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

Barbara J. Cade-Menun, Shannon M. Berch, Caroline M. Preston, and L.M. Lavkulich

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. 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.

Introduction

The Salal Cedar Hemlock Integrated Research Program (SCHIRP; Prescott and Weetman 1994) was initiated to investigate 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 ($Thuja canadensis$ (Lam.) Carr.), and MLP fir ($Abies lasiocarpa$ (Hook.) Nutt.). The results of this study suggest that the differences in nutrient cycling between CH and HA forests may be related to differences in soil P concentration and forms.
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 ad-
joining 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 replaced 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 (H₃PO₄). All native P in soils is originally de-

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 Hem-

lock 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 propor-
tion of deeply decomposed woody material overlying predominately moderately well to somewhat imperfectly drained Orthic Ferro-Humic Podzolic soils (Agriculture Canada Expert Commit-
tee 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 loca-
tion, 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 ± 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 sig-
nificant differences between HA and CH forests for horizon thick-

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 CaCl₂, 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. To-
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 colori-
metrictically 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 ovendried material using sodium pyrophosphate, acid ammonium oxalate extraction and citrate–bicarbonate–dithionite extraction (Bertsch and Bloom 1996; Loeppert and Inskeep 1996), followed by AAS.

Phosphorous methodology

Available P (P₄) was extracted from air-dried material by the Bray P1 method (Olsen and Sommers 1982), followed by colori-
metrictic analysis (Watanabe and Olsen 1965) using a Lachat FIA. Total P (P₅) was determined on oven-dried material by the
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 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 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 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.

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

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<th>Horizon</th>
<th>Forest type</th>
<th>Moisture (%)</th>
<th>pH</th>
<th>C (%)</th>
<th>N (%)</th>
<th>C/N</th>
<th>Extractable Ca (mg/kg)</th>
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<td>3.2 (0.14)*</td>
<td>46.6 (5.1)</td>
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<td>203 (122)</td>
<td>3.6 (0.27)</td>
<td>48.0 (4.3)</td>
<td>0.92 (0.11)</td>
<td>52.6 (6.2)</td>
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<td>2.9 (0.10)*</td>
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<td>0.17 (0.04)</td>
<td>41.0 (8.3)</td>
<td>222.3 (286.1)</td>
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</table>

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 (PNaOH) 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 (PNaOH), citrate–bicarbonate (PCB), citrate–bicarbonate–dithionite (PCBD), and HCl (PHCl) 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 31P-NMR spectroscopy. The samples selected were high in P2 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 Na2EDTA. After filtration with Buchner funnels and Whatman 41 filter paper, samples were freeze-dried, then re-dissolved in D2O for NMR analysis. The 31P-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 (Daai et al. 1996).
within a horizon, there were no significant differences between the HA and CH forest types for the variables presented in the table.

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.

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.

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.

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

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

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.

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Table 5. Correlation matrix.

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<td>0.63</td>
</tr>
</tbody>
</table>

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. H_2O, 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, H_2O, 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$_2$EDTA. Phon, phosphonate; ortho, orthophosphate; mono, orthophosphate monoester; diest, orthophosphate diester; pyro, pyrophosphate; poly, polyphosphate.
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$_2$EDTA. phon, phosphonate; ortho, orthophosphate; mono, orthophosphate monoester; diest, 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 (Condron 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 \( P_{O}/P_T \) 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 \( P_{O}/P_T \) ratios calculated for NMR are slightly lower than those from chemical analyses for organic and total P. The \( P_{O}/P_T \) ratios calculated for NMR are slightly higher for the LF and Bhf1 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 \( P_A \). 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 \( C/P_T \) 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

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

<table>
<thead>
<tr>
<th>Forest type</th>
<th>Horizon</th>
<th>Phon (%)</th>
<th>Orth (%)</th>
<th>Mono (%)</th>
<th>Dies (%)</th>
<th>Pyro (%)</th>
<th>Poly (%)</th>
<th>( P_{O}/P_T ) (%)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA-A</td>
<td>LF</td>
<td>0</td>
<td>31</td>
<td>38</td>
<td>18</td>
<td>13</td>
<td>0</td>
<td>56</td>
<td>99.6</td>
</tr>
<tr>
<td>H</td>
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<td>39</td>
<td>32</td>
<td></td>
<td>20</td>
<td>9</td>
<td>0</td>
<td>52</td>
<td>62.3</td>
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<tr>
<td>Bhf1</td>
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<td>35</td>
<td>34</td>
<td>24</td>
<td>7</td>
<td>0</td>
<td>58</td>
<td>53.0</td>
<td></td>
</tr>
<tr>
<td>Bhf2</td>
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<td>29</td>
<td>32</td>
<td>24</td>
<td>15</td>
<td>0</td>
<td>56</td>
<td>20.3</td>
<td></td>
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<tr>
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<td>45</td>
<td>17</td>
<td>5</td>
<td>0</td>
<td>62</td>
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<tr>
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<td>30</td>
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<td>26</td>
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<td>10</td>
<td>5</td>
<td>0</td>
<td>35</td>
<td>27.2</td>
<td></td>
</tr>
</tbody>
</table>

Note: \( P_{O}/P_T \) is the sum of phosphonate, orthophosphate monoester, and orthophosphate diester concentrations. Recovery is percentage of \( P_A \) extracted for NMR analysis. phon, phosphonate; orth, orthophosphate; mono, orthophosphate monoester; dies, orthophosphate diester; pyro, pyrophosphate; poly, polyphosphate.
**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 SCHRP 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 (Montigny et al. 1993), which are also indicative of incomplete decomposition 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 31P-NMR spectroscopy shows a higher ratio of carbohydrate to lignin C in CH samples and higher levels of lipids and total and labile polysaccharides (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 P₂O₅ and P₃O₅, which may be explained by the greater resorption of P by cedar than by western hemlock or amabilis fir (Keenan 1993). The ³¹P-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. Difference types of mycorrhizae may use different forms of P (Harley and Smith 1983). Although not significantly different, C/P₇ 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 clearcutting, burning, and replanting.

Conclusions

The diversity of P forms as revealed by ³¹P-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/P₇ 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 processes after logging and slash burning may not be due to inherent differences in soil P between the forest types.

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