

Characterization of soil P in coastal forest chronosequences of southern Vancouver Island: effects of climate and harvesting disturbance

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Preston, C. M. and Trofymow, J. A. 2000. **Characterization of soil P in coastal forest chronosequences of southern Vancouver Island: Effects of climate and harvesting disturbance.** *Can. J. Soil Sci.* **80**: 633–647. Limitation of tree growth due to inadequate P supply has been found for young plantations following harvesting of old-growth in high rainfall areas of coastal British Columbia. To understand the reasons for P limitation, we investigated P chemistry in mineral soil to 50 cm depth in sites from the Coastal Forest Chronosequence project on Vancouver Island. This allowed comparison of biogeoclimatic subzone (higher rainfall on west than east coast sites) and of time from harvesting disturbance (seral stage). Available (Bray 1) P was significantly higher ($P < 0.001$) on the drier east side (up to 50 mg kg^{-1}), than on the west side ($< 5 \text{ mg kg}^{-1}$), although total P values were less divergent (694 mg kg^{-1} , east and 534 mg kg^{-1} , west). There were no significant serral stage effects on total and available P. Extraction with 0.5 M NaOH recovered 50–60% of total P, except for samples from 10–30 cm depth on the west side, for which only 20% was recovered, an effect not found for C. Analysis of the NaOH extracts by ³¹P nuclear magnetic resonance (NMR) spectroscopy showed much higher proportions of orthophosphate P on the east side. West side extracts were higher in organic P forms, especially diesters, typical of forest ecosystems with restricted nutrient cycling and high precipitation. On the west side, low concentrations of available P, higher proportions of organic P in NaOH extracts, and depression of NaOH extractability at 10–30 cm are consistent with P being a limiting nutrient for tree growth, a problem that may be exacerbated by harvesting disturbance.

Key words: Forest chronosequences, harvesting disturbance, ³¹P NMR, P cycling, organic P

Preston, C. M. et Roy, J. A. 2000. **Caractérisation du P dans le sol de chronoséquences de la forêt côtière du sud de l'île Vancouver; effets du climat et des perturbations associées à la coupe du bois.** *Can. J. Soil Sci.* **80**: 633–647. Des contraintes à la croissance des arbres par carence de phosphore (P) ont été observées dans les jeunes plantations après la coupe des arbres exploitables dans les zones de forte pluviosité du littoral de la Colombie-Britannique. Pour connaître les causes de ces carences, nous avons examiné la nature des formes chimiques de P dans le sol minéral jusqu'à 50 cm de profondeur aux emplacements du projet de chronoséquences de la forêt côtière dans l'île Vancouver. Cela nous permettait de comparer entre les sous-zones biogéoclimatiques (pluviosité plus abondante sur la côte ouest que sur la côte est) et entre le temps écoulé depuis la coupe (stade séral). La teneur en P assimilable était très significativement plus élevée ($P < 0,001$) sur la côte est plus sèche, où elle pouvait atteindre jusqu'à 50 mg kg^{-1} , que sur la côte ouest où elle était inférieure à 5 mg kg^{-1} . Les valeurs de P total différaient moins, se chiffrant en moyenne à 694 mg kg^{-1} sur la côte est et à 534 mg kg^{-1} à l'ouest. Il n'y avait pas d'effets significatifs du stade séral sur le P total ni sur le P assimilable. L'extraction au 0,5 M NaOH permettait de récupérer 50 à 60 % du P total, sauf pour les prélèvements provenant de la couche de 10–30 cm de profondeur, où le taux de récupération n'était que de 20 %. Cet effet ne s'observait toutefois pas dans le cas de C. L'analyse des extraits au NaOH par spectroscopie de résonance magnétique nucléaire de ³¹P (RMN) révélait la présence de proportions beaucoup plus hautes de P sous forme d'orthophosphates sur la côte est. Les extraits provenant de la côte ouest étaient plus riches en formes organiques de P, en particulier les diesters, couramment associées aux écosystèmes forestiers à fortes précipitations caractérisées par des cycles de transformation restreints des éléments nutritifs. Les basses concentrations de P assimilable, les fortes proportions de P organique dans l'extrait au NaOH et la chute de l'extractibilité au NaOH dans la couche de 10 à 30 cm observées sur la côte ouest sont autant de facteurs permettant de conclure que P est un élément nutritif critique pour la croissance forestière dans cette région et que ce problème peut être aggravé par les perturbations associées à la coupe du bois.

Mots clés: Chronoséquence forestière, perturbations associées à la récolte, RMN de ³¹P, transformations de P, P organique

Soil P originates from mineral weathering, and is tightly conserved in forest ecosystems where it is often the second growth-limiting nutrient after N (Gressel and McColl 1997; Vitousek and Farrington 1997). Growth stagnation, a serious problem in young plantations on old-growth cutovers in areas of high rainfall on northern Vancouver Island, is alleviated by fertilization with both N and P (Weetman et al. 1989a, 1989b, 1993; Prescott et al. 1996). Climatic differences affect P cycling in forest ecosystems, and the high

rainfall in coastal British Columbia may increase the possibility of leaching losses of P after harvesting and slash-burning (Cade-Menun 1995).

Apart from specific silvicultural concerns, in BC there is also more general public concern over the effects of clearcutting and the conversion of coastal old-growth to managed forests (MacKinnon and Trofymow 1998). In response to this, and to assist in developing guidelines for sustainable management practices, the Canadian Forest

Service initiated the **Coastal Forest Chronosequence (CFC)** project, comprising a broad range of studies on ecosystem function in chronosequences of stands (i.e., different ages) from regeneration to old-growth sites in coastal forests on southern Vancouver Island (Trofymow et al. 1997). While most of coastal BC (including northern and western Vancouver Island) has a mild, wet climate, forests in the southeastern part of Vancouver Island have developed under drier and slighter warmer conditions. Establishment of the CFC sites has facilitated a wide range of ecosystem studies on the effects of both climate and successional changes after harvesting; in this study we investigate P forms and availability in mineral soil.

While it is difficult to analyse organic forms of soil P by conventional chemical techniques. Newman and Tate (1980) demonstrated the effectiveness of ^{31}P NMR spectroscopy to analyse inorganic and organic forms of P in NaOH extracts of soil. Since then, several studies have used ^{31}P NMR to demonstrate the importance of organic P forms in forest soils (Zech et al. 1985; Adams and Byrne 1989; Adams 1990; Forster and Zech 1993; Gressel et al. 1996; Guggenberger et al. 1996), although there has been only preliminary investigation of BC coastal forests (Cade-Menun and Preston 1996). We have applied this technique plus standard wet chemical analysis in our investigation of P forms and availability in mineral soil of coastal forests of Vancouver Island differing in climate (rainfall) and date from harvesting disturbance.

MATERIAL AND METHODS

Sites and Soil Sampling

For the CFC project, eight chronosequence study sites were established in 1991–1992 in coastal temperate rainforests on southern Vancouver Island, four on the east and four on the west side. Each site comprises stands of four seral stages (a chronosequence) in close proximity. The age ranges for each seral stage were (reference year 1990): regeneration (REG, 3–8 yr), immature (IMM, 25–45 yr), mature (MAT, 75–90 yr), and old growth (OG, >200 yr). Due to the extensive logging activities in the 20th century, it was difficult to locate sites that fulfilled all of the criteria, and the MAT stands at two sites, Koksilah (KOK) and Klanawa (KLA) originated from stand-destroying wildfire rather than harvest and slash-burning. Other criteria were that each chronosequence be within a $5 \times 5 \text{ km}^2$ area and that the different age stands have similar slope, elevation (within 200 m) and aspect. All of the 32 chronosequence plots are located within the Coastal Western Hemlock (CWH) biogeoclimatic zone (Pojar et al. 1991).

Chronosequences on the leeward east side (East) of Vancouver Island are in the very dry maritime subzone of the CWH biogeoclimatic zone (CWHxm, mean annual precipitation 1697 mm, mean annual temperature 9.1°C) (Klinka et al. 1991). They are designated: Greater Victoria Watershed North (VWN), Greater Victoria Watershed South (VWS), Nanaimo River (NAN), and Koksilah (KOK). Forests on the east side are dominated by Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco] with a small

component of western hemlock [*Tsuga heterophylla* (Raf.) Sarg] and western red cedar (*Thuja plicata* Donn.). They are predominantly on Dystric Brunisolic soils (Dystrochrept Inceptisol, U.S. Great Group equivalent) (Agriculture Canada Expert Committee on Soil Survey 1987) developed on morainal materials.

Sites on the west coast (West) of Vancouver Island (Red/Granite Creek (RGC), Nitinat (NIT), Klanawa (KLA) and Renfrew (REN)) are in the very wet maritime CWH subzone (CWHvm, mean annual precipitation 2787 mm, mean annual temperature 8.2°C). The forests are dominated by western hemlock with some amabilis fir (*Abies amabilis* Dougl.), western red cedar and Douglas-fir. West side sites are predominantly on Humo-Ferric Podzolic soils (Haplorthod Spodosol, U.S. Great Group equivalent) (Agriculture Canada Expert Committee on Soil Survey 1987) developed on colluvial materials. Further details of locations, plot layout and related studies are reported elsewhere (Trofymow et al. 1997; Preston et al. 1998).

Mineral soil was sampled from four subplots per plot at three depths (0–10, 10–30 and 30–50 cm), except in a few plots with shallow bedrock. There was no compositing of subplot samples for chemical analysis. Samples were stored at 2°C and then air-dried for 2–3 wk. The <2 mm fraction was separated by sieving and a subsample finely ground in a Siebtechnik mill for analysis. General soil chemical data for each site and seral stage by depth are given in Tables 1a and 1b [analyses according to Kalra and Maynard (1991)].

Chemical Analysis

Total N and C were determined by dry combustion with LECO FP-228 and LECO CR-12 analysers, respectively. Extractable P was determined using the Bray 1 procedure (Kalra and Maynard 1991), with analysis of the extracts by ICP atomic emission spectroscopy (ARL-FISONS 3410+ Sequential Analyser). Total P was determined by the *aqua regia* digestion procedure of Crosland et al. (1995) modified so that the samples did not go to dryness. A 500 mg sample was weighed into a 75 mL block digester tube and 15 mL of mixed acids (4:1 mix of conc. HCl/conc. HNO_3) was added. After digesting overnight at room temperature, the tubes were block-digested at 50°C for 1 h, 100°C for 1 h and 110°C for 3 h. After cooling, 10 mL of HCl (25% vol/vol) was added and the tubes re-heated at 90°C for 45 min. Digests were volumised to 75 mL with de-ionised water and the solutions analysed for total P by ICP as above. The procedure was verified using soil reference standards CAN-MET SO-4 (9000 mg g^{-1} P) and SO-3 (480 mg g^{-1} P) from the Canada Centre for Mineral and Energy Technology, Ottawa, Canada.

Extraction and ^{31}P NMR Spectroscopy

The ^{31}P NMR study was carried out on composite samples prepared using proportional weights from the four subplot samples from each depth. The extraction procedure used was that of Gressel et al. (1996), using 0.5 N NaOH, followed by a treatment with Chelex to reduce the content of paramagnetic cations. Twenty grams of air-dry soil (<2 mm) and 45 mL of 0.5 M NaOH were shaken for 2 h in a 100 mL

Table 1. Surface organic (LFH) and mineral soil chemical data for Coastal Forest Chronosequence plots summarized (a) by biogeoclimatic subzone, site, depth and (b) by biogeoclimatic subzone, seral stage, depth (after Trofymow et al. 1997)

Depth (cm)	Thickness (cm)	pH	Total C (g kg ⁻¹)	Total N (g kg ⁻¹)	Total P (mg kg ⁻¹)	Avail. P (mg kg ⁻¹)	CEC ^z (cmol kg ⁻¹)	Ca+Mg+K (mg kg ⁻¹)	Fe+Al ^y (g kg ⁻¹)	Fe+Al ^x (g kg ⁻¹)
<i>(a) by subzone, site, depth</i>										
<i>East (CWHxm^w)</i>										
<i>Victoria Watershed South</i>										
LFH	4	4.43	404.6	8.03	780	NA	NA	NA	NA	NA
0-10		4.50	41.5	1.25	575	50.6	22.1	875	6.9	11.5
10-30		4.59	20.3	0.71	620	51.8	16.1	491	7.1	13.3
30-50		4.69	14.2	0.53	481	27.3	14.2	435	6.1	13.9
<i>Victoria Watershed North</i>										
LFH	3	4.73	434.5	9.22	1090	NA	NA	NA	NA	NA
0-10		4.57	28.9	0.25	1138	66.7	17.7	645	5.8	17.7
10-30		4.60	22.1	0.45	1065	60.8	15.4	341	5.6	18.8
30-50		4.66	13.7	0.25	631	18.8	11.7	233	4.0	19.5
<i>Koksilah</i>										
LFH	3	4.90	400.2	9.33	1280	NA	NA	NA	NA	NA
0-10		4.88	41.9	0.70	913	30.3	20.7	1555	5.5	16.4
10-30		4.88	25.0	0.59	728	21.6	15.9	719	4.8	16.0
30-50		4.88	24.4	0.46	708	15.8	16.4	641	5.0	16.6
<i>Nanaimo River</i>										
LFH	5	4.37	429.8	7.73	867	NA	NA	NA	NA	NA
0-10		4.55	25.9	0.34	544	38.2	10.9	438	4.0	13.6
10-30		4.76	16.1	0.19	507	24.4	8.7	390	3.7	15.4
30-50		4.82	12.5	0.19	420	19.5	8.0	249	2.9	17.0
<i>West (CWHvm^y)</i>										
<i>Renfrew</i>										
LFH	7	3.42	441.3	9.41	788	NA	NA	NA	NA	NA
0-10		3.92	54.7	2.02	456	3.2	28.8	245	18.6	24.6
10-30		4.13	47.8	2.07	392	1.3	24.8	213	17.4	24.3
30-50		4.28	49.2	1.99	502	1.7	26.9	182	23.3	30.4
<i>Red/ Granite Creek</i>										
LFH	4	3.61	438.0	11.74	956	NA	NA	NA	NA	NA
0-10		4.25	52.7	2.64	651	4.6	28.0	281	20.6	28.3
10-30		4.49	39.3	1.70	626	3.4	22.5	195	17.6	30.3
30-50		4.49	26.3	0.86	522	2.1	17.1	142	15.1	27.3
<i>Nitinat</i>										
LFH	7	3.43	455.5	7.26	783	NA	NA	NA	NA	NA
0-10		4.04	79.5	3.52	947	3.3	37.8	375	23.2	28.7
10-30		4.25	59.7	2.09	780	3.4	31.0	200	20.1	29.5
30-50		4.76	32.9	2.03	889	4.8	25.1	390	18.5	32.5
<i>Klanawa</i>										
LFH	15	3.47	418.5	9.68	892	NA	NA	NA	NA	NA
0-10		4.24	69.9	2.44	321	1.5	28.9	233	25.6	28.6
10-30		4.45	57.2	2.09	317	0.9	29.4	182	24.5	31.0
30-50		4.61	52.9	1.81	365	0.7	25.8	118	26.3	36.4
<i>(b) by biogeoclimatic subzone, seral stage, depth</i>										
<i>East (CWHxm^w)</i>										
<i>Regeneration</i>										
LFH	3	4.48	396.3	7.82	911	NA	NA	NA	NA	NA
0-10		4.59	35.4	0.67	810	53.5	20.4	1155	5.5	14.9
10-30		4.71	21.4	0.48	738	38.9	15.6	450	5.5	15.7
30-50		4.76	16.5	0.29	568	21.5	14.0	314	4.7	17.6
<i>Immature</i>										
LFH	4	4.72	423.1	8.93	979	NA	NA	NA	NA	NA
0-10		4.55	34.9	0.83	703	41.8	18.5	674	5.7	14.7
10-30		4.67	22.8	0.45	764	43.1	15.7	523	5.7	15.9
30-50		4.71	16.7	0.40	628	20.8	13.7	352	5.3	18.2

Table 1. continued

Depth (cm)	Thickness (cm)	pH	Total C (g kg ⁻¹)	Total N (g kg ⁻¹)	Total P (mg kg ⁻¹)	Avail. P (mg kg ⁻¹)	CEC ^z (cmol kg ⁻¹)	Ca+Mg+K (mg kg ⁻¹)	Fe+Al ^y (g kg ⁻¹)	Fe+Al ^x (g kg ⁻¹)
<i>Mature</i>										
LFH	4	4.67	419.9	7.93	1051	NA	NA	NA	NA	NA
0-10		4.78	38.0	0.72	831	51.0	17.8	964	5.7	14.6
10-30		4.85	19.8	0.53	678	36.1	12.4	440	5.1	15.9
30-50		4.85	19.0	0.54	500	20.0	11.5	412	4.2	15.7
<i>Old Growth</i>										
LFH	5	4.55	429.9	9.63	1076	NA	NA	NA	NA	NA
0-10		4.57	29.9	0.32	828	39.5	14.8	719	5.3	15.0
10-30		4.60	19.4	0.48	740	40.4	12.5	527	4.9	16.0
30-50		4.74	12.6	0.19	544	19.1	11.0	480	3.8	15.6
<i>West (CWHvm^y)</i>										
<i>Regeneration</i>										
LFH	5	3.74	423.3	9.20	948	NA	NA	NA	NA	NA
0-10		4.24	59.0	2.07	412	1.0	29.5	205	22.6	31.6
10-30		4.43	41.9	1.68	460	1.5	27.3	148	16.5	29.4
30-50		4.52	37.4	1.33	330	0.7	18.4	58	17.6	29.0
<i>Immature</i>										
LFH	4	3.54	449.1	10.39	759	NA	NA	NA	NA	NA
0-10		4.04	57.1	2.74	434	1.6	28.4	400	16.8	20.0
10-30		4.16	51.6	2.05	407	1.4	27.1	341	18.5	23.0
30-50		4.29	45.5	2.08	503	1.5	26.8	371	24.1	30.0
<i>Mature</i>										
LFH	16	3.26	439.2	10.36	931	NA	NA	NA	NA	NA
0-10		4.30	72.6	3.57	692	3.6	34.2	225	27.9	35.6
10-30		4.60	54.9	2.31	605	2.2	28.7	118	26.4	37.3
30-50		4.73	40.6	1.61	623	3.0	25.1	128	20.0	36.0
<i>Old Growth</i>										
LFH	9	3.39	441.8	8.15	781	NA	NA	NA	NA	NA
0-10		3.87	68.0	2.24	706	6.5	31.5	304	20.7	23.0
10-30		4.09	54.1	1.84	737	4.1	22.5	177	17.4	24.3
30-50		4.55	36.7	1.00	666	3.0	20.1	99	21.8	29.8

^zCation exchange capacity.^ySodium pyrophosphate extractable.^xAcid oxalate extractable.^wCWHxm, very dry maritime Coastal Western Hemlock subzone.^vCWHvm, very wet maritime Coastal Western Hemlock subzone.

plastic tube, which was centrifuged for 20 min at 1150 relative centrifugal force, the solution decanted into a 250 mL plastic bottle and the process repeated. Five grams of Na-saturated Chelex-20 resin was added to the combined supernatants which were shaken for 10 min, and filtered through Number 42 Whatman filter paper. The filtrate was volumised with 0.5 M NaOH to 100 mL, of which 20 mL was stored for chemical analysis, and 80 mL was freeze-dried. Aliquots (2 mL) of the NaOH extracts were analysed for total C using the wet oxidation technique of Snyder and Trofymow (1984), and for total P using the same procedures as for the soil samples.

Solutions for NMR analysis were prepared by adding 2.3 mL D₂O and 0.3 mL 10 M NaOH to 0.2 g of freeze-dried extract. The solutions were shaken, left to stand overnight, centrifuged at 8000 rpm, and the supernatants filtered into NMR tubes of 10 mm diameter. Solution ³¹P NMR spectra were obtained at 121.49 MHz on a Bruker MSL 300 spectrometer, using inverse-gated decoupling, 45° pulse, 278 ms

acquisition time and 2.0 s relaxation delay, with approximately 24 h for each sample. Spectra were processed with 10 to 14 Hz linebroadening and baseline correction. Chemical shifts are reported relative to 85% phosphoric acid at 0 ppm, set occasionally using a capillary insert. Relative peak areas were determined from the integral traces (measured by hand, not as automatic readouts) and expressed as proportions of total spectral P. In a few cases where integrals were considered unreliable due to low signal-to-noise ratio, relative areas were determined by cutting and weighing. As the peaks for orthophosphate and monoester P were incompletely resolved, the integral was divided at the lowest point between the two peaks, the usual practice for analysis of ³¹P NMR spectra (Cade-Menun and Preston 1996).

Data Analysis

Analysis of variance (AOV) of the soil chemical P and C fractions and ratios were performed using the General

Table 2. Results (*P* values) of analyses of variance (AOV) of mineral soil P and C variables and ratios testing for (a) main effects of biogeoclimatic subzone (Zone), seral stage (Sere), Depth and the two-way and three-way interactions; and testing for main effects of site, sere, depth and two-way interactions with depth for the (b) east and (c) west biogeoclimatic subzones. *P* values <0.05 are in bold, *P* values <0.20 are underlined

DF	Total P	Avail. P	NaOH P	Avail. P	NaOH P	Total C	NaOH C	NaOH C	NaOH C	
	<i>P</i> > <i>F</i>	<i>P</i> > <i>F</i>	<i>P</i> > <i>F</i>	<i>P</i> > <i>F</i>	<i>P</i> > <i>F</i>	<i>P</i> > <i>F</i>	<i>P</i> > <i>F</i>	<i>P</i> > <i>F</i>	<i>P</i> > <i>F</i>	
<i>(a) Both subzones</i>										
Zone	1	0.043	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.295	< 0.001	
Sere	3	0.434	0.996	0.882	0.961	0.578	0.603	0.372	0.239	
Depth	2	0.302	0.013	0.026	<u>0.066</u>	< 0.001	< 0.001	0.289	< 0.001	
Zone × Sere	3	0.330	0.893	0.679	0.755	0.990	0.633	0.451	0.733	
Zone × Depth	2	0.486	0.023	0.001	0.263	< 0.001	0.676	0.231	0.382	
Sere × Depth	6	0.981	0.992	0.992	0.994	0.383	0.937	0.016	0.207	
Zone × Sere × Depth	6	0.999	0.986	0.900	0.879	0.862	0.958	<u>0.082</u>	0.263	
<i>(b) East (CWHxm²)</i>										
Site	3	< 0.001	< 0.001	0.018	< 0.001	0.004	0.007	0.213	<u>0.166</u>	
Sere	3	0.975	0.832	0.956	<u>0.159</u>	0.894	0.471	0.426	0.302	
Depth	2	0.013	0.019	0.006	0.005	0.004	< 0.001	0.942	0.008	
Site × Depth	6	0.366	0.779	0.570	0.531	0.249	0.501	0.358	<u>0.145</u>	
Sere × Depth	6	0.928	0.887	0.978	0.879	0.983	0.978	<u>0.069</u>	<u>0.144</u>	
<i>(c) West (CWHvm³)</i>										
Site	3	0.023	<u>0.165</u>	0.644	0.651	0.013	0.031	0.291	0.002	
Sere	3	<u>0.154</u>	<u>0.078</u>	0.277	0.407	0.804	0.447	0.503	0.333	
Depth	2	0.909	0.802	< 0.001	0.489	< 0.001	0.003	<u>0.171</u>	0.001	
Site × Depth	6	0.980	0.931	<u>0.196</u>	0.755	0.481	0.467	0.977	<u>0.160</u>	
Sere × Depth	6	1.000	0.986	0.618	0.692	0.364	0.891	<u>0.124</u>	0.032	

²CWHxm, very dry maritime Coastal Western Hemlock subzone.

³CWHvm, very wet maritime Coastal Western Hemlock subzone.

Linear Models procedure of the SAS statistical software (SAS Institute, Inc. 1985). For each variable, an initial three-way AOV was run to test for the effects of subzone, seral stage, depth and the two- and three-way interactions. Because of the blocked design of the study (four sites within each subzone) a separate AOV was run for the EAST and WEST side subzones to test for the effects of site, seral stage, depth and the two-way interactions of site or seral stage with depth. The same set of three-way AOVs was performed on the relative proportion values for each of the NMR spectral regions.

RESULTS

Soil P and C Chemistry

Data for the P and C analyses are shown in Table 3, AOV results in Table 2, and an overview for east vs. west side sites by depth in Fig. 1. For the west side, total P concentrations were significantly ($P = 0.023$) lower than for the east (534 vs. 694 mg kg⁻¹, Table 3), did not vary significantly with depth (Table 2c), and were similar to those for the east side at 30–50 cm (Fig. 1). On the east side, concentrations of total P were highest at 0–10 cm and declined significantly ($P = 0.013$) with depth. Levels of available P (Bray 1) were over 10 times higher on east side than west side sites (35 vs. 2.5 mg kg⁻¹) (Table 3) and showed a significant ($P = 0.019$) decline with depth only for sites in the east (Fig. 1, Table 2b, 2c). Concentrations of NaOH-extractable P were higher in the east compared to the west (396 vs. 207 mg

kg⁻¹, $P < 0.001$) and varied with both depth and subzone (Table 2). Compared to the east side where NaOH-extractable P levels generally declined with depth, west-side NaOH-extractable P had a minimum at 10–30 cm, compared to 0–10 and 30–50 cm depths (Fig. 1).

Seral stage effects on P chemistry were not significant by subzone (Table 2a) although for the west side, some weak trends were seen for available P ($P = 0.078$) and total P ($P = 0.154$). These tended to increase with stand age; from REG to OG sites, total P increased from 406 to 703 mg kg⁻¹, and available P from 1.1 to 4.9 mg kg⁻¹, although this did not hold for all depths (Table 1). In contrast to the weak trends associated with time from disturbance, site effects were found for total P ($P < 0.001$), available P ($P < 0.001$) and NaOH-extractable P ($P = 0.018$) on the east side, and for total P ($P = 0.023$) on the west (Table 2b, 2c). On the east side, the highest levels for all three chemical P variables were found at VWN and the lowest at NAN with the two other sites (VWS and KOK) intermediate (Table 3). On the west side, the highest total P levels were at NIT, and the lowest at KLA, with the other two sites (REN and RGC) intermediate (Table 3). There was a weak trend associated with site and depth on NaOH-P in the west ($P = 0.196$). The previously noted depression of NaOH-P at 10–30 cm was found at three of the four west side sites, with KLA not showing this effect.

Since total P declined with depth on the east and did not vary with depth on the west, the ratios of available P:total P and NaOH-extractable P:total P generally showed the same

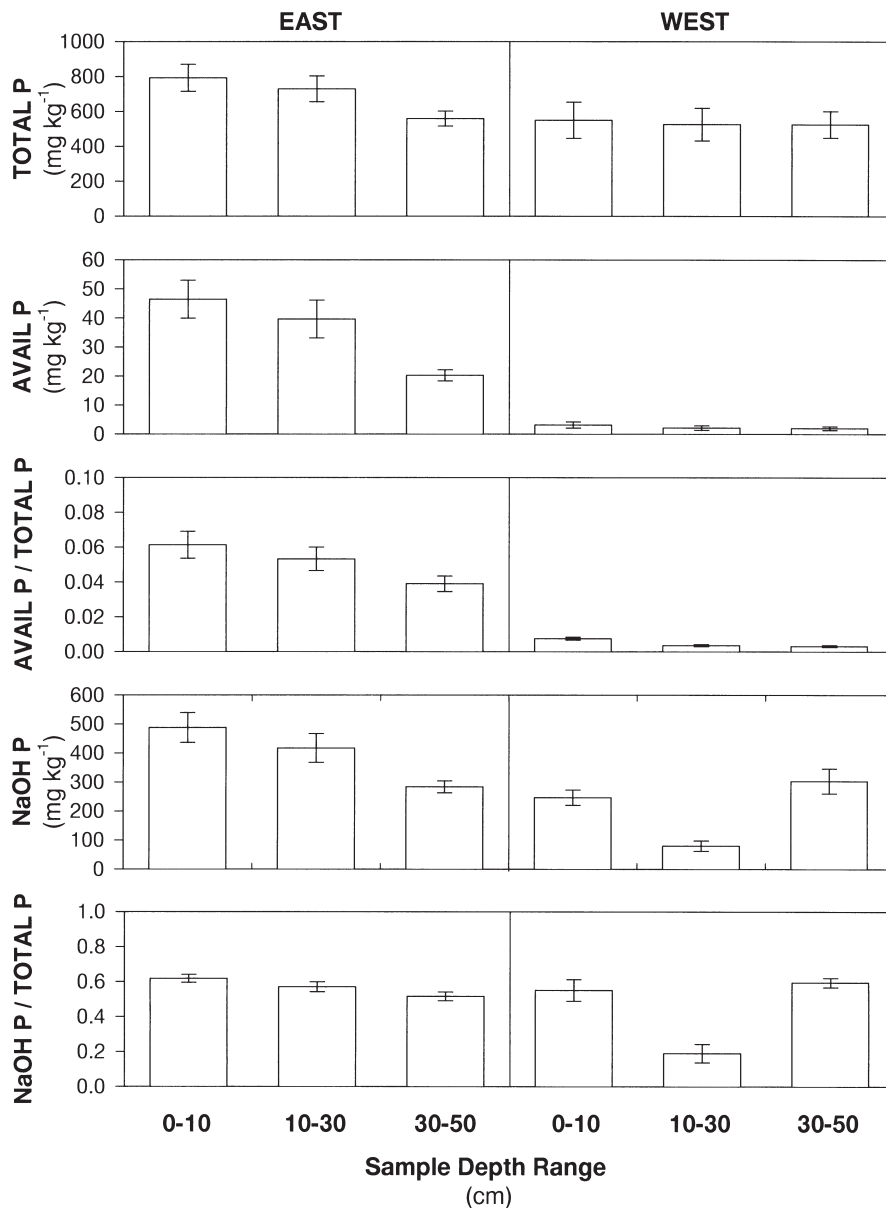


Fig. 1. Mineral soil P variables (total P, available P and NaOH-extractable P in mg kg^{-1}) and ratios (NaOH-P:Total P, Available P:Total P) in the Coastal Forest Chronosequence study by depth and biogeoclimatic subzone (East, West). Bars are standard errors.

effects of subzone and depth as seen for available P and NaOH-extractable P, respectively (Tables 2 and 3, Fig. 1). The proportion of available P represented less than 1% of total P for the west side and from 3–8% of total P for the east-side sites where it also varied significantly ($P < 0.001$) with site, averaging 8% at VWS vs. 3% at KOK (Table 3). The proportion of available P also varied with depth for the east, declining from 6% to 4%, but not for the west (Fig. 1).

NaOH extracted a range of 46–63% of total P for the east-side sites, which was significantly ($P < 0.001$) higher on average than for the west for which NaOH extracted 28–60% (Table 2, Table 3). The proportion extracted declined with depth and varied depending upon subzone.

For the west side sites, the proportions of P extracted by NaOH at 0–10 and 30–50 cm were comparable to those for the east side; however, recoveries were much lower at 10–30 cm (Fig. 1). The proportion extracted by NaOH varied with site in both the east and west (Table 2b, 2c). In the east, NaOH P extraction was highest at VWS, lowest at KOK, whereas in the west P extraction was highest at KLA, lowest at NIT (Table 3).

To determine whether the depression in NaOH-extractable P was related to low extractability of organic matter, we analysed for total and NaOH-extractable soil C. Total soil C concentrations were approximately twofold higher for west- than for east-side sites and declined signif-

Table 3. Concentrations of P (total P, available P, NaOH-extractable P), P ratios (available P: total P, NaOH P: total P), concentrations of C (total C, NaOH extractable C), and C ratios (NaOH C:total C, C:P ratio of NaOH extracts) of mineral soils and extracts. Means and standard errors (*italic*) across all depths are shown for each site by biogeoclimatic subzone

	East (CWHxm ²)					West (CWHvm ³)				
	Victoria Watershed South	Victoria Watershed North	Koksilah	Nanaimo River	Subzone	Renfrew	Red/Granite Creek	Nitinat	Klanawa	Subzone
Total P (mg kg ⁻¹)	558.5 <i>61.0</i>	944.6 <i>85.6</i>	783.0 <i>65.5</i>	490.5 <i>24.5</i>	694.2 <i>40.3</i>	444.4 <i>42.8</i>	599.8 <i>114.1</i>	858.7 <i>143.0</i>	335.5 <i>34.1</i>	533.6 <i>51.7</i>
Avail. P (mg kg ⁻¹)	43.2 <i>7.2</i>	48.8 <i>8.6</i>	22.6 <i>5.3</i>	27.4 <i>3.3</i>	35.5 <i>3.5</i>	2.1 <i>0.9</i>	3.4 <i>1.2</i>	3.7 <i>1.0</i>	1.0 <i>0.3</i>	2.5 <i>0.5</i>
NaOH P (mg kg ⁻¹)	365.9 <i>48.6</i>	550.5 <i>71.1</i>	367.0 <i>42.6</i>	301.2 <i>17.2</i>	396.2 <i>27.2</i>	200.1 <i>42.1</i>	207.1 <i>49.0</i>	224.1 <i>81.4</i>	200.5 <i>24.4</i>	206.5 <i>23.0</i>
Avail. P / Total P	0.076 <i>0.008</i>	0.048 <i>0.006</i>	0.026 <i>0.004</i>	0.055 <i>0.005</i>	0.051 <i>0.004</i>	0.008 <i>0.006</i>	0.004 <i>0.001</i>	0.004 <i>0.001</i>	0.003 <i>0.001</i>	0.005 <i>0.001</i>
NaOH P / Total P	0.63 <i>0.03</i>	0.56 <i>0.03</i>	0.46 <i>0.03</i>	0.62 <i>0.02</i>	0.57 <i>0.02</i>	0.43 <i>0.08</i>	0.38 <i>0.07</i>	0.28 <i>0.10</i>	0.60 <i>0.06</i>	0.44 <i>0.04</i>
Total C (mg kg ⁻¹)	25335 <i>4255</i>	21566 <i>2371</i>	30445 <i>3381</i>	18136 <i>2320</i>	23870 <i>1678</i>	50679 <i>2798</i>	39448 <i>4474</i>	62526 <i>9792</i>	59994 <i>4063</i>	52580 <i>2930</i>
NaOH C (mg kg ⁻¹)	7046 <i>868</i>	5340 <i>955</i>	5775 <i>819</i>	4642 <i>803</i>	5716 <i>435</i>	13698 <i>902</i>	13694 <i>864</i>	16172 <i>1278</i>	15932 <i>752</i>	14812 <i>488</i>
NaOH C / Total C	0.33 <i>0.06</i>	0.25 <i>0.04</i>	0.20 <i>0.03</i>	0.32 <i>0.08</i>	0.28 <i>0.03</i>	0.28 <i>0.02</i>	0.38 <i>0.03</i>	0.30 <i>0.04</i>	0.27 <i>0.02</i>	0.31 <i>0.02</i>
NaOH C / NaOH P	24.4 <i>5.3</i>	11.0 <i>2.2</i>	17.1 <i>3.0</i>	17.1 <i>4.0</i>	17.7 <i>2.0</i>	147.3 <i>52.4</i>	133.6 <i>35.0</i>	168.7 <i>61.2</i>	140.6 <i>63.0</i>	145.2 <i>25.0</i>

²CWHxm, very dry maritime Coastal Western Hemlock subzone.³CWHvm, very wet maritime Coastal Western Hemlock subzone.

icantly ($P < 0.001$, east and $P = 0.003$, west) with depth (Table 2, Fig. 2). Total C levels also varied significantly ($P = 0.007$, east and $P = 0.031$, west) with site, with mean total soil C in the east highest at KOK and lowest at NAN, and in the west highest at NIT and lowest at RGC (Table 2b and 2c, Table 3). Similarly, NaOH-extractable C levels were approximately twofold higher in the west than east though the amount extracted varied with depth and seral stage (Table 2). Levels of NaOH-extractable C were lowest at 30–50 cm in REG (0 cm, 10 856 mg kg⁻¹; 10 cm, 10 884 mg kg⁻¹; 30 cm, 8974 mg kg⁻¹) and OG (0 cm, 11641 mg kg⁻¹; 10 cm, 12 526 mg kg⁻¹; 30 cm, 7156 mg kg⁻¹) plots, did not vary with depth in IMM (0 cm, 9984 mg kg⁻¹; 10 cm, 8475 mg kg⁻¹; 30 cm, 9681 mg kg⁻¹) plots, and were highest at 30–50 cm in MAT plots (0 cm, 10 322 mg kg⁻¹; 10 cm, 9838 mg kg⁻¹; 30 cm, 12385 mg kg⁻¹).

In contrast to NaOH-extractable P, the proportion of NaOH-extractable C generally increased with depth for both subzones (Table 2, Fig. 2). Variations were greatest for the

west side plots where NaOH extracted 22–45% of total C in individual samples, and recoveries varied with site, and with seral stage with depth (Table 2). The highest recoveries were at RGC and lowest at KLA (Table 3). Percentage recoveries were highest at 30–50 cm in IMM (0 cm, 24; 10 cm, 26; 30 cm, 36) and MAT (0 cm, 22; 10 cm, 26; 30 cm, 46) plots, and showed less variation with depth in REG (0 cm, 26; 10 cm, 39; 30 cm, 33) and OG plots (0 cm, 29; 10 cm, 32; 30 cm, 30). The C/P ratios of the NaOH extracts varied with subzone and depth (Table 2); they were 8–10 times higher for the west side vs. east side sites (Table 3) and on the west side the 10–30 cm values were over twice those at 0–10 cm or 30–50 cm (Fig. 2).

Phosphorus-31 NMR Spectroscopy

Figure 3 shows typical spectra obtained in this study, with the characteristic signals for orthophosphate, monoester, diester, pyrophosphate and phosphonate P. Peak assignments are based on previous studies (Newman and Tate

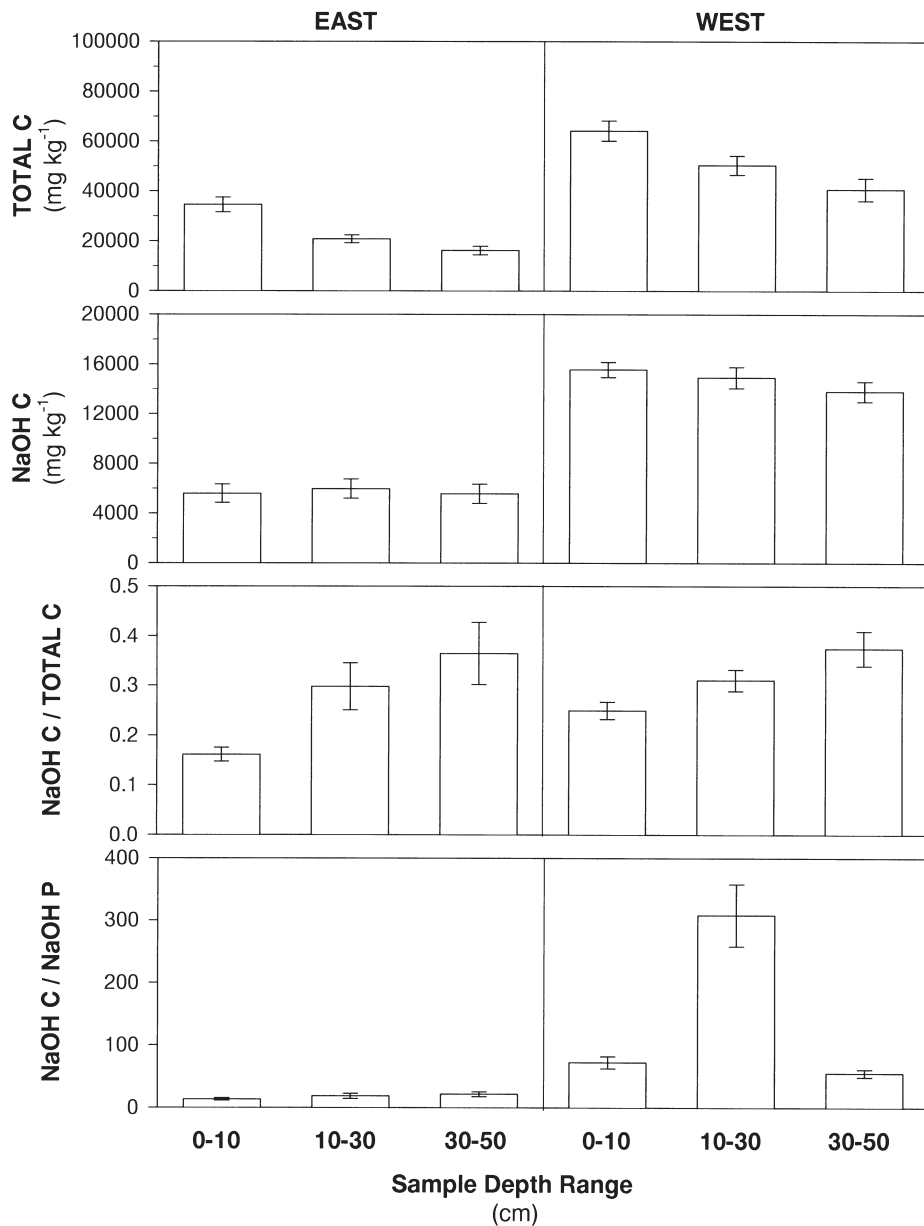


Fig. 2. Mineral soil total C and NaOH-extractable C (mg kg^{-1}), and ratios of NaOH-C:Total C and NaOH-P:NaOH-C in the Coastal Forest Chronosequence study summarised by depth and biogeoclimatic subzone (East, West). Bars are standard errors.

1980; Hawkes et al. 1984; Condon et al. 1985, 1990; Adams and Byrne 1989; Adams 1990). The sharp peak for orthophosphate P at 6.5 ppm was not completely resolved from the broader signal of phosphate monoesters at 4.9 ppm. The latter often showed incompletely resolved structure, in particular a relatively sharp peak at 4.3 ppm. Structures in this category may include inositol phosphates, sugar phosphates, mononucleotides and choline phosphate. The main peak for phosphate diesters (phospholipids, nucleic acids) is found at -0.1 ppm. Some spectra had broad, very weak signals around 1.0 to 2.0 ppm; these have been attributed to teichoic acid, a bacterial cell-wall component, and other unidentified diesters (Condon et al. 1990; Guggenberger et al. 1996; Sumann et al. 1998). Pyrophosphate was found at

-4.0 ppm and phosphonate at 20 ppm. The latter often had two peaks, at 19.1 and 20.6 ppm. Polyphosphate was not detected in any of the NMR spectra.

There was a dramatic difference in the nature of NaOH-extractable P from east- and west-side sites (Fig. 4, Tables 4 and 5). East-side sites had much higher proportions of orthophosphate P, with smaller amounts of monoester and pyrophosphate P. Traces of phosphonate were observed in only two samples. The west-side sites had a lower proportion of orthophosphate, with more P found as mono- and diesters and pyrophosphate. Phosphonate was also found in many west-side samples (16 of 44). In the west, the only significant ($P = 0.151$) depth effect was for pyrophosphate, which declined with depth, while in the east pyrophosphate

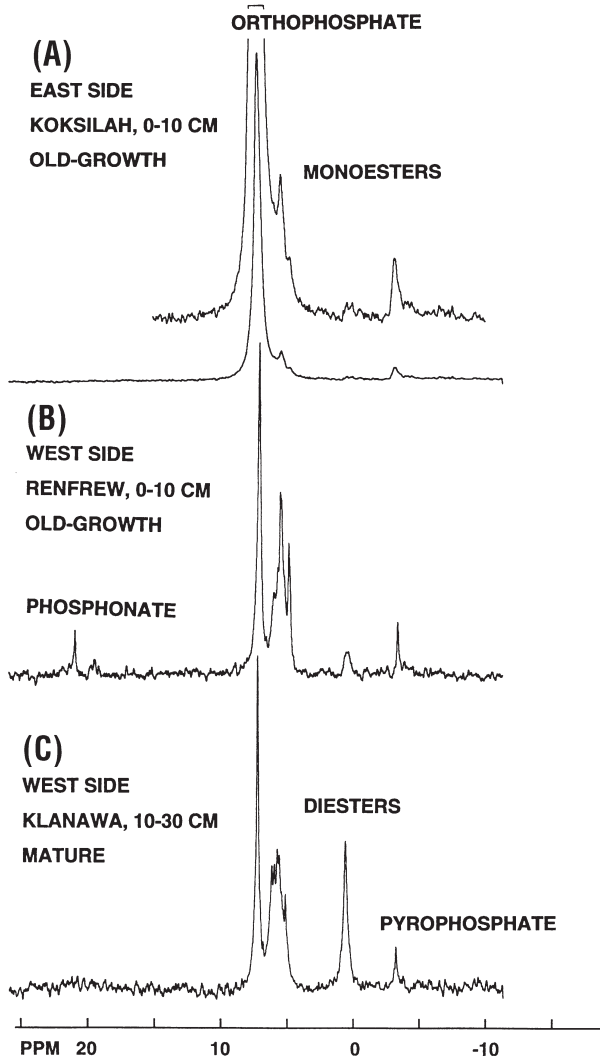


Fig. 3. Typical ^{31}P NMR spectra of NaOH extracts from plots from the two biogeoclimatic subzones of the Coastal Forest Chronosequence study: (a) East side; (b, c) West side.

tended to be lowest at 10–30 cm and highest at 30–50 cm. There were also weak trends in the west (Table 5c) for orthophosphate to increase and monoester and phosphonate to decrease with depth.

Significant site effects were noted for most variables (Table 5b, 5c). For the east side, KOK had the highest proportion of pyrophosphate and diester P, second highest monoester P and lowest orthophosphate while VVN had the highest proportion of orthophosphate and lowest monoester (Table 4). For the west side sites, RGC had the highest proportion of orthophosphate, second lowest monoester and lowest diester and pyrophosphate, while KLA had the lowest orthophosphate, highest monoester, and highest diester (Table 4). The only significant ($P = 0.056$) seral stage effect was for diester P in the east (Table 5b) which tended to be higher in REG (0.37) and OG (0.26) plots and lower in IMM

(<0.01) and MAT (0.06) plots. In the west, there was a weak trend for monoester P to be higher in IMM (38.4) and OG (36.6) plots and lower in REG (31.6) and MAT (31.2) plots.

DISCUSSION

Total and Available Soil P

Levels of available P were comparable to those found in other studies on Vancouver Island. For example, Van den Driessche (1988) found that available P in mineral soil in young Douglas-fir plantations on east Vancouver Island was 14–33 mg kg^{-1} at 0–15 cm and 24–35 mg kg^{-1} at 15–30 cm. In this study available P levels on the east side were 38–66 mg kg^{-1} at 0–10 cm, 21–60 mg kg^{-1} at 10–30 cm and 16–27 mg kg^{-1} at 30–50 cm. For wetter forest types at the north end of Vancouver Island, old-growth and recent cutovers (5–10 yr) had available P levels of 9–11 mg kg^{-1} in the upper mineral soil horizon and 5–7 mg kg^{-1} in the lower (Cade-Menun 1995). In this study available P in the west ranged from 1.0 to 6.5 mg kg^{-1} at 0–10 cm, from 1.4 to 4.1 mg kg^{-1} at 10–30 cm, and from 0.7 to 1.4 mg kg^{-1} at 30–50 cm.

The low levels of available soil P on north and west Vancouver Island are consistent with the high proportions found as organic forms, and P deficiency as already demonstrated by fertilization trials on similar forest types on northern Vancouver Island (Weetman et al. 1989a, b, 1993; Prescott et al. 1996). Consistent with this, Cade-Menun (1995) found that in north Vancouver Island forests, available P in surface organic layers increased immediately after harvest and slash-burning of old-growth but returned to pre-harvest levels after 5 to 10 yr.

This study only examined mineral soil, and in the wet forests of west and north Vancouver Island, the thick organic horizons and decaying wood are also important in P cycling. Organic horizons of old-growth cedar-hemlock forests of northern Vancouver Island had available P levels around 100 mg kg^{-1} (Prescott et al. 1993). In the west-side forests in this study, the amount of total P in detrital biomass (31–79 kg ha^{-1}) can equal 30% of the total P found in the upper 10 cm of mineral soil (156–261 kg ha^{-1}) (Blackwell and Trofymow 1998). Studies in coastal Washington state found no response of second-growth Douglas-fir and western hemlock stands to P fertilization, despite low available P and seedling response in greenhouse trials (Heilman and Ekuan 1980; Steinbrenner 1981; Radwan et al. 1991). Phosphorus is tightly conserved in forest stands and after canopy closure, P is increasingly supplied by retranslocation and from litter, with mycorrhizae playing a crucial role. While these factors resulted in adequate P supply for the above-mentioned Washington sites, western red cedar stands in coastal Washington did respond to P fertilization (Harrington and Wierman 1990), as have conifers on Northern Vancouver Island, as previously noted.

NaOH Extraction Efficiency

For the east-side sites, the two-stage extraction with 0.5 N NaOH recovered 46 to 63% of total P, with little variation by sere, and a significant ($P = 0.004$) decline with depth.

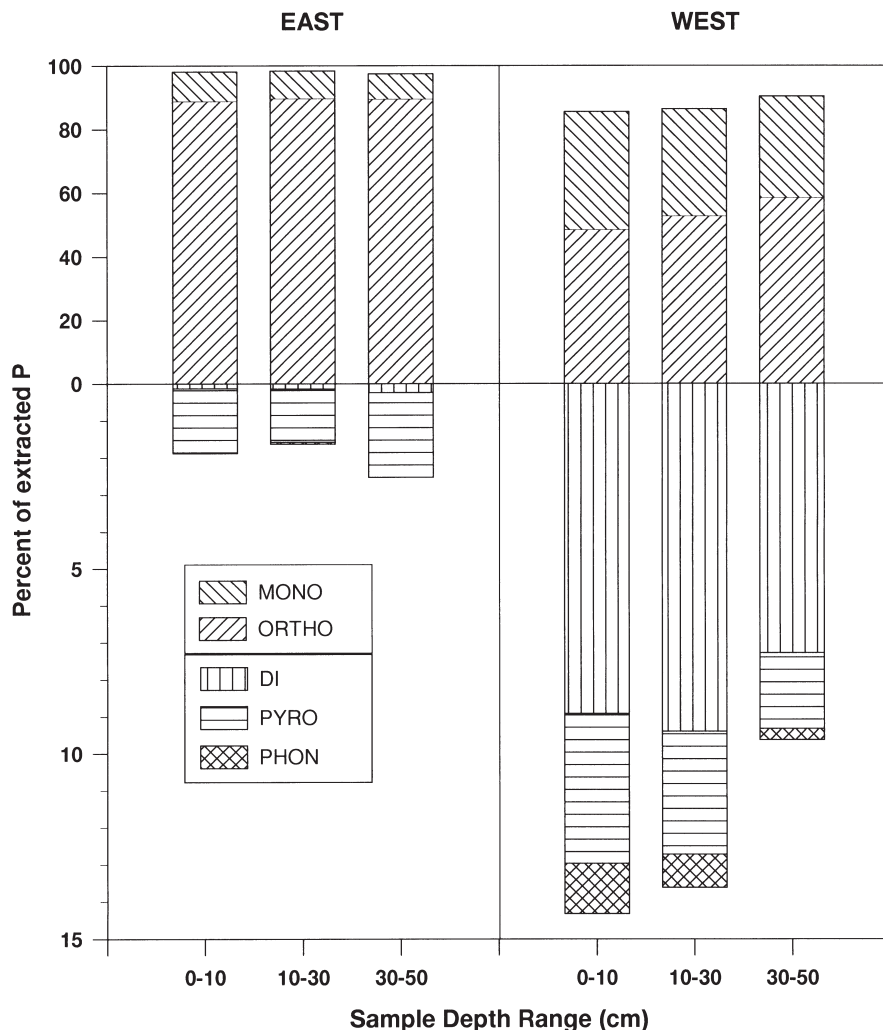


Fig. 4. Relative distribution of NaOH-extractable P forms by ^{31}P NMR by depth and biogeoclimatic subzone (East, West) in the Coastal Forest Chronosequence study. Note that orthophosphate (ORTHO) and monoester P (MONO) are on different scales than diester P (DI), pyrophosphate (PYRO) and phosphonate (PHON).

Similar recoveries have been reported for NaOH extraction for a wide range of soil types and for minor variants of the method (Newman and Tate 1980; Hawkes et al. 1984; Gil-Sotres et al. 1990; Forster and Zech 1993; Cade-Menun and Preston 1996; Gressel et al. 1996). For the west-side sites, recoveries for the 0–10 and 30–50 cm depths in the west were comparable to those for the east side; but recoveries at 10–30 cm depth were much lower for three out of four sites. Some site differences were also found in both the east and west.

As noted earlier, on the east side, the KOK site had the lowest proportion of both NaOH-extractable and available P (Table 3). This may be related to the high Ca concentrations in its limestone-derived soils, which is reflected in the relatively high cation contents and pH values for the KOK site (Table 1) with the result that a greater fraction of the total P at this site may be present in Ca salts, such as phytate (inositol hexaphosphate). In the west, recoveries of P in NaOH extracts were lowest at the NIT site, which also had soils with the highest total P and C contents such that a greater fraction of the total P at this site might be in less soluble

organic forms. Phosphorus recoveries at the KLA site were much higher than for other sites in the west, comparable to the highest of the east sites, but might be related to the low levels of total P and available P which were the lowest of all sites studied.

The low values of NaOH-extractable P at 30–50 cm for three out of four west-side sites were not associated with depression of NaOH-extractable C. This depth is typically where the Bf horizon occurs (Trofymow et al. 1997) and a zone of Fe and Al accumulation. Values for extractable (Fe + Al) are higher on the west side at all depths and seres (Table 1b). The site data (Table 1a) show that extractable (Fe + Al) increases from 0–10 to 10–30 cm for RGC, NIT and KLA, but not for REN, the site which did not show the depression in NaOH-P extractability. Yuan and Lavkulich (1994) found that the most important P sorbents in BC Spodosols were oxalate-extractable Fe and Al, especially Al. They suggested that P sorption capacity of these forest soils would be sensitive to disturbances and management practices that alter the fraction of Al complexed with organic matter. By contrast, anomalously low values for NaOH-

Table 4. Relative proportions (% of total spectra area) of NaOH-extractable P as identified by ³¹P NMR. Organic P is the sum of diester, pyrophosphate and phosphonate P. Means and standard errors (italic) across all depths are shown for each site by biogeoclimatic subzone

	East (CWHxm ²)					West (CWHvm ³)				
	Victoria Watershed South	Victoria Watershed North	Koksilah	Nanaimo River	Subzone	Renfrew	Red/Granite Creek	Nitinat	Klanawa	Subzone
orthophosphate	86.77 <i>1.01</i>	93.84 <i>0.51</i>	85.94 <i>0.61</i>	90.98 <i>0.74</i>	89.38 <i>0.59</i>	46.00 <i>2.72</i>	65.57 <i>3.77</i>	60.31 <i>5.63</i>	41.10 <i>2.23</i>	52.93 <i>2.33</i>
monester	12.31 <i>1.18</i>	4.93 <i>0.40</i>	10.42 <i>0.65</i>	6.76 <i>0.89</i>	8.61 <i>0.59</i>	40.76 <i>2.29</i>	28.89 <i>3.04</i>	24.19 <i>3.65</i>	41.50 <i>1.28</i>	34.34 <i>1.68</i>
diester	0.13 <i>0.13</i>	0.00 <i>0.00</i>	0.56 <i>0.15</i>	0.00 <i>0.00</i>	0.17 <i>0.06</i>	7.72 <i>2.15</i>	3.50 <i>1.69</i>	9.81 <i>2.03</i>	13.60 <i>1.87</i>	8.60 <i>1.10</i>
pyrophosphate	0.79 <i>0.31</i>	1.23 <i>0.28</i>	3.02 <i>0.22</i>	2.26 <i>0.31</i>	1.82 <i>0.19</i>	2.85 <i>0.35</i>	1.60 <i>0.44</i>	5.00 <i>0.77</i>	3.80 <i>0.60</i>	3.21 <i>0.32</i>
phosphonate	0.00 <i>0.00</i>	0.00 <i>0.00</i>	0.07 <i>0.07</i>	0.00 <i>0.00</i>	0.02 <i>0.02</i>	2.49 <i>0.53</i>	0.45 <i>0.32</i>	0.70 <i>0.40</i>	0.00 <i>0.00</i>	0.89 <i>0.23</i>
organic P	0.92 <i>0.36</i>	1.23 <i>0.28</i>	3.65 <i>0.24</i>	2.26 <i>0.31</i>	2.01 <i>0.21</i>	13.05 <i>2.17</i>	5.54 <i>2.07</i>	15.50 <i>2.53</i>	17.41 <i>1.82</i>	12.69 <i>1.25</i>
diester / monester	0.02 <i>0.02</i>	0.00 <i>0.00</i>	0.06 <i>0.02</i>	0.00 <i>0.00</i>	0.02 <i>0.01</i>	0.21 <i>0.06</i>	0.14 <i>0.07</i>	0.44 <i>0.09</i>	0.33 <i>0.05</i>	0.27 <i>0.04</i>

²CWHxm, very dry maritime Coastal Western Hemlock subzone.³CWHvm, very wet maritime Coastal Western Hemlock subzone.**Table 5. Results (*P* value) of analyses of variance (AOV) of NMR P fractions of NaOH extract, testing for (a) main effects of biogeoclimatic subzone (Zone), seral stage (Sere), Depth and the two-way and three-way interactions; and testing for the main effects of site, sere, depth and two-way interactions with depth for the (b) east and (c) west biogeoclimatic subzones. *P* values <0.05 are in bold, *P* values <0.20 are underlined**

	DF	orthophosphate	monoester	diester	pyrophosphate	phosphonate	organic P
		<i>P</i> > <i>F</i>	<i>P</i> > <i>F</i>	<i>P</i> > <i>F</i>	<i>P</i> > <i>F</i>	<i>P</i> > <i>F</i>	<i>P</i> > <i>F</i>
<i>(a) Both subzones</i>							
Zone	1	<0.001	<0.001	<0.001	0.002	<0.001	<0.001
Sere	3	0.939	0.289	0.325	0.660	0.989	0.449
Depth	2	0.224	0.339	0.796	<u>0.177</u>	<u>0.184</u>	0.405
Sere × Zone	3	0.982	0.615	0.357	0.204	0.993	0.596
Sere × Depth	6	0.999	0.995	0.771	0.937	0.965	0.845
Zone × Depth	2	0.318	0.675	0.748	0.009	<u>0.186</u>	<u>0.181</u>
Sere × Zone × Depth	6	0.977	0.981	0.753	0.836	0.950	0.806
<i>(b) East (CWHxm²)</i>							
Site	3	<0.001	<0.001	<0.001	<0.001	0.408	<0.001
Sere	3	0.565	0.466	<u>0.056</u>	0.624	0.408	0.398
Depth	2	0.646	0.474	0.603	<u>0.098</u>	0.381	<u>0.073</u>
Sere × Depth	6	0.669	0.819	0.970	0.976	0.446	0.947
Site × Depth	6	0.855	0.894	0.902	0.984	0.446	0.925
<i>(c) West (CWHvm³)</i>							
Site	3	<0.001	<0.001	0.016	0.008	<0.001	0.007
Sere	3	0.872	<u>0.179</u>	0.314	0.294	0.968	0.495
Depth	2	<u>0.111</u>	<u>0.151</u>	0.789	0.037	<u>0.136</u>	0.316
Sere × Depth	6	0.983	0.997	0.710	0.831	0.926	0.753
Site × Depth	6	0.972	0.933	0.865	0.938	0.341	0.866

²CWHxm, very dry maritime Coastal Western Hemlock subzone.³CWHvm, very wet maritime Coastal Western Hemlock subzone.

extractable P reported in two other studies (Gil-Sotres et al. 1990; Forster and Zech 1993) were attributed largely to low solubility of organic matter and calcium salts (phosphates and phytates).

³¹P NMR Analysis of P Forms

In our study, the overwhelming difference in P forms was by subzone (Table 4). On average, sites on the drier, slightly warmer east side of Vancouver Island had a very high pro-

portion of orthophosphate P (89%), and only 8.6% monoester, 1.8% pyrophosphate, 0.17% diester, and traces of phosphonate. By contrast, sites on the wetter, cooler west site had less orthophosphate (52.9%), followed by 34.3% monoesters, 8.6% diesters, 3.2% pyrophosphate and 0.89% phosphonate. The ratio of diester to monoester P was 0.27 compared to 0.02 for the east side, and the sum of diester, pyrophosphate and phosphonate P was 12.69% (west) compared to 2.0% (east).

As noted earlier, while there were some significant site effects in the ^{31}P NMR results, there was little effect by depth or time from disturbance. The only significant depth effect was a decline of pyrophosphate by depth in the west, and the only significant seral stage effect was that, in the east, diester P was higher in REG and OG plots than in IMM and MAT. The significant decline of diester P in IMM and MAT seral stages in the east may be related to the reduction and recovery of forest floor mass during stand succession (REG, 37 Mg ha $^{-1}$; IMM, 24 Mg ha $^{-1}$; 26, Mg ha $^{-1}$; OG, 38 Mg ha $^{-1}$), a reflection of increased decay and reduced litter fall in early stages of stand succession (Trofymow and Blackwell 1998).

Even the depressed NaOH extractability of P in the 10–30 cm west side samples in three out of four sites did not affect the distribution of P forms in the extract. In addition to the influence of climate, differences in the major tree species and their associated mycorrhizae possibly contributed to differences in P chemistry. Douglas-fir was the major species in east side sites, and western hemlock and western red cedar in the west. If this were the case, however, one would expect larger changes with disturbance. Similarly, there were no large differences in parent material or soil chemistry [Trofymow et al. (1997) and Table 1] that might account for such a large difference in P forms, with the exception of pH, which was lower on the west side. For the mineral soil, the differences in pH were generally less 0.5 pH units, although the discrepancies were greater for the LFH layers. A ^{31}P NMR study in the North American Great Plains also found that climate was the primary determinant for soil organic P, with no significant correlations with soil properties (Sumann et al. 1998).

Previous ^{31}P NMR studies with NaOH extracts have shown the sensitivity of P speciation to several factors. Cultivated soils and managed pastures tend to have a low diversity of organic P forms, mainly as monoesters, and a high proportion of orthophosphate P, both of which may increase with P fertilization (Hawkes et al. 1984; Condrón et al. 1985, 1990). Soils in natural ecosystems (forest, shrubland, alpine, grasslands) tend to have a lower proportion of orthophosphate P and a higher proportion and diversity of organic P forms, especially where decomposition is limited by cool, wet conditions (Tate and Newman 1982; Zech et al. 1985, 1987; Condrón et al. 1990; Gil-Sotres et al. 1990; Forster and Zech 1993; Dai et al. 1996; Gressel et al. 1996). Phosphonates have been found in protozoa (Deslauriers et al. 1982), and their soil occurrence is particularly associated with restricted decomposition and nutrient cycling in cool, wet or acid conditions (Tate and Newman 1982; Zech et al. 1987; Dai et al. 1996), including forest sites of northern

Vancouver Island (Cade-Menun 1995; Cade-Menun and Preston 1996).

Diester P is a relatively available pool of organic P that generally decreases or even disappears on disturbance or cultivation (Hawkes et al. 1984; Zech et al. 1985; Condrón et al. 1990). Mineralization of diester P was demonstrated in an incubation of sewage sludge (Hinedi et al. 1988), and also after addition of RNA to pasture and woodland sites in Victoria, Australia (Taranto et al. 2000). Mineralization of mono- and diester-P was also stimulated by conversion of low-fertility tussock grassland to conifers (*Pinus* spp.) in New Zealand (Condrón et al. 1996), where the enhanced mineralization of organic P was attributed to the introduction of conifer ectomycorrhizae, compared to the usually more severe effects of cultivation, in which organic matter is more exposed to microbial activity. However, diester P can accumulate under conditions less favourable to mineralization, in particular under wetter conditions as found in our study. Tate and Newman (1982) and Sumann et al. (1998) found a positive correlation of diester content with precipitation, and Zech et al. (1987) also found a high proportion of diester in a hydromorphic high-elevation soil.

By contrast, monoesters appear to be stabilised by strong associations with mineral matter, have lower availability and are less influenced by climate (Tate and Newman 1982; Hawkes et al. 1984; Adams and Byrne 1989; Adams 1990; Dai et al. 1996; Guggenberger et al. 1996; Sumann et al. 1998). However, our study showed a climate difference, with a higher proportion of monoesters on the west side (8.6% east vs. 34.3% west). Pyrophosphates are usually a minor fraction, although studies with NaOH-EDTA extraction reported higher proportions, up to 19% in mineral soil and forest floor (Cade-Menun 1995; Cade-Menun and Preston 1996; Dai et al. 1996), and Adams and Byrne (1989) found up to 13% in Chelex extracts of a eucalyptus forest. They were a minor fraction in this study (0.8–3.0% in the east and 1.6–5.0% in the west), although pyrophosphate was the main organic form for the east, and showed a significant ($P = 0.098$) decline with depth in the west. There is little information on the origin and role of pyrophosphates, although Condrón et al. (1985) and Gressel et al. (1996) suggested that they represent a fairly available pool of biological origin. Both pyro- and polyphosphate were found as storage forms in a ^{31}P NMR study of protozoa (Deslauriers et al. 1982), and pyrophosphate constituted 5% of a beech litter extract (Miltner et al. 1998).

For the east side, the distribution of P forms is more like a cultivated field or fertilised pasture than a forest soil, with very high proportions of orthophosphate P, followed by monoester and pyrophosphate P, very low diester P and traces of phosphonate in a few samples. Available (Bray 1) P is high, approximately 9% of NaOH-extractable P, and the NaOH extracts have a low C/P ratio of 18. For the west side, the distribution is typical of natural forest, grassland or alpine sites where decomposition is restricted by cool, wet conditions. There is less orthophosphate, and higher proportions of the other forms including phosphonate. The ratio of available P to NaOH P is only 0.01, and C/P ratios are higher, over 300 for the 10–30 cm depth.

Most previous studies have focused on surface horizons of mineral soil, or on forest floor and the underlying A horizons. Our study is unusual in investigating mineral soil down to 30–50 cm. It was also possible to take advantage of the soil sampling from the CFC study, with its robust statistical design of four replicate chronosequence sites for each subzone, and individual chemical analysis of samples from four subplots per plot. While the NaOH extractions and ^{31}P NMR analyses were carried out after compositing the subplot samples, the retention of site replication (four sites per subzone) made it possible to carry out statistical analysis of the relative areas obtained by ^{31}P NMR. The quality of the NMR data was also aided by the availability of sufficient NMR time to run over 90 samples for approximately 24 h each. With the 300 MHz spectrometer available for this study, these long acquisition times were necessary to obtain sufficient signal-to-noise ratio to quantify P forms present in small proportions, such as phosphonate.

These factors made it possible to examine the effects of site variation, in addition to those associated with climate and sere effects. Dai et al. (1996) and Cade-Menun (1995) found high variation in individual profiles, and significant site effects were found in this study. However, despite site variations, both chemical analyses and NMR demonstrated significant effects of climate on P forms and availability. The higher rainfall and slightly lower temperatures on the west side have led to the development of podzols, greater accumulation of C, lower pH, a higher proportion of P in organic forms and lower P availability due to low mineralization rates. Reduced litter input and plant uptake in the first few years after harvesting or fire disturbance, coupled with the higher rainfall on the west side, may be contributing factors that enhance leaching of P with accumulation of less soluble forms at lower depths.

CONCLUSIONS

In order to understand factors contributing to P limitation in young plantations following harvesting of old-growth in high rainfall areas of coastal British Columbia, this study investigated P chemistry in mineral soil to 50 cm depth in sites from forest chronosequences in contrasting biogeoclimatic subzones on the east and west sides of Vancouver Island. Sites on the wetter and slightly cooler west side had significantly lower levels of available P (by a factor of 10), while NaOH-extractable P had higher proportions of organic P forms, especially diesters, typical of forest ecosystems with restricted nutrient cycling and high precipitation. In three of the four west-side sites, the 10–30 cm samples showed a depression in the proportion of soil P extractable by NaOH, an effect not found for NaOH-extractable C. This result is consistent with greater leaching of P on the west side, and its accumulation at depth in less available forms. The divergences in P chemistry are more likely a result of the higher rainfall on the west side than differences in parent material or total P, and were in general, larger than effects associated with harvesting disturbance (i.e., seral stage).

This study, and previous work from similar forests on northern Vancouver Island (Weetman et al. 1989a, b, 1993; Prescott et al. 1996), suggest that cutovers on the west side

will be more vulnerable to leaching losses that will be exacerbated with intense slash-burning (Cade-Menun 1995). Young second-growth forests may require fertilization with P in addition to N. The small effects of seral stage found in this study may reflect the limited extent of disturbance (i.e., a single harvest), and the large legacy of organic matter (Trofymow and Blackwell 1998). Harvesting effects could intensify if shorter rotations lead to depletion of coarse woody debris (Wells and Trofymow 1997), more frequent periods of reduced plant uptake and more favourable conditions for decomposition. Sustainable logging on the west coast will require development of management practices to maintain the soil P reserve, minimise the potential for post-harvest leaching, and enhance conditions for mineralization of organic P.

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