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Linkages between phosphorus transformations and carbon decomposition in a forest soil

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Abstract. Phosphorus mineralization is chemically coupled with organic matter (OM) decomposition in surface horizons of a mixed-conifer forest soil from the Sierra Nevada, California, and is also affected by the disturbance caused by forest harvesting. Solution ^{13}C nuclear magnetic resonance (NMR) spectroscopy of NaOH extracts revealed a decrease of O-alkyl and alkyl-C fractions with increasing degree of decomposition and depth in the soil profile, while carbonyl and aromatic C increased. Solid-state ^{13}C-NMR analysis of whole soil samples showed similar trends, except that alkyl C increased with depth. Solution ^{31}P-NMR indicated that inorganic P (P_i) increased with increasing depth, while organic-P (P_o) fractions decreased. Close relationships between P mineralization and litter decomposition were suggested by correlations between P_i and C fractions ($r = 0.82, 0.81, -0.87$, and -0.76 for carbonyl, aromatic, alkyl and O-alkyl fractions, respectively). Correlations for diester-P and pyrophosphate with O-alkyl ($r = 0.63$ and 0.84) and inverse correlations with aromatics ($r = -0.74$ and -0.72) suggest that mineralization of these P fractions coincides with availability of C substrate. A correlation between monoester P and alkyl C ($r = 0.63$) suggests mineralization is linked to breakdown of structural components of the plant litter. NMR analyses, combined with Hedley-P fractionation, suggest that post-harvest buildup of labile P in decomposed litter increases the potential for leaching of P during the first post-harvest season, but also indicates reduced biological activity that transports P from litter to the mineral soil. Thus, P is temporarily stored in decomposed litter, preventing its fixation by mineral oxides. In the mineral horizons, ^{31}P-NMR provides evidence of decline in biologically-available P during the first post-harvest season.

Abbreviations: ESR – electron spin resonance spectroscopy; OM – organic matter; NMR – nuclear magnetic resonance spectroscopy; P_i – inorganic P; P_o – organic P.

Introduction

The chemical form of P is an important factor determining P cycling in forest soils, as P-forms differ in their reactions with minerals and availability

to plants and microorganisms (Stevenson 1986; Tate 1984). The organic P compounds (P_o) are particularly important as they comprise a major component of the total P. Definitions of P fractions based on sequential extractions have been used to index P availability in agricultural and grassland soils (Bowman & Cole 1978; Condron & Goh 1989; Hedley et al. 1982), but have contributed little to elucidation of P transformations in forest ecosystems (Attiwill 1991). Other attempts to define P availability in forest soils, such as those using phosphatase activity assays, have provided variable results (Adams 1992; Gil-Sotres et al. 1990), possibly because phosphatase activity seldom limits P mineralization (Tarafdar & Claassen 1988). Thus, unlike most important nutrient elements, characterization of P in soils has depended on 'operational' definitions, only partially revealing the real chemical nature and reactions involved. Decomposition studies of residues labeled with ^{32}P and ^{14}C provide evidence for the role of decomposition in P mineralization (Dalal 1979), but again, little is known about the important biochemical pathways in the field (Magid et al. 1995; Tate 1984). A combined approach that characterizes the biochemical forms of both P and C is therefore highly desirable.

Decomposition of organic matter (OM) is characterized by changes in C functional groups as a function of decomposition time (Inbar et al. 1989; Preston et al. 1990), down a gradient of litter and soil horizons (Gressel et al. 1995a; Kögel et al. 1988; Tam et al. 1991), or as a function of particle-size and density fractions (Baldock et al. 1992). Nuclear magnetic resonance (NMR) spectroscopy, especially ^{13}C-NMR, provides important insights into soil OM structure and the decomposition process in forests (Baldock & Preston 1995; Preston 1992; Preston et al. 1990). Solution ^{31}P-NMR has been used successfully on soil extracts to identify P functional groups (Condron et al. 1990; Forster & Zech 1993; Newman & Tate 1980). Although parallel analyses of P and C using NMR have been used in other biological disciplines, our study is the first application to soils.

There is current concern that forest harvest practices may result in decreased ecosystem productivity (Attiwill 1991; Powers 1991). Knowledge of the biological cycling of P and its potential disruption as a result of forest harvesting may be a key to preventing forest decline, because P is often in limited supply. Wood et al. (1984) hypothesized that after harvesting, mineralized P leaches to the lower part of the soil profile in Spodosols where it binds with Al and Fe-oxides, thus becoming unavailable for uptake by plants and microorganisms. Since replenishing of available P depends on slow weathering rates, major episodes of P loss may lead to rapid decline in ecosystem productivity. The same authors distinguished between important biological and geochemical subcycles, and found that the biological processes, dominant

in the litter and upper mineral horizons, and geochemical processes dominant in the mineral subsoil, were vertically stratified in Spodosols. In contrast, Walbridge et al. (1991) found that, in Ultisols and Inceptisols, the biological activity and the important geochemical indices for P availability (i.e. non-crystalline Fe and Al oxide content and P sorption capacity), were all greatest in the surface horizon. In this case, the biological and geochemical subcycles were not vertically separated, so that P released from decomposing litter and roots could be fixed after forest harvesting by mineral matter in the A horizon. This process would have little effect on total P in the soil horizons but would greatly reduce the amount of P available for rapid biological cycling.

Specific objectives of our study were: (1) to examine P fractions in soil and litter using ^{31}P-NMR; (2) to characterize the linkages between P transformations and OM decomposition in litter and upper mineral soil horizons; and (3) to determine the short-term effects of forest harvesting on dynamics of P and C transformations. Ideally, C decomposition and P transformations should be examined in whole samples of litter and soil using solid-state techniques rather than in laboratory extractions. However, such techniques for P, including solid-state ^{31}P-NMR, have yet to achieve sufficient resolution (Frossard et al. 1994; Hinedi et al. 1989; Newman & Condron 1995). It was therefore necessary for us to use solution ^{13}C and ^{31}P-NMR (as well as solid-state ^{13}C-NMR) as the primary tools in this study of C and P transformations.

Methods

Study site description

The study site adjoins the University of California Blodgett Research Forest, on Sierra-Pacific Lumber Co. property, near Georgetown, California on the western slopes of the Sierra Nevada Mountains (120°39′ W, 38°53′ N). Elevation is 1300 m; climate is Mediterranean with warm, dry summers and cool, wet winters. Precipitation averages 1650 mm annually, falling mostly as rain between late October and early May. Before harvesting, this mature, 80 year-old forest consisted (in order of abundance) of ponderosa pine (*Pinus ponderosa* Dougl. ex Laws.), incense-cedar (*Libocedrus decurrens* Torr.), white fir (*Abies concolor* (Gord. & Glend.) Hilderb.), Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco), sugar pine (*Pinus lambertiana* Dougl.) and tanoak (*Lithocarpus densiflorus* (Hook & Arn.) Rehd.). The soil, derived from andesitic parent material, is a fine-loamy, mixed, mesic Ultic Haploxeralf (Cohasset series), a widespread soil series with low P availability (Powers et al. 1978), summer soil moisture deficiencies and minor deficiencies of N (Powers 1983). Litter layers and mineral horizons were described

Table 1. Description of pre- and post-harvest litter and surface mineral horizons at the study site in a mixed-conifer forest in northern California.

Horizon	Depth (cm)	Description
Pre-harvest		
O_i	7–5	Conifer needles; desiccated; single particle; loose; acerose; no roots; some insects.
O_e	5–0	Desiccated; weak, non-compact matted; loose; acerose; few, fine roots; common white mycelia.
A_o	0–3	Desiccated; very dark brown; granular; loam; friable; plentiful roots and mycelia; abrupt boundary.
A_1	3–40	Dry; brown; granular; loam; friable; plentiful roots; gradual boundary.
B_t	40–150	Dry; reddish brown; subangular blocky; clay loam; friable; common fine roots, few medium and coarse roots; clay films; few weathered rock fragments; diffuse boundary.
R	150–200	Weathered brownish gray andesite.
Post-harvest		
O_i	12–5	Conifer woody slash; desiccated; single particle; loose; acerose; no roots or insects.
O_e	5–2	Desiccated; weak, compact; loose; acerose; no roots; few white mycelia.
O_a	2–0	Moist; compact matted; friable; gritty; few, fine roots and white mycelia.
A	0–40	Moist; brown; granular; loam; firm; gritty; some roots; gradual boundary.
B_t, R		Same as before harvesting.

using criteria of Green et al. (1993) and Soil Survey Staff (1990) (Table 1). The site was clearcut and skidded by tractor September, 1993 as part of the USDA Forest Service Long-Term Soil Sustainability Project (Powers 1991). Logging slash was left on the site.

Sample collection and preparation

Spatial heterogeneity at this forest site was typically large. To reduce variability, sampling locations with typical pre-harvest profiles were selected, and the exact locations were also used for post-harvest sampling. Samples were collected from three 1-m^2 plots before harvesting, in June 1993 and post-harvest in May 1994. Samples from the O horizons and the top 10 cm of the A horizon were immediately frozen in the field using dry ice. In the laboratory they were then freeze-dried prior to analysis. Litter samples were

ground to pass through a 0.85-mm mesh sieve after removal of obvious woody material. Soil samples were sieved through a 2-mm mesh sieve. Subsamples were ground to a fine powder on a ball-mill and replicate samples were wrapped in tin capsules for C and N analysis on a Carlo Erba NA 1500 C and N analyzer (Milan, Italy). Litter samples were prepared for determination of P, S, K, Ca, Mg, Fe, Mn and Al concentrations by digesting replicate 200 mg subsamples in 5 mL concentrated HNO_3 at 140 °C for 16 h (Zarcinas et al. 1987). Soil samples were prepared by fusion with Na_2CO_3 (Lim & Jackson 1982). A muffle furnace was used for heating instead of a Meker burner and concentrated HNO_3 was used to dissolve fusion cakes to prevent Pt crucible corrosion. Elemental concentrations were determined on a Plasma 40 (Perkin-Elmer, Norwalk, CT) inductively coupled plasma-atomic emission spectrometer (ICP-AES) equipped with a high-dissolved-solids nebulizer.

Sequential extraction of P from the O and A horizons followed the procedure of Hedley et al. (1982): three replicates of 0.5 g sample and 0.4 g anion-exchange resin bags (Dowex 1 × 8–50, >30 mesh, in HCO_3^- form) were shaken in deionized water for 16 h. The P extracted by the resin was eluted by shaking for 30 min with 20 mL 0.5 M NaCl. Resin-extracted samples were shaken for 16 h in 30 mL 0.5 M $NaHCO_3$, centrifuged and filtered to produce $NaHCO_3$-extractable P. The samples were then shaken for 16 h with 30 mL of 0.1 M NaOH, centrifuged and filtered to produce NaOH-extractable P. Another aliquot of NaOH solution was added to each sample, sonicated for 5 min in an ice bath and shaken for an additional 16 h to produce the sonicated-NaOH-extractable P. The residues were shaken with 30 mL 1.0 M HCl for 16 h, centrifuged and filtered to produce the HCl-extractable P. The residues were digested at 140 °C in 5 mL of concentrated H_2SO_4 and H_2O_2. The molybdate-blue method (Olsen & Sommers 1982) was used to determine inorganic P (P_i) in the $NaHCO_3$, NaOH and sonicated-NaOH extracts. Total P concentrations were measured after H_2SO_4/HCl digestion for all extracts. Organic P (P_o) was calculated as the difference between total P and P_i.

NMR analysis

For solution ^{13}C and ^{31}P-NMR analysis, 3 g of sample were dispersed in 30 mL 0.5 M NaOH in 50 mL centrifuge tubes and shaken for 4 h under N_2. Samples were centrifuged at 15,000 rpm for 20 min and filtered through a prewashed #1 Whatman filter, under reduced pressure. Residue was dispersed again in 0.5 M NaOH and the procedure was repeated twice more. The three consecutive extracts from each sample were combined. The extracts were treated with 2 g of Na-saturated Chelex-100 for 10 min to reduce concentrations of paramagnetic cations before filtering and freeze-drying the solution. Due to the long accumulation times required for NMR spectra

(16–60 h), only one representative sample of each horizon could be analyzed. Thus replicate extracts were combined prior to analysis. Freeze-dried material (800 mg) was dissolved in 2 mL of D_2O, centrifuged at 15,000 rpm for 20 min and filtered into a 10-mm NMR tube through a porous glass filter. The pH was determined to be >11 for all samples, to enable spectral separation between the orthophosphate (P_i) peak (4.9 ppm) and the monoester phosphate peak (3.2 ppm).

Solution ^{13}C- and ^{31}P-NMR spectra were acquired on a Bruker WM 250 NMR spectrometer at 62.9 MHz and 101.3 MHz for ^{13}C and ^{31}P, respectively. A 45° pulse with 2 s delay and inverse-gated decoupling were used for a total of 30,000–110,00 scans per spectrum. Line-broadening was 12–20 Hz for ^{31}P-NMR spectra depending on linewidth in individual spectra. Carbon-13 spectra were processed with two different values of line-broadening. This was done to enhance either the characteristic broad peaks of extracted humic substances (30–40 Hz) or the sharp lines attributed to low-molecular-weight organic acids (4 Hz). These were identified as carbonate (170 ppm), formate (172 ppm), oxalate (173 ppm) and acetate (183 and 25 ppm) by addition of pure standards.

Solid-state ^{13}C-NMR spectra were acquired on a Varian XL-200 spectrometer operating at 50.3 MHz. Each sample was packed in a 7-mm cylindrical, zirconia rotor and was retained with Kel-F end-caps; approximately 160 mg of litter or 300 mg of mineral soil entirely filled the rotor. Rotors were spun at 5 kHz in a Doty Scientific 'magic-angle spinning' (MAS) probe. Each 5 ms proton preparation pulse was followed by a 1 ms cross-polarization contact time, 15 ms of data acquisition and 300 ms of relaxation delay before the sequence was repeated. A total of 12,000–120,000 scans were collected and averaged per spectrum, depending on individual spectra.

To obtain proton spin relaxation edited (PSRE) subspectra we used a procedure modified from VanderHart and Perez (1986). Two solid-state ^{13}C-NMR spectra were obtained, one (labeled S) as described above and the other (labeled S′) using a pulse sequence in which the proton spins were inverted by a 180° pulse and allowed to recover for a relaxation interval 15 ms before the 90° proton preparation pulse was applied. Subspectra were separated by forming linear combinations of S and S′, using trial values of coefficients, until the results showed good mutual discrimination of selected signals without allowing any signal to become inverted (Preston & Newman 1992).

The mathematical basis for PSRE is summarized here. Suppose that a spectrum S is the sum of two components,

$$S = A + B \tag{1}$$

where A and B arise from categories of OM with distinguishable values of the proton spin-lattice relaxation time constant $T_1(^1H)$. Suppose that the two components are suppressed to different degrees by spin inversion and partial recovery:

$$S' = f_aA + f_bB \quad (2)$$

where f_a and f_b are functions of $T_1(A)$ and $T_1(B)$. Equations (1) and (2) can be solved for A and B:

$$A = kS + k'S' \quad (3a)$$

$$B = (1 - k)S - kS' \quad (3b)$$

where $k = f_b/(f_b - f_a)$, $k' = -1/(f_b - f_a)$. Coefficients k and k′ can be calculated from trial values of $T_1(A)$ and $T_1(B)$, or the calculation can be reversed to provide estimates of $T_1(A)$ and $T_1(B)$ from the optimized values of k and k′. The method has been described in more detail by Newman and Condron (1995).

Chemical shifts of ^{13}C-NMR spectra are reported relative to tetramethylsilane at 0 ppm, and interpreted based primarily on assignments by Malcolm (1989), deMontigny et al. (1993) and Wilson (1987). Chemical shifts of ^{31}P-NMR spectra are reported relative to 85% H_3PO_4 at 0 ppm, and interpreted based primarily on assignments by Newman and Tate (1980). Relative peak areas were measured using digital computerized integration.

ESR analysis

A Bruker ESR spectrometer operating at X-band frequency (9 GHz) was used at ambient temperature. Free-radical concentrations were quantified against a 'strong pitch' standard from Bruker. Samples were weighed and compacted such that equivalent mass and volumes were analyzed to improve the resolution of spin quantification (Ranby & Rabek 1977).

Statistical analysis

The effect of forest harvesting on soil nutrient concentrations was tested by paired t-test ($n = 3$). Correlations between the relative solution NMR signals of different functional groups were determined using all the pre- and post-harvest spectra (i.e. $n = 8$ for all correlations reported, each data point is one horizon at any given collection time). All statistics were computed using Statview 4.0 (Abacus Concepts, Berkeley, CA).

Results

Soil profile changes

At the sampling locations the Mormoder-type profile (Green et al. 1993) changed considerably due to harvesting. There was an addition of slash to the O_i horizon, and a highly decomposed organic O_a horizon developed at the litter-mineral interface which replaced the organic-rich A_o horizon (Table 1). Our observations did not indicate physical disturbance due to harvesting in the lower parts of the profile.

Solution ^{13}C-NMR spectroscopy

The NaOH extracted 30 ± 1% (mean±standard error) of the total C in the O layers and 62 ± 10% of the total C in the A horizons. The solution ^{13}C-NMR spectra with 30–40 Hz line-broadening (Figure 1) have features similar to those previously reported for NaOH extracts (Newman & Tate 1984) and fractionated humic substances (Preston 1987; Preston & Blackwell 1985). In the alkyl (aliphatic) region (0–50 ppm) of the ^{13}C-NMR spectra of O_i horizon extracts, there are peaks: at 25 ppm, this being the CH_3 of acetate, identified by standard addition and also evident in the 4 Hz line-broadening spectrum shown under the pre-harvest spectra in Figure 1; at 30 ppm, assigned to -CH_2- units of long chains, such as fatty acids and suberin (Preston et al. 1994); and at 39 ppm, assigned to -CH_2- units of branched chains. The relative intensity of these peaks and of the whole alkyl C region, decreased with increasing depth in the soil profile from 23 to 18% in the pre-harvest profile, and from 29 to 20% in the post-harvest profile (Table 2).

At 57 ppm, a peak typical of both methoxyl and amine C appears in pre- and post-harvest spectra (Figure 1). In the O-alkyl region (60–90 ppm), a peak at 63 ppm and a smaller one at 65 ppm would include the C_6 of carbohydrates. The peak at 73 ppm, dominates the O-alkyl region and may be attributed in part to ring-C of carbohydrates. The relative intensity of the O-alkyl region decreased in the pre-harvest profile from 21% in the O_i horizon to 14% in the A horizon and from 24 to 11% in the post-harvest profile (Table 2).

The di-O-alkyl region (90–110 ppm), which includes the anomeric C of carbohydrates, is dominated by a peak at 104 ppm (Figure 1). A peak at 95 ppm is present in the spectrum of the pre-harvest O_i horizon, but is not present in any other spectrum. Peak-resolution in the aromatic and phenolic regions (110–145 and 145–160 ppm, respectively) is less pronounced. Larger peaks at 119, 130 and 152 ppm might be assigned to aromatic units contained in lignin. Aromatic C increased in the pre-harvest profile from 15% in the O_i horizon to 21% in the A horizon and from 13 to 25% in the post-harvest profile

Table 2. Relative spectral areas of C and P functional groups in NMR spectra or pre- and post-harvest surface horizons of a mixed-conifer forest in northern California.

	^{13}C-NMR							^{31}P-NMR			
Fraction	alkyl	methoxyl	O-alkyl	di-O-alkyl	aromatic	phenolic	carbonyl	pyro-P	diester-P	monoester-P	P_i
Chemical Shift (ppm)	0–50	50–60	60–90	90–110	110–145	145–160	160–200	−6.5–−4.5	−3.5–−1.5	22.0–4.1	4.1–6.0
	% of total spectral area										
Solution NMR											
Pre-harvest											
O_i	23	5	21	7	15	5	23	13	13	62	12
O_e	26	6	18	6	17	6	23	8	15	63	14
A_o	21	4	15	5	19	4	30	5	11	58	27
A	18	3	14	6	21	6	32	7	7	49	37
Post-harvest											
O_i	29	5	24	5	13	6	18	11	10	64	15
O_e	25	5	17	6	17	5	25	8	9	65	18
O_a	27	6	19	4	14	6	24	4	11	71	13
A	20	6	11	6	25	7	26	0	5	67	28
Solid-state NMR											
Pre-harvest											
O_i	20	6	43	11	12	5	4				
O_e	26	6	36	10	12	5	5				
A_o	27	7	25	9	16	6	9				
A	27	6	23	9	21	5	10				
Post-harvest											
O_i	19	6	47	10	10	4	3				
O_e	22	7	40	9	11	5	5				
O_a	26	7	34	9	13	4	7				
A	33	6	22	8	18	5	8				

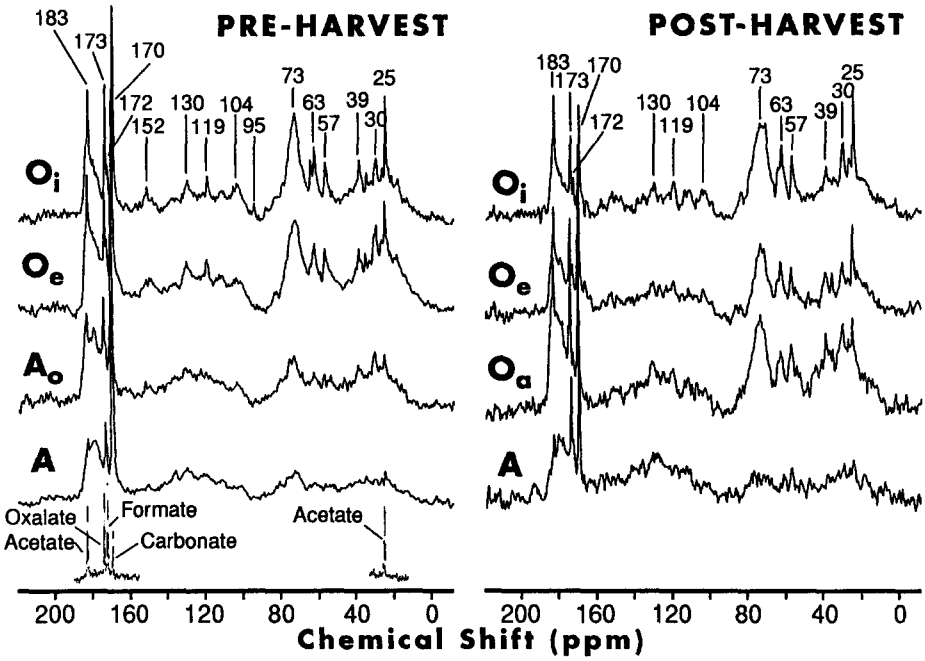

Figure 1. Solution ^{13}C-NMR spectra of NaOH extracts of pre- and post-harvest surface horizons from a California mixed-conifer forest soil. Line-broadening is 30–40 Hz for all spectra except for the bottom spectrum showing standard additions of low molecular-weight organic acids, which has line-broadening of 4 Hz.

(Table 2). The phenolic C region contributes a relatively constant 4–7% of the total signal.

The carbonyl region (160–200 ppm) is dominated by sharp, well resolved peaks that also appear in 4 Hz line-broadening spectra at 170, 172, 173 and 183 ppm, identified by standard additions as the carboxylics of carbonate, formate, oxalate and acetate, respectively (Figure 1). A broad peak at 179 ppm is featured in all 30–40 Hz line-broadening spectra, but is more apparent in the lower part of the profile where the acetate peak at 183 ppm is smaller. The intensity of the carbonyl region increased with depth in the profile, although the intensities of the formate, oxalate, and acetate peaks decreased with increasing depth (based on both 4 Hz and 30–40 Hz line-broadening spectra). Carbonyl C increased in the pre-harvest profile from 23% in the O_i horizon to 32% in the A horizon and from 18 to 26% in the post-harvest profile.

Solid-state ^{13}C-NMR spectroscopy

The solid-state ^{13}C NMR spectra (Figure 2) are typical for coniferous litter and forest soils with features similar to those reported previously (Baldock & Preston 1995). The alkyl region (0–50 ppm) of solid state ^{13}C-NMR spectra is dominated by a peak at 30 ppm in all spectra (Figure 2). The relative area of this region increased with increasing depth in the soil from 20 to 27% in the pre-harvest profile and from 19 to 33% in the post-harvest profile (Table 2). In the methoxyl region (50–60 ppm) there is a peak at 57 ppm which is clear in all the litter samples but not in the spectra of mineral soil. The O-alkyl region (60–90 ppm) is dominated by a strong peak at 73 ppm, with smaller peaks at 63 and 84 ppm in the spectra of the O_i horizon of both collection periods. This region decreased markedly with increasing depth from 43 to 23% in the pre-harvest profile and from 47 to 22% in the post-harvest profile. The di-O-alkyl region (90–110 ppm) exhibits a peak at 105 ppm with no apparent trends with depth. The aromatic region (110–145 ppm) increased with increasing depth from 11 to 21% in the pre-harvest profile and from 10 to 18% in the post-harvest profile, largely as a result of the increased intensity associated with the peak at 130 ppm. Peaks were also apparent at 145 and 155 ppm, especially in the O_i horizon. The relative proportion of the carbonyl region (160–200 ppm) also increased with increasing depth, from 4 to 10% in the pre-harvest profile and from 3 to 8% in the post-harvest profile.

Using PSRE, the spectrum of each sample was separated into 2 subspectra (Figure 3). All the strong peaks in the litter spectra appeared in the subspectra with long $T_1(^1H)$ constants, resembling recognizable plant components: resins (30 ppm); lignin (56 ppm); cellulose (C_6 at 63 ppm, $C_{2,3,5}$ at 73 ppm, C_4 at 84 ppm, and C_1 at 105 ppm); and possibly tannins (105, 145 and 155 ppm). The bulk of the aromatic C appears in the short $T_1(^1H)$ subspectra. Both long and short $T_1(^1H)$ subspectra change with increasing depth in the soil profile. O-alkyl C decreased with depth and alkyl C increased with depth in the long $T_1(^1H)$ spectra. Aromatic and carbonyl C increased and O-alkyl C decreased with increasing depth in the short $T_1(^1H)$ subspectra. The post-harvest O_i horizon had apparently more O-alkyl C in the short $T_1(^1H)$ subspectrum and less in the long $T_1(^1H)$ subspectrum compared to those of the pre-harvest spectra. In addition, $T_1(^1H)$ values became shorter and line-broadening increased with increasing depth, possibly because of increasing association with soil minerals.

Electron spin resonance spectroscopy

Electron spin resonance spectroscopy (ESR) was used to examine free-radical concentrations in the litter and A_o horizon (Table 3), but could not be used for

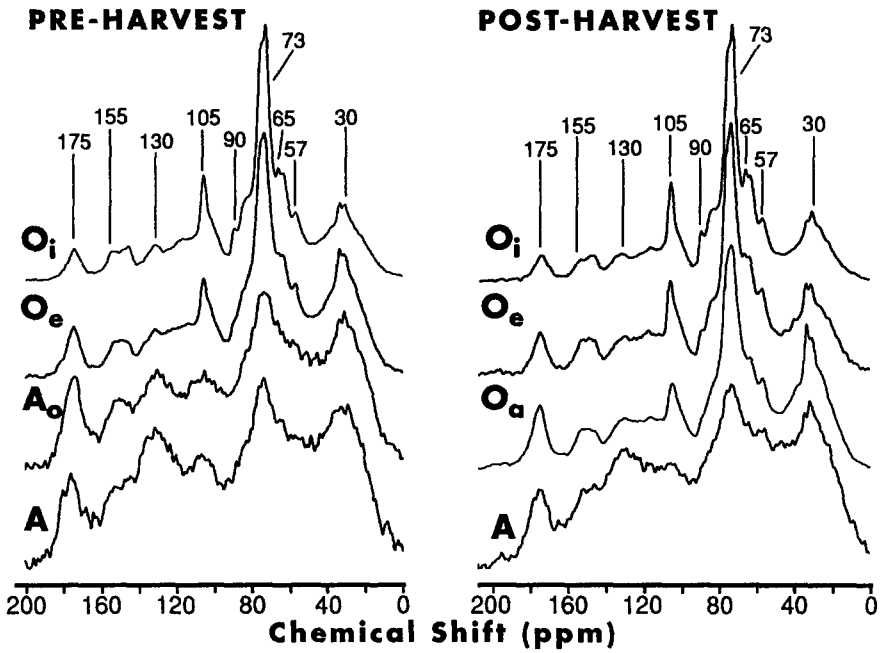

Figure 2. Solid-state ^{13}C-NMR spectra of pre- and post-harvest surface horizons from a California mixed-conifer forest soil.

the A horizon due to paramagnetic interferences (Senesi & Steelink 1989). Free-radical spin concentrations increased with increasing depth in the soil profile, as might be expected from increasing contributions of fungal constituents and humified material (Chen et al. 1978; Saiz-Jimenez & Shafizadeh 1985; Steelink & Tollin 1967). Our results are within the ranges reported previously for plant-derived lignins, ponderosa pine litter and dissolved OM, fungal melanin and humic substances of Mediterranean-region soils (Table 3). Increases in free-radical spin concentrations were most apparent in the pre-harvest profile, whereas after harvesting the O_e and O_a horizons have similar concentrations. Changes in the spectroscopic splitting factor (g-value) do not exhibit any consistent trend. Peak-to-peak line width increased with increasing profile depth for both pre- and post-harvest samples. The increase is attributed to increasing association of OM with paramagnetic elements, such as Fe and Mn (Table 4).

Elemental concentrations

Mean elemental concentrations in the pre- and post-harvest O and A horizons are presented in Table 4. Carbon concentrations decreased with increasing

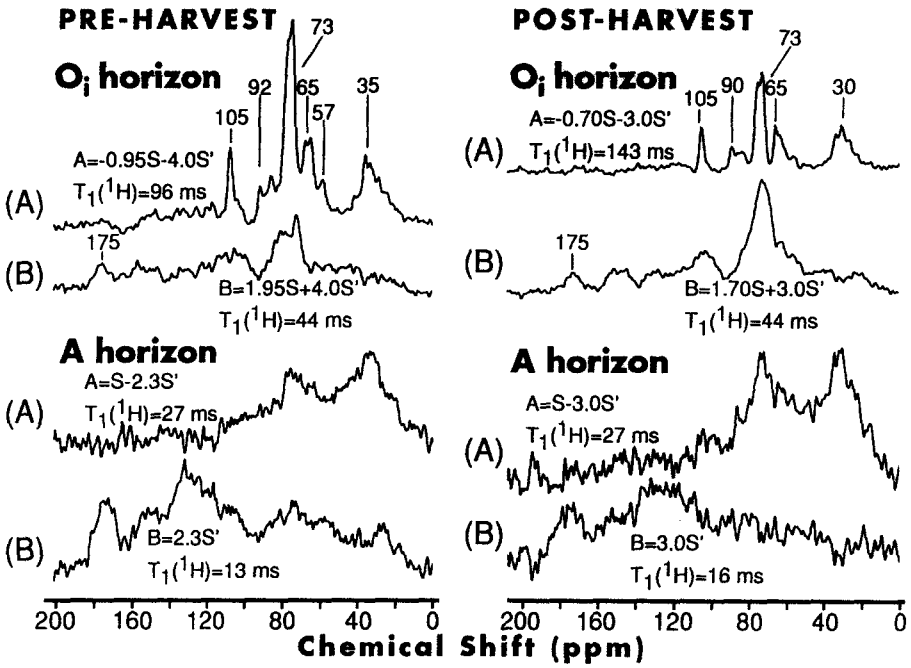

Figure 3. Solid-state ^{13}C-NMR PSRE subspectra of pre- and post-harvest horizons of a California mixed-conifer forest soil. The linear spectral combinations and $T_1(^1H)$ constants are indicated for each pair of (a) long and (b) short proton spin relaxation subspectra.

depth in the soil profile, while concentrations of Fe, Mn and Al, typical of mineral matter, increased. The concentration of K was lower in the pre-harvest O_i horizon compared to that of the post-harvest horizon (p = 0.03), but higher in the pre-harvest O_e horizon (p = 0.03). The concentration of Ca was lower in the pre-harvest A horizon compared to that of the post-harvest horizon (p = 0.03). Otherwise, element concentrations remained similar for both collection periods, although the change in the profile structure near the litter-mineral soil interface precludes comparison of the pre-harvest A_o and the post-harvest O_a horizons. The highest concentrations of N, P, K, S and Ca in the litter layers were found in the post-harvest O_a horizon.

Estimates of element concentrations on an aerial basis conducted by the USDA Forest Service (R.F. Powers, P.I.) suggest that litter contained 455 kg ha^{-1} N and 65 kg ha^{-1} P, and that the slash added to the site during harvest contained 387 kg ha^{-1} N and 55 kg ha^{-1} P. Assuming that element concentrations in the mineral soil samples are representative of the site, and using the mean bulk density measured for the 0–10 cm depth (640 kg m^{-3}), there was no change in P (367 kg ha^{-1}), but concentrations increased for

Table 3. ESR spectroscopic characteristics of pre- and post-harvest O and A_o horizons at the study site in a mixed-conifer forest in northern California.

Horizon	Spin concentration	Spectroscopic splitting factor	Line width	Ref.
	(spins $kg^{-1} \times 10^{19}$)	(*g*-value)	(Gauss)	
Pre-harvest				
O_i	2.95	2.0033	3.61	
O_e	3.44	2.0032	4.02	
A_o	22.63	2.0039	7.76	
Post-harvest				
O_i	1.91	2.0031	4.02	
O_e	6.22	2.0035	4.55	
O_a	5.17	2.0030	4.95	
Pinus ponderosa O layers	3.2–6.8	2.0034–2.0035	5.3–6.0	1
P. ponderosa Dissolved OM	1.38	2.0036	7.3	2
Lignins	3.0–40.0			3
Fungal melanin	7.0–200.0	2.0035–2.0041	2.9–5.9	3, 4
Mediterranean-soil humic substances	2.0–200.0	2.0031–2.0050	3.2–7.5	3, 4, 5

(1) Tam et al. (1991); (2) Gressel et al. (1995b); (3) Steelink and Tollin (1967); (4) Saiz-Jimenez and Shafizadeh (1985); (5) Senesi and Steelink (1989).

Ca (from 2844 to 3821 kg $ha^{-1)}$ and K (from 1028 to 1350 kg ha^{-1}) and decreased for N (from 3856 to 3322 kg ha^{-1}), during the first post-harvest season. However, these aerial-based concentrations are only rough estimates, because elemental analysis was limited to samples from the three profiles analyzed by NMR.

The C/N ratio of the pre-harvest O_i horizon was significantly higher than that of the post-harvest (48 versus 40; $p = 0.04$), due to addition of fresh plant material during harvesting that did not senesce naturally (Table 1). The C/N and C/P ratios decreased with increasing depth, both reaching values that were similar in the pre- and post-harvest A horizons (Table 4). The changes in concentrations of C and nutrients are typical responses to harvesting of temperate forests (Johnson 1992).

Solution ^{31}P-NMR spectroscopy

The NaOH solution extracted 69 ± 3% (mean ± standard error) of the total C in the O layers and 49 ± 2% of the total P in the A horizons. There were measurable amounts of Mn and Fe in the samples prepared for NMR analysis, even after the extracts were treated with the Chelex resin, especially

Table 4. Mean element concentrations (n = 3) and ratios in pre- and post-harvest surface horizons at the study site in a mixed-conifer forest in northern California.

Horizon	C	N	P	S	K	Ca	Mg	Fe	Al	Mn	C/N	C/P
	g kg^{-1}											
Pre-harvest												
O_i	484	10.07	0.58	0.72	0.86	12.67	1.13	1.11	2.21	0.57	48	834
O_e	410	13.72	0.68	0.98	0.73	17.14	1.35	5.19	10.30	1.53	30	605
A_o	178	8.09	0.65	0.57	1.90	6.62	1.55	28.59	33.63	0.87	22	272
A	114	5.14	0.54	0.37	1.48	3.51	1.75	31.30	33.32	0.52	22	211
Post-harvest												
O_i	471	11.66	0.62	0.67	1.21	11.38	1.07	0.67	1.36	0.33	40	757
O_e	427	13.51	0.70	1.01	0.48	14.63	1.17	3.32	6.33	0.57	32	610
O_a	406	17.00	0.79	1.30	1.45	24.60	1.46	4.49	8.07	1.18	24	513
A	116	5.19	0.57	0.49	2.11	5.97	1.74	23.05	36.27	0.54	22	203

in extracts of the mineral soil. Therefore, signal loss and decreasing resolution with increasing depth in the soil profile are attributed to a combination of increasing concentrations of paramagnetic elements and increasing chemical heterogeneity with increasing decomposition.

Relative increases of the P_i signal (4.9 ppm) with increasing depth were apparent for both pre- and post-harvest profiles (Figure 4 and Table 2). The change was most drastic in the pre-harvest profile where P_i increased from 12% of the total signal in the O_i horizon to 37% in the A horizon. After harvesting, P_i increased from 15 to 28% with increasing depth. Monoester P (3.2 ppm) decreased with increasing depth in the pre-harvest profile, but in the post-harvest profile was highest in the O_a and A horizons.

Peaks from diester phosphates (including phospholipids, DNA and RNA) centered at −2.2 ppm were apparent throughout the spectra for both collection periods (Figure 4). The relative signal intensity and its resolution decreased slightly with increasing depth in the pre-harvest profile but remained fairly constant in all three post-harvest O horizons. The relative intensity of diester P in the pre-harvest O_i and O_e horizons was greater than in the post-harvest horizons. A peak centered at −5.0 ppm assigned to pyrophosphates, was broader in spectra of the lower parts of the profile and cannot be distinguished from background noise in the post-harvest A horizon. Diester P, pyrophosphate and P_i fractions in the A horizon of the post-harvest spectra were lower than those in the pre-harvest spectra (Table 2).

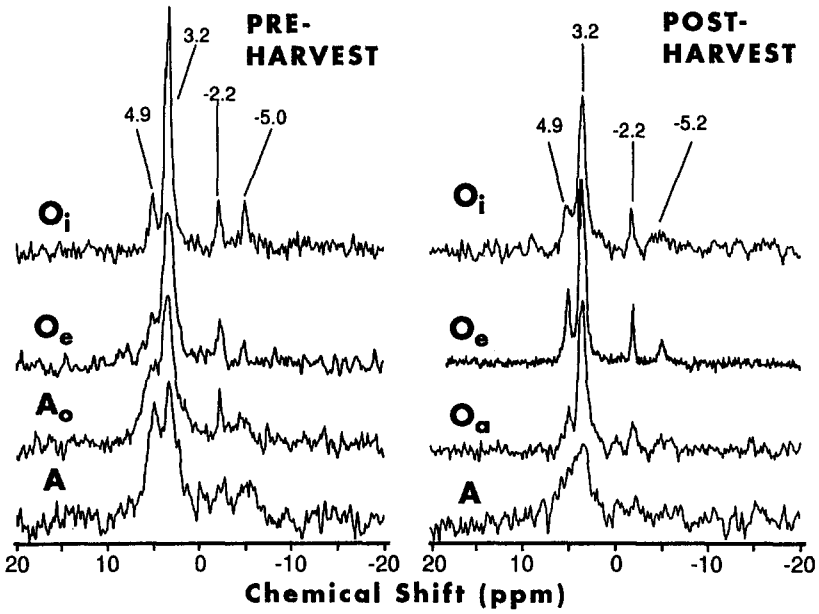

Figure 4. Solution ^{31}P-NMR spectra of NaOH extracts of pre- and post-harvest O_i and A horizons from a California mixed-conifer forest soil.

Sequential P-extraction

The relative concentrations of P in the fractions produced by the sequential extraction are presented in Figure 5. Because total P concentrations changed little with depth, trends for the relative proportions of each fraction and those for the actual concentrations were mostly similar. Recovery rates were 82–106% of the total P determined by HNO_3 digestion of litter and Na_2CO_3 fusion of the mineral horizons. Incomplete digestion of the residual mineral matter by the concentrated H_2SO_4 and H_2O_2 is most likely the cause for low recovery rates from the mineral soil.

Resin-extractable P and $NaHCO_3$ P_i and P_o decreased with increasing depth in the pre-harvest profile, but remained high in the post-harvest O horizons. The sum of these fractions, defined as labile P, constitute only 3–10% of the total P in the mineral horizons, which is typical for Ultisols (Cross & Schlesinger 1995). Relatively high concentrations of NaOH and sonicated/NaOH-extractable P_i were present only in the A horizons of both soil profiles. Organic P extracted in NaOH and sonicated/NaOH increased slightly with increasing depth in the O and A_o horizons, but decreased in the A horizon, and there were no clear trends for these fractions due to harvesting.

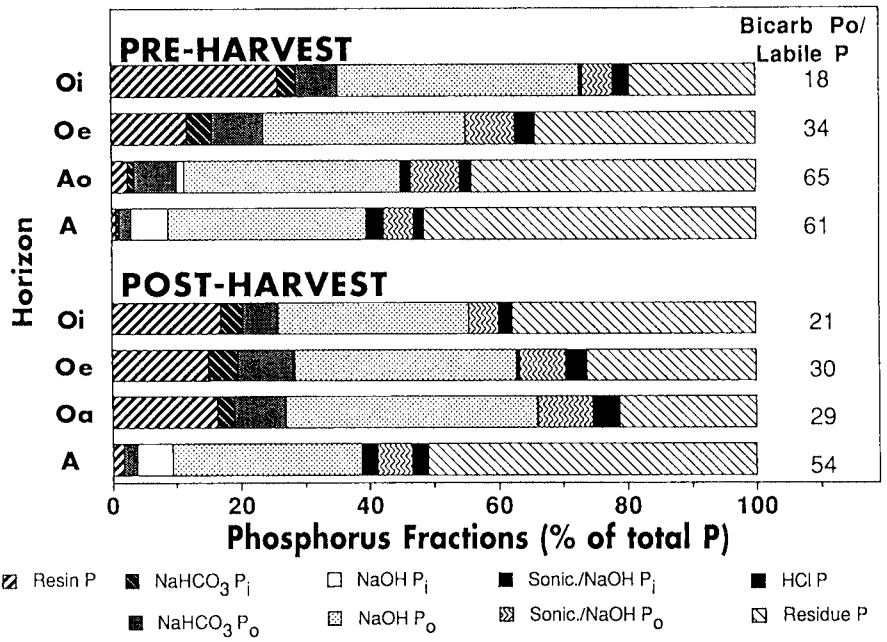

Figure 5. Phosphorus removed by sequential extraction of pre- and post-harvest surface horizons from a California mixed-conifer forest soil (standard error = 1.27).

HCl-extractable P_i were low throughout the profile for both collection periods, and no clear trends occurred for this fraction either. Residual P increased with increasing depth in the pre-harvest profile but decreased in the O horizons of the post-harvest profile. Geochemical P, defined as the sum of P_i fractions, resin, HCl and residual P in the A horizon was 63%, which is typical for highly weathered soils (Cross & Schlesinger 1995).

Discussion

Organic decomposition

Most studies that use a strong base for extraction, also fractionate OM into humic and fulvic acids (Stevenson 1994), but this fractionation arbitrarily divides the continuum of organic species based on their solubility. Although not generally recognized, such fractionation is mostly unnecessary for solution NMR investigations of samples with high OM, such as surface horizons of forest soils (Newman & Tate 1984). Thus, our study of a forest soil profile demonstrates the benefit of examining the full continuum of organic species,

including signals of the low molecular-weight organics, oxalate, formate and acetate which are important in pedogenic processes and nutrient cycling in forests (Figure 1). We have previously identified oxalate and acetate in Californian mixed-conifer forest litter, using other techniques (Pohlman & McColl 1988; Tam & McColl 1991). The decrease of low molecular-weight organics with increasing depth in the soil can be a result of increasing breakdown and association with mineral components, and has been reported by Tam et al. (1991) for California forest soils. Although some of these acids may be products of hydrolysis during the NaOH extraction, hydrolysis alone cannot explain the distinct decrease in their concentration with increasing depth in the soil profile.

The signals of recognizable plant components appear in the long $T_1(^1H)$ PSRE subspectra, while those found in the short $T_1(^1H)$ subspectra are typical of humic substances. The mere existence of such humified features in spectra of the O_i horizons reaffirms that decomposition begins well before plant material reaches the ground (Filip et al. 1991; Satchell 1974). Results of most decomposition studies, especially those involving NMR, suggest that aliphatic (alkyl C) structures are more recalcitrant, therefore increasing relative to other C fractions as decomposition proceeds. In contrast, aromatic C decomposition depends upon the interaction of plant composition, microbial community and climatic conditions (Baldock & Preston 1995). In our study, alkyl C increased with increasing depth in the soil profile for both the solid-state NMR spectra and the long $T_1(^1H)$ subspectra (Figures 2 and 3), in agreement with previous reports. However, results from solution ^{13}C-NMR and the short $T_1(^1H)$ subspectra showed small decreases in alkyl C with increasing depth from both collection periods. These results suggest that the humified, NaOH-extractable fraction of the otherwise-increasing alkyl C fraction, decreases with increasing depth in the soil. Increases in cross-linking, hydrophobic reactions and adsorption to mineral matter with increasing depth, may account for both reduced extractability in NaOH and greater resistance to decomposition of the alkyl fraction (Baldock & Preston 1995; Kögel-Knabner et al. 1992). Thus, the recalcitrant alkyl C derived from plants would show a relative increase in concentration, while humified alkyl C would be stabilized and resist NaOH extraction.

Aromatics were preferentially preserved relative to other organic forms, although changes in structure occurred with increasing depth. High aromatic C content has been previously noted in studies of burned soils (Almendros et al. 1990), paleosols (Calderoni & Schnitzer 1984), with increasing depth in the soil (Chen & Pawluk 1995) and in decomposed salt marsh plants (Filip et al. 1991) and pine needles (Baldock & Preston 1995; Wilson et al. 1983). High aromaticity has been attributed in these cases to either the formation

of polynuclear aromatic rings during decomposition, or to limitations of microbial activity by either allophanic mineralogy or long dry periods.

Chemical analysis, solution and solid-state ^{13}C-NMR provide a comprehensive description of OM decomposition in the upper profile (Tables 2 & 4 and Figures 1 & 2). Decomposition with increasing depth in the soil is characterized by decreases in C, N, S and Ca concentrations and the C/N ratio, increases in Fe, Mn and Al concentrations, decreases of low molecular-weight acids, O-alkyl and extractable alkyl C and increases of carbonyl and aromatic C. Correlations between the relative intensities (peak areas) of the solution ^{13}C-NMR fractions also show this decomposition pattern (Table 5). Positive correlations exist between alkyl and O-alkyl C (both decreasing with depth) and between carbonyl and aromatic C (both increasing with depth). There are also corresponding negative correlations between the C fractions. Correlations also exist with the C/N ratio, showing that the alkyl, O-alkyl, aromatic and carbonyl regions in the solution ^{13}C-NMR spectra are good indices of decomposition, to which patterns of P transformation can be related, as discussed below.

Phosphorus transformations

Tate and Newman (1982) examined solution ^{31}P-NMR spectra of soil extracts from Tussock grassland soils in New Zealand, and found that the amounts of diester-P and phosphonate, correlated with annual precipitation, biomass-C and ATP concentrations along a climosequence. Similarly, Condron et al. (1990) noted in their study of native Saskatchewan soils that ^{31}P-NMR spectral characters related to conditions of moisture, vegetation and cultivation. Our results of ^{13}C and ^{31}P-NMR analyses show interesting linkages between OM decomposition and P transformations. To our knowledge this is the first study of soils utilizing both ^{31}P and ^{13}C-NMR, demonstrating the potential of this approach for studying nutrient cycling and other soil-related processes.

Positive correlations between the relative peak area of the P_i signal with carbonyl and aromatic C, and negative correlations with alkyl and O-alkyl C (Table 5), suggest that P mineralization is coupled to C decomposition and increases with increasing breakdown of the litter material (Dalal 1979; Tate 1984). The negative correlation between P_i and the C/N ratio also supports this conclusion. Similar correlations also exist when P_i concentration is calculated on a semi-quantitative, mass basis (i.e. the relative NMR signal of P_i versus total P for each horizon). Diester P and pyrophosphates are biologically-available forms (Stevenson 1986; Tate & Salcedo 1988), and both correlate positively with O-alkyl C and negatively with aromatic C (Table 5), suggesting that diester P and pyrophosphates undergo mineralization concomitantly with utilization of available C substrate (i.e. carbo-

Table 5. Significant correlations (r-values) and their probability levels (p-values) for solution ^{13}C and ^{31}P-NMR results and indexes of organic decomposition and P fractions ($n = 8$; only correlations with $p < 0.10$ are shown).

Organic & P fractions	Carbonyl C		Alkyl C		O-Alkyl C		Aromatic C		Methoxyl		C/N	
	r	p	r	p	r	p	r	p	r	p	r	p
Decomposition												
Carbonyl C											−0.79	0.016
Alkyl C	−0.79	0.016										
O-Alkyl C	−0.80	0.015	0.81	0.012							0.81	0.012
Aromatic C	0.64	0.089	−0.88	0.003	−0.93	0.0003					−0.63	0.099
P fractions												
P_i	0.82	0.011	−0.87	0.003	−0.76	0.027	0.81	0.012	−0.64	0.088	−0.68	0.064
Monoester P			0.63	0.095					0.91	0.001		
Diester P					0.63	0.099	−0.74	0.036				
Pyrophosphate					0.84	0.006	−0.72	0.043			0.89	0.002
P_{Biol} †					0.84	0.006	−0.81	0.012			0.82	0.010
P_{Labile} ‡	−0.71	0.050	0.79	0.017	0.79	0.016	−0.86	0.004			0.78	0.020

† P_{Biol} (biologically available P) = diester P + pyrophosphate; calculated from the ^{31}P-NMR spectra.
‡ P_{Labile} = resin P + $NaHCO_3$ (P_i & P_o); calculated from the 'Hedley' fractionation.

hydrates). In contrast, monoester P correlates with NaOH-extractable alkyl C, suggesting joint physical compartmentation of these functional groups, i.e. monoester P mineralization is linked to decomposition of plant structural components that include alkyl C and also C in the 50–60 ppm region ('methoxyl' C). Much of the monoester P in the NaOH extracts may originate from hydrolyzed, plant-derived phospholipids (products include glycerophosphate, inositol phosphate, choline phosphate and others), that are associated with cuticle and middle lamella tissue and cellular membranes (Hance & Anderson 1963; Salisbury & Ross 1985). There is a surprising lack of data in the literature regarding P compounds remaining in senescent leaves (and decomposing litter) after retranslocation by the plant occurs, and about the actual physical location of P in the senescent leaf structures. Dependence of P release from litter on structural decomposition may explain why phosphatase activity assays and geochemical fractionation schemes have not provided appropriate mechanistic explanations for the P mineralization process (Attiwill 1991; Tarafdar & Claassen 1988).

McGill and Cole (1981) suggested that P_o mineralization is controlled on a biological time scale by extracellular phosphatase, produced in response to demand for available P. Analysis of trends in C and P contents of soil sequences (chrono, topo and climo) revealed that organic C increases steadily with soil development, but P_o increases until primary-mineral P is depleted, then it shows a slow decline. As a result, the C/P_o ratio is high during the very early and late stages of soil development. McGill and Cole (1981) explained this trend by low P availability at these stages, inducing phosphatase production by biota and subsequent mineralization of P_o. Their analysis resulted in the current working-paradigm for P cycling in soils, i.e. that P availability is independent of OM decomposition over both biological and pedogenic time scales (Crews et al. 1995; McGill & Cole 1981; Smeck 1985; Tate & Salcedo 1988). A recent study of a soil chronosequence on volcanic parent material in Hawaii found low decomposition rates, low litter quality and high C/P_o ratios in the earliest and latest stages of soil development (Crews et al. 1995). However, their data suggest that the C/P_o trend is controlled by ecological factors such as site conditions and initial litter quality, rather than by activity of phosphatase as suggested by McGill and Cole (1981). Under conditions of low P availability, the energy invested by plants in retranslocation increases with increasing P deficiency, but the efficiency of P mineralization and removal may decrease because a greater proportion is incorporated in structural tissues (Miller 1984). As a result, the concentration of P released in plant litter will decrease with decreasing availability of P and will also be less accessible for mineralization. Thus, P availability may depend on conditions that are conducive for decomposi-

tion of the C structures occluding P, as our results suggest, rather than on optimal conditions for phosphatase activity. Results of Tarafdar and Claassen (1988), who examined plant uptake of P from added inorganic and organic compounds, support this hypothesis; they found that uptake rates from P_i and P_o sources were similar, suggesting that phosphatase activity is not the rate-limiting factor for P_o mineralization. Thus, on a biological time-scale, P availability is most likely limited by its accessibility, rather than by phosphatase activity as McGill and Cole (1981) suggested.

We cannot explain the correlation between monoester P and the so-called methoxyl C region, and we emphasize that this spectral region is shared with amine and peptide C and overlaps with adjacent signals from alkyl and O-alkyl regions (Sohn & Rajski 1990). For example, the peak located at 52–55 ppm in spectra of humic acids from aquatic environments is derived primarily from amino acid and peptide C, but in soil humic acids it is derived primarily from methoxyl C (Sohn & Rajski 1990). The correlation between free-radical concentrations measured by ESR and methoxyl region was weak and not significant ($r = 0.44$, $p = 0.50$, $n = 6$), as was the correlation between the free-radical concentrations and monoester P ($r = 0.57$, $p = 0.27$, $n = 6$). These results suggest that the peak in this region of our spectra and the strong correlation with monoester P are influenced by functional groups other than methoxyl C, of which amino acid and peptide C are of special interest. A week correlation between the methoxyl region and total N content ($r = 0.62$, $p = 0.11$, $n = 8$) provides some support for this hypothesis. Further research is needed to elucidate the nature of this spectral region for litter samples, and the significance of its correlation with monoester P. Solid-state dipolar dephased ^{13}C-NMR (Sohn & Rajski 1990) or spin-sorting on solution ^{13}C-NMR spectra (Preston & Blackwell 1985), may be appropriate techniques for future investigations.

Labile P (P_{Labile}), measured using the Hedley extraction, decreased in the pre-harvest profile with increasing depth, but remained constant in the post-harvest O horizons (Figure 5). Our results support the previous use of the Hedley extraction, labile-P index to represent the status of P across a wide range of soils (Cross & Schlesinger 1995). Correlations between P_{Labile} and the NMR indices for decomposition are strikingly similar to those between diester P, pyrophosphates and their sum, considered to be 'biologically available P' ($P_{Biol.}$) and the decomposition indices (Table 5).

High N, P, K, S and Ca concentrations in the newly-developed O_a horizon suggest that harvesting increased susceptibility to leaching and mineral-fixation of important nutrients from litter and decomposing OM in the upper profile. The ratio of bicarbonate-extractable P_o to labile P decreased in the pre-harvest profile with increasing depth, but remained constant and low in

the post-harvest profile (Figure 5) similar to the trends for diester P (Table 2). We also noted that labile P, measured using the Hedley extraction, was high in post-harvest O horizons. These results support the suggestion by Wood et al. (1984) that forest harvesting may result in P mineralization which, with the lack of plant uptake, exceeds microbial demand. However, the formation of a post-harvest humified organic layer (O_a), in contrast to the original organic-rich, mineral horizon (A_o) at the litter-mineral interface (Table 1), suggests reduced faunal activity incorporating OM into the mineral soil. This, and the buildup of labile P in the post-harvest O horizons, suggests that less soil mixing by soil fauna may provide a negative feedback mechanism by which P is conserved in biologically-available forms, until plant growth and P uptake are restored. The concentrations of post-harvest total P and P_i in the A horizons were not different from pre-harvest concentrations. Similarly, estimates by Yanai (1991) for the Hubbard Brook hardwood forest in New Hampshire, suggest a negligible post-harvest increase in the P-movement from the litter to the mineral soil (0.7 kg ha^{-1} yr^{-1}), especially compared to the amount of P stored in the O layers (85 kg ha^{-1}). However, decreases of A horizon diester P and pyrophosphates, as shown in the ^{31}P-NMR spectra, support the notion that biologically available P in mineral horizons could be transformed and fixed during the first post-harvest season as a result of reduced plant uptake (Walbridge et al. 1991).

Conclusions

Solid-state and solution ^{13}C-NMR provided evidence that litter decomposition in this Mediterranean-climate, mixed-conifer forest is characterized by increasing aromatic C and plant-derived alkyl C with increasing depth in the soil without buildup of humified alkyl C, which generally occurs in other ecosystems. Inorganic P, monoester P, diester P and pyrophosphates were identified by the use of ^{31}P-NMR. In forest soils, where biological cycling of P is the dominant process controlling short-term P availability, NMR provides meaningful biochemical fractions, compared to the operational ones acquired using wet-chemistry techniques.

Strong correlations between inorganic P and C fractions in the surface horizons of a forest soil, support the hypothesis that P mineralization is coupled with decomposition of OM. Correlations with different C fractions suggest that diester P and pyrophosphates undergo mineralization that proceeds with a general increase in decomposition and decrease of available C substrate (carbohydrates). In contrast, we suggest the monoester P fraction is primarily associated with structural components of the senescent plant mate-

rial, and is therefore released from litter with the gradual breakdown of alkyl C structures.

Forest harvesting resulted in the rapid development of an O_a horizon above the mineral surface with high labile-P_i concentrations, suggesting a potential for leaching and subsequent mineral-fixation of the previously biologically-cycled P. However, post-harvest reduction in mixing of litter into the mineral soil by soil fauna is likely to provide a negative feedback mechanism and reduce potential losses. In contrast, there is evidence that biologically available P in the mineral soil is transformed and fixed.

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