

Phosphorus forms and related soil chemistry of Podzolic soils on northern Vancouver Island. II. The effects of clear-cutting and burning

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Abstract: When cedar–hemlock (CH) forests of northern Vancouver Island are clear-cut and replanted, growth of replanted trees is often poor. This growth check can be overcome with nitrogen (N) and phosphorus (P) fertilization, suggesting that it may be because of deficiencies of these elements. A widely used site-preparation tool in these forests is slash burning. Because fire is known to alter nutrient cycling in forests, this burning may be contributing to the problem of poor seedling growth. Thus, the objective of this study was to compare P in forest floor and soils from clear-cut CH stands 10 years, 5 years, and immediately after burning to P concentrations and forms in undisturbed old growth CH stands. Analytical methods included extraction and digestion procedures, fractionation and ^{31}P nuclear magnetic resonance spectroscopy. Soon after burning, an “ashbed effect” was noted, with increased pH and higher concentrations of available P in surface soil horizons. Available P concentrations and pH returned to preburn levels within 10 years. However, destruction of organic matter appeared to disrupt illuviation processes throughout the soil profile, producing long-term changes in organic matter, organic P, and organically complexed Fe and Al in lower mineral horizons. Total P concentrations were unchanged, but there was a shift from organic to inorganic P forms and changes in P forms with time at depth in the profile. These changes in P distribution and movement in the soil may contribute to the growth check observed in these forests.

Résumé : Quand les forêts de cèdre et de pruche (CP) du Nord de l'île de Vancouver sont coupées à blanc et reboisées, la croissance des arbres plantés est souvent pauvre. On peut remédier à cette croissance réduite avec une fertilisation azotée (N) et phosphatée (P), suggérant que cela peut être dû à des déficiences en ces éléments. Un mode de préparation de terrain largement utilisé dans ces forêts est le brûlage des déchets de coupe. Étant donné que le feu altère le recyclage dans les forêts, cette pratique pourrait contribuer au problème de la faible croissance des semis. L'objectif de cette étude était donc de comparer P dans la couverture morte et les sols des peuplements CP, 10 ans, 5 ans et immédiatement après feu aux concentrations et formes de P dans des peuplements CP matures non perturbés. Les méthodes analytiques incluent des procédures d'extraction et de digestion, le fractionnement et la spectroscopie ^{31}P -NMR. Peu de temps après le brûlage, un effet de lit de cendre était noté, avec une augmentation du pH et des concentrations plus élevées de P disponible dans les horizons de surface du sol. Les concentrations de P disponible et le pH sont revenus aux niveaux d'avant le brûlage à l'intérieur de 10 ans. Toutefois, la destruction de la matière organique semble avoir bloqué les processus d'illuviation à travers le profil de sol, produisant des changements à long terme de la matière organique, du P organique et des formes complexées de Fe et de Al avec la matière organique dans les horizons minéraux inférieurs. Les concentrations de P total étaient inchangées, mais il y avait un déplacement des formes organiques de P vers les formes inorganiques ainsi que des changements des formes de P avec le temps en profondeur dans le profil. Ces changements dans la distribution et le mouvement de P dans le sol peuvent contribuer aux diminutions de croissance observées dans ces forêts.

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Introduction

As was discussed in Cade-Menun et al. (2000), the Salal Cedar Hemlock Integrated Research Program (SCHIRP) was

initiated to investigate the causes of poor growth of conifer regeneration on northern Vancouver Island, British Columbia. Growth stagnation was observed in trees planted in cut-overs of old-growth western redcedar (*Thuja plicata* Donn.

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Table 1. Horizon thickness for LF, H, and Bhf1 horizons and sampling depth for the Bhf2 horizon.

Age (years)	Depth of horizon or sampling (cm)				
	LF	H	Bhf1	Bhf2	Total
OG	5.3 (2.6) <i>a</i>	9.7 (4.2) <i>a</i>	10.5 (8.0) <i>a</i>	20	44.4 (10.7) <i>a</i>
0	3.7 (2.2) <i>a</i>	4.6 (2.8) <i>b</i>	5.9 (2.8) <i>b</i>	20	34.2 (7.1) <i>ab</i>
5	5.1 (2.4) <i>a</i>	5.3 (2.5) <i>b</i>	4.1 (1.9) <i>b</i>	20	34.6 (5.1) <i>ab</i>
10	2.8 (1.7) <i>a</i>	4.3 (2.4) <i>b</i>	4.8 (2.2) <i>b</i>	20	31.9 (5.3) <i>b</i>

Note: Values are means, with SD given in parentheses ($n = 9$). Values with different letters are significantly different among the ages for a horizon at $p < 0.05$. OG, old growth.

ex D. Don) and western hemlock (*Tsuga heterophylla* (Raf.) Sarg.) (cedar-hemlock, CH) forests but not in trees planted in adjoining cutovers of second-growth hemlock and amabilis fir (*Abies amabilis* (Dougl.) Forbes) (HA forests) (Weetman et al. 1989a, 1989b). The low availability of N and P in CH cutovers was presumed to originate in the old-growth forests prior to clear-cutting (Prescott and Weetman 1994). However, the study by Cade-Menun et al. (2000) showed no significant differences in P concentrations between the CH and HA forest types, and only small differences in P forms. This suggested that P deficiencies observed in trees on the CH sites 5–8 years after clear-cutting and replanting were not due to inherent differences in P between the CH and HA forest types.

To achieve more rapid regeneration on the CH and HA sites, burning is used to reduce slash accumulations and to control the heavy cover of the ericaceous shrub salal (*Gaultheria shallon* Pursh), especially in CH forests (Prescott and Weetman 1994). During a fire, the nutrients incorporated in vegetation, litter, and soil can potentially be volatilized during pyrolysis or combustion, mineralized during oxidation, or lost by ash convection (Grier 1975). After a fire is out, nutrients left in ash may be redistributed by wind and water erosion or by leaching. Some frequently observed nutrient effects include increases in soil pH; increases in the availability of P, Ca, and Mg; and decreases in total N and S (Ahlgren and Ahlgren 1960; Ellis and Graley 1983; Khanna and Raison 1986; Macadam 1987; Tomkins et al. 1991; Romanyà et al. 1994). These nutrient changes generally occur in the forest floor and surface soil. The changes at depth in the soil profile are less distinct and occur more slowly as nutrients leach downward (Feller 1982; Brockley et al. 1992). The magnitude of these effects will depend on fire severity, site and soil characteristics, and fire intensity and duration (Brockley et al. 1992).

In forests, P is tightly conserved. The P cycle is virtually closed, with most plant P recycled by microbial breakdown of litter and organic matter and then taken up again by plants. Fire is one of the few agents of P loss in forests. Many researchers have reported large increases in available P in surface horizons immediately after fire. However, these are short-term increases that can produce long-term losses that may reduce forest productivity (DeBano and Klopatek 1988; Saá et al. 1993; Romanyà et al. 1994). Most studies of burning have investigated changes in available P. Little is known about the effect of fire on other P forms or the changes in P levels and forms that may occur with time after burning.

The objective of this research was to compare the P in forest floor and soils from cut CH stands 10 years, 5 years, and

immediately after slash burning to P concentrations and forms in undisturbed old growth CH stands. The P forms were characterized using extraction and digestion procedures, fractionation, and ^{31}P nuclear magnetic resonance (NMR) spectroscopy. Changes in P cycling were also studied by examining some aspects of the chemistry of these soils that could influence P forms and levels, to determine if changes after burning were producing the P deficiencies on CH cutovers.

Materials and methods

This study was conducted near Port McNeill (50°36'N, 127°15'W) on northern Vancouver Island, British Columbia, in late July and August 1991. Sites of four ages were used: old growth, 0-year, 5-year and 10-year, with three sites per age. The CH old-growth (OG) samples used in this study are the same ones used in Cade-Menun et al. (2000). The 0-year sites were sampled within 1 month of burning, with little rainfall between the times of burning and sampling. The 5-year and 10-year sites were sampled 5 and 10 years after burning, respectively. Sampling was restricted to Orthic Ferro-Humic Podzols, the predominant soil type on all sites. Using three pits per site per age, samples from nonwoody LF, H, and upper and lower Bhf horizons were collected from all but the 0-year sites, where an ash layer was collected for the LF horizon. The thickness of horizons is shown in Table 1. The lower Bhf horizon was sampled to 20 cm depth; horizon thickness was not measured for this horizon. The lower Bhf horizons are distinct in appearance and chemically from the Bhf1 horizons (see Cade-Menun et al. (2000) for more details about classification). After air-drying, samples were sieved to <2 mm. The forest floor samples were ground with a stainless steel coffee grinder prior to sieving.

Gravimetric moisture content was determined before air-drying. Soil pH was measured in 0.01 M CaCl_2 (McLean 1982). Total C was determined by a Leco induction furnace (Bremner and Tabatabai 1971). Total N was measured by a semi-micro-Kjeldahl procedure (Bremner 1996) and colorimetric analysis with a Lachat flow injection analyzer (FIA). Iron and Al were determined by sodium pyrophosphate, acid ammonium oxalate extraction, and citrate-bicarbonate-dithionite extraction (Bertsch and Bloom 1996; Loeppert and Inskeep 1996), followed by atomic absorption spectroscopy (AAS). Loss on ignition (LOI) was determined by igniting oven-dried samples in a muffle furnace for 1 h at 375°C and for 16 h at 550°C.

Available P (P_A) was determined by the Bray P1 method (Olsen and Sommers 1982) and colorimetric analysis (Watanabe and Olsen 1965) using Lachat FIA. Total P (P_T) was determined by the Parkinson and Allen (1975) digest and colorimetric analysis on the Lachat FIA. 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 auto-analyzer. The Chang and Jackson (1957) procedure, as described by Olsen and Sommers (1982) was utilized to fractionate P into

Table 2. Field moisture content, pH in (CaCl₂), total C, total N, C/N ratio, and loss on ignition (LOI).

Horizon	Age (years)	Moisture (%)	pH	C (%)	N _T (%)	C/N	LOI
LF	OG	203 (122) <i>a</i>	3.60 (0.27) <i>b</i>	48.0 (4.3) <i>a</i>	0.92 (0.11) <i>a</i>	52.56 (6.2) <i>a</i>	2145 (430) <i>a</i>
	0	67 (45) <i>b</i>	4.58 (0.40) <i>a</i>	35.5 (11.5) <i>a</i>	0.79 (0.17) <i>a</i>	46.3 (16.3) <i>a</i>	694 (588) <i>c</i>
	5	106 (132) <i>b</i>	3.81 (0.35) <i>b</i>	43.8 (5.5) <i>a</i>	0.96 (0.15) <i>a</i>	46.4 (7.7) <i>a</i>	1275 (484) <i>b</i>
	10	80 (94) <i>b</i>	3.66 (0.39) <i>b</i>	39.0 (8.3) <i>a</i>	0.82 (0.20) <i>a</i>	48.5 (5.5) <i>a</i>	774 (597) <i>bc</i>
H	OG	314 (149) <i>a</i>	3.12 (0.19) <i>b</i>	47.3 (6.2) <i>a</i>	0.91 (0.16) <i>a</i>	53.4 (11.6) <i>a</i>	2337 (432) <i>a</i>
	0	275 (85) <i>a</i>	3.76 (0.65) <i>a</i>	41.6 (9.7) <i>a</i>	0.93 (0.14) <i>a</i>	45.9 (15.1) <i>a</i>	980 (990) <i>bc</i>
	5	249 (87) <i>a</i>	3.32 (0.31) <i>ab</i>	41.0 (13.9) <i>a</i>	0.90 (0.22) <i>a</i>	47.2 (19.4) <i>a</i>	1580 (678) <i>b</i>
	10	188 (116) <i>a</i>	3.41 (0.23) <i>ab</i>	41.5 (4.69) <i>a</i>	0.84 (0.21) <i>a</i>	51.0 (10.0) <i>a</i>	700 (423) <i>c</i>
Bhf1	OG	249 (152) <i>a</i>	3.23 (0.17) <i>a</i>	14.3 (4.74) <i>a</i>	0.54 (0.20) <i>a</i>	29.8 (9.6) <i>a</i>	87.8 (64.5) <i>a</i>
	0	276 (93) <i>a</i>	3.67 (0.41) <i>a</i>	15.1 (7.01) <i>a</i>	0.51 (0.35) <i>a</i>	34.2 (9.5) <i>a</i>	87.5 (79.1) <i>a</i>
	5	183 (99) <i>a</i>	3.36 (0.30) <i>a</i>	19.4 (13.43) <i>a</i>	0.57 (0.22) <i>a</i>	34.9 (21.4) <i>a</i>	94.4 (51.9) <i>a</i>
	10	207 (211) <i>a</i>	3.26 (0.16) <i>a</i>	16.7 (6.31) <i>a</i>	0.41 (0.17) <i>a</i>	53.3 (50.8) <i>a</i>	98.8 (75.3) <i>a</i>
Bhf2	OG	84 (27) <i>a</i>	3.96 (0.29) <i>a</i>	6.7 (1.21) <i>a</i>	0.17 (0.04) <i>a</i>	41.0 (8.2) <i>a</i>	22.1 (4.3) <i>a</i>
	0	86 (35) <i>a</i>	4.31 (0.23) <i>a</i>	6.2 (2.71) <i>a</i>	0.14 (0.07) <i>a</i>	44.2 (10.5) <i>a</i>	20.8 (9.2) <i>ab</i>
	5	120 (99) <i>a</i>	4.28 (0.35) <i>a</i>	5.1 (2.6) <i>a</i>	0.13 (0.08) <i>a</i>	40.6 (10.3) <i>a</i>	15.9 (6.5) <i>bc</i>
	10	53 (10) <i>a</i>	4.61 (0.21) <i>a</i>	4.1 (2.2) <i>a</i>	0.08 (0.04) <i>a</i>	53.7 (22.4) <i>a</i>	13.4 (3.2) <i>c</i>

Note: Values are means, with SD given in parentheses ($n = 9$). Values with different letters are significantly different among the ages for a horizon at $p < 0.05$. OG, old growth; N_T, total N.

NaOH (P_{NaOH}), citrate–bicarbonate (P_{CB}), citrate–bicarbonate–dithionite (P_{CBD}), and HCl (P_{HCl}) extractable forms.

Two soil profiles for each of the OG and 0-, 5- and 10-year postburn sites were chosen for analysis by ³¹P-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. The LF, H, Bhf1, and Bhf2 horizons were analyzed for each profile. Description of the NMR sample preparation and analytical procedure can be found Cade-Menun and Preston (1996) and Cade-Menun et al. (2000).

Using a nested design (Hicks 1982), with location nested within age postburn, analysis of variance tests at $p < 0.05$ were conducted using SYSTAT (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

The field moisture content was significantly lower in the LF of all of the postburn sites relative to the OG sites (Table 2). The field moisture content was relatively uniform in the H and Bhf1 horizons but dropped in the Bhf2. There were no significant differences in moisture content among the ages in these horizons. There were significant differences in pH among the ages (Table 2). In the LF horizon of the 0-year sites, the pH was significantly higher than that of the other ages. The pH was also higher in the LF of the 5- and 10-year sites than in the OG samples, but the difference was not significant. This same pattern was seen in the H horizon, with increased pH values in all postburn samples relative to the OG but with only the values of the 0-year samples significantly different. There were no significant differences in pH in the Bhf1 horizon, but the values were still higher in the postburn soils than in those from the OG. In the Bhf2

horizon, the pattern changed, with the highest pH values for the 10-year sites.

There were no significant differences among the ages in any horizon for total C, total N, or the C/N ratio (Table 2). Generally, the C content was lower in the 0-year LF than in the LF of the other ages. The C content was lower in all of the postburn samples than in the OG samples in the LF and H horizons but was higher in the postburn samples in the Bhf1. In the Bhf2 horizon, the lowest C content was found in the 10-year sites. On the 0-year sites, total N was lowest in the LF horizon. In the H, Bhf1 and Bhf2 horizons, it was lowest in the 10-year samples. The C/N ratio was widest in the OG stand in the LF and H horizons. In the Bhf1 and Bhf2 horizons, it was widest on the 10-year sites. There were significant differences in LOI for the LF, H, and Bhf2 horizons but not the Bhf1. For all but the LF horizons, LOI was highest in the old growth samples and lowest in the 10-year samples. In the LF, it was lowest on the 0-year sites.

In the Bhf1 horizon, the 10-year sites were significantly lower in pyrophosphate-Fe than the 0-year stands (Table 3). Pyrophosphate-Fe was also significantly lower in the Bhf2 horizons of the 10-year stands than in soils from the other ages. There were no significant differences in pyrophosphate-Al in the Bhf1 horizons. In the Bhf2 horizon, the 10-year sites were significantly lower in pyrophosphate-Al. However, there was also a significant location effect. There were no significant differences among the ages in any horizon for citrate–bicarbonate–dithionite (CBD) extracted Fe or Al, or for Al and Fe extracted by acid ammonium oxalate (AAO) (Table 3). In the Bhf1 horizon, the concentrations of Fe-CBD were highest in the 0-year samples and lowest on the 10-year sites. In the Bhf2, the 5-year sites had the most Fe-CBD, while the 10-year sites contained the least. The Al-CBD concentrations were very similar among the ages in the Bhf1 horizon and were lowest in the 10-year stands for the Bhf2 horizon. The AAO extracted Fe levels were lowest on

Table 3. Pyrophosphate-extracted Fe and Al, citrate-bicarbonate-dithionite extracted Fe and Al, and acid ammonium oxalate extracted Fe and Al.

Horizon	Age (years)	Fe _p (%)	Al _p (%)	Fe _c (%)	Al _c (%)	Fe _a (%)	Al _a (%)	Fe _{cy} (%)	Al _{cy} (%)	Fe _{amph} (%)	Al _{amph} (%)
Bhf1	OG	1.42 (0.88) <i>ab</i>	0.56 (0.23) <i>a</i>	2.01 (1.21) <i>a</i>	0.47 (0.16) <i>a</i>	1.28 (0.69) <i>a</i>	0.52 (0.19) <i>a</i>	0.50 (0.43) <i>a</i>	0.00 (0.00) <i>a</i>	0.18 (0.23) <i>a</i>	0.02 (0.03) <i>a</i>
	0	1.53 (0.64) <i>a</i>	0.47 (0.25) <i>a</i>	2.39 (1.27) <i>a</i>	0.48 (0.22) <i>a</i>	1.37 (0.56) <i>a</i>	0.45 (0.18) <i>a</i>	1.02 (0.79) <i>a</i>	0.04 (0.07) <i>a</i>	0.06 (0.13) <i>a</i>	0.03 (0.04) <i>a</i>
	5	1.05 (0.52) <i>ab</i>	0.33 (0.10) <i>a</i>	1.98 (1.08) <i>a</i>	0.44 (0.15) <i>a</i>	1.18 (0.57) <i>a</i>	0.42 (0.14) <i>a</i>	0.80 (0.74) <i>a</i>	0.03 (0.06) <i>a</i>	0.18 (0.22) <i>a</i>	0.09 (0.05) <i>a</i>
Bhf2	10	0.77 (0.51) <i>b</i>	0.41 (0.16) <i>a</i>	1.36 (0.67) <i>a</i>	0.45 (0.19) <i>a</i>	0.88 (0.78) <i>a</i>	0.46 (0.22) <i>a</i>	0.48 (0.37) <i>a</i>	0.01 (0.02) <i>a</i>	0.20 (0.31) <i>a</i>	0.05 (0.11) <i>a</i>
	OG	0.91 (0.40) <i>a</i>	1.28 (0.44) <i>a</i>	3.00 (1.00) <i>a</i>	1.46 (0.38) <i>a</i>	2.09 (0.59) <i>a</i>	2.18 (0.94) <i>a</i>	0.96 (0.69) <i>a</i>	0.00 (0.00) <i>a</i>	0.84 (0.53) <i>a</i>	0.98 (0.86) <i>a</i>
	0	0.89 (0.53) <i>a</i>	1.12 (0.48) <i>a</i>	3.46 (1.19) <i>a</i>	1.53 (0.32) <i>a</i>	2.11 (0.91) <i>a</i>	2.33 (0.67) <i>a</i>	1.35 (0.51) <i>a</i>	0.00 (0.00) <i>a</i>	1.22 (0.75) <i>a</i>	1.21 (0.68) <i>a</i>
	5	0.83 (0.71) <i>a</i>	0.95 (0.49) <i>a</i>	3.92 (1.67) <i>a</i>	1.56 (0.63) <i>a</i>	2.10 (0.70) <i>a</i>	2.23 (0.76) <i>a</i>	1.82 (1.24) <i>a</i>	0.00 (0.00) <i>a</i>	1.27 (0.36) <i>a</i>	1.28 (0.56) <i>a</i>
	10	0.29 (0.12) <i>b</i>	0.64 (0.17) <i>b</i>	3.20 (0.72) <i>a</i>	1.26 (0.17) <i>a</i>	1.62 (0.60) <i>a</i>	2.44 (0.88) <i>a</i>	1.58 (0.93) <i>a</i>	0.00 (0.00) <i>a</i>	1.32 (0.57) <i>a</i>	1.80 (0.89) <i>a</i>

Note: Values are means, with SD given in parentheses ($n = 9$). Values with different letters are significantly different among the ages for a horizon at $p < 0.05$. OG, old growth. Fe_p and Al_p, pyrophosphate extraction; Fe_c and Al_c, citrate-bicarbonate-dithionite extraction; Fe_a and Al_a, acid ammonium oxalate extraction; Fe_{cy}, crystalline; Fe_{amph} and Al_{amph}, amorphous.

the 10-year sites in the Bhf1 horizon. In the Bhf2 horizon, the concentrations were very similar for all ages. The values of Al-AAO were also very similar for all ages in the Bhf1 and Bhf2 horizons. Little amorphous Fe (AAO minus pyrophosphate) was found in the Bhf1 horizon. The Fe of this horizon is predominantly in organic (pyrophosphate extracted) and crystalline (CBD minus AAO) forms. In the Bhf2 horizon, Fe is found in amorphous, crystalline, and organic forms. The 10-year sites contain less organic Fe and more amorphous Fe. The OG stands contain the lowest concentration of crystalline Fe. These differences, however, were not significant. Aluminium was almost entirely in organic form in the Bhf1 horizon of all ages. In the Bhf2 horizon, the 10-year samples contained significantly more amorphous Al.

The results from the analysis for P_A, P_T, P_O, and the P_O/P_T ratio are displayed in Table 4. Available P was significantly higher for the 0-year sites in the LF horizon and for the 0- and 5-year sites in the H horizon. There were no significant differences in P_A in the Bhf1 and Bhf2 horizons. There were no differences among the ages for P_T for any horizon, but there were significant differences in P_O. In the LF horizon, P_O was lowest in the 0-year sites and highest in the 5-year sites. In the H and Bhf1 horizons, it was lowest in the 0-year sites and highest in the 5- and 10-year sites. In the Bhf2 horizon, P_O was significantly lower in the 5- and 10-year sites. The P_O/P_T ratio shows that most of the P in the LF, H, and Bhf1 horizons was organic. The P_O/P_T ratio was significantly lower for the 0-year sites than the other sites in the LF horizon, while the 0- and 5-year sites had the lowest P_O/P_T ratios for the H and Bhf1 horizons. In the Bhf2 horizon, all ages were significantly different from one another. In the OG stands, P was mostly organic (56.4% P_O), but 10 years after burning, P was mostly inorganic (31% P_O).

The Chang and Jackson fractionation procedure measured P_{HCl}, P_{NaOH}, and P_{CBD} (Table 5). The P_{NaOH} fraction is thought 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 nonincluded apatite fraction (Williams et al. 1980; Olsen and Sommers 1982). There were no significant differences among the ages for P_{HCl} or P_{CBD} in either the Bhf1 or Bhf2 horizons. P_{NaOH} was significantly higher in the Bhf1 horizon of the 0-year sites than the OG or 10-year sites and was lowest in the 10-year sites, but there was also a location effect. There were no significant differences in the Bhf2 horizon.

Table 6 displays the correlation matrix for the performed soil analyses. Aluminum extracted by CBD, AAO, and pyrophosphate all correlated positively with one another and with Fe-AAO, Fe-CBD, pH, P_{HCl}, and P_{CBD}. They were all negatively correlated with C, P_{NaOH}, N, P_A, P_O, and P_T. Available P correlated positively with C, N, P_{NaOH}, P_T, and P_O and negatively with P_{HCl}, P_{NaOH}, and Fe extracted by CBD, AAO, and pyrophosphate. Organic P and P_T correlated positively with one another C, N, and P_{NaOH} and negatively with P_{HCl}, P_{CBD}, and with all three Fe extractions. Carbon correlated positively to total N and LOI.

The ³¹P-NMR spectra for the two OG profiles are found in Figs. 1A and 1B. The percentages of P found within each

Table 4. Available P (P_A), total P (P_T), organic P (P_O), and the ratios of P_O/P_T and C/P_T .

Horizon	Age (years)	P_A (mg/kg)	P_T (mg/kg)	P_O (mg/kg)	P_O/P_T (%)	C/P_T
LF	OG	30.5 (10.0) <i>b</i>	602.2 (78.4) <i>a</i>	479.6 (78.9) <i>b</i>	79.6 (6.8) <i>a</i>	815 (135) <i>a</i>
	0	88.0 (31.25) <i>b</i>	713.9 (181.4) <i>a</i>	358.2 (129.7) <i>d</i>	51.3 (16.5) <i>b</i>	539 (242) <i>a</i>
	5	27.2 (9.38) <i>b</i>	695.0 (136.1) <i>a</i>	578.7 (107.8) <i>a</i>	83.5 (4.5) <i>a</i>	673 (162) <i>a</i>
	10	17.2 (7.15) <i>b</i>	517.3 (125.0) <i>a</i>	420.3 (109.7) <i>c</i>	81.0 (4.3) <i>a</i>	878 (295) <i>a</i>
H	OG	20.6 (9.65) <i>b</i>	458.4 (105.7) <i>a</i>	377.0 (88.5) <i>b</i>	82.3 (4.7) <i>a</i>	1055 (389) <i>a</i>
	0	44.1 (24.89) <i>a</i>	482.8 (131.1) <i>a</i>	349.7 (93.4) <i>c</i>	72.7 (4.2) <i>b</i>	958 (536) <i>a</i>
	5	39.0 (21.37) <i>a</i>	580.4 (107.1) <i>a</i>	441.3 (76.3) <i>a</i>	76.3 (4.8) <i>a</i>	826 (368) <i>a</i>
	10	12.6 (5.08) <i>b</i>	515.4 (150.9) <i>a</i>	417.0 (133.9) <i>a</i>	80.8 (7.2) <i>a</i>	866 (258) <i>a</i>
Bhf1	OG	6.1 (2.92) <i>a</i>	361.3 (106.2) <i>a</i>	284.9 (98.2) <i>b</i>	78.1 (8.9) <i>a</i>	392 (152) <i>a</i>
	0	8.8 (8.12) <i>a</i>	349.4 (199.5) <i>a</i>	234.3 (148.6) <i>c</i>	65.2 (14.2) <i>c</i>	450 (111) <i>a</i>
	5	9.2 (6.54) <i>a</i>	438.2 (147.0) <i>a</i>	323.8 (118.6) <i>a</i>	73.9 (8.5) <i>b</i>	343 (112) <i>a</i>
	10	8.6 (1.78) <i>a</i>	384.6 (134.1) <i>a</i>	293.9 (134.6) <i>ab</i>	74.6 (8.3) <i>a</i>	468 (151) <i>a</i>
Bhf2	OG	6.3 (1.02) <i>a</i>	262.5 (58.7) <i>a</i>	147.9 (63.7) <i>a</i>	56.4 (19.1) <i>a</i>	252 (90) <i>a</i>
	0	6.4 (1.12) <i>a</i>	257.2 (97.4) <i>a</i>	129.9 (93.4) <i>a</i>	46.7 (16.7) <i>b</i>	268 (104) <i>a</i>
	5	6.1 (1.05) <i>a</i>	214.7 (66.9) <i>a</i>	91.2 (47.1) <i>b</i>	40.4 (11.3) <i>c</i>	221 (65) <i>a</i>
	10	6.6 (0.51) <i>a</i>	214.2 (74.1) <i>a</i>	65.4 (31.5) <i>b</i>	31.6 (13.2) <i>d</i>	193 (71) <i>a</i>

Note: Values are means, with SD given in parentheses ($n = 9$). Values with different letters are significantly different among the ages for a horizon at $p < 0.05$. Available P was determined by Bray P1; total P, by Parkinson and Allen (1971) digest; and organic P, by ignition. OG, old growth.

Table 5. P extracted by HCl, NaOH and citrate–bicarbonate–dithionite (CBD), during the Chang and Jackson fractionation procedure.

Horizon	Age (years)	P_{HCl} (mg/kg)	P_{NaOH} (mg/kg)	P_{CBD} (mg/kg)
Bhf1	OG	7 (0.5) <i>a</i>	37 (28.0) <i>b</i>	22 (17.0) <i>a</i>
	0	8 (1.3) <i>a</i>	58 (34.8) <i>a</i>	34 (20.5) <i>a</i>
	5	7 (1.0) <i>a</i>	42 (13.6) <i>ab</i>	26 (19.3) <i>a</i>
	10	7 (0.7) <i>a</i>	27 (16.9) <i>b</i>	15 (13.9) <i>a</i>
Bhf2	OG	19 (13.6) <i>a</i>	25 (12.4) <i>a</i>	74 (23.6) <i>a</i>
	0	24 (12.1) <i>a</i>	23 (12.0) <i>a</i>	59 (24.8) <i>a</i>
	5	22 (24.0) <i>a</i>	17 (10.8) <i>a</i>	68 (35.8) <i>a</i>
	10	30 (14.5) <i>a</i>	18 (6.8) <i>a</i>	50 (14.7) <i>a</i>

Note: Values are means, with SD given in parentheses ($n = 9$). Values with different letters are significantly different among the ages for a horizon at $p < 0.05$. The LF and H horizons were not extracted. OG, old growth.

class of compounds, calculated from the spectra by integration, are shown in Table 7. Figure 2 shows the spectra from the 0-year sites; Fig. 3 displays spectra from 5-year sites; and Fig. 4, from 10-year sites. A guide for the interpretation of NMR spectra can be found in Cade-Menun and Preston (1996).

As discussed in Cade-Menun et al. (2000), orthophosphate diesters and monoesters were the main P forms in the two OG profiles (Figs. 1A and 1B, Table 7) in all but the Bhf2 horizon of profile B. 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 (Condron et al. 1990). However, because this peak is poorly resolved, it will be considered as part of the orthophosphate diester peak.

On the 0-year sites (Figs. 2A and 2B, Table 7), there were differences in the spectra obtained for the two profiles. The orthophosphate and orthophosphate monoester peaks were distinctly separated in the Bhf1 and Bhf2 horizons of profile A, but not in the LF and H horizons, and they were not clearly separated in any horizon of profile B. Orthophosphate was the predominant P form in the LF horizon of profile A. Orthophosphate monoesters were also present, as well as traces of orthophosphate diesters and pyrophosphate. In the H horizon, orthophosphate monoesters and diesters were the predominant P forms. The percentage of orthophosphate decreased relative to the LF horizon, while that of pyrophosphate increased. In the Bhf1 horizon, orthophosphate increased relative to the H horizon, while orthophosphate diesters and pyrophosphate were similar to the H horizon. In the Bhf2, orthophosphate was the predominant P form, with a small amount of orthophosphate monoesters. The LF and H horizons of profile B had orthophosphate and orthophosphate diesters at equal levels and a higher percentage of orthophosphate monoesters. In the Bhf1, phosphonate and pyrophosphate were present, in addition to orthophosphate and orthophosphate monoesters and diesters. The P of the Bhf2 horizon occurred mainly as orthophosphate monoesters, with some orthophosphate and orthophosphate diesters.

Five years after burning (Figs. 3A and 3B, Table 7), orthophosphate monoesters were the predominant P form in all horizons of profile A. The LF and H also contained orthophosphate diesters, orthophosphate, and polyphosphate peaks. There was a phosphonate peak in the H horizon, and pyrophosphate peaks in the H and Bhf1. In the Bhf2, the main P forms were orthophosphate monoesters, with some

Table 6. Correlation matrix.

	Al _A	Al _C	Al _P	C	C/N	C/P	Fe _A	Fe _C	Fe _P	H ₂ O	LOI	P _A	P _O	pH	P _{HCl}	P _{NaOH}	P _{CBD}	N _T	P _T	
Al _A	1.00																			
Al _C	0.86	1.00																		
Al _P	0.71	0.85	1.00																	
C	-0.61	-0.54	-0.70	1.00																
C/N	ns	ns	ns	0.27	1.00															
C/P	-0.60	-0.49	-0.55	0.80	0.38	1.00														
Fe _A	0.51	0.63	0.43	-0.52	ns	-0.47	1.00													
Fe _C	0.44	0.64	0.37	-0.43	ns	-0.37	0.88	1.00												
Fe _P	-0.31	ns	0.56	-0.57	-0.30	-0.45	0.36	0.34	1.00											
H ₂ O	-0.44	-0.36	ns	0.31	ns	0.31	ns	ns	ns	1.00										
LOI	-0.52	-0.49	-0.31	0.81	ns	0.72	ns	-0.34	ns	0.42	1.00									
P _A	ns	-0.31	-0.43	0.51	ns	ns	-0.40	-0.38	-0.40	ns	0.37	1.00								
P _O	-0.61	-0.59	-0.57	0.66	ns	ns	-0.63	-0.54	-0.44	ns	0.40	0.62	1.00							
pH	0.72	0.58	0.29	-0.39	ns	-0.54	0.44	0.39	ns	-0.51	-0.38	ns	ns	1.00						
P _{HCl}	0.80	0.61	0.51	-0.40	ns	-0.44	0.38	0.32	-0.26	-0.34	-0.35	-0.08	-0.41	0.59	1.00					
P _{NaOH}	-0.51	-0.47	-0.34	0.41	ns	ns	-0.26	-0.27	0.23	0.39	0.39	0.46	0.46	ns	-0.40	1.00				
P _{CBD}	0.59	0.72	0.61	-0.37	ns	-0.32	0.52	0.55	ns	-0.22	-0.30	-0.21	-0.40	0.44	0.46	-0.24	1.00			
N _T	-0.63	-0.57	-0.67	0.88	ns	0.57	-0.43	-0.36	-0.41	0.34	0.64	0.46	0.74	-0.32	-0.41	0.47	-0.32	1.00		
P _T	-0.33	-0.30	-0.45	0.64	ns	ns	-0.27	-0.28	-0.29	ns	0.37	0.55	0.86	ns	ns	0.47	-0.24	0.79	1.00	

Note: Al_A and Fe_A were extracted by acid ammonium oxalate; Al_C and Fe_C, by citrate-bicarbonate-dithionite; Al_P and Fe_P, by pyrophosphate; P_A, by Bray. H₂O, field moisture content; P_O, organic P by ignition; P_T, total P by Parkinson and Allen digest; N_T, total N. Values shown are all significant at $p = 0.05$; $n = 144$ for P_A, C, C/N, H₂O, P_O, pH, N_T, and P_T; for all others, $n = 72$. ns, not significant ($p > 0.05$).

Fig. 1. (A and B) ^{31}P NMR spectra for two soil profiles from mature CH sites, extracted with a 1:1 (v/v) 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.

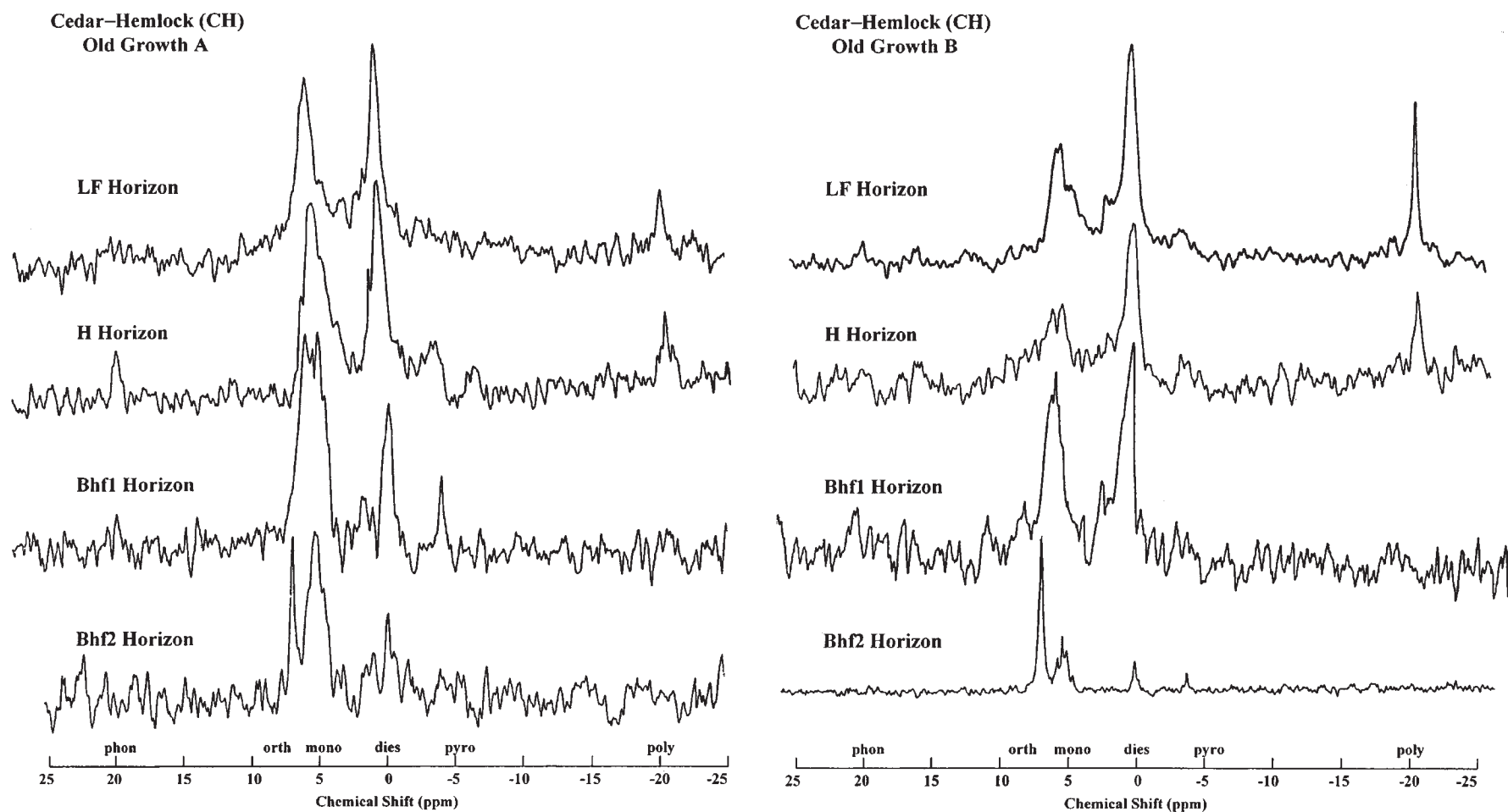


Table 7. Percentage of P found within each P form after ^{31}P -NMR spectroscopy.

Age (years) and profile	Horizon	Phon (%)	Orth (%)	Mono (%)	Dies (%)	Pyro (%)	Poly (%)	$\text{P}_\text{O}/\text{P}_\text{T}$ (%)	Recovery (%)
OG-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	77	16.1
OG-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
0-A	LF	0	51	32	11	6	0	43	89.1
	H	0	12	52	23	12	0	75	58.6
	Bhf1	0	25	43	24	8	0	67	43.0
	Bhf2	0	85	15	0	0	0	15	9.5
0-B	LF	0	22	53	19	13	0	72	95.2
	H	5	28	32	31	0	4	68	94.7
	Bhf1	10	13	40	30	7	0	80	39.8
	Bhf2	0	13	62	25	0	0	87	6.3
5-A	LF	0	23	40	18	7	12	58	78.5
	H	4	15	36	25	0	20	65	41.6
	Bhf1	0	12	55	29	4	0	84	48.4
	Bhf2	0	30	60	10	0	0	70	32.8
5-B	LF	0	33	44	23	0	0	67	76.7
	H	0	23	59	18	0	0	77	69.1
	Bhf1	0	23	51	26	0	0	77	64.8
	Bhf2	0	18	37	45	0	0	82	51.6
10-A	LF	0	17	27	32	10	14	59	89.3
	H	4	14	39	24	6	13	67	31.8
	Bhf1	0	31	51	14	4	0	65	36.6
10-B	LF	0	36	53	11	0	0	64	80.2
	H	0	8	69	18	5	0	87	57.6
	Bhf1	0	12	36	42	10	0	78	26.4
	Bhf2	0	65	25	0	0	10	25	4.1

Note: Values were calculated from the ^{31}P -NMR spectra by integration. Recovery is percent of P_T that was extracted for NMR analysis. $\text{P}_\text{O}/\text{P}_\text{T}$, sum of phosphonate and orthophosphate monoester and diester concentrations; phon, phosphonate; orth, orthophosphate; mono, monoester P; diest, diester P; pyro, pyrophosphate; poly, polyphosphate. OG, old growth.

orthophosphate and diester phosphate. In profile B, peaks were seen only for orthophosphate and orthophosphate monoesters and diesters. Orthophosphate monoesters were the dominant P forms in all but the Bhf2, where orthophosphate diesters were highest.

The spectra for the two profiles from the 10-year sites were very different from one another (Figs. 4A and 4B, Table 7). In profile A, the orthophosphate and orthophosphate monoester peaks overlapped in the LF and H horizons but were separate in the Bhf1. A spectrum could not be obtained for the Bhf2 horizon because of the low P level in this soil and the high level of interfering paramagnetic ions such as Fe. There was a range of P forms in the LF horizon of profile A. Orthophosphate diesters were highest, followed by orthophosphate monoesters. Orthophosphate and pyrophosphate were also present, as well as a sharp polyphosphate peak. The spectrum for the H horizon was similar to that of the LF but with a smaller polyphosphate peak. A small

phosphonate peak was also present in the H horizon. In the Bhf1, most of the P occurred as orthophosphate monoesters. The percentages of orthophosphate had increased from in the LF and H, while orthophosphate diesters had decreased. There was also a small amount of pyrophosphate. In profile B, the orthophosphate and orthophosphate monoester peaks were separated only in the Bhf2 horizon. In the LF, the P was predominantly found as monoester phosphate, with smaller quantities of diester phosphate. In the H horizon, the proportion of orthophosphate dropped, while the orthophosphate monoesters and diesters increased. Pyrophosphate was also present. Orthophosphate monoesters and diesters were almost equal in the Bhf1, with lower levels of orthophosphate and pyrophosphate. The Bhf2 horizon contained mainly orthophosphate, with low levels of orthophosphate monoesters and polyphosphate. The signal-to-noise ratio was low for this horizon, and it was difficult to distinguish peaks from the background noise. This was due to the low P concentration in

Fig. 2. (A and B) ^{31}P NMR spectra for two soil profiles from 0-year CH sites, extracted with a 1:1 (v/v) 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.

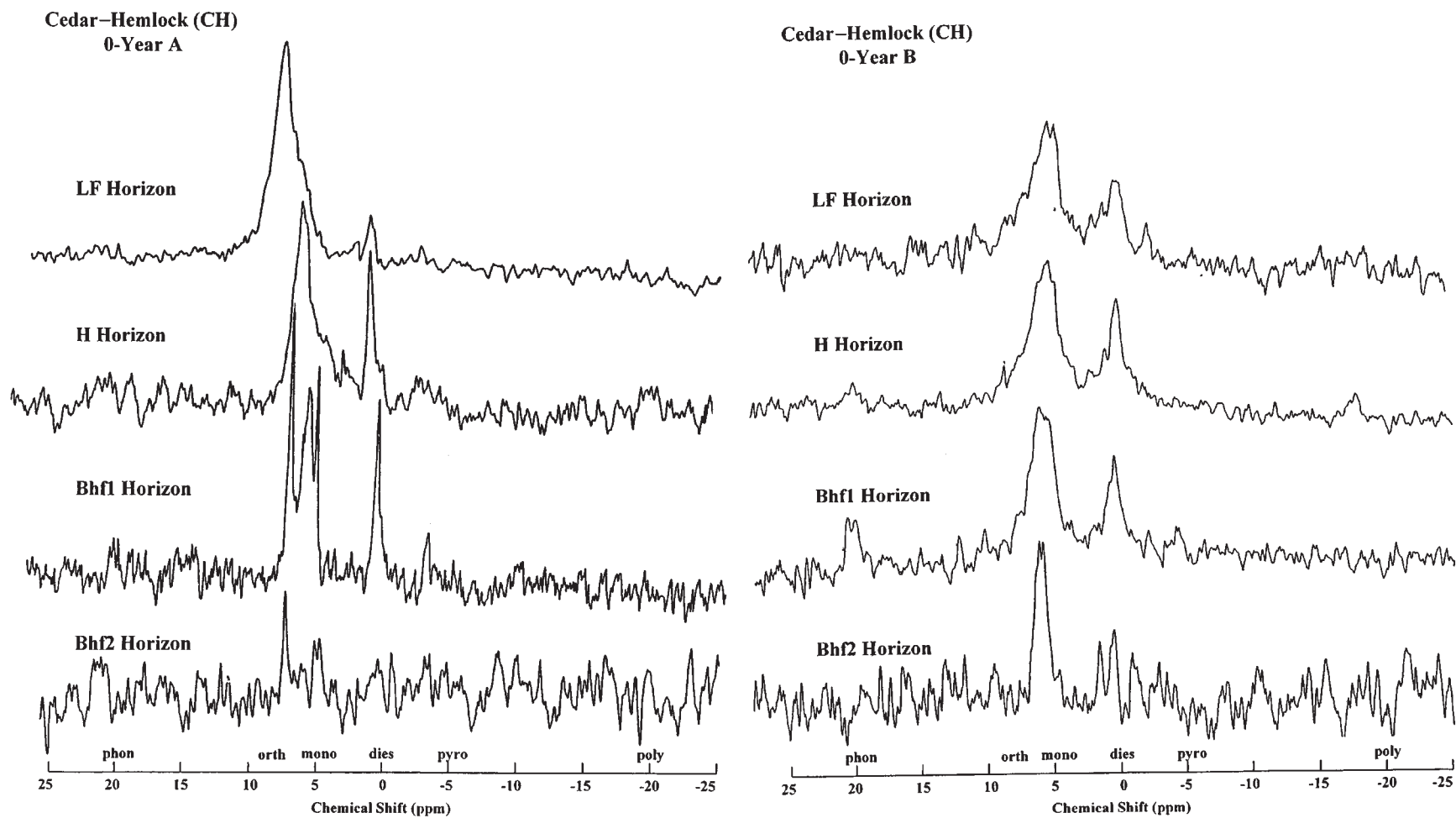


Fig. 3. (A and B) ^{31}P NMR spectra for two soil profiles from CH sites 5 years after burning, extracted with a 1:1 (v/v) mixture of 0.25 M NaOH and 0.05 M Na_2EDTA . Phon, phosphonate; ortho, orthophosphate; mono, orthophosphate monoester; diest, orthophosphate diester; pyro; pyrophosphate; poly, polyphosphate.

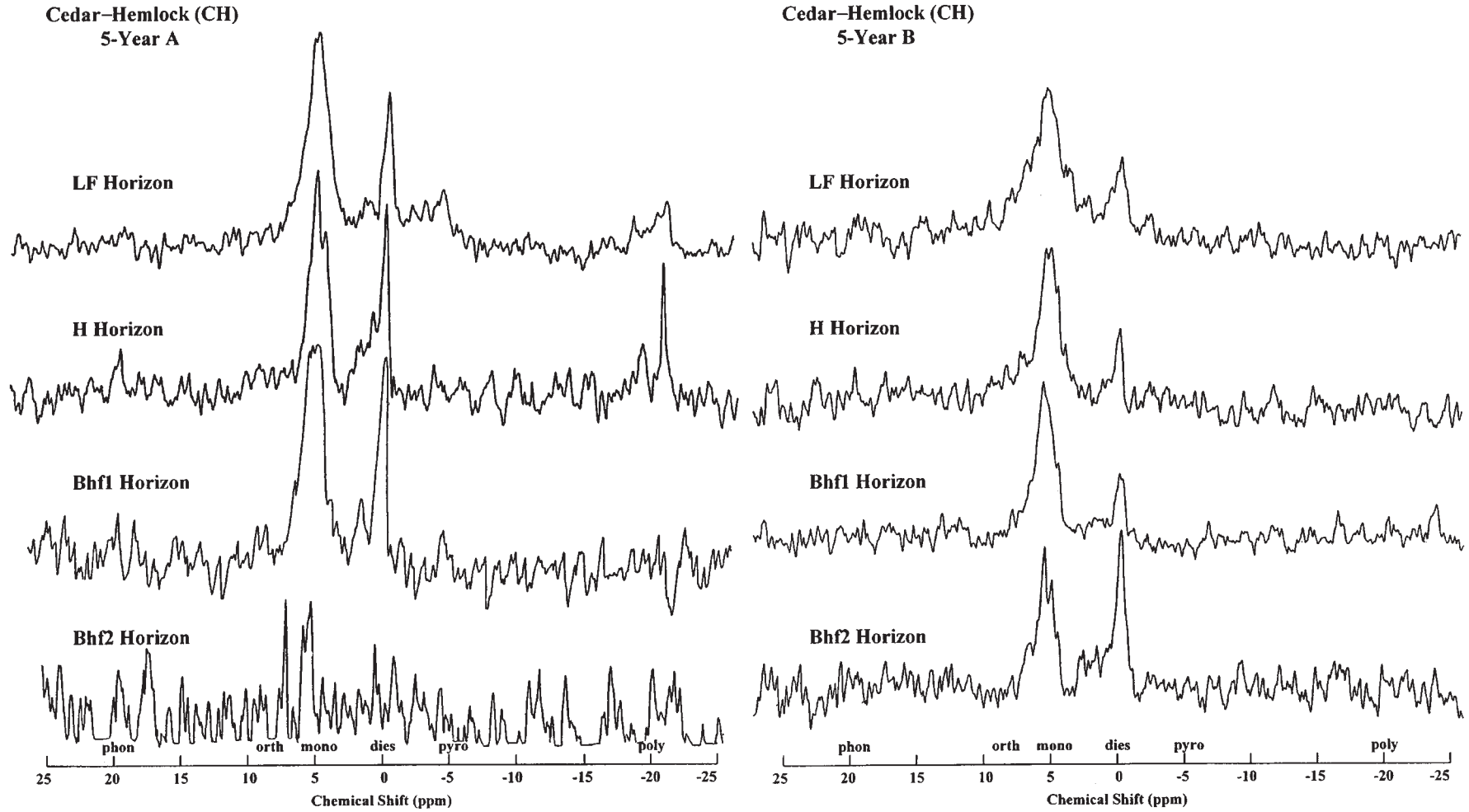
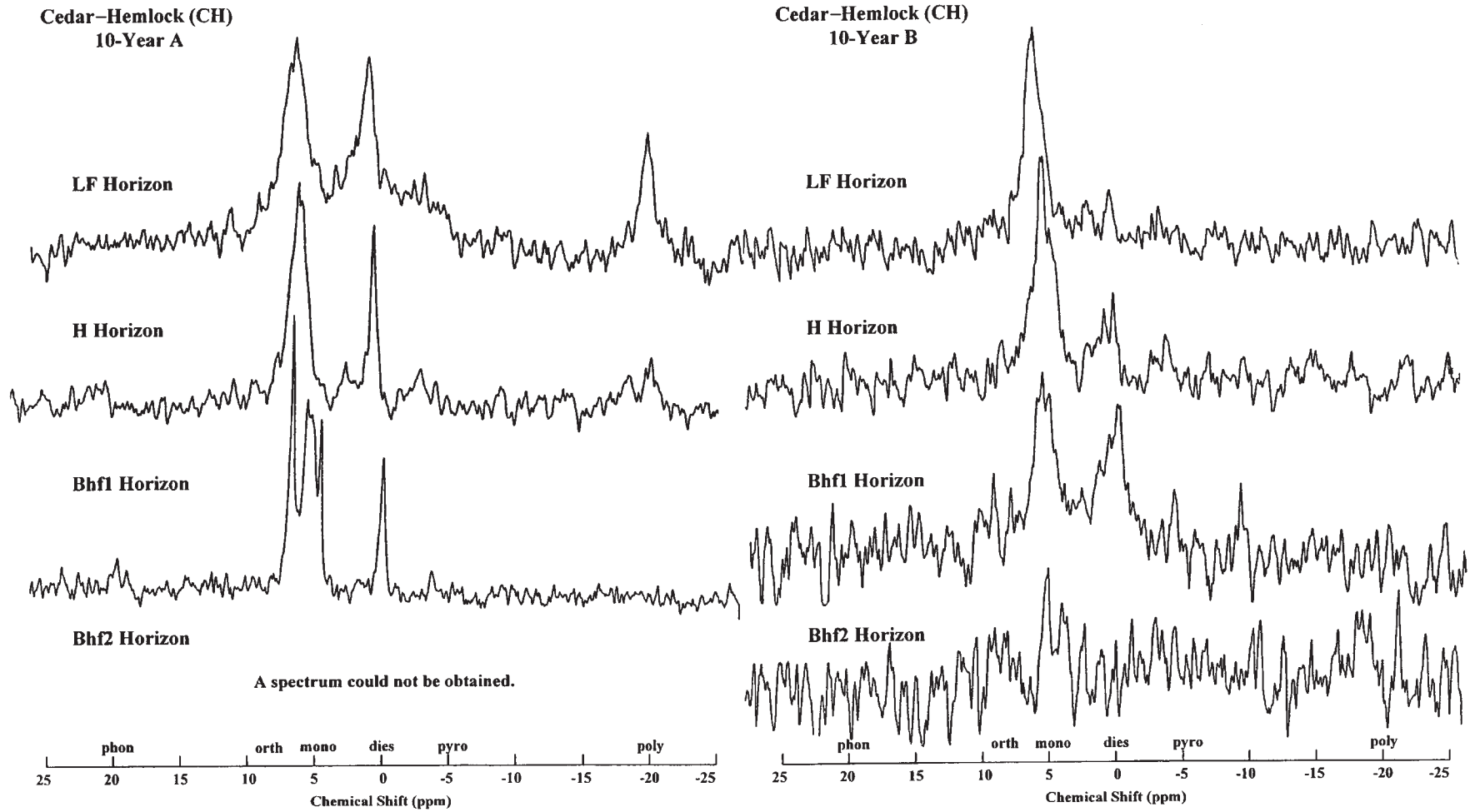


Fig. 4. (A and B) ³¹P NMR spectra for two soil profiles from CH sites 10 years after burning, extracted with a 1:1 (v/v) mixture of 0.25 M NaOH and 0.05 M Na₂EDTA. Phon, phosphonate; ortho, orthophosphate; mono, orthophosphate monoester; diest, orthophosphate diester; pyro; pyrophosphate; poly, polyphosphate.



this sample and the high concentration of interfering paramagnetic ions.

The P_O/P_T ratios of Table 7 were calculated from the NMR spectra by adding the percentages of organic P compounds: phosphonates and orthophosphate monoesters and diesters. These ratios are generally comparable with those determined by chemical extraction in Table 4, especially given that the ratios of Table 4 are means from nine samples, whereas those of Table 7 are for single samples. The recovery rate (concentration of P_T extracted for NMR analysis) was highest in the organic horizons and lowest in the mineral horizons.

Discussion

Changes in soil chemistry

As has been widely reported, burning increased the pH in the surface horizons (e.g., Vlamis et al. 1955; Ellis and Graley 1983; Tomkins et al. 1991; Romanyà et al. 1994; Marcos et al. 1995) (Table 2). This is part of the so-called "ashbed effect" of fire on soils (Humphreys and Lambert 1965). The significant pH increase in the H horizon of the recent burn may reflect contamination of the samples with the ash layer during sampling, because there had been no rain to move ash down the horizon between the burning and sampling dates. For the 5-year samples, the significant pH increase in the H horizon reflects movement of alkaline salts and ash down the horizon (Tomkins et al. 1991), which also accounts for the significantly elevated pH in the Bhf2 of the 10-year postburn sites. Ellis and Graley (1983) and Tomkins et al. (1991) also report pH increases at depth with time after burning.

The lowest total N concentrations in the LF were for the 0-year sites; for other horizons, they were lowest on the 10-year sites. Those differences, however, were not significant. There are varied reports in the literature on total N levels after fire. Some researchers report decreases (Beaton 1957; Grier 1975; St. John and Rundel 1976; Ellis and Graley 1983; Khanna and Raison 1986; Macadam 1987); others report increases (Vlamis et al. 1955; Mangas et al. 1992). Nitrogen is readily volatilized during fire (Mroz et al. 1980), and the amount of N lost is relative to the intensity of the burn. However, the correlation of total N to LOI and other components of soil organic matter such as P_O (Table 5) suggests that the changes seen in this study reflect changes in organic matter, rather than volatilization losses of N.

There was a significant decrease in organic matter, as measured by LOI, in the burn sites relative to the OG for all but the Bhf1 horizon (Table 2). Fire reduces organic matter content in surface horizons (Macadam 1987; Tomkins et al. 1991), especially in mor humus forms, where organic matter is not incorporated into soil but accumulates on the mineral surface (Feller 1982). Litter inputs, which are initially reduced after fire (Grigal and McColl 1975), would be expected to increase with the reestablishment of vegetation. However, the significant differences in LOI in all burned sites relative to OG suggest that organic matter is still reduced in burned sites. The significantly lower organic matter content of the Bhf2 horizon 10 years after burning suggests that burning the surface organic matter will affect the movement of organic matter through the profile. The C concentra-

tion was also lower, although the difference was not significant. Macadam (1987) also reported a decrease in C with time in mineral soil after fire. It should be noted that the 10-year sites were burned in the fall, while the 0- and 5-year sites were burned in the spring. The slash and litter were drier in the fall, which can result in a more intense burn (Giovannini and Lucchesi 1997). This may account for the differences in organic matter between the 5- and 10-year sites, which were significantly different in LOI in the H horizon.

Pyrophosphate-Fe was significantly lower in the 10-year sites in the Bhf1 and Bhf2 horizons, while pyrophosphate-Al was significantly lower in the 10-year Bhf2. There were no significant differences in CBD-extracted Fe and Al or in AAO-extracted Fe and Al. Pyrophosphate extracts the organically complexed Fe and Al. Natural, undisturbed Podzols are characterized by high concentrations of organically complexed Fe and Al in the mineral horizons, reflecting the illuviation of organic matter and organometallic complexes (Oades 1989). Humphreys and Lambert (1965) observed a decrease in oxalate-soluble Al in mineral soils 9 years after burning, while Kwari and Batey (1991) demonstrated that heating soils in laboratory ovens could increase CBD-extracted Al and Fe, which they considered to be a measure of free Fe and Al oxides. Neither reported changes in pyrophosphate-Fe or -Al after heating or fire.

Ten years after burning, the illuviation of organic matter and organometallic complexes appears to have been altered. The same changes do not appear to have occurred on the 5-year sites, either because there has been insufficient time since burning for changes to manifest or because more organic matter was present on the 5-year sites (Table 2), leaving the illuviation processes relatively unaffected. The changes in C and pyrophosphate Fe concentrations on the 10-year Bhf2 horizon have, in fact, changed the classification of this horizon to a Bfj horizon and not a Bhf2 horizon as on the other sites (Agriculture Canada Expert Committee on Soil Survey 1987). We have no reason to believe that this horizon would have differed significantly from the Bhf2 horizons of the OG sites prior to logging and burning, based on silvicultural reports. Therefore, we can only surmise that logging and burning have induced this change.

Changes in phosphorus

There were no significant differences among the ages for P_T , which agrees with other research (Humphreys and Lambert 1965; Marion and Black 1988; DeBano and Klopatek 1988; Saá et al. 1998). Levels of P_T , unlike N, do not generally decrease after fire, because the volatilization temperature of P is much higher than that of N (Hernández et al. 1997).

Fire is an effective mineralizing agent, significantly decreasing P_O in the LF horizon of the 0-year sites relative to the other ages. Previous studies also report decreased P_O after fire (Kwari and Batey 1991; Saá et al. 1993; Romanyà et al. 1994). This decrease in P_O results in a significant increase in P_A due to the shift from organic to inorganic forms. This increase in P_A after burning has been reported by other researchers and is one of the most consistent effects of fire on soils (e.g., Ahlgren and Ahlgren 1960; DeBano and Klopatek 1988; Saá et al. 1993; Romanyà et al. 1994; Saá et

al. 1998). The P_A increase is relative to the severity of the fire, is of short duration, and decreases with time (Macadam 1987; DeBano and Klopatek 1988; Tomkins et al. 1991; Romanyà et al. 1994; Lynham et al. 1998). On the sites in our study, P_A had returned to OG levels for all horizons in the 10-year postburn sites. As was observed with soil pH, significant increases in P_A in the H horizon of the recent burn probably reflect contamination with ash during sampling.

The ^{31}P -NMR spectra show changes in P forms after fire. As was noted in Cade-Menun et al. (2000), the NMR spectra are specific to each profile examined, making generalizations difficult. In the OG samples, the LF and H horizons had spectra typical of wet areas with high microbial immobilization, as illustrated by the high diversity of P forms and the persistence of relatively labile compounds such as orthophosphate diesters (Tate and Newman 1982; Condon et al. 1990; Gil-Sotres et al. 1990). In the Bhf1 and Bhf2 horizons, the diversity of P forms was reduced, and orthophosphate predominated, although organic P forms were found, even in the Bhf2. Immediately after burning, P in the surface horizons was converted to orthophosphate. The lower horizons appear to be unchanged from those of the old growth, with the same general trends. Five years after burning, there was more P as orthophosphate in the LF and H horizons than for the old-growth sites. Polyphosphate peaks are also present for one profile. Khanna and Raison (1986) suggest that P mineralized by soil heating may be deposited in ash in slowly soluble forms such as polyphosphates. Polyphosphates are easily formed in the laboratory by heating orthophosphate (Kulaev 1979), and their presence in these horizons may be an effect of burning. However, they are also products of mycorrhizae and soil microbes, and thus, their origin may be biological. The spectra for the Bhf1 and Bhf2 horizons are not unlike those of the old growth and 0-year profiles, except for the Bhf2 of the 5-year A profile, which produced a poor-quality spectrum because of its low P concentration.

Litter fall from re-established vegetation resulted in spectra for the LF and H horizons of 10-year profile A that were comparable with those for the old growth. In profile B, though, monoester phosphate was the predominant P form in all but the Bhf2 horizon. The most noticeable difference of the 10-year sites, relative to the other ages, was the poor quality of the spectra obtained for the Bhf2 horizon. In fact, a spectrum could not be obtained for the Bhf2 of profile A. This was due to low P concentrations in these horizons, reflecting lower organic P levels.

There are few published studies showing ^{31}P NMR spectra of forest soils following burning. Zech et al. (1987) state that cutting and burning of *Pinus mugo* Turra and establishment of pasture did not significantly influence the patterns of ^{31}P NMR spectra of the surface horizons, but they give no information on the length of time since burning or the intensity of the fire, and they only looked at one sample. Adams and Byrne (1989) report higher concentrations of inorganic P forms in surface soils in recently burned *Eucalyptus diversicolor* F. Muell. forests and an increase in P_O forms with time after burning. They did not examine P forms at depth in the soil profile or changes in organic horizons.

The significantly lower concentration of P_O in the Bhf2 horizon 10 years postburn, but lack of differences for P_T ,

suggest that there must be a shift from organic to inorganic P forms in this horizon. This is not reflected in the fractionation results, which show no differences in inorganic phosphate (P_I) forms. The Bhf2 horizon of the 10-year sites had no significant increases relative to the other ages for P_{HCl} , P_{CBD} , or P_{NaOH} , which might be expected if inorganic P were moving down the profile and reacting with soil surfaces. However, the 10-year Bhf2 samples do appear to have increased levels of P_{HCl} , which is thought to measure calcium phosphates. Ellis and Graley (1983), Kwari and Batey (1991), and Saá et al. (1993) have also reported the formation of calcium phosphates in surface soils after fire. It is possible that the higher intensity fires on the 10-year sites, together with the elevated pH, caused the Ca and P released from organic matter by burning to recombine into calcium phosphates. These subsequently moved down the soil profile to the Bhf2 horizon, where they have persisted, because the pH was still significantly elevated over OG levels. However, the positive correlation of P_{HCl} to Al extracted by AAO and CBD suggests that the extraction procedure for P_{HCl} may be measuring P associated with Al rather than Ca, as discussed in Cade-Menun et al. (2000). Increased aluminium phosphate concentrations have been reported after fire (Humphreys and Lambert 1965; Khanna and Raison 1986; Kwari and Batey 1991), as well as increased P sorption capacity, probably due to Al released from organic matter after burning (St. John and Rundel 1976; Kwari and Batey 1991; Romanyà et al. 1994). The significant change in P_O suggests that there should also be a significant change in P_I . The fact that this was not seen suggests that the Chang and Jackson method does not completely extract P_I forms from soil.

Clear-cutting and burning also reduced the depth to the Bhf2 horizon, especially on the 10-year sites (Table 1). In OG CH forests, feeder roots are usually found in the H and Bhf1 horizons. However, with the reduction of the surface horizons, feeder roots were seen in the Bhf2 horizon on the 10-year sites. Any shifts from P_O to occluded, unavailable P_I forms in the Bhf2 would reduce the P available for plant uptake on these sites.

Our results suggest that clear-cutting and burning reduce organic matter in Podzolic soils. With time, this produces a shift throughout the soil profile, reducing the characteristic illuviation patterns that move organic matter through these soils. Burning also converts P from organic forms, which can be mineralized to release plant-available P, to inorganic forms, resulting in a short-lived increase in its availability to plants. However, over time the P_I forms are converted to occluded Al-phosphates that are unavailable to plants. The results from this paper and Cade-Menun et al. (2000) suggest that illuviation of P_O is an important aspect of P cycling in Podzolic soils and is responsible for the P_O at depth as much as in situ formation by soil microbes. This disruption of illuviation, and subsequent changes in P movement through these soils, may be responsible for the P-related growth check seen in these forests.

Clear-cutting versus burning

For this paper, we have focussed on the effects of burning, although these sites were both clear-cut and burned. We were unable to analyse clear-cut sites separately from clear-cut and burn sites, because there were no 5- or 10-year sites

available that had not been burned. Many of the observed changes in pH, organic matter, and P are consistent with fire effects, as discussed above. However, clear-cutting is known to produce a variety of effects related to the removal of the forest canopy and disturbance of the forest floor. Litter fall will be decreased in clearcuts (France 1997), and decomposition is often increased (Fuller et al. 1988; Tsobel 1991). Therefore, clear-cutting may also have contributed to the significant changes in organic matter on the logged and burned sites relative to the OG forests. The thickness of the forest floor may be decreased by clear-cutting, because of increased decomposition, erosion (Fuller et al. 1988), or compaction (Brais and Camiré 1998). Therefore, both logging and burning may have produced the significant changes in horizon thickness on all logged and burned sites versus old growth (Table 1). Residual compaction may still be present 6–10 years after logging (Brais and Camiré 1998). There can also be increased rainfall on soils after clear-cutting because less water is deflected by the tree canopy (McCull 1978). In the high rainfall environment of the SCHIRP sites, this could result in increased illuviation or leaching losses, contributing to the reduced C, P_O, and organically complexed Fe and Al in the Bhf2 horizon of the 10-year sites. Unless erosion occurs, nutrient losses from clear-cutting are usually minimal due to retention in litter and soil and to uptake by rapidly growing vegetation invading clear-cut sites (McCull 1978). On similar SCHIRP sites, Keenan et al. (1994) found no significant differences in pH, extractable nitrate or extractable phosphate in soils from recent clearcuts, as compared with OG soils.

We are also aware of the limitations of the chronosequence approach. Silvicultural records were used during site selection to carefully choose sites with similar vegetation, slope, and aspect to the OG sites. Care was also taken to avoid sites with known differences in logging, such as scarification. One known difference, as discussed above, was the timing of burning, whereby the 10-year sites were burned in the fall, while the 0- and 5-year sites were burned in the spring. The 10-year sites had also been replanted with different tree species. Sitka spruce (*Picea sitchensis* (Bong) Carr.) and Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) were found on the 10-year sites in addition to the western hemlock and western redcedar that were planted on the 5-year sites.

Conclusions

After clear-cutting and burning, the soils of the CH forest types experience an ashbed effect, with increased pH and higher concentrations of available P in the surface horizons. These return to preburn levels within 10 years in the surface horizons, but changes are seen at depth. Destruction of organic matter by logging and burning appears to disrupt illuviation processes throughout the soil profile, and may produce long-term changes in lower mineral horizons, with decreased organic matter, organically complexed Fe and Al, and organic P at depth 10 years after cutting and burning. Although total P levels were not changed, there was a shift from organic P forms to inorganic P forms and changes in P forms with time at depth in the profile. These changes in the P cycle are probably responsible for the reduced P availability on these sites after clear-cutting and replanting.

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