée (P), ce qui suggère qu'il existe des différences dans le recyclage des nutriments entre les forêts CP et PS. Cette étude avait pour but d'examiner le P du sol dans des forêts CP et PS matures et non coupées. Les résultats indiquent qu'il n'y a pas de différences inhérentes dans la concentration de P du sol entre les forêts CP et PS. La diversité des formes de P, telle que révélée par la spectrométrie ^{31}P -NMR, était typique des forêts fraîches, humides et acides avec une forte immobilisation de P. Les diesters phosphates ont été trouvés dans tout le profil de sol, bien qu'en très faible concentration dans les horizons minéraux. Les formes de P et le recyclage étaient stratifiés verticalement du haut vers le bas du profil. La majorité de P dans l'horizon LF était sous des formes organiques typiques de la litière tombant au sol. Dans l'horizon H dont l'humification était plus avancée, les formes de P étaient plus typiques des organismes du sol. Les rapports C/N et C/P élevés dans les horizons LF et H du site CP sont consistants avec une immobilisation microbienne. Dans la partie supérieure de l'horizon Bhf, le P inorganique était d'une manière prédominante non occlus. Le P organique était présent, principalement sous forme de monoesters de phosphate, lesquels étaient probablement adsorbés sur les colloïdes du sol. Dans la partie inférieure de l'horizon Bhf, la majorité du P était occlus dans les sesquioxides amorphes, avec de faibles niveaux de P organique, principalement sous forme de monoesters de phosphate.

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Introduction

The Salal Cedar Hemlock Integrated Research Program (SCHIRP; Prescott and Weetman 1994) was initiated to in-

vestigate the causes of poor growth of conifer regeneration on northern Vancouver Island, British Columbia. Chlorosis and growth stagnation have been observed in Sitka spruce (*Picea sitchensis* (Bong.) Carr.), western redcedar (*Thuja*

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plicata Donn. ex D. Don), and western hemlock (*Tsuga heterophylla* (Raf.) Sarg.) planted in clearcuts of old-growth cedar–hemlock (CH) forests but not in trees planted in adjoining clearcuts of second growth hemlock and amabilis fir (*Abies amabilis* (Dougl.) Forbes) (HA forests) (Weetman et al. 1989a). Germain (1985) and Weetman et al. (1989a, 1989b) indicated that the replanted CH stands were deficient in N and P, with a positive response to fertilization. This poor growth was attributed to the low availability of N and P in CH old-growth forests prior to clear-cutting (Prescott and Weetman 1994). Decomposition of the forest floor in the CH sites appears to be less complete than that of the HA: all layers of the CH forest floor have lower concentrations of total and extractable N, and mineralized less N during laboratory aerobic incubations (Prescott and Weetman 1994); there is a higher ratio of carbohydrate to lignin moieties in the CH forest (de Montigny et al. 1993); and forest floors of CH forests are wetter and have less soil fauna (Prescott and Weetman 1994).

Although carbon (C) and N forms on these sites have been examined in detail (e.g., de Montigny et al. 1993; Keenan 1993; Chang 1995), P cycling has not been studied in these forests, despite responses to P fertilization in replanted trees (Weetman et al. 1989a, 1989b). In soil, P is found largely in its oxidized state as orthophosphate or derivatives of phosphoric acid (H_3PO_4). All native P in soils is originally derived from apatite (Stevenson and Cole 1999), from which P is released by weathering and then formed into inorganic pyrophosphates and polyphosphates, inorganic Ca, Fe, or Al phosphates, the occluded P of Fe and Al oxides, or organic P (P_O) compounds. Soil P_O compounds include: orthophosphate monoesters (ROPO_3^{2-} , where *R* is an unspecified organic moiety) such as inositol phosphates, mononucleotides, and sugar phosphates (Newman and Tate 1980; Tate and Newman 1982); orthophosphate diesters ($\text{R}_1\text{OROPO}_2^-$, where *R* and *R*₁ are unspecified organic moieties) such as phospholipids, RNA, and DNA (Kowalenko and McKercher 1971; Tate and Newman 1982); teichoic acids, which are acidic polysaccharides attached to the cell walls of Gram-positive bacteria; consisting of repeating units of either glycerol or ribitol and are connected by phosphate esters (Brock and Madigan 1988); and phosphonates, containing C–P bonds, which are very resistant to oxidation and hydrolysis (Corbridge 1990). In cool, wet, acidic forest soils such as those of northern Vancouver Island, Fe and Al phosphates predominate, and P_O forms will accumulate (Stevenson and Cole 1999).

We hypothesized that the observed differences in litter decomposition on the CH and HA forest types could result in different levels and forms of P in these forests, which may contribute to the nutrient deficiencies in replanted CH forests. Therefore, the objectives of this research were (i) to characterize P forms in forest floor and soils of mature, uncut CH and HA stands using extraction and digestion procedures, fractionation, and ^{31}P nuclear magnetic resonance (NMR) spectroscopy; (ii) to study P cycling in these forests by examining relevant aspects of the chemistry of these soils that could influence P forms and levels; and (iii) to determine differences in P forms and cycling between CH and HA forests that could result in P deficiencies after clear-cutting and replanting.

Materials and methods

Study area

This study was conducted on Tree Farm License 25 near Port McNeill (50°36'N, 127°15'W) in the wetter Coastal Western Hemlock biogeoclimatic zone (Pojar et al. 1991) on northern Vancouver Island, British Columbia. The mean annual temperature is 7.9°C, and mean daily temperatures vary from 3.0°C in January–February to 13.7°C in July–August (Lewis 1982). The annual precipitation is 1700 mm, mainly falling between October and February as rain. This area is characterized by a gently undulating topography. There is a thick (typically >45 cm) mor humus layer with a large proportion of deeply decomposed woody material overlying predominantly moderately well to somewhat imperfectly drained Orthic Ferro-Humic Podzolic soils (Agriculture Canada Expert Committee on Soil Survey 1987) or Typic Haplorthods (Soil Survey Staff 1975).

Sample collection

Sampling was conducted in July and August 1992. There were three locations per forest type (CH or HA) and three pits per location, and only pits lacking nonwoody horizons were sampled. The thickness of the horizons, in centimetres, were as follows: LF: HA, 5.1 ± 2.8 (mean \pm SD); CH, 5.3 ± 2.6 ; H: HA, 7.1 ± 2.6 ; CH, 9.7 ± 4.2 ; upper Bhf (Bhf1): HA, 9.1 ± 7.2 ; CH, 10.5 ± 8.0 ; lower Bhf (Bhf2): sampled to 20 cm in both forest types. There were no significant differences between HA and CH forests for horizon thickness at $p < 0.05$. This sampling depth was chosen to include the zone where most roots were observed, and horizon differentiations were based on observed differences in the field. The lower Bhf horizons were distinct from the upper Bhf in appearance and chemical properties. The pyrophosphate Fe concentration is high enough that the Bhf2 horizons could be classified as Bf horizons. However, the C content is too high for Bf horizons (Agriculture Canada Expert Committee on Soil Survey 1987), so we are calling them Bhf2 horizons to recognize their differences from the upper Bhf. Samples were placed in plastic bags in coolers and later frozen for transportation. In the laboratory, samples were thawed, air-dried at 25°C, and sieved to <2 mm. The forest floor samples were ground with a stainless steel coffee grinder prior to sieving. All samples were subsequently stored at room temperature in airtight plastic containers.

Chemical analysis

Gravimetric moisture content was determined by oven-drying at 105°C for 16 h, using thawed, but not air-dried, samples. Soil pH was measured in 0.01 M CaCl_2 , using a 1:2 (w/v) soil:liquid ratio for mineral horizons and a 1:5 (w/v) ratio for forest floor material (McLean 1982). Total C was estimated with a Leco induction furnace (Bremner and Tabatabai 1971), using oven-dried material. Total N was measured on oven-dried samples by a semi-micro-Kjeldahl procedure to convert the N to ammonium (Bremner 1996). The ammonium in solution was then determined colorimetrically with a Lachat flow injection analyzer (FIA). Calcium was extracted from air-dried samples by the Mehlich III method (Mehlich 1984) and read with atomic absorption spectroscopy (AAS). Iron and Al were determined on oven-dried material using sodium pyrophosphate, acid ammonium oxalate extraction and citrate–bicarbonate–dithionite extraction (Bertsch and Bloom 1996; Loeppert and Inskeep 1996), followed by AAS.

Phosphorus methodology

Available P (P_A) was extracted from air-dried material by the Bray P1 method (Olsen and Sommers 1982), followed by colorimetric analysis (Watanabe and Olsen 1965) using a Lachat FIA. Total P (P_T) was determined on oven-dried material by the

Table 1. Field moisture content, pH, total C, total N, the C/N ratio, and extractable Ca.

Horizon	Forest type	Moisture (%)	pH	C (%)	N (%)	C/N	Extractable Ca (mg/kg)
LF	HA	226 (120)	3.2(0.14)*	46.6 (5.1)	1.06 (0.18)	44.5 (4.8)	1853.0 (307.3)
	CH	203 (122)	3.6 (0.27)	48.0 (4.3)	0.92 (0.11)	52.6 (6.2)	3354.3 (616.5)
H	HA	230 (76)	2.9(0.10)*	40.8 (7.9)	1.01 (0.10)	40.5 (7.7)	1660.9 (762.1)
	CH	314 (149)	3.1 (0.19)	47.3 (6.2)	0.91 (0.16)	53.4 (11.6)	2720.9 (1027.4)
Bhf1	HA	206 (109)	3.2 (0.32)	20.0(4.7)*	0.77 (0.14)	26.1 (4.5)	945.0 (1045.2)
	CH	249 (152)	3.2 (0.17)	14.3 (4.7)	0.54 (0.20)	29.8 (9.6)	1272.8 (1325.5)
Bhf2	HA	97 (48)	4.0 (0.31)	8.8(2.6)*	0.24 (0.06)	37.0 (5.0)	39.4 (11.1)
	CH	84 (27)	4.0 (0.29)	6.7 (1.2)	0.17 (0.04)	41.0 (8.3)	222.3 (286.1)

Note: Values are means with SD given in parentheses ($n = 9$). An asterisk indicates a significant difference between the HA and CH forest types for a horizon at $p < 0.05$.

Parkinson and Allen (1975) digest, with colorimetric analysis on a Lachat FIA. This was demonstrated to be a suitable method for soils of this type in Cade-Menun and Lavkulich (1997). Organic P (P_O) was determined by the Saunders and Williams (1955) ignition procedure, as per Olsen and Sommers (1982), followed by colorimetric analysis on a Technicon autoanalyzer. The Chang and Jackson (1957) procedure, as described by Olsen and Sommers (1982), was utilized to fractionate P into NaOH (P_{NaOH}), citrate-bicarbonate (P_{CB}), citrate-bicarbonate-dithionite (P_{CBD}), and HCl (P_{HCl}) extractable forms. This procedure was chosen over the currently more popular Hedley fractionation procedure (Hedley et al. 1982) primarily because the extractants of the Chang and Jackson procedure paralleled those used for Al and Fe, allowing us to relate P fractions to Fe and Al forms. Additionally, at the time this work was done there had been few published papers showing the suitability of Hedley fractionations for C-rich acid soils (Cross and Schlesinger 1995), and our preliminary trials with the Hedley procedure showed problems with reproducibility from organic matter precipitation.

NMR spectroscopy

Two soil profiles for each of the CH and HA forest types were chosen for ^{31}P -NMR spectroscopy. The samples selected were high in P_T , and had chemical characteristics close to the mean values for the forest type they represented. Air-dried soils were extracted overnight at room temperature using 100 mL of a 1:1 mixture of 0.25 M NaOH and 0.05 M Na_2EDTA . After filtration with Buchner funnels and Whatman 41 filter paper, samples were freeze-dried, then re-dissolved in D_2O for NMR analysis. The ^{31}P -NMR spectra were generated at 101.27 MHz on a Bruker WM 250 high-resolution NMR spectrometer with inverse-gated decoupling using a 45° pulse with a 1.5-s delay and an acquisition time of 0.508 s (Cade-Menun and Preston 1996). Accumulation times ranged from 24 to 48 h. Peak assignments were based on Newman and Tate (1980), and peak areas were determined by integration. Overlapping of orthophosphate and orthophosphate monoester peaks was seen in some spectra. Because a valley between peaks occurs at 6 ppm when there is clear separation, this was chosen as the dividing line where overlapping occurred (Dai et al. 1996).

Statistical analysis

Using a nested design (Hicks 1982), with location nested within each forest type, analysis of variance tests at $p < 0.05$ were conducted with the SYSTAT programme (Wilkinson 1990) followed by Tukey's HSD tests. Pearson pairwise product-moment correlations were calculated, and the probabilities associated with each correlation were Bonferroni adjusted. Homogeneity of variance was determined by plotting residuals against estimates. Log and $\log(n + 1)$ transformations were performed where necessary, but means are reported on untransformed data.

Results

There were no significant differences between the CH and HA forest types in field moisture contents (Table 1), which were relatively uniform for the surface horizons but dropped in the Bhf2. The pH of the CH litter was significantly higher than the HA in the LF and H horizons (Table 1). The HA forests contained significantly more C in the Bhf1 and Bhf2 horizons than the CH (Table 1). However, there was a location effect, indicating that much of this difference in C came from one of the three locations used within the HA forest type. There were no significant differences between the CH and HA in total N or C/N (Table 1), although the HA forests generally contained more N in all horizons and had a lower C/N ratio. Generally, the CH contained more extractable Ca (Table 1). However, the variability was high, and the differences were not significant.

Pyrophosphate, acid ammonium oxalate (AAO), and CBD each extract a different fraction of the soil Fe and Al (Table 2). Pyrophosphate extracts the Fe and Al associated with organic matter. The AAO-extracted organic Al and Fe plus the amorphous Al associated with allophane and imogolite, and the amorphous Fe of ferrihydrite (Parfitt and Childs 1988). The CBD procedure extracts crystalline Fe, as well as amorphous and organic forms of Fe and Al. A measure of the amorphous component was obtained by subtracting the pyrophosphate results from the AAO results. Subtracting the AAO concentrations from those obtained by CBD gave the crystalline Fe concentration. There were no significant differences between the CH and HA forests for amorphous or crystalline Fe or Al (Table 2). There were, however, differences between the Bhf1 and Bhf2 horizons. Iron associated with organic matter dominated both the Bhf1 and Bhf2 horizons. There was no amorphous Fe in the Bhf1 and relatively equal concentrations of crystalline and amorphous Fe in the Bhf2. Only organic Al was present in the Bhf1 horizons.

There were no significant differences between the two forest types for P_A , P_T , P_O , or the P_O/P_T or C/P_T ratios for any of the horizons (Table 3). There was a decrease in P_A with depth in the soil profile, from a high of 38.2 mg/kg in the LF to 4.8 in the Bhf2. Both P_O and P_T were highest in the LF and decreased with depth. The ratio of P_O/P_T showed that P was about 80% organic in the litter and Bhf1 and about 50% organic in the Bhf2.

The Chang and Jackson fractionation shows the presence of inorganic P forms: P_{NaOH} , P_{CBD} , and P_{HCl} (Table 4). No P was extracted by citrate-bicarbonate (P_{CB}). P_{NaOH} is thought

Table 2. Pyrophosphate-extracted Fe and Al, citrate–bicarbonate–dithionite-extracted Fe and Al, and acid ammonium oxalate-extracted Fe and Al and the calculated concentrations of crystalline Fe and Al and amorphous Fe and Al.

Horizon	Forest type	Fe _P (%)	Al _P (%)	Fe _C (%)	Al _C (%)	Fe _A (%)	Al _A (%)	Fe _{Cry} (%)	Al _{Cry} (%)	Fe _{Amph} (%)	Al _{Amph} (%)
Bhf1	HA	1.53 (0.66)	0.57 (0.15)	1.80 (0.95)	0.52 (0.19)	1.23 (0.52)	0.56 (0.20)	0.57 (0.49)	0.01 (0.02)	0.00 (0.00)	0.03 (0.03)
	CH	1.39 (0.93)	0.58 (0.23)	2.01 (1.30)	0.48 (0.17)	1.28 (0.69)	0.52 (0.18)	0.50 (0.43)	0.011 (0.03)	0.18 (0.23)	0.02 (0.03)
Bhf2	HA	1.44 (0.48)	1.56 (0.30)	3.28 (0.44)	1.80 (0.44)	2.41 (0.34)	2.27 (0.58)	0.86 (0.30)	0.00 (0.00)	0.97 (0.36)	0.71 (0.33)
	CH	0.91 (0.40)	1.19 (0.36)	2.64 (1.11)	1.46 (0.38)	1.78 (0.48)	2.39 (1.10)	0.96 (0.69)	0.00 (0.00)	0.84 (0.53)	0.98 (0.86)

Note: Values are means with SD given in parentheses ($n = 9$). Fe_P and Al_P are extracted by pyrophosphate. Fe_C and Al_C are extracted by citrate–bicarbonate–dithionite. Fe_A and Al_A are extracted by acid ammonium oxalate. Al_{Cry} and Fe_{Cry} are crystalline Al and Fe. Fe_{Amph} and Al_{Amph} are amorphous Fe and Al. Within a horizon, there were no significant differences between the HA and CH forest types for the variables presented in the table.

Table 3. Available P (Bray-extracted), total P (Parkinson and Allen digest), organic P (ignition method), P_O/P_T, and C/P_T.

Horizon	Forest type	Available P (mg/kg)	Total P (mg/kg)	Organic P (mg/kg)	P _O /P _T (%)	C/P _T
LF	HA	38.2 (6.2)	714.0 (67.5)	580.2 (49.8)	81.5 (5.5)	659 (102)
	CH	30.5 (10.0)	602.2 (78.4)	479.6 (78.9)	79.6 (6.8)	815 (135)
H	HA	20.6 (6.7)	561.4 (98.3)	442.3 (90.1)	79.4 (11.8)	736 (135)
	CH	20.6 (9.6)	485.4 (105.7)	377.0 (88.5)	82.3 (4.7)	1055 (389)
Bhf1	HA	10.2 (7.0)	495.8 (76.4)	388.0 (72.7)	78.2 (8.2)	384 (67)
	CH	6.1 (2.9)	361.3 (106.2)	284.9 (98.2)	78.1 (8.7)	392 (152)
Bhf2	HA	4.8 (0.9)	361.0 (105.5)	188.8 (51.3)	53.2 (8.0)	256 (82)
	CH	6.3 (1.0)	262.2 (58.7)	147.9 (63.7)	56.4 (19.1)	252 (90)

Note: Values are means with SD given in parentheses ($n = 9$). Available P was determined with Bray P1, total P by the Parkinson and Allen (1975) digest, and organic P by the ignition method. Within a horizon, there were no significant differences between the HA and CH forest types for the variables presented in the table.

Table 4. P extracted by HCl, NaOH, and citrate–bicarbonate–dithionite (CBD) during the Chang and Jackson fractionation procedure.

Horizon	Forest type	P _{HCl} (mg/kg)	P _{NaOH} (mg/kg)	P _{CBD} (mg/kg)
Bhf1	HA	7 (0.5)	44 (15.4)	30 (9.8)
	CH	7 (0.5)	37 (28.0)	22 (17.0)
Bhf2	HA	16 (7.7)	23 (8.4)	96 (15.9)
	CH	19 (13.6)	25 (12.4)	74 (23.6)

Note: Values are means with SD given in parentheses ($n = 9$). The LF and H horizons were not extracted. Within a horizon, there were no significant differences between the HA and CH forest types for the variables presented in the table.

to be the nonoccluded phosphate bound to the surfaces of Al or Fe hydrous oxides (Olsen and Sommers 1982). The P_{CBD} fraction is comprised of P occluded within the matrices of Fe and Al oxides and hydrous oxides, while the P_{HCl} is thought to be the extracted calcium phosphates of the non-included apatite fraction (Williams et al. 1980; Olsen and Sommers 1982). The P_{HCl} concentrations were much lower than those were for P_{NaOH} and P_{CBD}. There were no significant differences between the CH and HA forests. The P_{NaOH} concentrations were highest in the Bhf1, while the P_{CBD} levels were highest in the Bhf2.

The correlation matrix (Table 5) shows the relationships that were significant at $p < 0.05$. Aluminum extracted by CBD, AAO, and pyrophosphate all had high positive correlations with one another. Acid ammonium oxalate aluminum (AAO-Al) was also positively correlated with P_{HCl} and pH. Aluminum extracted by CBD was positively correlated with P_{CBD} and both pH methods. There was a positive relationship between Fe extracted with CBD and AAO. Total N correlated positively with C, extractable Ca, and P_O. There was a negative relationship between C and pH, and a positive one with P_T to P_O.

The ³¹P-NMR spectra for the two HA soil profiles are shown in Figs. 1A and 1B; those for the CH profiles are found in Figs. 2A and 2B. The percentage of P found within each class of compounds, calculated from the spectra by integration, is displayed in Table 6. A detailed guide for the interpretation of NMR spectra can be found in Cade-Menun and Preston (1996). In the HA profiles (Figs. 2A and 2B, Table 6), orthophosphate monoesters and orthophosphate were the predominant P forms. The percentage of orthophosphate diesters was always lower than that of orthophosphate monoesters. Profile A had pyrophosphate peaks in all horizons; in profile B, pyrophosphate peaks only occurred in the LF and H horizons. There were no polyphosphate peaks in any horizons of the HA profiles, and only the H horizon of the HA-B profile had a phosphonate peak.

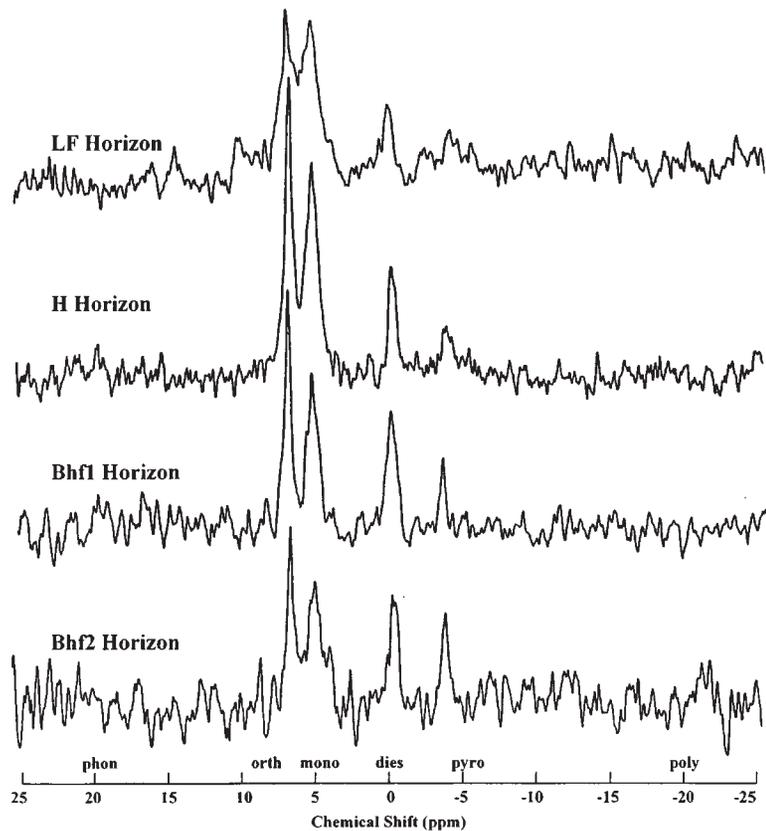
Table 5. Correlation matrix.

	Al _A	Al _C	Al _P	C	C/N	C/P _T	Ca	Fe _A	Fe _C	Fe _P	H ₂ O	P _A	P _O	pH	P _{HCl}	P _{NaOH}	P _{CBD}	N _T	P _T	
Al _A	1.00																			
Al _C	0.92	1.00																		
Al _P	0.88	0.94	1.00																	
C	-0.59	-0.59	-0.49	1.00																
C/N	0.69	0.62	0.57	-0.45	1.00															
C/P _T	ns	ns	ns	ns	ns	1.00														
Ca	-0.51	-0.57	-0.50	0.51	-0.50	ns	1.00													
Fe _A	0.43	0.61	0.51	-0.53	0.45	ns	-0.62	1.00												
Fe _C	0.37	0.56	0.41	-0.47	0.45	ns	-0.58	0.89	1.00											
Fe _P	ns	ns	ns	ns	ns	0.44	ns	0.47	0.50	1.00										
H ₂ O	-0.52	-0.54	-0.52	0.30	-0.68	ns	0.47	-0.59	-0.49	ns	1.00									
P _A	-0.32	-0.40	ns	0.49	-0.38	ns	0.32	-0.59	-0.61	ns	0.27	1.00								
P _O	-0.48	-0.52	-0.44	0.68	-0.52	ns	0.38	-0.53	-0.57	ns	0.45	0.43	1.00							
pH	0.73	0.75	0.67	-0.70	0.46	0.33	-0.32	0.53	0.44	ns	-0.45	-0.40	-0.49	1.00						
P _{HCl}	0.82	0.64	0.59	-0.39	0.59	ns	ns	ns	ns	-0.42	-0.38	ns	ns	0.63	1.00					
P _{NaOH}	-0.53	-0.52	-0.52	ns	-0.47	ns	ns	ns	ns	ns	0.43	ns	ns	-0.37	-0.46	1.00				
P _{CBD}	0.67	0.77	0.67	-0.57	0.51	ns	-0.39	0.64	0.49	ns	-0.47	-0.32	-0.43	0.69	0.51	-0.45	1.00			
N _T	-0.68	-0.69	-0.60	0.93	-0.69	ns	0.64	-0.65	-0.58	ns	0.53	0.58	0.71	-0.69	-0.47	ns	-0.62	1.00		
P _T	ns	-0.35	ns	0.66	-0.39	ns	ns	-0.34	-0.40	ns	ns	0.42	0.74	-0.47	ns	ns	-0.33	0.63	1.00	

Note: Al_A and Fe_A were extracted by acid ammonium oxalate, Al_C and Fe_C by citrate-bicarbonate-dithionite, and Al_P and Fe_P by pyrophosphate. P_A was extracted by Bray. Ca was extracted by Mehlich. H₂O, field moisture content; N_T, total N; P_O, organic P by ignition; P_T, total P by Parkinson and Allen digest. Values shown are all significant at $P = 0.05$; $n = 72$ for P_A, C, C/N, Ca, H₂O, P_O, pH, N_T, and P_T; for all others, $n = 36$. ns, not significant ($P > 0.05$).

Fig. 1. (A and B) ^{31}P -NMR spectra for two soil profiles from mature HA sites, extracted with a 1:1 mixture of 0.25 M NaOH and 0.05 M Na_2EDTA . Phon, phosphonate; ortho, orthophosphate; mono, orthophosphate monoester; diest, orthophosphate diester; pyro, pyrophosphate; poly, polyphosphate.

**Hemlock–Amabilis Fir (HA)
Old Growth A**



**Hemlock–Amabilis Fir (HA)
Old Growth B**

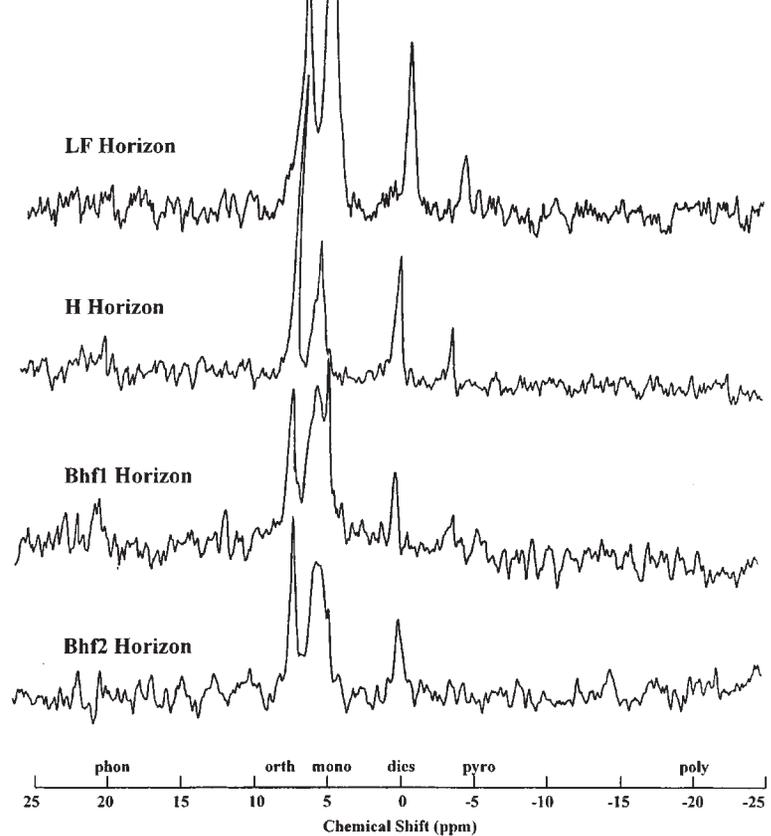


Fig. 2. (A and B) ^{31}P -NMR spectra for two soil profiles from mature CH sites, extracted with a 1:1 mixture of 0.25 M NaOH and 0.05 M Na_2EDTA . phon, phosphonate; ortho, orthophosphate; mono, orthophosphate monoester; diest, orthophosphate diester; pyro, pyrophosphate, poly, polyphosphate.

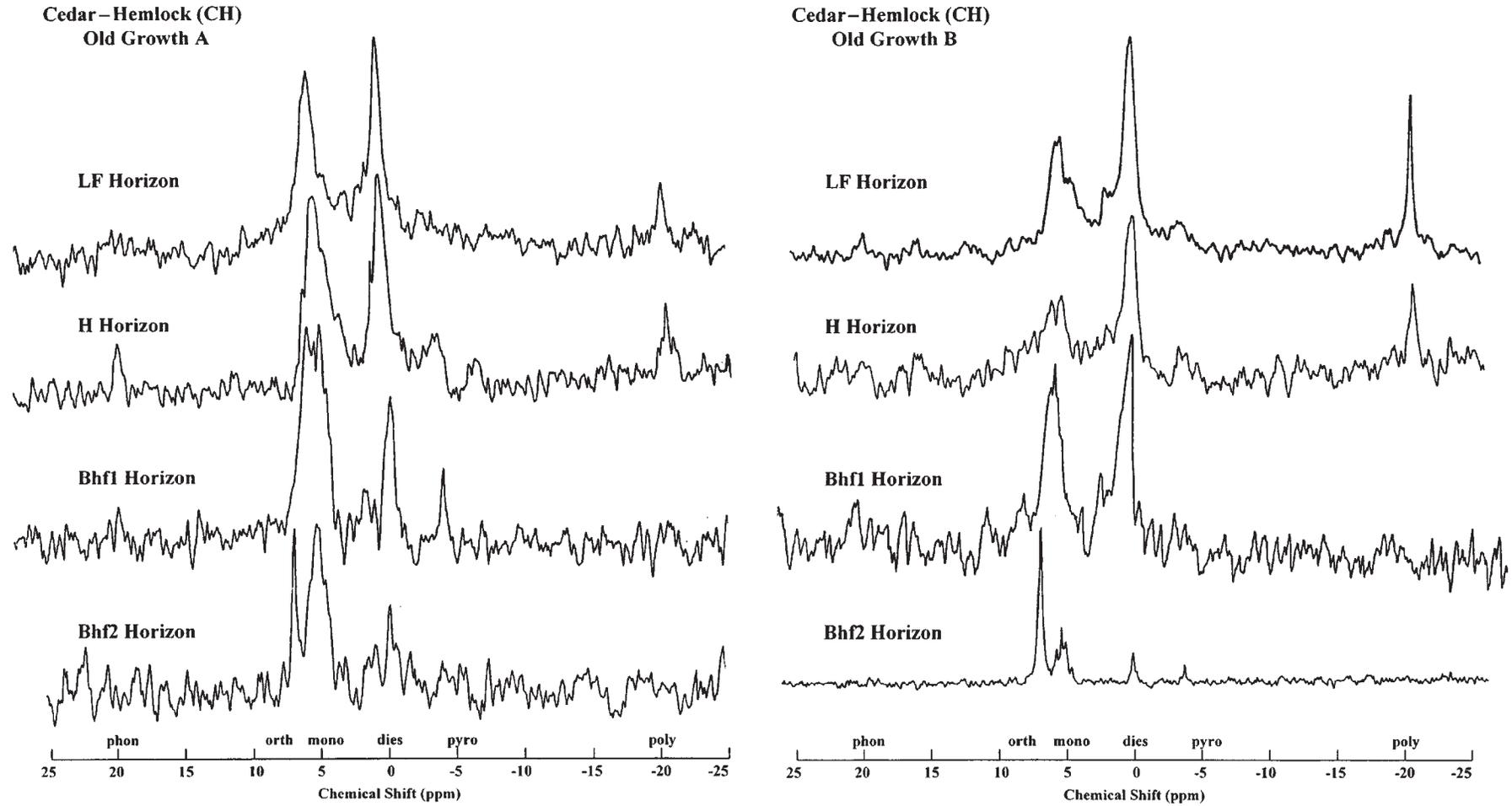


Table 6. The percentage of total P in solution found within each P form revealed by ^{31}P -NMR spectroscopy.

Forest type	Horizon	Phon (%)	Orth (%)	Mono (%)	Dies (%)	Pyro (%)	Poly (%)	$\text{P}_\text{O}/\text{P}_\text{T}$ (%)	Recovery (%)
HA-A	LF	0	31	38	18	13	0	56	99.6
	H	0	39	32	20	9	0	52	62.3
	Bhf1	0	35	34	24	7	0	58	53.0
	Bhf2	0	29	32	24	15	0	56	20.3
HA-B	LF	0	33	45	17	5	0	62	91.6
	H	9	30	30	26	5	0	65	71.1
	Bhf1	7	21	54	11	7	0	72	61.1
	Bhf2	0	31	51	18	0	0	69	21.2
CH-A	LF	0	9	33	45	0	13	78	71.3
	H	5	7	38	36	5	7	79	67.6
	Bhf1	4	23	36	32	5	0	72	47.6
	Bhf2	0	21	58	21	0	0	79	16.1
CH-B	LF	4	7	24	39	11	15	67	85.5
	H	0	15	19	50	4	12	69	43.1
	Bhf1	10	18	28	44	0	0	82	32.1
	Bhf2	0	60	25	10	5	0	35	27.2

Note: $\text{P}_\text{O}/\text{P}_\text{T}$ is the sum of phosphonate, orthophosphate monoester, and orthophosphate diester concentrations. Recovery is percentage of P_T extracted for NMR analysis. phon, phosphonate; orth, orthophosphate; mono, orthophosphate monoester; dies, orthophosphate diester; pyro, pyrophosphate; poly, polyphosphate.

Orthophosphate diesters and monoesters were the main P forms in the two CH profiles (Figs. 2A and 2B, Table 6) in all but the Bhf2 horizon. There were very distinct polyphosphate peaks in the LF and H horizons of both profiles. The pyrophosphate peaks of the CH profiles were much smaller than those of the HA profiles. Phosphonate peaks occurred in the H and Bhf1 horizons of profile A, and the LF and Bhf1 horizons of profile B. Orthophosphate comprised a much smaller percentage of total P in the CH profiles than the HA profiles in all but the Bhf2 horizon of CH-B. A small peak in the LF and H horizons at 1–3 ppm may be teichoic acid (Condrón et al. 1990). However, because this peak is poorly resolved, it will be considered as part of the orthophosphate diester peak. Table 6 also includes the ratios of $\text{P}_\text{O}/\text{P}_\text{T}$ that were calculated from the NMR spectra. These can be compared with the ratios of Table 3, which were calculated from separate chemical analyses for organic and total P. The $\text{P}_\text{O}/\text{P}_\text{T}$ ratios calculated for NMR are slightly lower than those from chemical analyses for the LF and H horizons and slightly higher for the Bhf1 and Bhf2 horizons. The recovery rates are higher for the LF horizons and lowest in the Bhf2.

Discussion

Phosphorus cycling within the soil profile

The LF is the horizon with the highest concentration of P_T . The P_A is also highest in this horizon, indicating an abundance of labile, easily leached P. This horizon most reflects the P forms and contents of litter fall, and most of the P is in organic form, as orthophosphate monoesters and diesters. This horizon also contains the highest concentrations of C, N, and extractable Ca because of the relatively undecomposed litter. Acid conditions such as those in the CH and HA forests generally suppress bacteria and actinomycetes, resulting in decomposition that is primarily fungal

(Harris 1988). Fungal mats are common in the F layers of these forests (de Montigny 1992). Fungal decomposition is slower than bacterial and results in the wide variety of P forms in the LF and H horizons of these sites. The high C/N and C/P ratios indicate microbial immobilization of nutrients (Blair 1988; Saggar et al. 1998).

The lower P_A concentrations in the H horizon, relative to the LF, are due to the loss of labile P compounds by leaching or through uptake by plant roots or microbes. In the H horizon, the P forms are similar to those seen in the LF, but there are changes in the relative abundances of P forms. For all but the CH-A profile, the percentage of P as orthophosphate monoesters is lower, and that of orthophosphate diesters is higher. The percentages of P as phosphonate and pyrophosphate were also changed in the H from the LF horizon. These changes suggest that P in this horizon is more influenced by soil microbes and less by the kind of litter. This is supported by the increased $\text{C}/\text{P}_\text{T}$ ratio in the H over the LF horizon for both sites, indicating increased microbial immobilization in the H horizon (Saggar et al. 1998). The orthophosphate diesters in this horizon are probably lipids, which de Montigny (1992) also found in the forest floor of these forests. Lipids are usually considered quite labile in soil (Stevenson and Cole 1999); their presence is indicative of reduced decomposition, as is the high C/P ratio. Decomposition is usually slower in the H than the LF horizon, because the more labile materials are no longer available. However, more nutrients are mineralized per C atom in the H than in the LF (Hart et al. 1994). Plant uptake is also high in this horizon; feeder roots are abundant in the H and Bhf1 horizons in these forests.

The Podzols of coastal British Columbia have an abrupt transition from forest floor to mineral soil, and lack A horizons (Sanborn 1987). These soils also have distinctively high C concentrations (Martin and Lowe 1989). In the Bhf1 horizon of these forests, the P_{NaOH} fraction is higher than the

P_{CBD} and P_{HCl} fractions, suggesting that inorganic phosphate (P_i) is nonoccluded, most likely with organically associated Fe, as shown by the positive correlation to pyrophosphate-extracted Fe. The diversity of P forms in the Bhf1 is reduced relative to the forest floor, with orthophosphate and orthophosphate monoesters predominating. The accumulation of orthophosphate monoesters in the Bhf1 and Bhf2 is due to their adsorption onto surface hydroxyls of soil colloids (Miltner et al. 1998; Ognalaga et al. 1994). Orthophosphate diesters do not appear to adsorb to soil colloids (Hawkes et al. 1984), although some orthophosphate diesters are present in the Bhf1 and Bhf2 of the CH and HA forests. They may be microbial, or Al or Fe bridges to humic substances (Gerke 1992) may link them. Pyrophosphate is also present in some Bhf1 and Bhf2 horizons. The high affinity of pyrophosphate for organically bound Fe and Al has led to its use as an extractant for these Fe and Al forms. Therefore, pyrophosphate may be linked to organic matter complexes with Al and (or) Fe.

Iron and Al were quantified thoroughly because of their known role in P retention in Podzolic soils (Sanborn 1987; Yuan and Lavkulich 1994). The predominance of organic-associated Fe and Al reflects the characteristic illuviation of organic matter and organometallic complexes in Podzolic soils (Oades 1989). The presence of crystalline Fe but not Al is typical of Podzols on Vancouver Island (Lewis 1976; Sanborn 1987). The amorphous Fe and Al in the Bhf2 horizons reflect the volcanic parent material of this region. The positive correlation of AAO-Al to pH and C indicates that the partitioning of Al between organically complexed and allophanic forms is controlled by pH and soil organic matter content, an observation also made by Sanborn (1987). The higher organic Al in the HA Bhf2 than the CH Bhf2 may reflect a number of factors: tree species differences in Al content; differences in the organic ligands transporting the Al to the Bhf2 horizon (Keenan 1993); or faunal activity, which is higher in the HA forests and which may alter the illuviation patterns (Sanborn 1987). The intercorrelation of all of the Al extraction procedures suggests that these methods are less selective for particular Al fractions than they are for Fe fractions (Sanborn 1987) and also reflects fewer Al forms relative to Fe forms in these soils.

The concentrations of P_A , P_T , and P_O are lower in the Bhf2 horizon than the Bhf1, as are C and N. The P_{NaOH} fraction is lower, while the P_{HCl} and P_{CBD} fractions have increased relative to the Bhf1. It would appear from the increased P_{HCl} fractions in the Bhf2, relative to the Bhf1, that apatite is present in this horizon. However, the strong correlation of P_{HCl} to AAO-extracted Al suggests that P sorbed to amorphous Al may have been extracted instead of, or in addition to, calcium phosphate. Orthophosphate and orthophosphate monoesters are the main P forms revealed by ^{31}P -NMR spectroscopy. It has been suggested (Dolfing et al. 1999; Fares et al. 1974) that P_O does not actually occur in B horizons but that the P_O determined by ignition or extraction procedures is instead inorganic P bridged to humic substances. The results from ^{31}P -NMR spectroscopy show that this may be likely for some of the P, because orthophosphate is the predominant P form in the Bhf2. However, organic P compounds are also present in these horizons. The largest inorganic P fraction in the Bhf2 horizon is P_{CBD} , and it cor-

relates strongly to amorphous Al and Fe, suggesting that much of the P in this horizon is occluded and is sequestered in amorphous sesquioxides. This is typical of podzolic Bhf and Bf horizons (Sanborn 1987; Yuan and Lavkulich 1994). Although P sorption capacities were not determined for these soils, P sorption has been found to be highly correlated with amorphous Al and Fe in many soils (Burnham and Lopez-Hernandez 1982; Walbridge et al. 1991; Zhang et al. 1997). Yuan and Lavkulich (1994) have also shown that, in British Columbia Podzols, the most important P sorbants are amorphous Fe and Al, especially Al. Thus, these soils would be expected to have high P sorption capacity.

These results suggest that P cycling is vertically stratified in these soils. In the surface horizons, biological processes such as decomposition and plant uptake and microbial immobilization control P cycling. In the Bhf2 horizon, it is controlled by sorption to amorphous Al and Fe. This vertical stratification has also been observed in Spodosols in the United States (Wood et al. 1984; Walbridge et al. 1991). It is assumed that biological P cycling is very tightly controlled in the upper horizons. Any P released by decomposition and mineralization is probably taken up by plants and microbes very quickly. Otherwise, in this high rainfall environment, it would be leached to the Bhf2 horizon where it would become less available to plants by sorption to Al and Fe.

Phosphorus cycling in soils of CH and HA forest types

Although this study sampled only nonwoody Orthic Ferro-Humic Podzols, the results from the general chemical analyses are very similar to those obtained by other SCHIRP researchers, who sampled all of the soils present on these sites. The results here indicate a higher moisture content in the CH samples, although the differences were not significant. CH forest floors tend to be wetter than adjacent HA forest floors (Prescott and Weetman 1994), and the mineral horizons are more frequently gleyed (de Montigny 1992). This may be a consequence of less windthrow disturbance in CH forests, which could cause them to be less drained, or it may be because the CH forests are on lower slope positions (Prescott and Weetman 1994). The pH was significantly higher in the LF and H horizons of the CH forests than it was in the HA, probably because of differences in litter. The higher C concentrations in the LF and H horizons of CH forests also suggest differences in litter, although these differences were not significant. Decomposition rates appear to be the same in these forest types (Prescott et al. 1995), but decomposition on CH sites is thought to be less complete later in the process, resulting in humus buildup (Prescott et al. 1995). Analysis by ^{13}C -NMR spectroscopy shows a higher ratio of carbohydrate to lignin C in CH samples and higher levels of lipids and total and labile polysaccharides (de Montigny et al. 1993), which are also indicative of incomplete decomposition in the CH forest floor. The change in the Bhf1 and Bhf2 horizons, with the C content significantly higher in the HA forests, suggests increased mixing of organic and mineral material, either by windthrow disturbance or by the higher abundance and biomass of soil fauna than in the CH forests (Battigelli et al. 1994). This higher C concentration may also be due to increased root decomposition on the HA sites or to increased illuviation of organic compounds. Differences were not significant for total N, although

N was generally lower in CH samples. This is due to the lower foliar N concentrations and a significantly higher rate of N resorption in cedar than western hemlock or amabilis fir (Keenan 1993), resulting in lower N concentrations in the soil organic matter of CH forests. Differences were also not significant for the C/N ratio, which is higher in the CH than HA forests for all horizons. Extractable Ca was higher in the CH samples. Cedar is a Ca accumulator, with high foliar Ca (Ballard and Carter 1986). Consequently, the higher Ca on the CH sites may be due to the incorporation of cedar foliage into the soil organic matter.

There were no significant differences between the CH and HA forest types for any of the P measurements. The HA LF horizon had slightly higher concentrations of P_O and P_T , which may be explained by the greater resorption of P by cedar than by western hemlock or amabilis fir (Keenan 1993). The ^{31}P -NMR spectra showed more orthophosphate in the LF and H horizons of the HA forests and more orthophosphate monoesters than diesters throughout the profile. The HA forests had little phosphonate and no polyphosphate relative to the CH forests. These differences could be due to differences in foliar P among the trees resulting in differences in P inputs from litter (Hawkes et al. 1984). They may also be due to differences in mycorrhizae between the forest types: cedars form arbuscular mycorrhizae, whereas hemlock and amabilis fir form ectomycorrhizae. Different types of mycorrhizae may use different forms of P (Harley and Smith 1983). Although not significantly different, C/ P_T ratios were higher for the CH sites for all but the lower Bhf horizon. This suggests that microbial immobilization may be higher on the CH sites. This is supported by the differences in P forms, because orthophosphate diesters and phosphonates are found where biological activity and mineralization are low (Condron et al. 1990; Tate and Newman 1982). However, because these differences in P were not significant, they suggest that the two forest types are not inherently different in P contents and cycling. Phosphorus differences in existing forests are unlikely to fully explain the P deficiencies seen on CH sites, but not HA sites, after clear-cutting, burning, and replanting.

Conclusions

The diversity of P forms as revealed by ^{31}P -NMR spectroscopy was typical of cool, moist acidic forests, as was the persistence of diester phosphates throughout the soil profile, albeit at very low levels in the mineral horizons. Phosphorus forms and cycling were vertically stratified down the profile. Most of the P in the LF was in organic forms that are typical of litterfall. In the H horizon there was more humification, with P forms more typical of soil organisms and high C/ P_T ratios indicative of microbial immobilization. In the upper Bhf horizon, inorganic phosphorus was predominantly non-occluded. Organic P was present mainly as orthophosphate monoesters, which were probably adsorbed on soil colloids. In the lower Bhf horizon, most P was occluded in amorphous sesquioxides, with low levels of organic P, mainly as monoester phosphates. No significant differences in P forms or concentrations were found between the CH and HA forest types, suggesting that P-related nutrient cycling problems after logging and slash burning may not be due to inherent differences in soil P between the forest types.

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