

## Chemical and $^{31}\text{P}$ NMR Characterization of Soil P in Coastal Forest Chronosequences of Southern Vancouver Island: Effects of Climate and Disturbance

### Introduction

After N, P is the second-most important nutrient limiting growth in old-growth cutovers in areas of high rainfall on northern Vancouver Island, a situation which may affect large areas of coastal British Columbia (BC) (Prescott and Weetman 1995). Climatic differences affect P cycling in forests; after harvest disturbance, the high rainfall on most of the west coast may increase the possibility of losses of P due to leaching. Despite the controversies surrounding forestry in coastal BC, little is known about key nutrients such as P. In forests, much of the plant-available P is in organic forms that can be analysed by solution  $^{31}\text{P}$  nuclear magnetic resonance (NMR) spectroscopy of NaOH extracts (Cade-Menun and Preston 1996, Gressel et al. 1996). This study examined zonal differences in P forms and availability in the Coastal Forest Chronosequence (CFC) sites (see Trofymow and Porter, this issue) of Vancouver Island.

### Methods and Materials

Mineral soil (<2 mm fraction) was sampled from four pits per plot of the CFC sites at depths of 0-10, 10-30, and 30-50 cm. Extractable P was determined using the Bray 1 procedure, and total P of soils and NaOH extracts were determined by an aqua regia digestion followed by inductively coupled plasma atomic emission spectroscopy. The  $^{31}\text{P}$  NMR study was carried out on plot-level composite samples. They were extracted with 0.5 N NaOH, followed by a Chelex treatment to reduce the content of paramagnetic cations (Gressel et al. 1996). Solutions for  $^{31}\text{P}$  NMR were prepared in NaOD using 0.2 g of freeze-dried extract. Solution  $^{31}\text{P}$  NMR spectra were obtained on a Bruker MSL 300 NMR spectrometer (Cade-Menun and Preston 1996; Gressel et al. 1996). Peak areas were integrated and expressed as percentages of the total spectral area.

### Results and Discussion

Table 1 summarizes data for total, available and NaOH-extractable P by depth and subzone (stand age (sere) data not shown). Available P was much higher on the east side. For the west side, available P tended to increase with stand age, with the old-growth stands having the highest available P values (all <10 ppm). There was much less contrast by subzone for total P than for available P. For the east side, total P ranged from 500 to 850 ppm, and did not differ significantly by sere. For the west side, total P values tended to increase with stand age, although the effect was not significant.

TABLE 1. Total available (Bray 1) and NaOH-extractable P (mg/g) by depth and subzone in <2 mm mineral soil of the CFC plots (standard error in brackets).

Total P	EAST		WEST	
0-10cm	792.7	(310.3)	550.0	(371.6)
10-30cm	730.0	(296.3)	525.9	(351.3)
30-50cm	559.8	(171.8)	525.4	(275.1)
	694.2	(279.4)	533.6	(327.2)
Available P				
0-10cm	46.4	(26.2)	2.8	(3.8)
10-30cm	39.6	(26.0)	2.3	(2.9)
30-50cm	20.3	(7.7)	2.0	(2.3)
	35.5	(24.1)	2.3	(3.0)
NaOH Extract P				
0-10cm	487.7	(205.3)	246.3	(95.2)
10-30cm	417.1	(199.3)	80.0	(67.7)
30-50cm	283.6	(82.6)	303.0	(155.2)
	396.2	(188.7)	206.5	(145.3)

The NaOH extracted 50-65% of total P, except for the 10-30 cm west-side samples; P extracted in these samples was much lower and increased from 10% to 42% with stand age. This may indicate a higher proportion of P bound in non-extractable organic matter or occluded mineral phosphates. Figure 1 shows typical  $^{31}\text{P}$  NMR

spectra and structural assignments (Cade-Menun and Preston 1996, Gressel et al. 1996). The sharp peak for orthophosphate P at 6.5 ppm is not completely resolved from the broader signal of phosphate monoesters at 4.9 ppm. Phosphate diesters are found at -0.1 ppm, pyrophosphate at -4.0 ppm and phosphonate at 20 ppm.

Figure 1 illustrates the dramatic subzonal difference in NaOH-extractable P forms. East-side sites had a much higher proportion of orthophosphate P, with smaller amounts of monoester and pyrophosphate P. West-side sites had a lower proportion of orthophosphate, with more P as mono- and diesters and pyrophosphate; many samples also contained phosphonate. Soils in natural sites tend to have a lower proportion of orthophosphate P and a higher diversity of organic P forms, especially where decomposition is limited by cool, wet conditions. Diesters are a relatively available pool of organic P that are associated with high precipitation, and generally decrease or disappear with disturbance or cultivation.

The NMR results are consistent with greater nutrient availability and faster cycling on east-side sites. While total P is only slightly lower on west-side sites, available P levels are much lower. Variations in NaOH extractability indicate that P may be deposited in less available forms at 10-30 cm depth on the west side. This effect decreases with increasing stand age, and is back in the normal range for the old-growth plots. This suggests that on the west side, harvesting may have increased leaching of labile P, and its sequestration in less available forms at 30-50 cm depth, with the effects lasting longer than 80 years (the mean age of the mature plots).

Similar results were found in a study from northern Vancouver Island, up to ten years after harvesting (Cade-Menun 1995). These sites also had low available P and a high diversity of or-

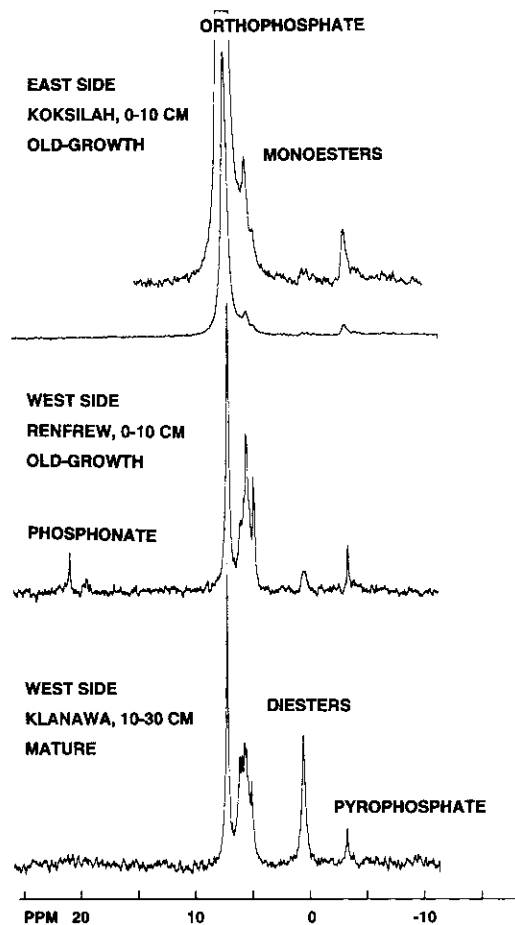


Figure 1. Typical solution  $^{31}\text{P}$  NMR spectra of NaOH extracts from the CFC plots.

ganic P forms. Intense slashburning caused a flush of available P. However, low plant uptake in the first few years after harvesting, coupled with high rainfall and lack of fresh litter input, allowed more P to leach to lower depths and be deposited in insoluble forms.

## Literature Cited

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