

Characterization and Transformations of Organic Carbon Pools by ^{13}C CPMAS NMR in Coastal Forest Chronosequences of Southern Vancouver Island

Introduction

Studies of forest C pools rarely characterize the organic C components. Analysis is difficult because of the complexity of the biomass inputs and their subsequent microbial and chemical transformations. We are using solid state nuclear magnetic resonance spectroscopy with cross-polarization and magic-angle spinning (^{13}C CPMAS NMR) (Baldoek and Preston 1995; Preston et al. 1990, in press) to characterize selected organic matter pools of the coastal forest chronosequence (CFC) project.

Methods and Materials

Detailed information on the CFC study sites and sampling is provided elsewhere (Trofymow and Porter, this issue). The NMR study was carried out on plot-level composite samples, except for coarse woody debris (CWD), for which selected samples were analysed. Two categories of woody debris were examined: fine woody debris (FWD) <1 cm in diameter, and CWD >12 cm diameter. The CWD was identified to species—Douglas-fir (*Pseudotsuga menziesii*), western hemlock (*Tsuga heterophylla*) and western redcedar (*Thuja plicata*)—where possible, and assigned a decay class of I to V in the field (Preston et al. 1990, in press). Forest floor (sieved to <8 mm) was separated into LFH and live roots (LFH-ROOTS). Water-floatable organic matter/roots were separated from the 2-8- and <2-mm fractions of 10-30-cm depth mineral soil. CPMAS ^{13}C NMR was carried out using a Bruker CXP-100 spectrometer (Preston et al. in press). Spectra were divided into chemical shift regions whose areas were integrated and expressed as a percentage of total area. Proportions of lignin and polysaccharide C were determined for CWD only (Preston et al. 1990, in press). Data for other pools were analysed using principal component analysis (PCA) with the relative NMR areas as variables.

Results and Discussion

As previously found (Preston et al. 1990), CWD samples from both east- and west-side sites (zone) and all stand ages (sere) showed an initial phase of non-selective loss (decay classes I to III), followed by selective loss of polysaccharide and accumulation of lignin in classes IV and V (Preston et al. in press). Figure 1 shows the progression for Douglas-fir wood, with decrease of the sharp polysaccharide peak (73 ppm), and increasing prominence of the lignin features, including methoxyl C at 57 ppm and phenolic C at 148 ppm. This pattern suggests a transition from white-rot fungi to brown-rot fungi in the final stages, with little alteration of the remaining lignin (Baldoek and Preston 1995).

Representative spectra of the other organic carbon pools are shown in Figure 2. Spectra of FWD (Figure 2a) were similar to fresh or slightly decomposed wood. They had relatively sharp features dominated by the peaks for polysaccharide, but also showed features due to tannins (phenolic peaks at 145 and 155 ppm) and suberin (alkyl peak at 30 ppm) from bark. The FWD spectra were similar to each other, with little effect of sere or zone. Spectra of LFH-ROOTS had sharp features, and considerable variation in their tannin and suberin contents; note that the aromatic C signals originate largely from tannins rather than lignin. Older and west-side sites tended to have higher aromatic, phenolic, and alkyl C (e.g. Figure 2b), presumably associated with increasing proportions of tannin and suberin in roots.

The LFH spectra had broader peaks than those of FWD or LFH-ROOTS, due to an increased extent of decomposition (Figure 2c). For LFH, positive scores on the first principal component (PC1) were associated with increasing lignin (woody origin), and negative PC1 scores with forest floor derived from litter and roots, with prominent

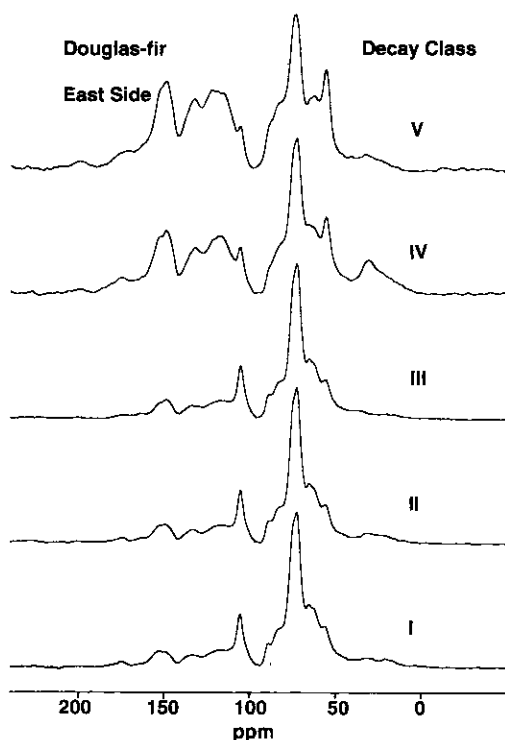


Figure 1. Solid-state ^{13}C CPMAS NMR spectra of Douglas-fir CWD of different decay classes.

features of tannins, cutin (sharper alkyl signal at 30 ppm) and suberin. For PC2, the largest loading was positive for carboxyl C, associated with increasing oxidation. There was a zonal effect, with more of the west-side samples having higher PC1 scores (more woody input). This is consistent with the greater detrital C accumulations on the west side (Trofymow and Blackwell, this issue). The lack of a sere effect in this and other pools may reflect the limited history of logging in this region, so that disturbed sites still largely reflect accumulated legacy carbon.

Spectra of the 2-8 mm floatables showed high variability, which was not generally related to sere or zone, but to individual site inputs of charcoal (aromatic peak at 130 ppm, Figure 2d), tannin (similar to Figure 2b), or wood (brown-rot residue, similar to Figure 1, decay class V). The samples with a charcoal fingerprint were all from the east side, while the two samples with a distinctive woody signature were from the west side. Similarly, the spectra of the <2-mm floatables did not show consistent sere or zone variation, but more attenuated features of woody or tannin in-

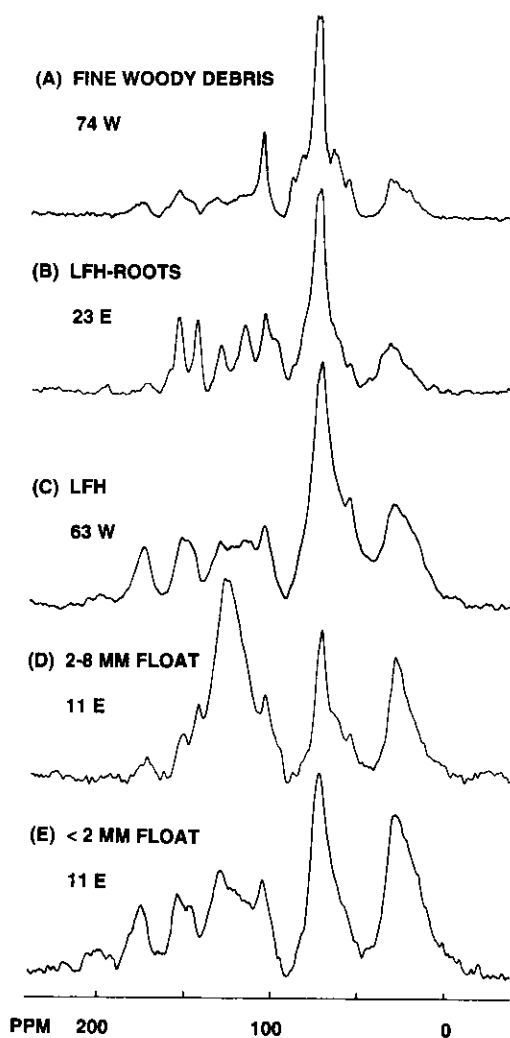


Figure 2. Solid-state ^{13}C CPMAS NMR spectra of organic matter from CFC sites (code gives plot and zone).

put (increasing lignin content along PC1). They also showed more variation in degree of decomposition, with PC2 associated with increasing carboxyl C and higher alkyl/O-alkyl C ratio (Baldock and Preston 1995) (Figure 2e).

In summary, ^{13}C CPMAS NMR spectroscopy was used to characterize organic matter pools in CFC sites. The use of PCA provided site-specific insight into inputs, decomposition processes, and nature of past disturbances, and indicated that natural biogeoclimatic forces still dominate carbon pools in CFC project sites.

Literature Cited

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