Reproduced from Journal of Environmental Quality. Published by ASA, CSSA, and SSSA. All copyrights reserved.

# Chemical and Carbon-13 Cross-Polarization Magic-Angle Spinning Nuclear Magnetic Resonance Characterization of Logyard Fines from British Columbia

C. M. Preston* and P. D. Forrester


## ABSTRACT

**Phasing out beehive burners and rising costs for landfilling have increased the need to widen options for utilization of the smaller size fractions of woody wastes generated during log handling and sawmilling in British Columbia. We characterized several size classes of logyard fines up to 16 mm sampled from coastal and interior operations. Total C, total N, ash, and condensed tannin concentrations were consistent with properties derived largely from wood, with varying proportions of bark and mixing with mineral soil. Especially for <3-mm fractions, the latter resulted in high ash contents that would make them unsuitable for fuel. Solid-state $^{13}C$ cross-polarization magic-angle spinning (CPMAS) nuclear magnetic resonance (NMR) spectra were consistent with the chemical data, with high O-alkyl intensity and similarity to naturally occurring woody forest floor; no samples were high in aromatic or phenolic C. Aqueous extracts of two <16-mm fines, which accounted for only a small proportion of the total C, were enriched in alkyl C and had low or undetectable tannins. Application to forest sites might cause short-term immobilization of N, but also might include possible longer-term benefits from reduction of N loss after harvesting and restoration of soil organic matter in degraded sites.**


Logyard residues are generated during the handling of logs before their introduction into sawmilling or pulping facilities. For many years, beehive burners and their smoke emissions were a familiar part of the British Columbia landscape, as much of this woody waste was disposed of in this manner or buried in landfills. Due to increasing concern with air quality, these burners are being phased out, while increasing disposal costs and environmental concerns are also reducing the opportunities for landfilling (Forrester, 1999).

Much of the residue generated in logyards is already reclaimed and used for wood chips, hog fuel (used for on-site power generation), and rock for surfacing, but the fines present a challenge (MacDonald, 2001; Forrester, 1999). This material, of approximately 5 cm or less, is often high in ash and moisture, and therefore not suitable as a fuel or as feedstock for pulp or fiberboard. Possible alternative uses include landscaping products, land rehabilitation, and composting with agricultural wastes and sewage sludge. However, utilization has been hindered both by economic considerations (e.g., high transport costs) and by environmental concerns, especially the potential for leachate production (Folk and Campbell, 1990).

C.M. Preston, Pacific Forestry Centre, Natural Resources Canada, 506 West Burnside Road, Victoria, BC, Canada V8Z 1M5. P.D. Forrester, Forest Engineering Research Institute of Canada, 2601 East Mall, Vancouver, BC, Canada V6T 1Z4. Received 14 May 2003. *Corresponding author (cpreston@pfc.cfs.nrcan.gc.ca).

Published in J. Environ. Qual. 33:767–777 (2004).
© ASA, CSSA, SSSA
677 S. Segoe Rd., Madison, WI 53711 USA

Previous research specifically on logyard fines has been limited to a few studies on physical and chemical properties (Folk and Campbell, 1990), utilization as a soil amendment (Zeng et al., 1993), and options for marketing and utilization (Campbell and Tripepi, 1992; MacDonald, 2001). Our ability to predict the behavior of land-applied logyard fines requires more comprehensive information on their chemical composition, especially the carbon-containing building-blocks. Once material has been reduced to small particle sizes, mixed with mineral matter (many British Columbia logyards are unpaved), or stored for varying lengths of time, it is poorly served by traditional wet chemical methods such as proximate analysis (Preston, 1996; Preston et al., 1997).

The technique of nuclear magnetic resonance spectroscopy with cross-polarization and magic-angle spinning ($^{13}C$ CPMAS NMR) is well suited for characterizing directly the bulk organic composition of complex, insoluble samples as dry powders. It has been applied to many types of organic matter (Preston, 1996), including decomposing wood in forest ecosystems (McColl and Powers, 1998; Preston et al., 1990, 1998b), sewage sludge, and composts (Pichler et al., 2000; Preston et al., 1998a; Veeken et al., 2001).

In 1996, the Forest Engineering Research Institute of Canada (FERIC) and the Pacific Forestry Centre started a project to characterize logyard residues and test equipment to separate the organic and inorganic components under operational conditions. The original objective was to reduce the mineral content of fines to enhance their potential for production of energy. However, this remains largely uneconomic, while their potential as soil amendments is becomingly increasingly attractive. We present chemical and spectroscopic characterization of fines from British Columbia logyards, including results from a commercial composting operation, and water-extractable carbon. Our purpose is to provide information to assess the suitability of these materials as soil amendments, in particular for forestry applications.

## MATERIALS AND METHODS

### Lavington Logyard Site

In this paper, we use the term *logyard* to include log sortyards. Technically, a logyard is an area where sorted logs are stockpiled at a sawmilling or pulping facility, and a log sortyard is an area where logs are accumulated for measuring and

**Abbreviations:** C–DOC, combined colloidal and dissolved organic carbon fraction; CP, cross-polarization; CS, clean, sorted; CU, clean, unsorted; CT, condensed tannins; DD, dipolar-dephasing; DOC, dissolved organic carbon; DS, dirty, sorted; DU, dirty, unsorted; MAS, magic-angle spinning; NMR, nuclear magnetic resonance; POC, particulate organic carbon; TOSS, total suppression of sidebands.

Reproduced from Journal of Environmental Quality. Published by ASA, CSSA, and SSSA. All copyrights reserved.

grading before being forwarded to a processing facility. In general, the former installation is common in the interior of British Columbia, whereas the latter is more often found on the coast.

The main study was performed in summer 1996 during cleanup of a one-year accumulation of logyard residues by Tolko Industries Limited at its Lavington Planer Mill Division, east of Vernon, in the central-interior of British Columbia. A contractor was brought in with a separation system to reduce the residue flow to a landfill by reclaiming rock for logyard maintainance and wood and bark for burning, and also to find an alternate use for the fines component of the residue. The main species were lodgepole pine (*Pinus contorta* Douglas ex Loudon var. *latifolia* Engelm.) and Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco].

The objectives of the research project were threefold: (i) characterize residue types in the logyard, (ii) assess the costs and efficacy of the operational separation, and (iii) characterize the smallest size fractions before and after separation. For the first objective, five residue types were identified in this sortyard:

- Dirty, sorted (DS): Residues accumulated (after larger wood removed for chipping) when the logyard gravel surface was wet.
- Dirty, unsorted (DU): As above but with larger wood not removed.
- Clean, sorted (CS): Residues accumulated (after larger wood removed for chipping) when the logyard gravel surface was frozen.
- Clean, unsorted (CU): Residues accumulated (larger wood not removed) on the paved apron at the log infeed deck to the sawmill.
- Deal processor (DP): Material accumulated after residues were processed through a Deal processor (i.e., classifier–debarker; V.K. Brunet Ltd., New Westminster, BC, Canada) to reclaim chippable wood.

Examples of these residue types were manually sorted on site to determine their distribution in nine size classes (>100 cm, 60–100 cm, 30–60 cm, 15–30 cm, 7.5–15 cm, 3.2–7.5 cm, 13–32 mm, 3–13 mm, and <3 mm). Proportions of wood, slab, bark, branch, rock, and glass were determined for the four largest size classes. After completion of this preliminary survey, the accumulated residues were separated using a system based on a Powerscreen (Dungannon, Northern Ireland) 830 trommel (a cylindrical rotating screen) and a General Kinematics (Crystal Lake, IL) destoner. Recoveries were 10 to 15% by weight for reclaimed rock for logyard surfacing and 4 to 16% of wood and bark for burning, bringing the total residue utilized to 16 to 26%. The fines fraction from the separation was that retained by the 16-mm trommel screen. More detailed reports are available on the sorting and trommel screen separation, including weight and volume data, and economic analysis (Forrester, 1999; Forrester and Preston, 2002).

## Vancouver Island Samples

Another sample of <16-mm fines was obtained from a similar trommel screen operation at Port Alberni on Vancouver Island and three compost samples from a commercial operation near Port McNeill on northern Vancouver Island. The main species were western hemlock [*Tsuga heterophylla* (Raf.) Sarg.] and western red cedar (*Thuja plicata* Donn ex D. Don). The compost process also used <16-mm trommel screen fines for composting with ensiled wastes (fish morts) from local fish farms. The three compost samples were taken from different positions in one pile (left, middle, right).

Reference samples of wood and bark were obtained from top, middle, and base sections along the stem of a 45-yr-old Douglas-fir. This tree was cut in a forest site near Victoria on southern Vancouver Island to provide baseline samples for studies of wood decomposition. Two other samples of thicker Douglas-fir bark were obtained from sites of logging debris on the western coast of Vancouver Island in May 1997. Heartwood of old-growth western hemlock was that used for the Canadian Intersite Decomposition Experiment (CIDET) (Preston et al., 2000).

## Sample Processing and Leaching Study

Chemical characterization of the Lavington logyard wastes for this study was limited to the two smallest size classes, 3 to 13 mm and <3 mm. Of the five replicates from the site, two of each residue type were taken for analysis. The 3- to 13-mm fraction was obviously a mixture of woody fragments and small rocks, except for CU, which was essentially all organic. To facilitate chemical and NMR analyses, the organic fraction was separated by floatation and the rock fragments dried at 70°C, weighed, and discarded. The other samples (<3-mm fraction, <16-mm trommel screen fines, and composts) were used as received. Subsamples for analysis were dried at 70°C and ground through a Wiley mill to pass a 60-mesh (250-μm) screen (woody materials) or finely ground in a Siebtechnik (Mülheim an der Ruhr, Germany) mill (<3-mm fraction).

To give some indication of their possible leaching behavior, the <16-mm trommel screen fines were extracted with water. Two liters of distilled water were added to 1000 g (wet weight) of the fines in a large carboy that was shaken for 2 h. This resulted in a suspension that was poured through a 1-mm sieve. The residue was returned to the carboy and the process repeated. The resulting 4-L volume from the Alberni fines was run through a succession of filters down to a 2.7-μm glass-fiber filter. The retained material, designated as particulate organic carbon (POC; 2.7 μm–1 mm), was dried at 70°C. The 2.7-μm filter was used to define a combined colloidal and dissolved organic carbon fraction (C–DOC), as very little of the solution could be passed though a 1.0- or 0.45-μm filter. The aqueous phase (<2.7 μm) was reddish-amber in color, scattered light, and remained in suspension apparently indefinitely; a 2-L portion was freeze-dried for analysis.

Extraction of the Lavington <16-mm fines produced a very dark gray soupy mixture (<1 mm) that proved impossible to filter directly. Two liters were processed by centrifugation at 8000 rpm, and the resulting pale yellow solution was filtered to 2.7 μm. Although this solution did not scatter light and could pass through a smaller pore size, it was decided to use the same filter pore size for both extracts. As for the Alberni extraction, 2 L of the aqueous phase (C–DOC) was freeze-dried, and the 2.7 μm- to 1-mm material (POC) was dried at 70°C and a subsample finely ground for analysis. The extraction residue (>1 mm) was obviously high in rock fragments, which were separated, weighed, and discarded, as for the 3- to 13-mm logyard wastes. A subsample of the organic fraction was ground in a Wiley mill for analysis.

## Chemical Analysis

Sample total C was analyzed by automatic combustion using a LECO (St. Joseph, MI) CR12 analyzer and total N by a Kjeldahl method (Preston et al., 1998b), due to the very low N concentration of many samples. Ash was determined by heating at 650°C for 16 h. The butanol–HCl (*proanthocyanidin*) assay was used to determine condensed tannin content

Reproduced from Journal of Environmental Quality. Published by ASA, CSSA, and SSSA. All copyrights reserved.

of the samples, as the sum of extractable (70:30 acetone to water) and residual insoluble tannins as described in detail previously (Preston, 1999; Lorenz et al., 2000), with standardization against a purified condensed tannin from balsam fir [*Abies balsamea* (L.) Mill.].

### Carbon-13 Cross Polarization Magic Angle Spinning Nuclear Magnetic Resonance Spectroscopy

Solid-state $^{13}C$ CPMAS NMR spectra were run on a MSL 300 spectrometer (Bruker Instruments, Karlsruhe, Germany) operating at 75.47 MHz. To facilitate magic-angle spinning, subsamples of the 60-mesh materials were more finely ground using liquid nitrogen and a mortar and pestle. Samples were spun at 4.7 kHz in 7-mm-diameter zirconium oxide rotors. Spectra were acquired with a 1-ms contact time and 2-s recycle time, and up to 80 000 scans for the samples lowest in C. Spectra were processed using 30- to 40-Hz line-broadening and baseline correction. Due to their low C content, spectra of the <3-mm fractions were distorted by a broad background signal from the probe and rotor cap. This was corrected by subtraction of the free induction decay obtained from an empty rotor, scaled to match the number of scans (Preston, 2001). Chemical shifts are reported relative to tetramethylsilane (TMS) at 0 ppm, with the reference frequency set using adamantane. Dipolar-dephased (DD) spectra were generated by inserting a 40- to 50-μs delay period without $^{1}H$ decoupling between the cross-polarization and acquisition portions of the CPMAS pulse sequence. For most samples with >100 g kg$^{-1}$ C, the DD spectra were obtained using the total suppression of sidebands (TOSS) sequence for total suppression of spinning sidebands.

Spectra were divided into chemical shift regions as follows: 0 to 45 ppm, alkyl C; 45 to 93 ppm, methoxyl and O-alkyl C; 93 to 112 ppm, di-O-alkyl C and some aromatics; 112 to 140 ppm, aromatic C; 140 to 165 ppm, phenolic C; and 165 to 190 ppm, carboxyl C. Areas of the chemical shift regions were determined after integration and expressed as percentages of total area ("relative intensity"). Areas were not corrected for spinning sidebands, as these were relatively small, and their effect would be similar among most of the samples. The low signal to noise ratio of many <3-mm samples also precluded accurate measurement of the spinning sideband integrals. There are other limitations in the quantitative reliability of CPMAS spectra, but it is appropriate to use them to compare intensity distributions among similar samples and to use DD spectra to point out general structural features (Preston, 2001). The TOSS spectra can suffer from additional distortions, but this technique was only used in combination with DD for qualitative interpretation.

## RESULTS AND DISCUSSION

### Chemical Analysis of Logyard Fines

Chemical data for samples from the Lavington logyard survey are shown in Table 1. Except for the CU category, the 3- to 13-mm samples were very high in rock fragments, which constituted up to 90% of their dry weight. The organic components that had been separated by water floatation and hand-sorting were still high in mineral content, with 373 to 559 g kg$^{-1}$ ash, 220 to 300 g kg$^{-1}$ C, and 1.6 to 2.9 g kg$^{-1}$ N. The intact CU samples from the paved deck were cleaner, with the duplicate samples having 256 and 87 g kg$^{-1}$ ash, 368 and 469 g kg$^{-1}$ C, and 2.1 and 2.8 g kg$^{-1}$ N. The <3-mm fractions were even lower in organic matter, with 36 to 185 g kg$^{-1}$ C and 0.7 to 2.1 g kg$^{-1}$ N and lower C to N ratios than the corresponding 3- to 13-mm fractions. The CU materials had the highest organic content for both size fractions. Properties of the 3- to 13-mm fines are similar to those reported by Folk and Campbell (1990) and Zeng et al. (1993). The high mineral content of fines of both size classes would make them unsuitable as fuel (Folk and Campbell, 1990).

Chemical data for wood and bark samples, which are representative of the main organic inputs to the woody wastes in this study, are shown in Table 2. Fresh Douglas-fir and western hemlock heartwood have high total C and C to N ratio, and low total N, ash, and condensed tannins (CT). Compared with wood, the bark samples have generally higher total C contents, up to 588 g kg$^{-1}$ and CT up to 85.6 g kg$^{-1}$. Ash values are higher, and C to N ratios lower, due to higher N content than wood. With increasing age and thickness, bark from the freshly felled Douglas-fir of 45 yr has decreasing N and ash, and increasing CT, to more than 8% of total weight. Compared with the fresh base bark, the thicker bark samples picked up from the landing site differed mainly in having slightly higher total C, but only about half of the tannin content. Results for C, N, and ash concentrations of wood and bark are similar to those reported for Douglas-fir (Schowalter and Morrell, 2002), red fir (*Abies magnifica* A. Murr.; McColl and Powers, 1998), and several coastal conifer species (Edmonds, 1987).

Condensed tannin contents were up to 4 g kg$^{-1}$, except for the 3- to 13-mm CU samples, with up to 17.8 g kg$^{-1}$. This may reflect higher bark content, although they

**Table 1. Analytical data for the <3- and 3- to 13-mm logyard fines.**

| | | <3-mm Total sample | | | | | 3- to 13-mm Organic fraction | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Residue type | Code | C | N | Ash | CT† | C to N ratio | Mass | C | N | Ash | CT | C to N ratio |
| | | g kg$^{-1}$ | | | | | % of total | g kg$^{-1}$ | | | | |
| Dirty, sorted | DS 16 | 67 | 1.1 | 836 | 0.2 | 61 | 22.4 | 220 | 2.1 | 559 | 1.4 | 105 |
| | DS 25 | 48 | 0.7 | 896 | 0.2 | 68 | 12.8 | 222 | 1.8 | 544 | 1.5 | 123 |
| Dirty, unsorted | DU 4 | 36 | 0.7 | 919 | 0.1 | 51 | 9.6 | 237 | 1.6 | 529 | 1.7 | 148 |
| | DU 35 | 52 | 1.0 | 877 | 0.2 | 52 | 31.5 | 246 | 2.3 | 545 | 2.3 | 107 |
| Clean, sorted | CS 18 | 104 | 1.3 | 787 | 0.4 | 80 | 64.8 | 286 | 2.5 | 373 | 4.0 | 114 |
| | CS 56 | 98 | 1.4 | 800 | 0.3 | 70 | 42.5 | 253 | 2.9 | 499 | 1.7 | 87 |
| Clean, unsorted | CU 2 | 185 | 2.1 | 635 | 3.4 | 88 | 100.0 | 368 | 2.1 | 256 | 15.0 | 175 |
| | CU 11 | 154 | 1.6 | 688 | 2.0 | 97 | 100.0 | 469 | 2.8 | 87 | 17.8 | 168 |
| Deal processor | DP 9 | 53 | 1.3 | 889 | 0.2 | 41 | 11.3 | 299 | 2.7 | 397 | 1.1 | 111 |
| | DP 64 | 60 | 1.4 | 871 | 0.1 | 43 | 13.8 | 261 | 2.9 | 478 | 0.8 | 90 |

† Condensed tannins.

Reproduced from Journal of Environmental Quality. Published by ASA, CSSA, and SSSA. All copyrights reserved.

**Table 2. Analytical data for <16-mm trommel fines and fractions from leaching study.†**

| Fraction | Lavington | | | | | Alberni | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Mass | C | N | CT‡ | C to N ratio | Mass | C | N | CT | C to N ratio |
| | % of total | g kg$^{-1}$ (% recovery) | | | | % of total | g kg$^{-1}$ (% recovery) | | | |
| Fines (<16 mm) | 100.0 | 117 | 1.5 | 0.6 | 77 | 100.0 | 443 | 3.4 | 4.5 | 130 |
| Residue (>1 mm) | 16.9§, 51.3¶ | 430§ (62.2) | 2.1§ (23.4) | 2.8 (75.6) | 205 | 83.9 | 443 (83.9) | 2.8 (69.1) | 5.3 (99.4) | 158 |
| POC# (2.7 μm–1 mm) | 21.2 | 191 (34.6) | 3.0 (41.9) | 0.7 (23.9) | 64 | 8.4 | 370 (7.0) | 3.3 (8.2) | 0.7 (1.2) | 112 |
| C–DOC†† (<2.7 μm) | 0.3 | 364 (0.8) | 4.2 (0.8) | 0.3 (0.2) | 87 | 0.6 | 402 (0.5) | 12.9 (2.1) | ND‡‡ (0) | 31 |
| Recovery, % | 89.7 | 97.6 | 66.1 | 99.7 | | 92.9 | 91.4 | 79.4 | 100.6 | |

† Ash content was 558 g kg$^{-1}$ for Lavington and 205 g kg$^{-1}$ for Alberni.
‡ Condensed tannins.
§ Organic component after hand-separation.
¶ Mineral component not analyzed.
# Particulate organic carbon.
†† Combined colloidal and dissolved organic carbon fraction.
‡‡ Not detected.

were well below the 37 to 86 kg kg$^{-1}$ range of the bark samples (Table 2). Tannin contents of wood samples were much lower. None was detected in western hemlock wood, and Douglas-fir was around 1 g kg$^{-1}$, similar to values found by Dellus et al. (1997). In fact, concentrations in this range are difficult to measure, due to large background absorbances, and may include structures modified by reactions of the B ring (Dellus et al., 1997). The CT concentrations are comparable with those found in forest litter and humus layers, which are usually <5 g kg$^{-1}$ (Preston, 1999; Lorenz et al., 2000; Kranabetter and Banner, 2000), although up to 40 g kg$^{-1}$ were reported for some black spruce [*Picea mariana* (Mill.) Britton et al.] sites in northern Ontario (Lorenz et al., 2000).

## Trommel Screen Fines and Wood-Fish Composts

The <16-mm trommel screen fines from Lavington (117 g kg$^{-1}$ C, 1.5 g kg$^{-1}$ N; Table 3) were obviously contaminated with soil and small rock fragments, with a black color mixed with gray particles. The Alberni sample, which came from a paved sortyard, was reddish-brown with very few rock fragments, consistent with its higher C, N, and tannin contents. To characterize the general nature of components that might be released under leaching conditions, we extracted the <16-mm fines with water and generated three fractions; insoluble residue of >1 mm in diameter, material 2.7 μm to 1 mm that remained in suspension (POC), and dissolved plus colloidal material of <2.7 μm (C–DOC). For both samples, no fraction showed unduly high tannin levels (maximum 5.3 g kg$^{-1}$ in the Alberni insoluble residue). In particular, the C–DOC fractions accounted for less than 1% of total mass and carbon, and had the lowest tannin concentrations, with tannins in the Alberni C–DOC fraction below detection.

**Table 3. Analytical data for coastal fish–wood composts and some reference wood and bark samples (Spar, Landing) from Douglas-fir (DF) or western hemlock (WH).**

| Sample | C | N | Ash | CT | C to N ratio |
|---|---|---|---|---|---|
| | g kg$^{-1}$ | | | | |
| **Composts** | | | | | |
| Left | 452 | 3.5 | 187 | 2.6 | 129 |
| Middle | 395 | 4.2 | 297 | 0.8 | 94 |
| Right | 404 | 5.0 | 291 | 0.9 | 81 |
| **Wood** | | | | | |
| WH wood | 498 | 0.4 | 4.0 | 0 | 1245 |
| DF wood | 498 | 1.1 | 0.3 | 1.2 | 449 |
| **Douglas-fir bark** | | | | | |
| DF top | 486 | 2.5 | 11.8 | 53.4 | 194 |
| DF mid | 547 | 1.7 | 8.9 | 68.6 | 322 |
| DF base | 545 | 1.5 | 6.5 | 85.6 | 363 |
| Spar | 588 | 1.5 | 9.7 | 37.0 | 392 |
| Landing | 584 | 1.8 | 9.8 | 39.2 | 324 |

The compost samples represent operational conditions for processing wood with fish farm wastes on northern Vancouver Island. Samples taken from the middle and right side of the pile were similar, and had a higher degree of decomposition than the left-side sample (Table 3). The latter was higher in C, C to N ratio, and ash, and lower in CT and ash. The less-decomposed left-side sample appears similar to the 3- to 13-mm samples from Lavington and the 16-mm Alberni trommel screen fines, whereas the more decomposed samples mainly differ in having higher total N and lower CT. These commercially produced composts still had the look and feel of woody fragments and seem to be less altered, with higher C and lower N contents than some reported composts from wood and fish or seafood wastes (Jellum et al., 1995; Liao et al., 1997; Laos et al., 1998) which were prepared with richer initial mixes and more optimal conditions for decomposition.

## Carbon-13 Cross Polarization Magic Angle Spinning Nuclear Magnetic Resonance—Bark and Wood

To facilitate interpretation of the residue spectra, we first show normal and DD $^{13}$C CPMAS NMR spectra of wood and bark (Fig. 1), the main organic inputs to the logyard fines. Relative areas of all spectra are found in Table 4. The spectrum of fresh Douglas-fir wood (Fig. 1a) is typical of gymnosperms with guaiacyl lignin (Czimczik et al., 2002; McColl and Powers, 1998; Preston et al., 1998b), and dominated by strong signals from cellulose at 63 and 65 ppm (C6), 73 and 75 ppm (C2, C3, C5), 83 and 89 ppm (C4), and 105 ppm (C1). Guaiacyl lignin produces the sharp signal for methoxyl at 56 ppm and the broader peaks in the aromatic and phenolic region, and acetate the small peaks at 22 and 173 ppm. For guaiacyl lignin, the phenolic region typically has a peak at 147 to 148 ppm with a shoulder at 152 ppm.

Reproduced from Journal of Environmental Quality. Published by ASA, CSSA, and SSSA. All copyrights reserved.

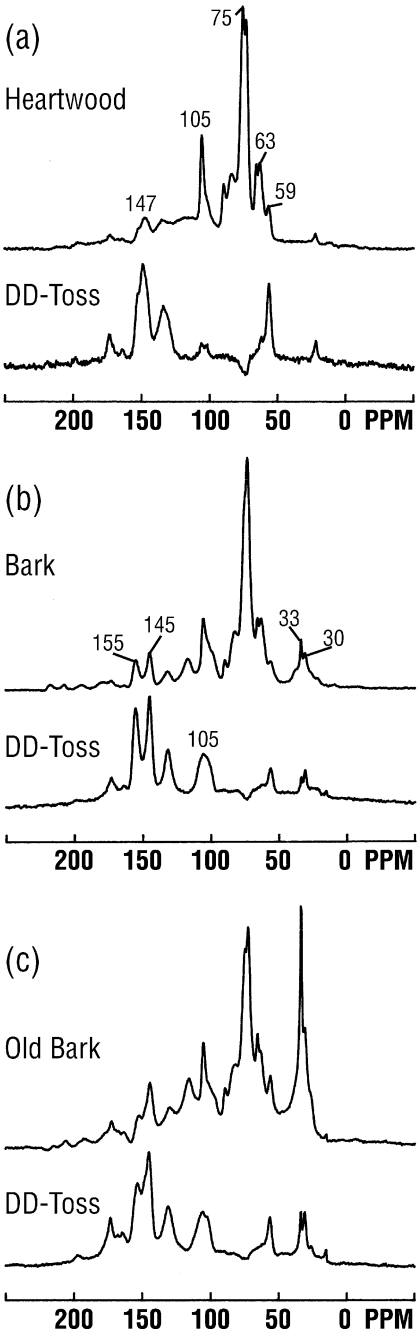


**Fig. 1. Solid-state $^{13}C$ nuclear magnetic resonance spectra with cross-polarization magic-angle spinning (CPMAS NMR) of (a) heartwood and (b) bark from the mid-section of a Douglas-fir stem and (c) weathered Douglas-fir bark from a roadside log handling site. Lower spectra are with dipolar-dephasing and total suppression of sidebands (DD–TOSS).**

The DD–TOSS spectrum is also typical, with the main peaks due to methoxyl C, C- and O-substituted aromatic C, and carboxyl C. Spectra of heartwood from old-growth western hemlock (not shown) were very similar. The relative areas (Table 4) reflect the dominance of cellulose and hemicellulose structures, with highest intensity in the O-alkyl region and low alkyl to O-alkyl ratios.

The spectrum of bark from the mid-section of a 45-yr-old Douglas-fir (Fig. 1b) has much more intensity in the alkyl region, while the phenolic region has two peaks at 145 and 155 ppm. The lower intensity of the methoxyl signal in both the normal and DD spectrum, and the large splitting of the phenolic signal, indicate a high proportion of condensed tannins compared with lignin (Preston, 1999; Preston and Sayer, 1992). Barks also contain suberin, a complex material with both phenolic and aliphatic components, the latter producing the alkyl intensity with peak maxima at 30 and 33 ppm (Perra et al., 1995; Bernards, 2002; Yan and Stark, 2000).

Similar contrasts between bark and wood spectra were found by McColl and Powers (1998) for red fir. We previously reported spectra run at lower magnetic fields of the three fresh Douglas-fir bark samples from the 45-yr-old tree (Preston, 1996). As shown there, spectra of the other two samples had similar features, and from the top to the bottom section, had decreasing O-alkyl intensity and increasing intensity in the alkyl, aromatic, and phenolic regions. Consistent with the chemical data for total C and condensed tannins, these trends indicate increasing proportions of suberin and tannins for older bark.

The thick bark from an old-growth Douglas-fir (Fig. 1c) has even lower O-alkyl intensity characteristic of carbohydrate, and higher alkyl, aromatic, and carboxy intensity. These indicate higher proportions of suberin and perhaps secondary compounds such as resin acids. There is a higher proportion of lignin to tannin, with greater methoxyl intensity and broadening and increased intensity of the peak at 145 ppm due to the overlap with the lignin peak at 148 ppm. For both bark samples, the broad peak at 105 ppm in the DD–TOSS spectra is a characteristic marker of tannins; by comparison the heartwood spectrum has a very weak signal in this region. Both NMR and chemical analysis indicate lower tannin contents for the older barks.

The DD–TOSS spectra of the bark samples also retain intensity for the methoxyl signal of lignin, and peaks at 30 and 33 ppm in the alkyl region for $CH_2$ in long chains. Intensity is lost at a faster rate for the peak at 33 ppm, which represents components with lower molecular mobility than at 30 ppm (Pichler et al., 2000).

## Carbon-13 Cross Polarization Magic Angle Spinning Nuclear Magnetic Resonance—Logyard Fines

Spectra of <3- and 3- to 13-mm fines (Fig. 2) are represented by three of the five categories. The spectra can be interpreted by considering them as mainly wood mixed with some bark, and modified by leaching, decomposition, and incorporation of soil particles from manipulation and outdoor storage for up to one year. In most cases there was good agreement between the relative areas of the two replicates (Table 4), and in all cases, similarity in spectral features between the two. Especially for the <3-mm samples, the discrepancies in relative area between replicates may be related largely to paramagnetic effects of mineral soil components, and variations introduced by background correction, and

Reproduced from Journal of Environmental Quality. Published by ASA, CSSA, and SSSA. All copyrights reserved.

**Table 4. Relative areas (percentage of total area) for chemical-shift regions of nuclear magnetic resonance (NMR) spectra.**

| Sample | Type or code | NMR chemical shift region (ppm) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Alkyl (0–45) | O-alkyl (45–93) | Di-O-alkyl (93–110) | Aromatic (110–140) | Phenolic (140–160) | Carboxyl (160–190) |
| | | % of total area | | | | | |
| **Reference samples** | | | | | | | |
| Western hemlock | wood | 1 | 63 | 13 | 13 | 6 | 4 |
| Douglas-fir (DF) | wood | 3 | 59 | 13 | 14 | 7 | 4 |
| DF, fresh 45-year | bark | 10 | 58 | 12 | 9 | 8 | 3 |
| DF, old | bark | 22 | 42 | 10 | 13 | 9 | 4 |
| **<3-mm Logyard fines** | | | | | | | |
| Dirty, sorted | DS 16 | 11 | 50 | 11 | 17 | 6 | 5 |
| | DS 25 | 15 | 43 | 13 | 13 | 9 | 7 |
| Dirty, unsorted | DU 4† | | | | | | |
| | DU 35 | 19 | 49 | 10 | 12 | 6 | 4 |
| Clean, sorted | CS 18 | 14 | 49 | 11 | 14 | 6 | 6 |
| | CS 56 | 16 | 48 | 12 | 13 | 7 | 4 |
| Clean, unsorted | CU 2 | 19 | 49 | 11 | 9 | 7 | 5 |
| | CU 11 | 16 | 50 | 12 | 12 | 6 | 4 |
| Deal processor | DP 9 | 15 | 38 | 9 | 18 | 10 | 10 |
| | DP 64 | 12 | 48 | 10 | 14 | 9 | 7 |
| **3- to 13-mm Logyard fines** | | | | | | | |
| Dirty, sorted | DS 16 | 17 | 56 | 10 | 10 | 4 | 3 |
| | DS 25 | 14 | 57 | 11 | 10 | 6 | 2 |
| Dirty, unsorted | DU 4 | 17 | 53 | 10 | 11 | 6 | 3 |
| | DU 35 | 15 | 54 | 13 | 7 | 8 | 3 |
| Clean, sorted | CS 18 | 16 | 57 | 11 | 9 | 4 | 3 |
| | CS 56 | 18 | 47 | 11 | 13 | 7 | 4 |
| Clean, unsorted | CU 2 | 15 | 54 | 11 | 10 | 7 | 3 |
| | CU 11 | 20 | 50 | 11 | 10 | 7 | 3 |
| Deal processor | DP 9 | 12 | 53 | 12 | 12 | 6 | 5 |
| | DP 64 | 14 | 51 | 11 | 13 | 7 | 4 |
| **<16-mm Trommel screen fines, Lavington** | | | | | | | |
| Fines | <16 mm | 20 | 51 | 11 | 9 | 5 | 4 |
| Residue | >1 mm | 13 | 58 | 12 | 9 | 5 | 3 |
| Suspended | 2.7 μm–1 mm | 18 | 50 | 10 | 12 | 6 | 4 |
| C–DOC‡ | <2.7 μm | 34 | 44 | 8 | 6 | 2 | 6 |
| **<16-mm Trommel screen fines, Alberni** | | | | | | | |
| Fines | <16 mm | 18 | 54 | 10 | 10 | 5 | 3 |
| Residue | >1 mm | 16 | 47 | 11 | 13 | 7 | 6 |
| Suspended | 2.7 μm–1 mm | 15 | 51 | 11 | 12 | 6 | 5 |
| C–DOC | <2.7 μm | 30 | 33 | 8 | 12 | 6 | 11 |
| **Fish–wood composts** | | | | | | | |
| Sample | left | 14 | 54 | 10 | 12 | 6 | 4 |
| | mid | 14 | 54 | 11 | 12 | 5 | 4 |
| | right | 15 | 51 | 11 | 12 | 6 | 5 |

† No spectrum.
‡ Combined colloidal and dissolved organic carbon fraction.

difficulties of phasing and baseline correction of low-carbon samples.

Except for the CU samples (Fig. 2c), spectra of the other four 3- to 13-mm fractions (Fig. 2a, 2e) had similar features. Compared with fresh wood, they are mainly higher in alkyl and carboxyl C and slightly lower in O-alkyl, aromatic, and phenolic C, and also have broader features. The methoxyl C of lignin (57 ppm) is only a weak shoulder on the O-alkyl peak, but lignin is the main contributor to the aromatic and phenolic signals from 110 to 160 ppm. The DD–TOSS spectra are also very similar, with most samples having a broad alkyl signal with a sharper maximum at 30 ppm for long-chain $CH_2$, and at 57 ppm for the $CH_3$ of methoxyl. Peaks in the aromatic and phenolic region are typical of guaiacyl lignin of softwood (130 ppm, 148 ppm with a shoulder at 152 ppm). However, the spectra also have the characteristic broad tannin peak at 106 ppm. Tannins and suberin of bark are probably the main source of the alkyl and carboxyl C, although these can also result from accumulation of microbial biomass.

The CU samples have higher C, N, and CT contents, and their NMR spectra are much better resolved. In both CP and DD–TOSS spectra, the peaks at 145 and 154 ppm in the phenolic region are more characteristic of tannin than of lignin. The "sawtooth-like" pattern in the aromatic and di-O-alkyl regions is also characteristic of condensed tannins. The differences between the CU and the other 3- to 13-mm fractions do not extend to relative areas, illustrating the importance of also examining details of peak positions and linewidths.

The lower carbon contents of the <3-mm fractions result in lower signal to noise ratio and greater broadening (no useful spectrum could be acquired for DU 4), although the peak positions are similar to those of the 3- to 13-mm samples (Fig. 2b). The main features are found at 30 ppm (alkyl C), 73 ppm (O-alkyl C including carbohydrates), 105 ppm (di-O-alkyl C including ano-

Reproduced from Journal of Environmental Quality. Published by ASA, CSSA, and SSSA. All copyrights reserved.

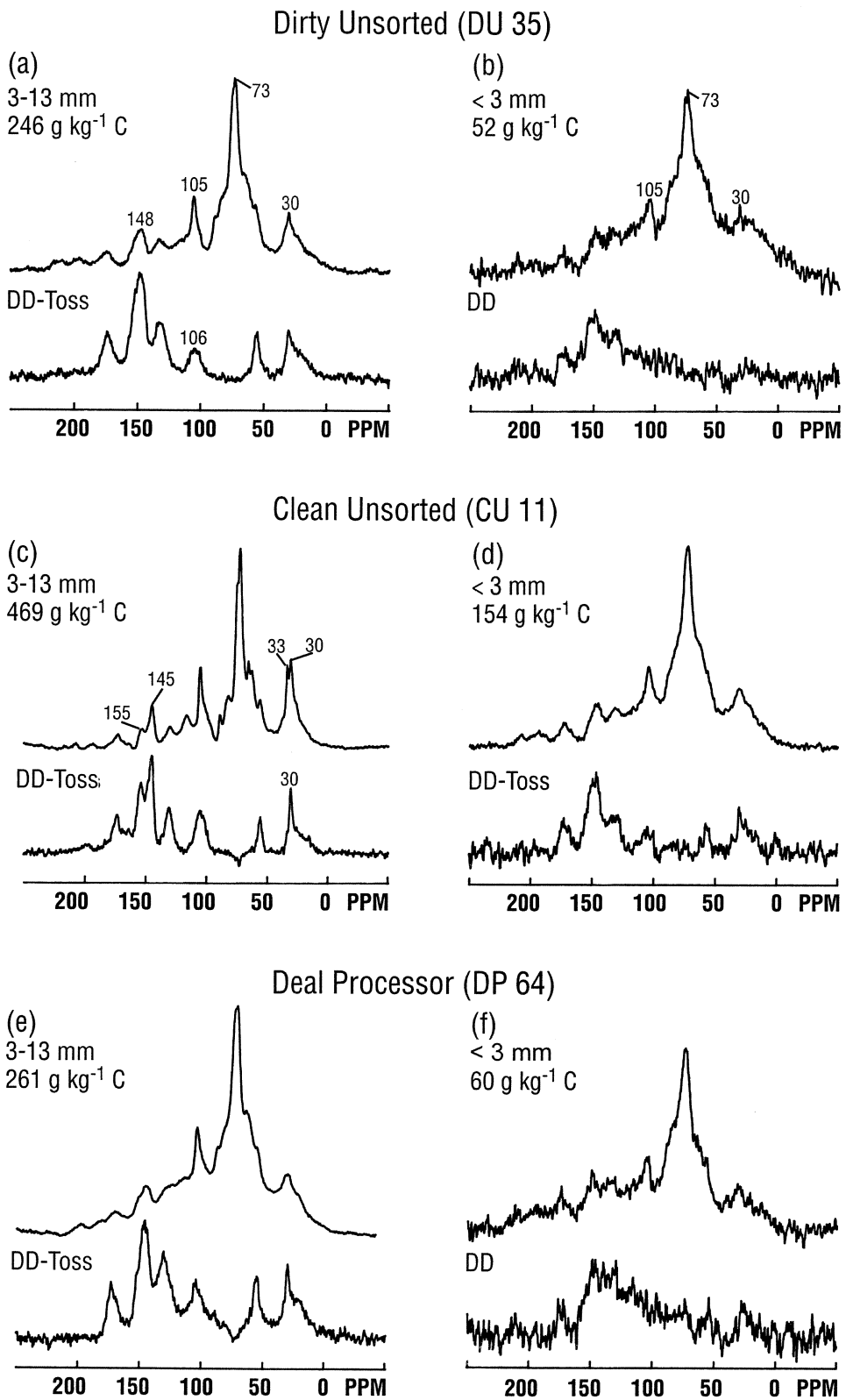


**Fig. 2. Solid-state $^{13}C$ nuclear magnetic resonance spectra with cross-polarization magic-angle spinning (CPMAS NMR) representing three of the five categories of (a, c, e) 3- to 13- and (b, d, f) <3-mm fines from the Lavington logyard. Lower spectra are with dipolar-dephasing (DD) or with dipolar-dephasing and total suppression of sidebands (DD–TOSS) as indicated.**

Reproduced from Journal of Environmental Quality. Published by ASA, CSSA, and SSSA. All copyrights reserved.

meric C of carbohydrates), aromatic and phenolic (110–160 ppm), and a broad, weak region for carboxyl, amide, and ester C (170–190 ppm). The <3-mm CU samples again have the highest total C, resulting in the best spectral quality. Compared with the 3- to 13-mm samples, differences in relative intensity distributions are small, with the <3-mm samples tending to be slightly lower in O-alkyl C and higher in carboxyl C. However, the increasing dilution of C with mineral matter and probably direct effects of paramagnetic and ferromagnetic components, as well as the aforementioned difficulties with spectral processing, reduce the reliability of the area measurements.

No DD spectrum could be obtained for DS 28, and the DD spectra of DS 35 and DS 64 are of poor quality, probably due to background signal in the aromatic and phenolic region. However, the spectra of the other <3-mm fractions had features similar to the corresponding 3- to 13-mm spectra. In general, the <3-mm samples also gave spectra consistent with a composition mainly of wood mixed with some bark, but degraded by close association with mineral soil particles. There was no accumulation of aromatic, phenolic, or alkyl C, the former consistent with the low levels of condensed tannins found by chemical analysis.

## Carbon-13 Cross Polarization Magic Angle Spinning Nuclear Magnetic Resonance—Trommel Screen Fines and Composts

Both CP and DD–TOSS spectra of the <16-mm trommel screen fines (Fig. 3a, 3c) have characteristics similar to those of the Lavington 3- to 13-mm fractions. The Alberni sample (Fig. 3a), with sharper features and higher C concentration, is more like the CU samples, although not as high in tannins. Spectra of the insoluble residues (<1 mm, not shown) were well-resolved, and showed only small differences in relative areas from the intact material; the main difference being lower alkyl intensity for the Lavington sample. Spectra of the suspended POC fractions also showed only minor differences from the starting materials and are not shown. However, the C–DOC fractions (Fig. 3b, 3d) have higher relative intensity for alkyl and carboxyl C, and lower for O-alkyl C. The C–DOC fraction is slightly higher in aromatic + phenolic C for the Alberni sample, and slightly lower for the Lavington samples. The DD–TOSS and DD spectra differ from those of all other samples, being dominated by carboxyl C and a more mobile fraction of alkyl C, the latter especially prominent for the Lavington C–POC.

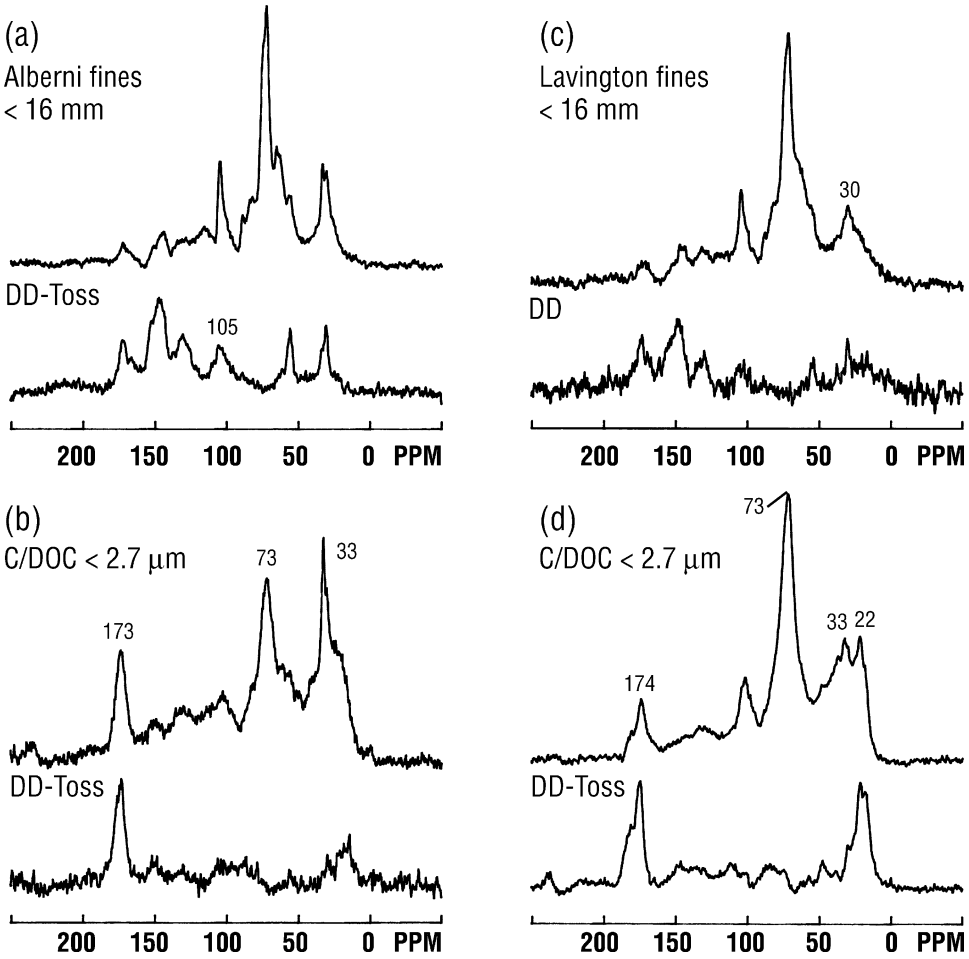


**Fig. 3. Solid-state $^{13}C$ nuclear magnetic resonance spectra with cross-polarization magic-angle spinning (CPMAS NMR) of <16-mm trommel screen fines from (a) Alberni and (c) Lavington and (b) and (d) corresponding aqueous extracts. Lower spectra are with dipolar-dephasing (DD) or with dipolar-dephasing and total suppression of sidebands (DD–TOSS) as indicated.**

Reproduced from Journal of Environmental Quality. Published by ASA, CSSA, and SSSA. All copyrights reserved.

The main point is that the C–DOC fractions leached from the <16-mm trommel screen fines, which constitute a very small proportion of the total mass and C, are enriched in alkyl, rather than phenolic or aromatic C structures, consistent with their very low tannin contents. They are also similar to forest DOC samples collected in summer and autumn (Kaiser et al., 2001) that were higher in alkyl, aromatic, and carboxyl C, and structures of high molecular weight produced from microbial decomposition of forest floor and lignin. By contrast, winter and spring forest DOC, mainly derived from fresh microbial biomass, had a higher proportion of hydrophilic fraction, and was higher in carbohydrates, amino sugars, and low molecular weight compounds.

Spectra of the fish waste–wood composts are not shown, as they were similar to those of the DS, DU, and CS 3- to 13-mm fines in Fig. 2. Relative areas of the three samples (Table 4) were essentially the same, except for slightly higher alkyl to O-alkyl intensity ratio for the right-side sample. There was thus little effect of the composting on the bulk organic composition of the Alberni fines, consistent with the small changes shown by chemical analysis.

## Implications for Utilization

Chemical analysis and $^{13}C$ CPMAS NMR spectra of the woody wastes in this study are consistent with a bulk organic composition due mainly to wood, mixed with varying amounts of bark and mineral soil, and further influenced by leaching and microbial decomposition during storage (Preston et al., 1990, 1998b, 2002; McColl and Powers, 1998). Our results for total C, N, and mineral content are similar to previous studies of logyard fine fractions (Zeng et al., 1993; Folk and Campbell, 1990). Neither NMR or tannin analysis indicate high phenolic content or accumulation of aromatic C, and the C–DOC fraction extracted by water was enriched mainly in alkyl C. The bulk properties of the larger fractions (3–13 and <16 mm) were also similar to those of woody forest floor, which is especially characteristic of British Columbia coastal forests (Preston, 1999; Preston et al., 2002), and it appears that most phenolics are present as structural polymers (lignins, tannins, suberins) of high molecular weight and low solubility. The incorporation of mineral soil into the <3-mm fractions mainly resulted in higher ash content, lower total C, C to N ratio, and tannins (either on a mass basis, or as g $kg^{-1}$ of total C, not shown), and degradation of the quality of the NMR spectra.

Uncertainty concerning possible adverse environmental effects, especially due to leachates, is an important concern for the land application of logyard and harvesting residues to forest sites. Toxic effects have been demonstrated for bark wastewater tannins (Field et al., 1988), leachate from aspen chips (Taylor et al., 1996), and pulping effluents high in resin acids (Dorado et al., 2000), and leaching of both organic components and nutrients is exacerbated for residues or logs piled in heaps or windrows (Rosén and Lundmark-Thelin, 1987; Parfitt et al., 1998; Taylor et al., 1996). However, at least the resin acids and tannins in bark and heartwood are poorly soluble under conditions of rainwater leaching (Field et al., 1988; Dellus et al., 1997; Matthews et al., 1997), and such effects can be minimized under appropriate conditions of application. Due to accumulation and storage of logyard fines on site, leaching could be more of an issue at the origin than in a later application.

Wood and wood co-composts have long been used as soil amendments in both field and greenhouse applications (King, 1979; Martin et al., 1978; Salomon, 1953; Schuman and Belden, 1991; N'Dayegamiye and Angers, 1993; Tremblay and Beauchamp, 1998). Similar to the composting process of most organic residues, the phytotoxic effects of wood and bark wastes in the composting process are transient (Hardy and Sivasithamparam, 1989; Martin et al., 1978). In a pot and field trial, logyard fines contributed organic matter, nutrients, and improved soil physical properties, but reduced plant availability of N, typical of amendments with high C to N ratio (Zeng et al., 1993).

There are some reports on application, or retention of harvesting residues in forestry, although not specifically using logyard residues. Application of chipped aspen residue to an aspen regeneration site in northern Alberta showed little effect on a range of plant and soil properties, including mycorrhizal fungi (Corns and Maynard, 1998; Visser et al., 1998). Application or retention of residues with high C to N ratio may adversely affect tree growth (Bulmer, 2000; Zabowski et al., 2000), mainly due to immobilization of N. In other situations, however, this can provide longer-term benefits by reducing loss of nitrate in recently harvested systems (Vitousek and Matson, 1985; Piirainen et al., 2002). Studies of decomposition and nutrient release from logging residues have demonstrated the importance of the coarser materials for long-term nutrient release and maintenance of organic matter, especially in sites of low fertility (Barber and Van Lear, 1984; Hyvönen et al., 2000; Nzila et al., 2002; Parfitt et al., 1998, 2001; Smith et al., 2000).

Results from these many studies of soil amendment with woody materials, including logyard fines, indicate that logyard fines should be useful, or at least not detrimental as a soil amendment, although initial immobilization of N may be expected. In addition, applying or dumping these materials inappropriately so that leachate could enter streams would have a negative effect, due to BOD load, suspended fines, and components with direct toxicity (Field et al., 1988; Taylor et al., 1996). Under natural conditions, the large amounts of DOC with highly variable composition leached out of litter (needles, wood, cones, dead roots) and forest floor move into the mineral soil, where the competing processes of absorption and decomposition are a natural part of soil development (Jandl and Sollins, 1997; Kaiser et al., 2001; Kalbitz et al., 2000; Guggenberger et al., 1998).

This should also be the case with application of woody wastes under acceptable, appropriate practice for soil amendment, although few studies have been reported. Cronan et al. (1992) found that increases in O-horizon

Reproduced from Journal of Environmental Quality. Published by ASA, CSSA, and SSSA. All copyrights reserved.

DOC after application of sawdust were within the range of natural variation for hardwood sites in the region (Maine). Increases in DOC from clearcutting slash also in a hardwood site (Appalachian Mountains, North Carolina) were balanced by absorption and decomposition in the C horizon of the mineral soil (Qualls et al., 2000). Their study also showed that leaching of DOC and DON could occur if hydrologic flowpaths near streams bypass the strongly adsorbing soil horizons, emphasizing the importance of appropriate site selection and application. In contrast to toxic effects, increases in soil microbial biomass and activity following retention or extra addition of blue gum (*Eucalyptus globulus* Labill.) harvesting residues were attributed to soluble C leaching from the residues to provide a readily available energy source (Mendham et al., 2002).

The samples in this study, while low in number, all represent materials produced under operational conditions in British Columbia. Extension to field application is now in progress in a related study, where a variety of woody residues including sortyard wastes have been applied for rehabilitation and reforestation of logging roads and areas disturbed by log handling and storage (preliminary results in Venner et al., 1999). Our studies indicate that the effects of fragmentation, leaching, microbial activity, and mixing with mineral soil on logyard wastes are similar to those that occur naturally in soil and forest floor. Decisions for management of logyard debris will inevitably be influenced by a mix of economic, societal, and environmental considerations (MacDonald, 2001), but incorporation into composting operations or returning the material to the forest ecosystem as a soil amendment or road cover should at least be compatible with its origin and chemical properties.

## ACKNOWLEDGMENTS

This work was supported by the Federal Panel on Energy R&D (PERD) through the ENFOR program of Forestry Canada, Project P-404. We also thank Kevin McCullough, Allison Barriscale, and Carol Cutforth for excellent technical support, Don Waugh (Feenix Forest Technologies, Nanaimo, BC) for compost samples, and Kim Young from Tolko Industries Ltd. for coordinating the Lavington study.

## REFERENCES

Barber, B.L., and D.H. Van Lear. 1984. Weight loss and nutrient dynamics in decomposing woody loblolly pine logging slash. Soil Sci. Soc. Am. J. 48:906–910.

Bernards, M.A. 2002. Demystifying suberin. Can. J. Bot. 80:227–240.

Bulmer, C. 2000. Reclamation of forest soils with excavator tillage and organic amendments. For. Ecol. Manage. 133:157–163.

Campbell, A.G., and R.R. Tripepi. 1992. Logyard residues: Products, markets and research needs. For. Prod. J. 42(9):60–64.

Corns, I.G.W., and D.G. Maynard. 1998. Effects of soil compaction and chipped aspen residue on aspen regeneration and soil nutrients. Can. J. Soil Sci. 78:85–92.

Cronan, C.S., S. Lakshman, and H.H. Patterson. 1992. Effects of disturbance and soil amendments on dissolved organic carbon and organic acidity in red pine forest floors. J. Environ. Qual. 21:457–463.

Czimczik, C.I., C.M. Preston, M.W.I. Schmidt, R.A. Werner, and E.-D. Schulze. 2002. Effects of charring on mass, organic carbon, and stable carbon isotope composition of wood. Org. Geochem. 33:1207–1223.

Dellus, V., I. Mila, A. Scalbert, C. Menard, V. Michon, and C.L.M. Herve du Penhoat. 1997. Douglas-fir polyphenols and heartwood formation. Phytochemistry 45:1573–1578.

Dorado, J., F.W. Claassen, G. Lenon, T.A. van Beek, J.B.P.A. Wijnberg, and R. Sierra-Alvarez. 2000. Degradation and detoxification of softwood extractives by sapstain fungi. Bioresour. Technol. 71: 13–20.

Edmonds, R.L. 1987. Decomposition rates and nutrient dynamics in small-diameter woody litter in four forest ecosystems in Washington, U.S.A. Can. J. For. Res. 17:499–509.

Field, J.A., M.J.H. Leyendeckers, R.S. Alvarez, G. Lettinga, and L.H.A. Habets. 1988. The methanogenic toxicity of bark tannins and the anaerobic biodegradability of water soluble bark matter. Water Sci. Technol. 20:219–240.

Folk, R.L., and A.G. Campbell. 1990. Physical and chemical properties of classified logyard trash: A mill study. For. Prod. J. 40(4):22–24.

Forrester, P.D. 1999. Logyard residue reclamation in Central-Interior British Columbia. FERIC Tech. Note TN-287. For. Eng. Res. Inst. of Canada, Vancouver, BC.

Forrester, P.D., and C.M. Preston. 2002. Utilization of the fines component in logyard residues. Advantage 3, no. 28. For. Eng. Res. Inst. of Canada, Vancouver, BC.

Guggenberger, G., K. Kaiser, and W. Zech. 1998. Mobilization and immobilization of dissolved organic matter in forest soils. Z. Pflanzenernaehr. Bodenkd. 161:401–408.

Hardy, G.E.St.J., and K. Sivasithamparam. 1989. Microbial, chemical and physical changes during composting of a eucalyptus (*Eucalyptus calophylla* and *Eucalyptus diversicolor*) bark mix. Biol. Fertil. Soils 8:260–270.

Hyvönen, R., B.A. Olsson, H. Lundqvist, and H. Staaf. 2000. Decomposition and nutrient release from *Picea abies* (L.) Karst. and *Pinus sylvestris* L. logging residues. For. Ecol. Manage. 126:97–112.

Jandl, R., and P. Sollins. 1997. Water-extractable soil carbon in relation to the belowground carbon cycle. Biol. Fertil. Soils 25:196–201.

Jellum, E.J., S. Kuo, and U. Sainju. 1995. Mineralization and plant availability of nitrogen in seafood waste composts in soil. Soil Sci. 160:125–135.

Kaiser, K., G. Guggenberger, L. Haumaier, and W. Zech. 2001. Seasonal variations in the chemical composition of dissolved organic matter in organic forest floor layer leachates of old-growth Scots pine (*Pinus sylvestris* L.) and European beech (*Fagus sylvatica* L.) stands in northeastern Bavaria, Germany. Biogeochemistry 55:103–143.

Kalbitz, K., S. Solinger, J.-H. Park, B. Michalzik, and E. Matzner. 2000. Controls on the dynamics of dissolved organic matter in soils: A review. Soil Sci. 165:277–304.

King, L.D. 1979. Waste wood fiber as a soil amendment. J. Environ. Qual. 8:91–95.

Kranabetter, J.M., and A. Banner. 2000. Selected biological and chemical properties of forest floors across bedrock types on the north coast of British Columbia. Can. J. For. Res. 30:971–981.

Laos, F., M.J. Mazzarino, I. Walter, and L. Roselli. 1998. Composting of fish waste with wood by-products and testing compost quality as a soil amendment: Experiences in the Patagonia region of Argentina. Compost Sci. Util. 6:59–66.

Liao, P.H., L. Jones, A.K. Lau, S. Walkemeyer, B. Egan, and N. Holbek. 1997. Composting of fish wastes in a full-scale in-vessel system. Bioresour. Technol. 59:163–168.

Lorenz, K., C.M. Preston, S. Raspe, I.K. Morrison, and K.-H. Feger. 2000. Litter decomposition and humus characteristics in Canadian and German spruce ecosystems: Information from tannin analysis and $^{13}C$ CPMAS NMR. Soil Biol. Biochem. 32:779–792.

MacDonald, A.J. 2001. Energy balance, carbon emissions, and costs of sortyard debris disposal. Advantage 2, no. 38. For. Eng. Res. Inst. of Canada, Vancouver, BC.

Martin, J.P., R.L. Branson, and W.M. Jarrell. 1978. Decomposition of organic materials used in planting mixes and some effects on soil properties and plant growth. Agrochimica 22:248–261.

Matthews, S., I. Mila, A. Scalbert, and D.M.X. Donnelly. 1997. Extractable and non-extractable proanthocyanidins in barks. Phytochemistry 45:405–410.

McColl, J.G., and R.F. Powers. 1998. Decomposition of small diameter woody debris of red fir determined by nuclear magnetic resonance. Commun. Soil Sci. Plant Anal. 29:2691–2704.

Reproduced from Journal of Environmental Quality. Published by ASA, CSSA, and SSSA. All copyrights reserved.

Mendham, D.S., K.V. Sankaran, A.M. O'Connell, and T.S. Grove. 2002. *Eucalyptus globulus* harvest residue management effects on soil carbon and microbial biomass at 1 and 5 years after plantation establishment. Soil Biol. Biochem. 34:1903–1912.

N'Dayegamiye, A., and D. Angers. 1993. Organic matter characteristics and water-stable aggregation of a sandy loam after 9 years of wood-residue applications. Can. J. Soil Sci. 73:115–122.

Nzila, J.D., J.-P. Bouillet, J.-P. Laclau, and J. Ranger. 2002. The effects of slash management on nutrient cycling and tree growth in *Eucalyptus* plantations in the Congo. For. Ecol. Manage. 171:209–221.

Parfitt, R.L., D.J. Ross, and G.J. Salt. 1998. Nitrogen and phosphorus mineralization in *Pinus radiata* harvest residue samples from a coastal sand. N. Z. J. For. Sci. 28:347–360.

Parfitt, R.L., G.J. Salt, and S. Sagger. 2001. Post-harvest residue decomposition and nitrogen dynamics in *Pinus radiata* plantations of different N status. For. Ecol. Manage. 154:55–67.

Perra, B., J.-P. Haluk, and M. Metche. 1995. IR, $^{1}H$ and $^{13}C$ NMR spectroscopic studies of suberin from beech barks (*Fagus sylvatica* L.). Holzforschung 49:99–103.

Pichler, M., H. Knicker, and I. Kögel-Knabner. 2000. Changes in the chemical structure of municipal solid waste during composting, as studied by solid-state dipolar-dephasing and PSRE $^{13}C$ NMR and solid-state $^{15}N$ NMR spectroscopy. Environ. Sci. Technol. 34:4034–4038.

Piirainen, S., L. Finér, H. Mannerkoski, and M. Starr. 2002. Effects of forest clear-cutting on the carbon and nitrogen fluxes through podzolic soil horizons. Plant Soil 239:301–311.

Preston, C.M. 1996. Possibilities for the application of $^{13}C$ nuclear magnetic resonance spectroscopy to biomass feedstocks and conversion processes. p. 131–142. *In* J. Karau (ed.) Proc. of the Canadian Energy Plantation Workshop, Gananoque, ON. 2–4 May 1995. Nat. Resour. Canada, Canadian For. Serv., Science Branch, Ottawa, ON.

Preston, C.M. 1999. Condensed tannins of salal (*Gaultheria shallon* Pursh): A contributing factor to seedling "growth-check" on northern Vancouver Island? p. 825–841. *In* G.G. Gross, R.W. Hemingway, and T. Yoshida (ed.) Plant polyphenols 2: Chemistry, biology, pharmacology, ecology. Kluwer Academic/Plenum Publ., New York.

Preston, C.M. 2001. Carbon-13 solid-state NMR of soil organic matter—Using the technique effectively. Can. J. Soil Sci. 81:255–270.

Preston, C.M., and B.G. Sayer. 1992. What's in a nutshell: An investigation of structure by carbon-13 cross-polarization magic-angle spinning nuclear magnetic resonance spectroscopy. J. Agric. Food Chem. 40:206–210.

Preston, C.M., B.G. Sayer, and B. Cade-Menun. 1998a. Characterization of Canadian backyard composts; chemical analysis and $^{13}C$ CPMAS and $^{31}P$ NMR spectroscopy. Compost Sci. Util. 6:53–66.

Preston, C.M., P. Sollins, and B.G. Sayer. 1990. Changes in organic components for fallen logs in old-growth Douglas-fir forests monitored by $^{13}C$ nuclear magnetic resonance spectroscopy. Can. J. For. Res. 20:1382–1391.

Preston, C.M., J.A. Trofymow, and C.I.D.E.T. Working Group. 2000. Variability in litter quality and its relationship to litter decay in Canadian forests. Can. J. Bot. 78:1269–1287.

Preston, C.M., J.A. Trofymow, J. Niu, and C.A. Fyfe. 1998b. CPMAS $^{13}C$ NMR spectroscopy and chemical analysis of coarse woody debris in coastal forests of Vancouver Island. For. Ecol. Manage. 111:51–68.

Preston, C.M., J.A. Trofymow, J. Niu, and C.A. Fyfe. 2002. Harvesting and climate effects on organic matter characteristics in British Columbia coastal forests. J. Environ. Qual. 31:402–413.

Preston, C.M., J.A. Trofymow, B.G. Sayer, and J. Niu. 1997. $^{13}C$ nuclear magnetic resonance spectroscopy with cross-polarization and magic-angle spinning investigation of the proximate analysis fractions used to assess litter quality in decomposition studies. Can. J. Bot. 75:1601–1613.

Qualls, R.G., B.L. Haines, W.T. Swank, and S.W. Tyler. 2000. Soluble organic and inorganic nutrient fluxes in clearcut and mature deciduous forests. Soil Sci. Soc. Am. J. 64:1068–1077.

Rosén, K., and A. Lundmark-Thelin. 1987. Increased nitrogen leaching under piles of slash—A consequence of modern forest harvesting techniques. Scand. J. For. Res. 2:21–29.

Salomon, M. 1953. The accumulation of soil organic matter from wood chips. Soil Sci. Soc. Am. Proc. 17:114–118.

Schowalter, T.D., and J.J. Morrell. 2002. Nutritional quality of Douglas-fir wood: Effect of vertical and horizontal position on nutrient levels. Wood Fiber Sci. 34:158–164.

Schuman, G.E., and S.E. Belden. 1991. Decomposition of wood-residue amendments in revegetated bentonite mine spoils. Soil Sci. Soc. Am. J. 55:76–80.

Smith, C.T., A.T. Lowe, M.F. Skinner, P.N. Beets, S.H. Schoenholtz, and S. Fang. 2000. Response of radiata pine forests to residue management and fertilization across a fertility gradient in New Zealand. For. Ecol. Manage. 138:203–223.

Taylor, B.R., J.S. Goudey, and N.B. Carmichael. 1996. Toxicity of aspen wood leachate to aquatic life: Laboratory studies. Environ. Toxicol. Chem. 15:150–159.

Tremblay, J., and C.J. Beauchamp. 1998. Fractionnement de la fertilization azotée d'appoint à la suite de l'incorporation au sol de bois raméaux fragmentés: Modifications de certaines propriétés biologiques et chimiques d'un sol cultivé en pomme de terre. Can. J. Soil Sci. 78:275–282.

Veeken, A.H.M., F. Adani, K.G.J. Nierop, P.A. de Jager, and H.V.M. Hamelers. 2001. Degradation of biomacromolecules during high-rate composting of wheat straw-amended feces. J. Environ. Qual. 30:1675–1684.

Venner, K.H., C.E. Prescott, C.M. Preston, and M.-J. Douglas. and C.E Bulmer. 1999. Wood wastes: A valuable addition to compacted forest soils? p. 33–45. *In* Proc. Residue-to-Revenue Residual Wood Conf., Vancouver, BC, Canada. 8–9 Nov. 1999. Logging and Sawmilling Journal, North Vancouver, BC.

Visser, S., D. Maynard, and R.M. Danielson. 1998. Response of ecto- and arbuscular mycorrhizal fungi to clear-cutting and the application of chipped aspen wood in a mixedwood site in Alberta, Canada. Appl. Soil Ecol. 7:257–269.

Vitousek, P.M., and P.A. Matson. 1985. Disturbance, nitrogen availability, and nitrogen losses in an intensively managed loblolly pine plantation. Ecology 66:1360–1376.

Yan, B., and R.E. Stark. 2000. Biosynthesis, molecular structure, and domain architecture of potato suberin: A $^{13}C$ NMR study using isotopically labeled precursors. J. Agric. Food Chem. 48:3298–3304.

Zabowski, D., B. Java, G. Scherer, R.L. Everett, and R. Ottmar. 2000. Timber harvesting residue treatment: Part 1. Responses of conifer seedlings, soil and microclimate. For. Ecol. Manage. 126:25–34.

Zeng, M., A.G. Campbell, and R.L. Mahler. 1993. Log yard fines as a soil amendment: Pot and field studies. Commun. Soil Sci. Plant Anal. 24:2025–2041.