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A ^{13}C NMR study of decomposing logging residues in an Australian hoop pine plantation

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Abstract

Purpose Residue retention is important for nutrient and water economy in sub-tropical plantation forests. We examined decomposing hoop pine (*Araucaria cunninghamii* Ait. Ex D. Don)

residues – foliage, branches and stem wood – to determine the changes in structural chemistry that occur during decomposition.

Materials and methods Residues were incubated *in situ* using 0.05-m^2 microplots. We used solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy to determine the structural composition of harvest residues in the first 24 months of decomposition.

Results and discussion The spectral data for branch and stem residues were generally similar to one another and showed few changes during decomposition. The lignin content of branch and foliage residues decreased during decomposition. When residues were mixed together during decomposition the O-alkyl fraction of foliage decreased initially then increased up to 24 months, while the alkyl carbon (C) fraction exhibited the opposite pattern. The decomposition of woody hoop pine residues (branch and stem wood) is surprisingly uniform across the major C forms elucidated with ^{13}C NMR, with little evidence of preferential decomposition. When mixed with branch and stem materials, foliage residues showed significant short- and long-term compositional changes. This synergistic effect may be due to the C:N ratio of the treatments and the structure of the microbial decomposer community.

Conclusions Twenty-four months of decomposition of hoop pine residues did not result in substantial accumulation of recalcitrant C forms, suggesting that they may not contribute to long-term C sequestration.

Keywords Australia • Carbon • Decomposition • Forestry • Litter • Nuclear magnetic resonance spectroscopy • Residue management • Tissue chemistry

1 Introduction

Hoop pine (*Araucaria cunninghamii* Ait. Ex D. Don) plantations occupy approximately 45,000 ha of the forestry estate in southeast Queensland, Australia (Mathers et al. 2003). Valued for use in plywood and for artisanal woodworking, hoop pine is also culturally important, as it is one of a few softwoods indigenous to Australia. Burning of logging residues after harvesting has resulted in high nutrient losses and reductions in soil organic matter (SOM) contents in hoop pine plantations (Ryan and Gilmour 1985; Xu et al. 2008), leading to the recommendation that harvest residues be windrowed in second-rotation stands (Costantini et al. 1997; Xu et al. 2008).

Residue retention in forest plantations can improve water and nutrient retention in the early years of the new rotation. Residue management is therefore crucial for the development of sustainable forest harvesting in soils that are nutrient-poor or that have poor water-retention characteristics. The first few years after harvesting are especially important in sub-tropical plantation forests, where residue decomposition rates are high and the new forest canopy closes relatively quickly. Understanding the structural transformations that occur during the decomposition of harvest residues can provide insight into nutrient cycling and SOM processes, and ultimately inform forest management policies.

Blumfield et al. (2004a) used 0.05-m^2 microplots to study the decomposition of ^{15}N-labeled hoop pine logging residues – foliage, branch and stem materials – in a hoop pine plantation in southeast Queensland. They found that much of the residue-derived N was retained in surface soils. Interestingly, they found that the rate of foliage decomposition was 30% lower in mixed foliage-branch-stem microplots, compared to foliage-only plots. In contrast, stem and branch decomposition rates were significantly higher in the combined-residue microplots. Blumfield et al. (2004a) ascribed this synergistic effect to microclimatic conditions in the combined-residue treatments and the alteration of the overall quality of the residue substrates when mixed together. Analyses of foliage residues using ^{13}C nuclear magnetic resonance (NMR) spectroscopy indicated that methoxyl C, aryl C and phenolic C were significantly correlated to either mass loss, residue N concentration or both. In this paper, we extend the work of Blumfield et al. (2004a) by including new ^{13}C NMR analyses of branch and stem residues and additional characterization of foliage residues. We hypothesized that the organic composition of hoop pine harvest residues would undergo significant transformation during decomposition, with resonances associated with the more recalcitrant fractions of alkyl and aromatic C increasing in intensity and the carbohydrate-dominated O-alkyl C resonances decreasing in intensity as decomposition proceeds. Furthermore, although harvest residues decompose at different rates when mixed than they do when separated, we hypothesized that there would be no difference in the carbon chemistry of decomposing residues at similar stages of decomposition.

2 Materials and methods

2.1 Site description and experimental design

This work was conducted after harvesting of a first-rotation hoop pine stand at the Imbil State Forest in southeast Queensland, Australia (26° 31′ S, 152° 38′ E), approximately 150 km north of Brisbane. The Imbil forest experiences cool, dry winters and warm, wet summers. Average annual rainfall varies considerably, ranging from 495 to 1964 mm. During the period of this study, April 1999 to March 2001, annual rainfall was near the historical average of 1188 mm in both years (Blumfield et al. 2004a). Average monthly temperatures during the study period ranged from 20°C to 32°C. Detailed information about the site can be found elsewhere (Mathers et al. 2003; Blumfield et al. 2004a, b, 2006).

Hoop pine harvest residues were incubated *in situ* in microplots made from sections of PVC pipe with diameter 25 cm and wall thickness 3.5 mm. Each 30-cm long PVC section was pushed about 20 cm into the ground. The residues were taken from three ^{15}N-labeled hoop pine trees, which were harvested at an age of approximately 10 yr and air-dried to constant weight. The foliage was collected, as were sections of branch and stem material. The amounts of residue materials placed in the microplots were based on measurements of residue mass in nearby windrows. One of five treatments was randomly assigned to each microplot: foliage-only (102.5 g per microplot), branch-only (184 g), stem only (90 g), combined-residue (102.5 g foliage + 184 g branch + 90 g stem), and control (no residues). The diameter of the branch residues was approximately 50 mm, while stem residues had diameters ranging from 150-200 mm. Branch residues were approximately 200 mm long, while stem residues were discs about 25 mm in thickness, based on the desired weight. Wire mesh was placed over the microplots and the area around each was kept weed-free to prevent shading and litter input. Additional information about the experimental design and installation of the microplots may be found in Blumfield et al. (2004a).

2.2 Sample collection and analysis

Samples for this study were collected 3, 6, 12, and 24 months after establishment of the microplots. Additional foliage samples from the foliage-only microplots were collected at 30 months. At each sampling date, one microplot was randomly chosen for each treatment in each of the three experimental blocks (Blumfield et al. 2004a). Residues were carefully removed by hand and stored in plastic bags for transport to the laboratory, where they were dried at 60°C and

weighed. Residues from the combined foliage+branch+stem microplots were separated by hand and analyzed separately. All samples were ground to a fine powder for chemical analysis.

Solid-state ^{13}C NMR analyses were performed using cross-polarization with magic-angle spinning (CPMAS). Spectra were obtained using a Varian Unity400 spectrometer operating at a ^{13}C frequency of 100.59 MHz. The samples were packed in 7-mm silicon nitride rotors and spun at 5000 Hz. For the CPMAS analyses, 2000 transients were collected for each sample, with a contact time of 2 ms, an acquisition time of 14 ms, and a recycle delay of 2.5 s. Chemical shift values were externally referenced to hexamethylbenzene at 132.1 ppm. Foliage samples were re-analyzed for this study using these experimental conditions, which are slightly different than those used by Blumfield et al. (2004a). Samples from different micro-plots were not composited, providing an opportunity to assess the variability in NMR spectra for each sampling time and treatment.

The relative contributions of various C forms to the NMR spectra were estimated by integrating the spectra using the chemical shift regions described in Table 1. The spinning sideband (SSB) for carboxyl C, which occurs at about 223 ppm, was generally negligible, as can be seen in the spectra in this paper. Nevertheless, we subtracted the integrated intensity of the 212-230 ppm spectral region from the aromatic region and added twice that amount to the carboxyl region to correct for this effect. The SSB for O-aryl C occurs at 200 ppm, which is also where resonances related to ketonic C are found. We therefore did not correct for this SSB. Consequently, our estimates of aromatic C may be slightly underestimated, and our estimates of carbonyl C may be slightly overestimated. After integration, we summed the integral values for the appropriate spectral regions to compute the alkyl C (0-46 ppm), O-alkyl C (46-110 ppm), aromatic C (110-160 ppm), and carbonyl C (160-220 ppm).

3 Results

Example spectra for branch and stem wood residues are shown in Figs. 1 and 2, respectively. As expected, the ^{13}C CPMAS NMR spectra for branch and stem material are very similar. The smaller diameter branch material contains proportionally more bark than the stem residues, but there are no great differences in the spectra. During decomposition, both branch and stem residues showed a change in the nature of the broad peak at 70-75 ppm, corresponding to the C2, C3, and C5 carbons in cellulose (Atalla and VanderHart 1999). In all of the branch and stem

samples, the peak at 74 ppm was dominant in younger-aged residues, with only a shoulder at 72 ppm. By 24 months, however, we observed a clear split peak, with the 72 ppm peak often larger than the one at 74 ppm (see Figs. 1 and 2). In the stem wood residues, the relative size of the peak at 89 ppm increased relative to the peak at 83 ppm. These results suggest that the relative abundance of crystalline cellulose increases, relative to amorphous cellulose, during decomposition. The 89 ppm peak can be attributed to the C4 carbon in crystalline cellulose, whereas the 83 ppm could be C4 carbon in amorphous cellulose, or hemicellulose (Kim and Newman 1995). However, hemicellulose would also produce peaks at 21 ppm (acetyl methyl C) and 174 ppm (carboxyl C), yet these peaks, though present, were very small in our spectra. Barron et al. (1985) also found little evidence of hemicellulose-related acetate in hoop pine wood.

In the branch residues, the resonance region associated with phenolic C (141-160 ppm) decreased in intensity as decomposition proceeded (see Fig. 1). These peaks, at 148 and 153 ppm in our spectra, along with peaks at 115 and 133 ppm are indicative of guaiacyl lignin, the predominant lignin form in softwoods (Preston et al. 1990; Mathers et al. 2003). The diminution of these peaks in the branch spectra from both branch-only and combined-residue plots suggests that lignin is lost relatively quickly from these residues during the first 12 months of decomposition. Interestingly, this is not the case with stem wood (see Fig. 2), suggesting that physical fragmentation of the smaller branch material, and differences in the ratio of surface area to volume may be important.

The loss of lignin-related C was also evident in the spectra of foliage incubated in the foliage-only microplots, which also showed sharp decreases in spectral intensity in the phenolic C region (Fig. 3). There were no other major patterns visible in the foliage-only spectra. In contrast, there was no evidence that the lignin content of foliage in the combined-residue plots was affected by decomposition. The relative intensity in the alkyl C region (0-45 ppm) increased in the first six months of decomposition in the combined-residue spectra, and declined thereafter. The peaks in the O-alkyl C region (45-110 ppm) showed the opposite trend.

By 24 months, the alkyl C peak for foliage in the combined-residue spectra was considerably smaller than the corresponding peak in the foliage-only spectra (see Fig. 3). Accordingly, the integrated intensity for the alkyl C region after 24 months was significantly lower for the combined-residue plots than the foliage-only plots (Fig. 4). The integrated intensity of O-alkyl C

was greater in the combined-residue spectra, offsetting much of the difference in alkyl C, but the difference was not significant. For branch and stem residues, the integrated intensities for the single-component spectra and the combined-residue spectra were almost identical, and the differences were not statistically significant (see Fig. 4).

In general, the carbon speciation of branch and stem residues was unaffected by the time of decomposition (Fig. 5). The significant decrease in the contribution of aromatic C in branch residues over time was due to the decrease observed in phenolic C (see Fig. 1). The integrated intensities of the major spectral regions for foliage in the foliage-only plots also showed little change during the course of decomposition (see Fig. 5). Foliage in the combined-residue plots, on the other hand, increased in alkyl C in the first 12 months, then decreased sharply. This was balanced by O-alkyl C, which decreased quickly, from 54% of spectral intensity at 3 months to 47% at 6 months, then increased back to 56% at 24 months (see Fig. 5).

4 Discussion

4.1 Decomposition effects on major C fractions in woody residues

Numerous ^{13}C NMR studies of the decomposition of natural organic matter in forest ecosystems have documented that different C fractions are preferentially lost or retained in the decomposing substrate (e.g., Kögel et al. 1988; Baldock and Preston 1995; Preston et al. 1998; Ganjegunte et al. 2004). The O-alkyl C resonance region, which is dominated by peaks related to carbohydrate structures, represents a particularly labile form of C for microbial organisms. We anticipated that this fraction would decrease during the decomposition of hoop pine residues, while the alkyl C and aromatic C fractions, which represent more recalcitrant forms of C such as waxes, resins, and lignin (Preston et al. 1990), would increase in importance. On the contrary, our spectral integration data indicate that the relative intensities of the four major spectral regions in branch and stem materials were largely unaffected by the time of decomposition (Fig. 5). The 18% decline in the aromatic C fraction in branch residues was the only statistically significant change that we observed. We observed little variation in the spectral properties of replicate samples collected at each sampling date (note the small error bars in Figures 4 and 5). The absence of significant compositional changes during decomposition is not, therefore, an artifact of high statistical variation.

The chemistry of decomposing branch and stem residues remained relatively constant despite substantial mass loss. After 24 months of decomposition, we observed up to 45% mass loss in branch residues and up to 62% mass loss in stem residues (Table 2). Thus, it appears that the decomposition of woody hoop pine residues is not particularly selective (with the exception of the lignin component, discussed in section 4.3). Davis et al. (1994a,b,c) used solid-state ^{13}C CPMAS NMR to study the decomposition of the softwood *Picea pungens* and the hardwood *Betula papyrifera* by white rot and brown rot fungi. They found that decomposition of *Picea pungens* wood by three white rot species was largely non-preferential (Davis et al. 1994a), whereas brown rot decomposition resulted in the preferential loss of the O-alkyl C fraction (Davis et al. 1994c), a pattern also observed by others (Kim and Newman 1995; Filley et al. 2002; Irbe et al. 2001). Our data are generally consistent with the patterns observed by Davis et al. (1994a,b) during white rot decomposition. Preston et al. (1998) also observed little change in ^{13}C CPMAS NMR spectral properties in the early stages of decomposition of coarse woody debris from three softwood species on Vancouver Island, Canada. In a study of small-diameter woody debris decomposition, the same researchers observed few compositional changes up to 19 years (corresponding to approximately 65% mass loss), which they attributed to the dominance of white-rot decomposition (Preston et al. 2012). After 19 years, they observed a change in the carbohydrate-to-lignin ratio, suggesting that brown-rot decomposition became increasingly important in the latter stages of decomposition. In a study of the decomposition of chipped logging slash (mixed softwoods) in the Sierra Nevada mountains of Northern California, small but significant differences were observed in the composition of chips from the bottom of chip piles compared to the top of the piles after ten years (Preston et al. 2011). Chips from the bottom of the piles had significantly lower O-alkyl and di-O-Alkyl C, and significantly higher carbonyl, methoxyl and alkyl C. As in our study, Preston et al. (2011) observed a high degree of reproducibility among replicate samples. Using proton spin relaxation editing (PSRE) to examine slowly relaxing and rapidly relaxing C fractions, they found that the rapidly relaxing component appears to reflect the chemistry of decomposing wood, with lower O-alkyl C and higher aromatic and alkyl C than the slowly relaxing component. The PSRE technique is thus a promising tool for teasing out small compositional changes during decomposition.

There were no significant differences in the distribution of C among the four major spectral regions when branch and stem residues from the single-component plots were compared to those

in the combined-residue plots (see Fig. 4). This was true despite the higher decomposition rates observed for branch and stem residues in the combined-residue plots (see Table 2; Blumfield et al. 2004a). Therefore, while the mixing of residues in the combined treatments increased the rate of branch and stem decomposition, it does not appear to have significantly altered the biochemistry of the decomposition process.

4.2 Decomposition effects on major C fractions in foliar residues

Studies of litter decomposition have often revealed a consistent pattern of increasing alkyl C content and decreasing O-alkyl C content over time (e.g., Baldock and Preston 1995). Indeed, an increasing alkyl:O-alkyl C ratio has been used as a measure of the extent of organic matter decomposition in soil (Baldock et al. 1997). A particularly relevant example is a nearby study of the decomposition of mulga (*Acacia aneura* F. Muell. Ex. Benth.) foliage at a semi-arid site in Queensland, Australia (Mathers et al. 2007). They found a steady decline in O-alkyl C and an increase in alkyl and carbonyl C over 18 months of *in situ* decomposition. In contrast, we observed no significant changes in any of the major C forms over the first 24 months of decomposition of hoop pine foliage (see Fig. 5), despite up to 65% mass loss. Mulga and hoop pine foliage are similar in ^{13}C NMR composition, and in both studies the foliage samples were incubated at the ground surface. The two sites differ greatly in climate, with greater average temperature and rainfall at the hoop pine site than the mulga site, yet the first-order rate constants for foliar mass loss were similar (0.47 yr^{-1} for hoop pine, 0.41 yr^{-1} for mulga: Blumfield et al. 2004a; Mathers et al. 2007). Other researchers have also observed species-related differences in the chemistry of decomposition. Almendros et al. (2000) observed substantial variations in the relative gains and losses of different ^{13}C NMR fractions in decomposing foliage of 12 Mediterranean species, with several of the species showing little or no change in overall composition after six months of decomposition. Similarly, Preston et al. (2009) observed little or no change in the average ^{13}C NMR spectral composition of 10 foliar litters after two years of decomposition in Canada, while noting large variations in decomposition patterns among species.

Unlike branch and stem material, foliage residues decomposed differently in the combined-residue microplots compared to the foliage-only microplots (see Figs. 3, 4, 5). The O-alkyl C content of foliage residues in the combined-residue plots decreased significantly and the alkyl C

content increased significantly between 3 and 6 months (see Fig. 5). After six months, the contribution of O-alkyl C increased, while the contribution of alkyl C decreased. By 24 months, the foliage from the combined-residue plots had significantly less alkyl C than the foliage from the foliage-only plots (see Fig. 4).

Our data suggest that the mixing of branch, stem and foliage residues has a synergistic effect on the decomposition of foliage (but not branch or stem residues). This may be related to the composition of the microbial community responsible for the decomposition. Hoop pine branch and stem residues have a C:N ratio of approximately 300 and 200, respectively, while foliage residues have a C:N ratio of about 40 (Mathers et al. 2003). Fungal decomposition dominates when substrates are N-limited, whereas bacterial decomposition is prevalent when C:N ratios are lower (e.g., Berg and Laskowski 2006). Therefore, the decomposer community in the combined-residue plots may have included a diverse assemblage including both fungal and bacterial microbes, whereas the single-residue plots may have featured largely fungal-dominated or largely bacterial-dominated microflora. Further research into the microbial community structure of mixed residue systems would provide insight into this synergistic pattern (Zhang et al. 2007a, b, 2009; Xu et al. 2009). Another potential factor is microclimate. McColl and Powers (1998) observed striking differences in the composition of decomposing red fir (*Abies magnifica* A. Murr.) debris in thinned versus unthinned plots, a result that they attributed to stand-thinning effects on microclimate at the soil surface. The greater mass of residues present in our combined-residue plots likely resulted in increased moisture retention and fewer temperature extremes than in the foliage-only plots (Blumfield et al. 2004a).

4.3 Lignin and cellulose decomposition

Although the relative proportions of the major C fractions in the single-residue treatments did not change very much during decomposition (see Fig. 5), the ^{13}C CPMAS NMR spectra did reveal some preferential decomposition patterns. The spectra for the branch residues clearly showed a decrease in the phenolic C peaks at 148 and 153 ppm during decomposition (see Fig. 1), indicating a decrease in the relative amount of lignin. In the stem wood residues (see Fig. 2), the peak at 89 ppm became sharper and larger relative to the 83 ppm peak as decomposition progressed, suggesting an increasing importance of crystalline cellulose relative to amorphous cellulose. Davis et al. (1994a,b) found that white rot fungi showed a slight preference for

decomposition of amorphous cellulose, resulting in an increase in the importance of crystalline cellulose, in both *Picea pungens* (a softwood) and *Betula papyrifera* (a hardwood). They suggested that it was more difficult for the enzymes responsible for the degradation of cellulose to penetrate the crystalline structures than the amorphous regions. Although Davis et al. (1994a) did not observe a relative decrease in phenolic C, or other indications of preferential decomposition of lignin, they did observe that white rot fungi were effective in attacking guaiacyl lignin in *Picea pungens*. They suggested that lignin decomposition occurred through cleavage of the C_α-C_β bond, creating a monomer similar to vanillic acid. A similar pathway may be relevant in our residues, perhaps followed by alteration of the phenolic-OH group.

5 Conclusions

Despite mass losses of up to 62%, we observed only minor preferential decomposition of woody residues from hoop pine logging over the two-year study period. Branch wood residues experienced some preferential loss of aromatic C due to the decomposition of lignin, and there was evidence for a slight preferential decomposition of amorphous cellulose over crystalline cellulose. In general, however, the relative amounts of alkyl C, O-alkyl C, aromatic C and carbonyl C in the woody residues remained approximately constant through two years of decomposition, regardless of whether they were incubated separately or part of the combined foliage+branch+stem treatment. In contrast, decomposition of foliage residues exhibited a synergistic pattern when combined with the branch and stem materials. Residues from the foliage-only treatment demonstrated few preferential decomposition patterns. However, foliage in the combined-residue treatment experienced significant short-term decreases in O-alkyl C and increases in alkyl C, followed by longer-term increases in O-alkyl C and decreases in alkyl C. Further research into the microbial community structure in mixed-residue environments may help shed light on this interesting result.

After 24 months of decomposition we found little evidence for the relative enrichment of more recalcitrant forms of C – alkyl and aromatic C in particular. Therefore, while the decomposing residues provide short-term insulation and water-holding capacity (Blumfield et al. 2004a,b), they do not appear to be undergoing a substantial amount of humification, and may not contribute significantly to the long-term sequestration of C in hoop pine plantation soils. If this is a management goal, it may be necessary to incorporate the residues into the upper soil layers.

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Table 1 Chemical shift assignments for carbon structures and spinning sidebands (SSB). Assignments are based on those of Baldock and Smernik (2002) and Mathers et al. (2003)

Chemical shift region	Assignment	Key resonances
0-46 ppm	Alkyl C	Methyl C, short- and long-chain aliphatic C
46-59 ppm	Methoxyl and N-Alkyl C	—OCH_3, amino groups
59-94 ppm	O-Alkyl C	Carbohydrate C, cellulose, alcohols, amino sugars
94-110 ppm	Di-O-Alkyl C	Anomeric C1 of celluloses, tannin components
110-141 ppm	Aryl and Unsaturated C	C- and H-substituted aromatic C, olefinic C, lignin and tannin components
141-160 ppm	O-Aryl C	Phenolic C, lignin and tannin compounds, O- and N-substituted aromatic C, olefinic C
160-190 ppm	Carbonyl and Amide C	Carboxyl C, amide and ester C
190-212 ppm	Ketone C, O-aryl SSB	Ketones and aldehydes, spinning sideband for O-aryl C occurs at 200 ppm
212-250 ppm	Carboxyl SSB	Spinning sideband for carboxyl C occurs at 223 ppm

Table 2 Percent mass remaining of hoop pine residues after 24 months of decomposition in single-component and combined-residue microplots. Values shown are means ± standard error. The differences between single-component and combined-residue values are statistically significant for stem and foliage ($P < 0.05$)

Residue	Single-component microplots	Combined-residue microplots
Branch	69.9 ± 5.4	62.8 ± 4.5
Stem	74.3 ± 6.3	49.5 ± 6.7
Foliage	35.1 ± 1.6	63.2 ± 2.1

Figure Captions

Fig. 1 ^{13}C CPMAS NMR spectra of hoop pine branch residues at different stages of decomposition

Fig. 2 ^{13}C CPMAS NMR spectra of hoop pine stem-wood residues at different stages of decomposition

Fig. 3 ^{13}C CPMAS NMR spectra of hoop pine foliage residues at different stages of decomposition. Examples are shown for foliage from foliage-only microplots and from microplots in which foliage, branch and stem wood were combined

Fig. 4 Integrated intensity values for major ^{13}C CPMAS NMR spectral regions in hoop pine residues incubated in microplots for 24 months. Error bars indicate one standard error, and statistically significant differences between single-component and combined-residue plots are shown with an asterisk (*, $P < 0.05$)

Fig. 5 Changes in the contributions of the major spectral regions to the overall spectral intensity of hoop pine logging residues during decomposition. Error bars indicate plus or minus one standard error, and in some cases are smaller than the symbol. For branch and stem residues there were no significant differences between single-component and combined-residue spectra (Fig. 4), so those data are pooled in this figure

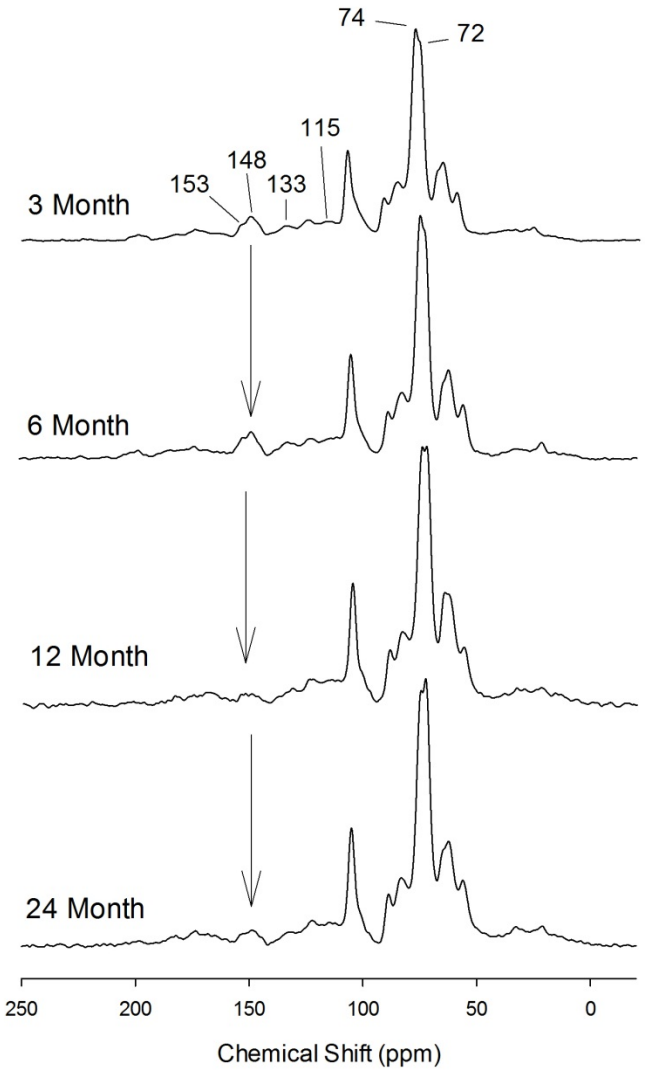
74
72
115
148
153
133
3 Month
6 Month
12 Month
24 Month
250
200
150
100
50
0
Chemical Shift (ppm)

Figure 1

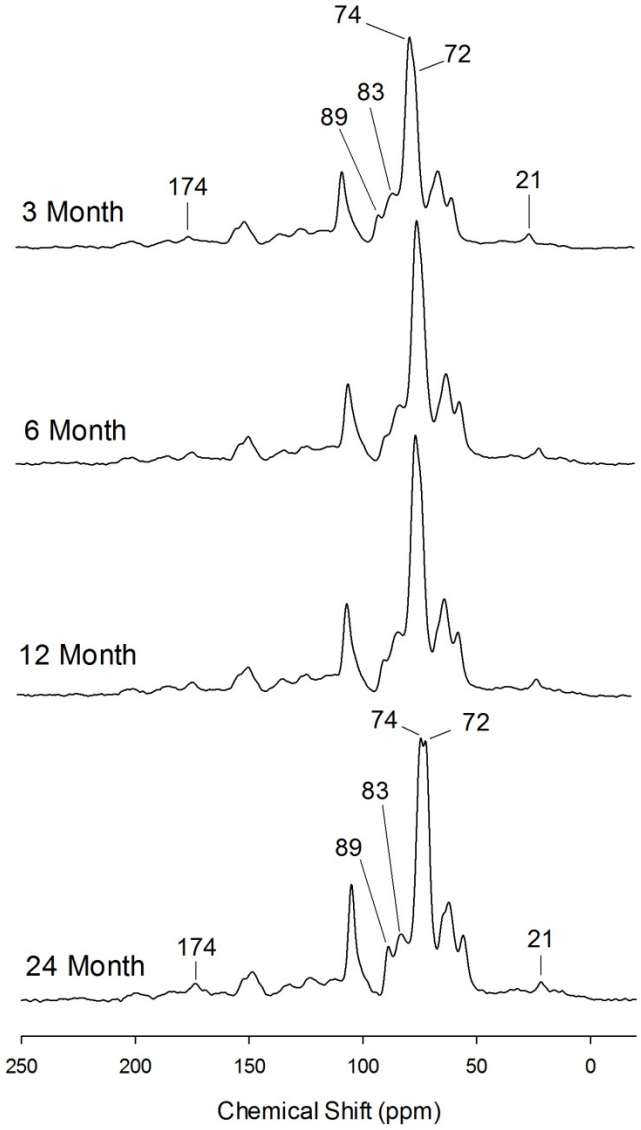
74
72
83
89
174
21
3 Month
6 Month
12 Month
74
72
83
89
174
21
24 Month
250
200
150
100
50
0
Chemical Shift (ppm)

Figure 2

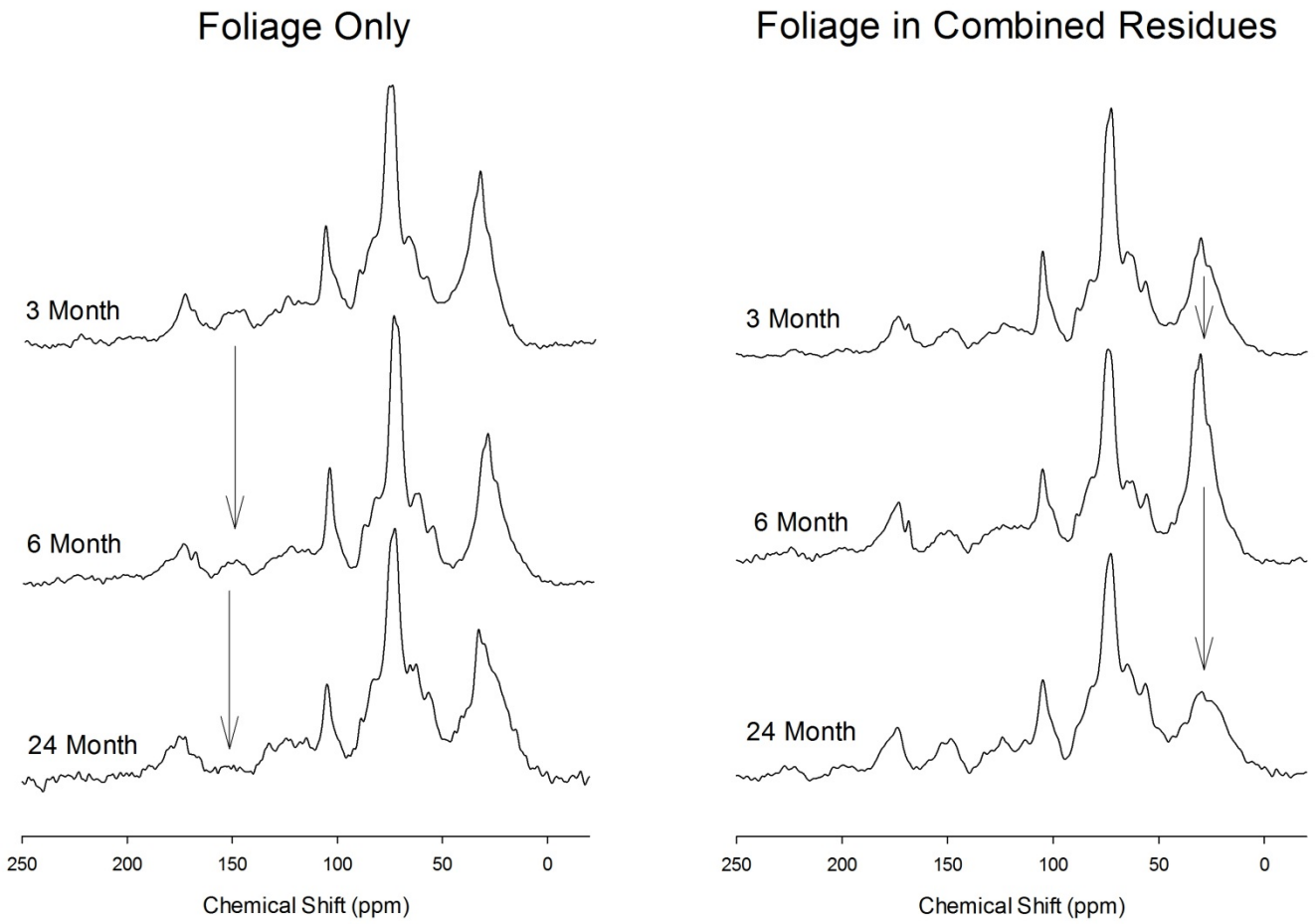
Foliage Only
3 Month
6 Month
24 Month
250
200
150
100
50
0
Chemical Shift (ppm)
Foliage in Combined Residues
3 Month
6 Month
24 Month
250
200
150
100
50
0
Chemical Shift (ppm)

Figure 3

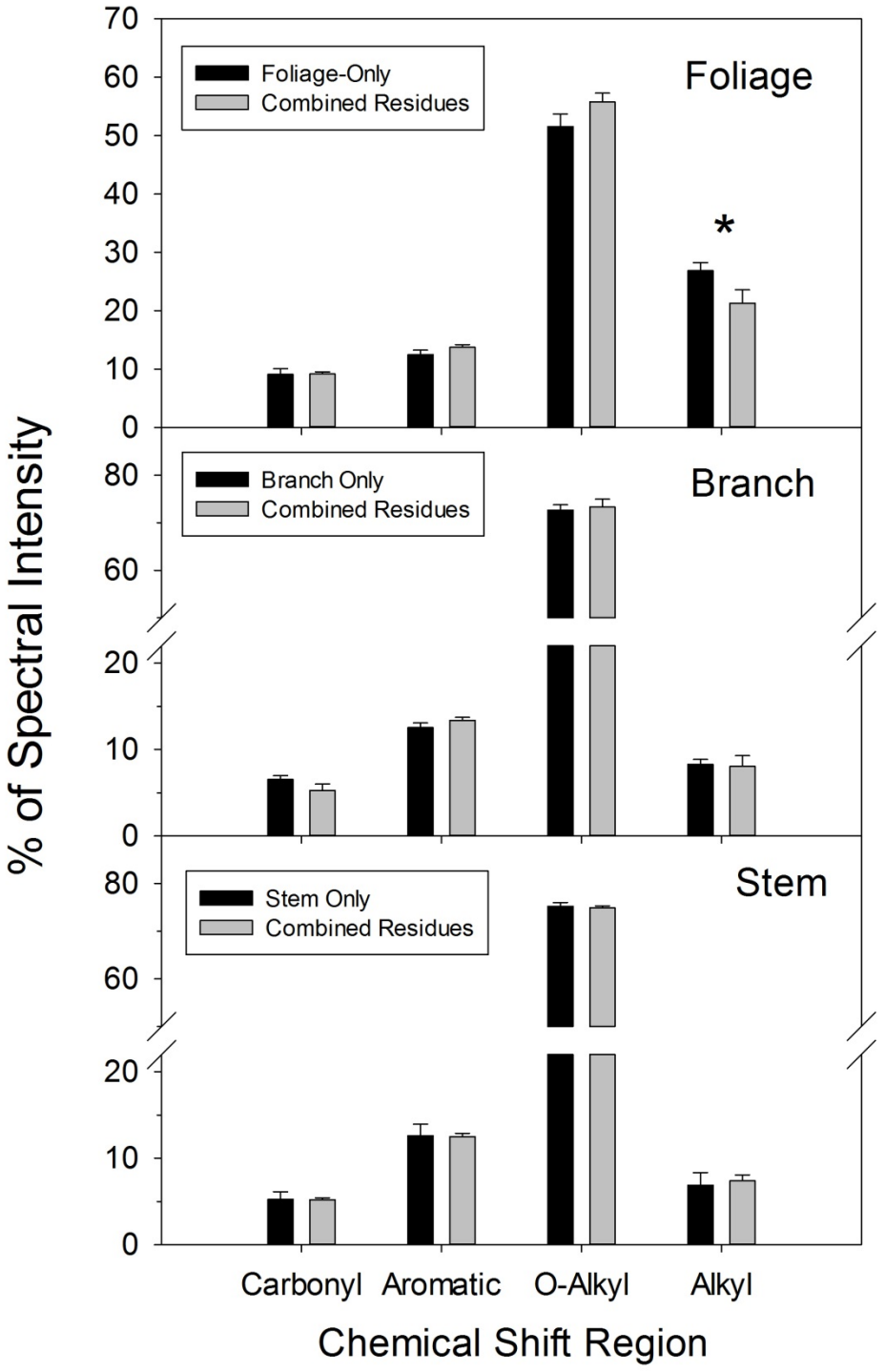
% of Spectral Intensity
Foliage-Only
Combined Residues
Foliage
*
Branch Only
Combined Residues
Branch
Stem Only
Combined Residues
Stem
Carbonyl
Aromatic
O-Alkyl
Alkyl
Chemical Shift Region

Figure 4

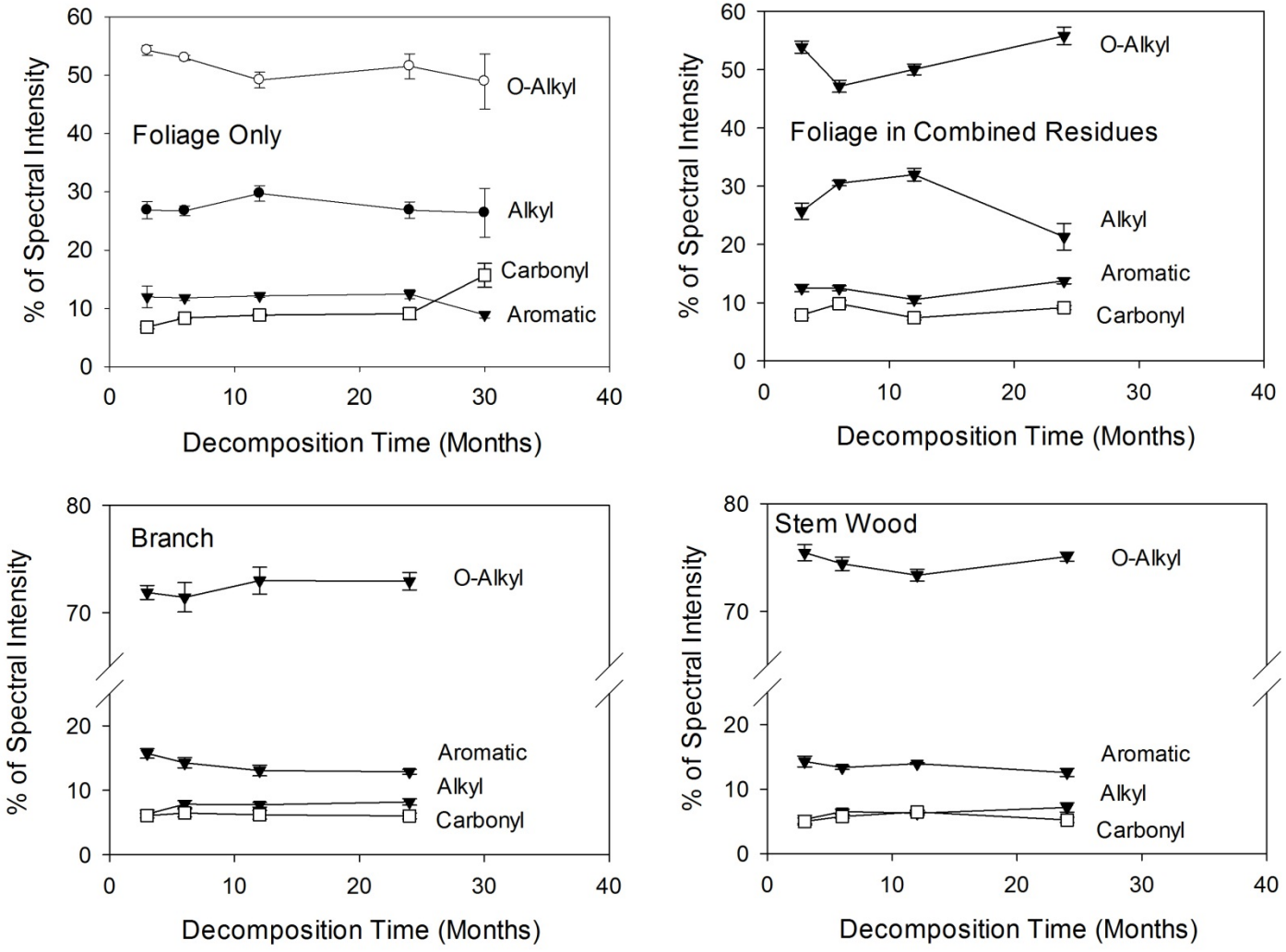
Foliage Only
O-Alkyl
Alkyl
Carbonyl
Aromatic
% of Spectral Intensity
Decomposition Time (Months)
Foliage in Combined Residues
O-Alkyl
Alkyl
Aromatic
Carbonyl
% of Spectral Intensity
Decomposition Time (Months)
Branch
O-Alkyl
Aromatic
Alkyl
Carbonyl
% of Spectral Intensity
Decomposition Time (Months)
Stem Wood
O-Alkyl
Aromatic
Alkyl
Carbonyl
% of Spectral Intensity
Decomposition Time (Months)

Figure 5