Chemical transformations of deadwood and foliar litter of mixed boreal species during decomposition

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Abstract: Deadwood constitutes an important input of carbon to soil, but its role in carbon sequestration over the long term is not well documented in the eastern boreal forests of Canada, especially when compared with foliar litter. The objectives of this study were to characterize and compare patterns of mass loss and changes in chemical composition of deadwood and foliar litter of trembling aspen (*Populus tremuloides* Michx.), white spruce (*Picea glauca* (Moench) Voss), and balsam fir (*Abies balsamea* (L.) Mill.) during a 5- to 6-year period of field decomposition, using litterbags, solid-state ^{13}C nuclear magnetic resonance analysis, and lignin monomer quantification by cupric oxide oxidation. The maximum decomposition limit was similar between foliar litter and wood material, but foliar litter decomposed faster, reached the estimated maximum decomposition limit, and converged to a composition rich in alkyl, phenolic, and carbonyl carbon. However, wood did not reach the estimated maximum decomposition limit and underwent relatively little chemical changes, remaining with high carbohydrate content. At the end of the experiment, aspen wood still had a lower lignin concentration than that of conifers, but contained higher proportions of alkyl and carbonyl carbon. Although wood contributes to a greater diversity in the chemical composition of the forest floor, foliar litter, which keeps a high alkyl C content throughout its decay, could generate more recalcitrant residual organic matter.

Résumé : Une quantité importante de carbone dans les sols vient du bois mort mais son rôle dans la séquestration du carbone à long terme, comparativement à celui des litières de feuilles, n'est pas bien documenté dans les forêts boréales de l'Est du Canada. Les objectifs de cette étude étaient de caractériser et de comparer les patrons de perte de masse et les changements dans la composition chimique du bois mort et des litières de feuilles du peuplier faux-tremble (*Populus tremuloides* Michx.), de l'épinette blanche (*Picea glauca* (Moench) Voss) et du sapin baumier (*Abies balsamea* (L.) Mill.) pendant une période d'incubation in situ de 5 à 6 ans, au moyen de sacs de litières, d'analyses par résonance magnétique nucléaire du ^{13}C en phase solide et de la quantification des monomères de lignine par oxydation à l'oxide de cuivre. La limite maximale de décomposition des litières de feuilles et du bois mort était similaire, mais les litières de feuilles se décomposaient plus rapidement, atteignaient la limite maximale de décomposition estimée et convergeaient vers une composition riche en carbone alkyle, phénolique et carbonyle. Au contraire, le bois n'atteignait pas la limite maximale de décomposition estimée, subissait peu de changements chimiques et conservait une teneur élevée en cellulose. A la fin de l'expérimentation, le bois de peuplier faux-tremble avait toujours une concentration en lignine plus faible que celle des conifères, mais des concentrations plus élevées en carbone alkyle et carbonyle. Alors que le bois contribue à augmenter la diversité chimique de la couverture morte, les litières de feuilles, qui conservent un contenu plus élevé en composés alkyles tout au long de la décomposition, pourraient générer une matière organique résiduelle plus récalcitrante.

[Traduit par la Rédaction]

Introduction

In Canada, boreal forests cover 304 Mha, representing a carbon (C) pool of 186 Pg (Bhatti et al. 2003), 84% of which is contained in soils (IPCC 2001). Historically, wildfire and insect outbreaks were the dominant disturbances affecting boreal forests, but harvesting contributes to an increasing fraction of the overall disturbance effects (Seedre et al. 2011). Forest harvesting modifies soil C dynamics through input of logging slash, alteration of litter input from remaining vegetation, increased microbial respiration, and increased leaching (Jandl et al. 2007). In particular, partial and selective cutting promoted by ecosystem management to diversify silvicultural practices has an impact on the chemical quality of litter input, as it changes the balance between foliar litter fall, deadwood, and dead roots recruitment (Harvey and Brais 2007; Lee et al. 2002).

Litter quality is a significant factor controlling decomposition and then carbon sequestration in soils and may influence its early decay rate (Prescott 2010), its maximum decomposi-

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tion limit (Berg 2000; Berg et al. 1996), and in some cases, composition of the residual soil organic matter (Quideau et al. 2001). Nitrogen (N) is one of the key components of litter quality, initially enhancing decomposition but reacting with lignins to form recalcitrant complexes in later stages of decay (Berg 2000). Although lignins were traditionally considered a major source of stable carbon, recent evidence suggests that some lignin components have a relatively rapid turnover (Thevenot et al. 2010). Tannins can sequester proteins, forming complexes resistant to decomposition (Kraus et al. 2003), whereas aliphatic compounds, including cutin, suberin, and lipids, are considered the most recalcitrant compounds (Lorenz et al. 2007).

Litter quality, mainly described for foliar litter, is often characterized using parameters incorporating nitrogen and lignin content, and the relationship of these parameters to ease of decomposition is assessed by means of correlations with litter decay rates (Taylor et al. 1989). However, in many studies, lignin is loosely defined as the acid-unhydrolyzable residue (AUR) of the proximate analysis, although this may include other recalcitrant compounds such as tannins and cutin (Preston et al. 2009*b*). Moreover, the negative exponential model used to estimate decay rates (Trofymow et al. 1995) may not describe C dynamics adequately as it assumes a constant decay rate and a complete decomposition (Berg et al. 1995). In northern forests, decay rates are not constant over time and eventually drop to very low levels (Prescott 2005, 2010), corresponding to the maximum decomposition limit of the litter (Berg et al. 1996). Quantifying changes in chemical properties with decay and the maximum decomposition limit of litters should further our understanding of how litter contributes to long-term forest soil C sequestration (Berg 2000; Prescott 2005, 2010).

Among boreal tree species, aspen has a relatively easily decomposable litter compared with conifers (Flanagan and Van Cleve 1983). Aspen leaves contain more labile material and less AUR than conifers needles (Trofymow et al. 2002). Because they are demethylated faster, the syringyl units from deciduous lignins are thought to be preferentially degraded over the vanillyl units found in all plants (Otto and Simpson 2006). Also, phenols and tannins present mainly in conifers can hinder decomposition (Hernes and Hedges 2004; Kraus et al. 2003). Wood contains more lignin than foliage but very low amounts of nitrogen and aliphatic compounds (Alban and Pastor 1993; Preston et al. 2009*a*; Trofymow et al. 1995); it also has lower decay rates (Alban and Pastor 1993; Moore et al. 2006). An important intersite study realized in western Canada (Preston et al. 2009*a*, 2009*b*; Trofymow et al. 2002, 1995) showed that foliar litters became closer in chemical composition after 6 years of decomposition when compared with their initial composition; specifically, they became more concentrated in AUR arising from a collective increase in lignins, tannins, and cutin. However, few studies have compared the decomposition of foliar litter and coarse woody debris from the same species (Krzyszowska-Waitkus et al. 2006) and their respective contribution to C retention in soils.

The objective of this study was to characterize and compare patterns of mass loss and changes in chemical composition of wood and foliar material for three boreal species of contrasting quality using a litter bag experiment, solid-state nuclear magnetic resonance (NMR) spectroscopy, and cupric oxide (CuO) oxidation analyses. (*i*) We expected wood to have a higher maximum decomposition limit than foliar litter, despite its slower decomposition rate, because of its low N content (Berg et al. 1996). (*ii*) Foliar litters, containing aliphatic compounds, were hypothesized to converge to a composition rich in alkyl C, whereas wood containing little aliphatic compounds were expected to converge to a composition rich in aromatic C from lignins. (*iii*) We also expected lignins from aspen to be less recalcitrant than those of conifers and to change their composition and content during decomposition.

Materials and methods

Study area and experimental design

The study area is located in the Lake Duparquet Research and Teaching Forest in the Abitibi region of northern Quebec, 45 km northwest of Rouyn–Noranda, Quebec (48°86′N–48°32′N, 79°19′W–79°30′W). Mean annual temperature is 0.7 °C, and mean temperatures of the warmest and coldest months (July and January) are 16.9 and –18.2 °C, respectively. Annual precipitation is 890 mm, of which 614 mm falls as rain from April to November (Environment Canada 2010). Soils have evolved from fine clayey to fine loamy textured glaciolacustrine deposits formed by sedimentation at the bottom of glacial Lake Barlow-Ojibway (Veillette et al. 2000) under fresh to moist moisture regimes (Brais and Camiré 1992) and are classified as Gray Luvisols (Agriculture et Agro-Alimentaire Canada 2002). The region is situated in the mixedwood zone of the boreal shield within the western balsam fir – white birch bioclimatic domain. Forest succession on rich mesic sites generally begins with the establishment of pure or mixed stands of white birch (*Betula papyrifera* Marsh.), trembling aspen (*Populus tremuloides* Michx.), and jack pine (*Pinus banksiana* Lamb.) that maintain dominance for over 100 years. In the absence of a major disturbance, these species are gradually replaced by a mixture of shade-tolerant species such as white spruce (*Picea glauca* (Moench) Voss), black spruce (*Picea mariana* (Mill.) B.S.P.), and balsam fir (*Abies balsamea* (L.) Mill.) (Bergeron and Dubuc 1989).

The study was conducted within the SAFE (Sylviculture et Aménagement Forestier Écosystémiques) project, a series of silvicultural experiments testing an ecosystem management model based on natural dynamics (Brais et al. 2004). The project is set in three natural stand types (Table 1) originating from forest fires dating from 1923 (ASPEN stand), 1910 (MIXED stand), and 1760 (OLD stand). Trembling aspen represented 92% of the basal area of the ASPEN stand and 81% of the MIXED stand, whereas white spruce and balsam fir accounted for 18% of the total basal area of the latter stand. The oldest stand type (OLD) was affected by the 1970–1987 outbreak of spruce budworm (*Choristoneura fumiferana*) (Morin et al. 1993) and was characterized by a mixed composition of white birch, white spruce, and balsam fir.

This study was limited to control (unharvested) stands and included three replications in each stand type for a total of nine experimental units (1–2 ha). In all experimental units,

Table 1. Forest stand descriptions and chronology of litterbag collections.

		Year of collection (time (t) of decay)				
Stand type	Litter type	Initial	1st	2nd	3rd	4th
ASPEN	Trembling aspen leaves and wood	1999* (t = 0)	2000* (1 year)	2002* (3 years)	2004 (5 years)	2005* (6 years)
MIXED	White spruce needles and wood	2001* (t = 0)	2002* (1 year)	2005 (4 years)	2007* (6 years)	—
OLD	Balsam fir needles and wood	2000* (t = 0)	2001* (1 year)	2004 (4 years)	2005* (5 years)	—

*Samples from these collections were analyzed by NMR and CuO oxidation.

five permanent sampling plots (400 m^2) were established at the onset of the study.

Litterbag decomposition experiment

Freshly fallen leaves of aspen were collected in the fall, whereas fresh needles of fir and spruce were sampled directly on trees. Wood blocks were cut (10 × 5 × 5 cm) from dimensional lumbers of each species. Foliar material (±10 g) and wood blocks (100–150 g) were enclosed in litterbags (±10 × 8 cm) made of fiberglass (1 mm mesh size), with their initial moist mass printed on DYMO tape. Five to 10 subsamples of each litter type (n = 42) were dried (48 h, 65 °C) to determine the moist-to-dry mass conversion factor and to characterize initial litter chemical composition. Five litterbags containing wood blocks and five containing foliage from one of the stands dominant species were positioned in each permanent sampling plot and left in situ to decompose. A total of 300 litterbags were collected 1 to 6 years after the start of the experiment (Table 1).

After collection, the exterior of each litterbag was carefully cleaned with a brush. Foliar material or wood blocks were removed from the bags and manually sorted to eliminate any mineral soil or plant remains. Material was dried (48 h, 65 °C) and weighed. Initial moist mass was converted to dry mass, and mass loss was estimated. Materials for each collection date and litter type were pooled over experimental units, leading to 60 samples. A total of 102 samples (42 nondecomposed samples and 60 field-incubated samples) were ground to 0.5 mm for chemical analyses. A subset of 60 samples (three undecayed samples per litter type and samples at different times of decay; see Table 1) was analyzed by NMR and CuO oxidation.

Laboratory analyses

Solid-state ^{13}C cross-polarization with magic angle spinning (CPMAS) NMR analyses were carried out using a Bruker Avance 400 spectrometer (B_0 = 9.4T, $\nu_L(^{13}C)$ = 100.6 MHz) with ramped cross-polarization (RAMP-CP) according to the procedure followed by Thiffault et al. (2008) and Turcotte et al. (2009). Spectra were acquired with a ^{1}H 90° pulse length of 4 μs, a pulse delay of 5.0 s, a cross-polarization contact time of 1.0 ms, an acquisition time of 17.1 ms, and a spinning frequency of 13 kHz. A ramped ^{1}H pulse was used to circumvent spin modulation of Hartmann–Hahn conditions. Four or eight thousand scans were processed, depending on the samples, using line broadening set at 200 Hz. Chemical shifts were reported relative to tetramethylsilane (TMS) at 0 ppm, with the reference frequency set using adamantane. The Bruker's WIN-NMR package was used to estimate the relative integrated areas of the different spectral regions between 0 and 222 ppm, after corrections for spinning sidebands. Spectra were divided into a total of seven chemical shift regions according to the studies of Baldock et al. (1992) and Knicker and Lüdemann (1995): (1) alkyl C (0–46 ppm) region from lipids, cutin, and amino acids; (2) methoxyl C (46–58 ppm), (3) *O*-alkyl C (58–93 ppm), and (4) di-*O*-alkyl C (93–111 ppm) regions from carbohydrates, amino acids, and methoxyl C of lignins (= *O*/*N*-alkyl C, which includes regions 2, 3, and 4); (5) aromatic C (111–142 ppm) and (6) phenolic C (142–166 ppm) regions from lignins, tannins and olefins; and (7) carbonyl C (166–222 ppm) region from carboxylic acid, amide, ester, aldehyde, and ketone in lignins, proteins, lipids, carbohydrates, and tannins. Although there are limitations in the quantitative reliability of CPMAS spectra (Preston et al. 1990), it is appropriate to use NMR to compare intensity distribution and study structural features when samples do not differ widely in composition and are run under similar experimental conditions (Preston 1996), as was the case for our study. To obtain further information on C structures, dipolar dephased (DD) spectra were generated for six samples (one of each initial litter type) by inserting a delay period of 40 μs without ^{1}H decoupling between the cross-polarization and acquisition portions of the CPMAS pulse sequence (Thiffault et al. 2008). All DD spectra were obtained using the TOSS sequence for total suppression of spinning sidebands (Lorenz et al. 2000).

The analysis of lignin monomers by CuO oxidation provides additional information on the nature of lignins, their degradability, and their oxidation state (Dignac et al. 2005). Cupric oxide oxidation was carried out according to the method developed by Hedges and Ertel (1982) and modified by Kögel and Bochter (1985) and Turcotte (2009). Each sample (50 mg) was added to a PARR stainless steel Teflon bomb (no. 4749) containing CuO (1 g), iron (II) ammonium sulphate hexahydrate (0.1 g), and 15 mL of 2 mol·L^{-1} NaOH. The bomb was placed in an oven (model no. 1330GMS, VWR International, Cornelius, Oregon) and heated at 150 °C for 3 h. After cooling under running water, the sample was centrifuged at 4000 rpm for 20 min. The supernatant was transferred into a beaker, and the litter residue was washed with 10 mL deionized water, vortexed, centrifuged, and added to the beaker containing the supernatant. The solution was acidified with 6 mol·L^{-1} HCl to a pH of 1.8–2.2. Ethylvanillin (100 μL at 200 ppm) was added to the sample as a recovery standard. After being kept in the dark overnight,

the sample was filtered through a SPE C18 column (50 μm particle size, 60 Å pore size, 8 cm^3 column size) (Alltech Associates, Inc., Deerfield, Illinois). The final phenolic products were eluted with 0.8 mL ethyl acetate, dried, and derivatized to their silylated forms by adding BSTFA (*N*,*O*-Bis(trimethylsilyl)trifluoroacetamide) as the derivatizing agent and pyridine as the final solvent. Phenylacetic acid (100 μL at 200 ppm) was added as an internal standard. Samples were analysed immediately by a gas chromatograph – flame ionization detector (GC-FID) on a HP GC 5890 equipped with a HP Ultra 2 (cross-linked Ph Me Silicone) (25 m × 0.32 mm × 0.52 μm). The initial temperature was 120 °C for 2 min, increased to 160 °C at a rate of 8 °C·min^{-1}, increased to 170 °C at a rate of 4 °C·min^{-1}, and increased to 300 °C at a rate of 20 °C·min^{-1}. The injector was kept at 280 °C, and the detector was kept at 350 °C. Samples were injected in split mode (1:5). Results from GC-FID analyses with a recovery below 30% were discarded.

From the GC-FID chromatographs, 11 lignin phenols were quantified. The sum of vanillin (Val), vanillic acid (Vac), and acetovanillone (Vc) constitutes the vanillyl phenols (V); the sum of syringaldehyde (Sal), syringic acid (Sac), and acetosyringone (Sc) comprises the syringyl phenols (S); the *p*-hydroxy phenols (P) include *p*-hydroxybenzaldehyde (Pal), *p*-hydroxybenzoic acid (Pac), and *p*-hydroxyacetophenone (Pc); and the sum of *p*-coumaryl acid (Cco) and ferulic acid (Cfe) corresponds to the cinnamyl phenols (Cn). The sum of vanillyl, syringyl, cinnamyl, and *p*-hydroxy phenols represents the total phenolic constituents (TPC). The resolution of GC peaks of the syringyl phenols in foliage was not well resolved, so we removed these data from the results.

Total C and N contents were determined by dry combustion using a CNS 2000 analyzer (LECO Corporation, St. Joseph, Michigan).

Data analyses

The proportion of initial mass remaining (residual mass), as well as the percentage of initial mass of N and C remaining at each collection date, were calculated for all individual litterbags. The maximum decomposition limit was estimated for each litter type using a single negative exponential model with an asymptote (Harmon et al. 2009):

$$[1] \qquad M_t = M_0 \times e^{-kt} + S_0$$

where M_t is the residual mass (%) at time t (years), M_0 is the initial mass of material subject to loss (%), S_0 is the asymptote (%), and k is the decomposition rate. The sum of M_0 and S_0 is 100%, and an estimate of one can be used to derive the other (Harmon et al. 2009). Parameters of the model were estimated using a nonlinear regression with the nls function from the nlrwr library of the R software (version 2.12.0, R Development Core Team (http://www.r-project.org/)). The amount of N remaining (as a percentage of initial mass) was plotted over the amount of C remaining (as a percentage of initial mass). The polynomial regression was used to predict the C content remaining at the maximum N content (Moore et al. 2006) and then establish the critical C:N quotient, indicating the point after which there was a net loss of N.

The effects of material (wood vs. foliage), tree species, and time of decomposition on litter characteristics were assessed by means of linear mixed models and Wald's *t* test (Pinheiro and Bates 2000) using the lme function included in the nlme library of R software. Experimental units within stand types were treated as a random factor. Material, species (two contrasts: C1, aspen vs. conifers; C2, fir vs. spruce) and time of decomposition, as well as their double and triple interactions, were treated as fixed factors. Interactions were removed from the models when found to be nonsignificant. Response variables were C and N concentrations, C:N ratio, alkyl:*O*/*N*-alkyl ratio, which corresponds to the division of alkyl (0–46 ppm) by the sum of methoxyl, *O*-alkyl, and di-*O*-alkyl (46–111 ppm) (Baldock and Preston 1995), phenolic:*O*-alkyl ratio (Dignac et al. 2002), as well as ratios of lignin phenols, the acid:aldehyde ratios (Vac:Val, Sac:Sal, Pac:Pal), which can be used to estimate the oxidation state of lignins, the S:V ratio, as an indicator of angiosperm contribution, the Cn:V ratio, an indicator of nonwoody tissues contribution, and the P:V ratio (Hedges et al. 1988). The corCAR argument was used to account for the correlation between measures with time. Normality and homogeneity of variances were verified by visual assessment of residuals. When these assumptions were not met, square-root or logarithmic transformations were applied.

To synthetize information generated by NMR spectroscopy, spectral NMR areas from all litter types and collection dates were analyzed using the nonmetric multidimensional scaling (NMS) method (Kruskal 1964) with the PC-ORD software (version 5, MjM Software Design, Gleneden Beach, Oregon). This ordination method is well suited to nonnormal or semiquantitative data such as the integrated spectral NMR areas. The Sorensen (Bray–Curtis) distance measure was used. The variables included in the first matrix were the seven integrated spectral NMR areas (alkyl, methoxyl, *O*-alkyl, di-*O*-alkyl, aromatic, phenolic, and carbonyl), relativized by row and standardized using the arcsine square-root transformation. The second matrix contained the NMR areas to map these vectors over the first matrix, as well as three variables: material (wood vs. foliage), tree species, and time of decomposition. In addition, the multiresponse permutation procedure (MRPP) analysis with the Sorensen distance was used to compare distances in the ordination space between different litter types and decomposition times to determine whether these groups of litters were statistically different. In addition to the p value, MRPP results include the T value, which indicates separation among groups (with larger values for stronger separation), and the A value, which indicates within-group homogeneity compared with random expectation.

Results

Maximum decomposition limit, decay rates, and residual biomass

Predicted residual organic matter (S_0, asymptote) ranged from 22.4% to 53.8% (Table 2*a*; Figs. 1A, 1B, and 1C). Maximum decomposition limits were similar between foliar litters and wood blocks and among species (overlap of confidence intervals; Table 2*a*). Balsam fir needles decayed significantly faster than other foliar litters, and aspen wood decayed faster than spruce wood. Decay rates did not differ

Table 2. (*a*) Residual biomass of foliar litters and wood blocks from three boreal species after one year and at the end of a field decomposition experiment and model of residual mass (Figs. 1A, 1B, 1C). (*b*) Carbon and nitrogen remaining and model of nitrogen remaining (Figs. 1D, 1E, 1F).

(*a*) Residual mass vs. time model.

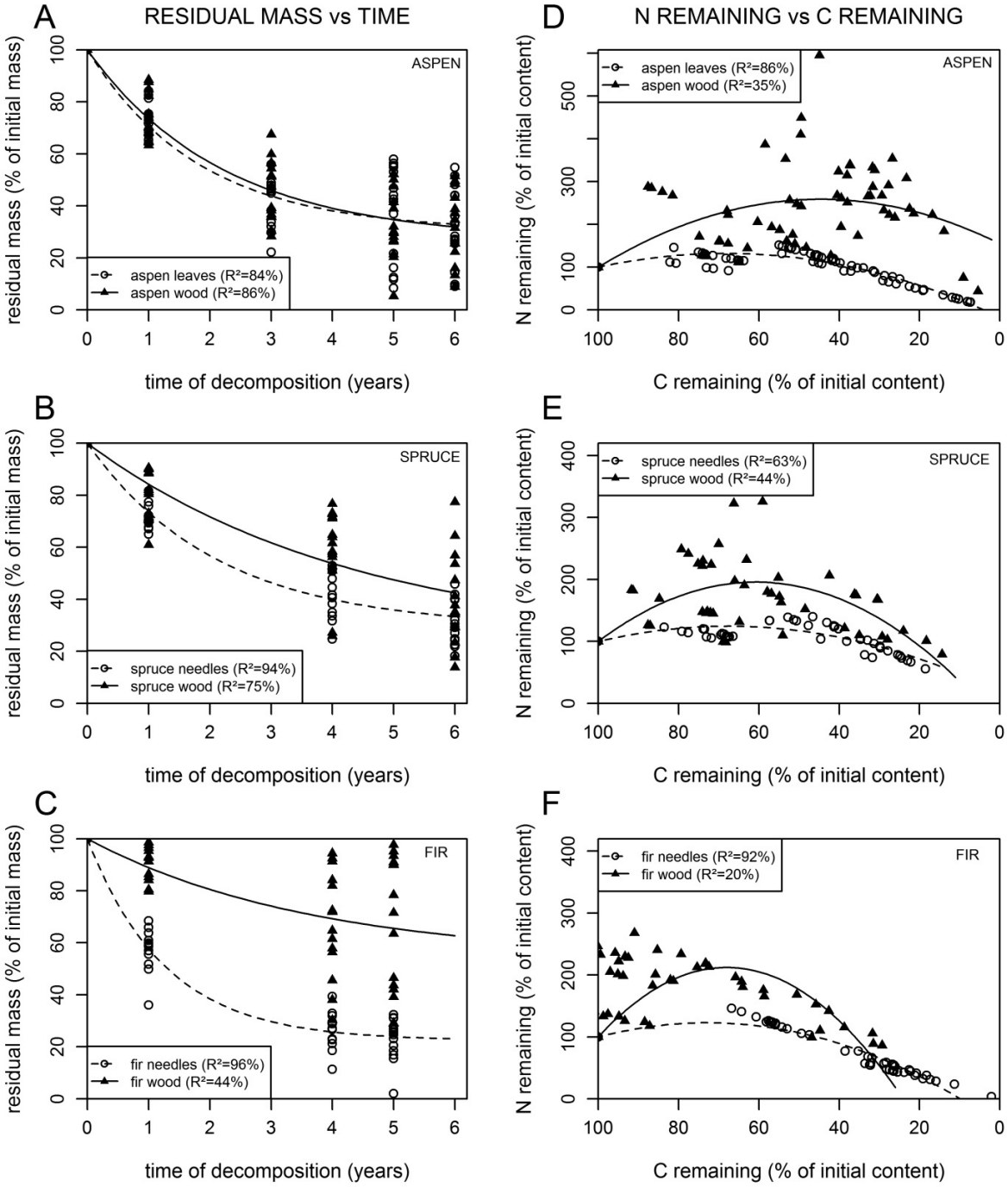
	Residual mass (% of initial mass)		Model of residual mass with time: $M_t = M_0 \times e^{-kt} + S_0$				
Litter types	After 1 year	After 5–6 years	Asymptote S_0 (%)	M_0 (= 1 – S_0) (%)	p	k (years^{-1})	p
Aspen leaves	72.7±3.2	32.4±7.3	30.4±6.5	69.6±6.5	<0.001	0.550±0.168	<0.001
Spruce needles	71.4±2.1	31.2±4.3	29.2±5.5	70.8±5.5	<0.001	0.472±0.109	<0.001
Fir needles	57.6±3.9	23.5±4.0	22.4±3.0	77.6±3.0	<0.001	0.788±0.115	<0.001
Aspen wood	73.9±4.2	33.0±7.1	27.1±7.9	72.9±7.9	<0.001	0.451±0.138	<0.001
Spruce wood	78.7±4.8	39.7±8.9	22.9±36.7	77.1±36.7	<0.001	0.229±0.199	0.028
Fir wood	91.5±3.7	66.7±13.2	53.8±51.5	46.2±51.5	0.084	0.274±0.578	0.358

(*b*) N remaining vs. C remaining model.

	C remaining (% of initial content)		N remaining (% of initial content)		Model of N remaining with C remaining: $N = a \times C^2 + b \times C + (1 - a - b)$				
							Maximum of curve		
Litter types	After 1 year	After 5–6 years	After 1 year	After 5–6 years	Equation	$p(a, b)$	C_m (%)	N_m (%)	C:N_m
Aspen leaves	71.9±3.0	29.9±7.2	117.8±7.6	83.3±21.4	$N = -3.20C^2 + 4.37C - 0.17$	<0.001	68	132	35.8
Spruce needles	71.8±2.5	31.9±4.4	112.0±2.8	97.0±13.4	$N = -2.33C^2 + 3.14C + 0.18$	<0.001	68	124	32.7
Fir needles	55.3±3.8	24.3±4.2	119.8±8.3	41.9±7.1	$N = -3.10C^2 + 4.51C - 0.41$	<0.001	73	123	25.7
Aspen wood	73.6±4.1	33.9±7.2	182.2±33.7	270.8±61.0	$N = -5.19C^2 + 4.64C + 1.55$	<0.001	45	259	149.1
Spruce wood	75.9±5.8	40.9±9.1	139.9±14.1	176.2±37.5	$N = -6.21C^2 + 7.55C - 0.34$	<0.001	61	196	244.7
Fir wood	93.6±3.9	69.2±13.4	159.5±20.6	196.9±35.4	$N = -11.0C^2 + 14.96C - 2.97$	<0.001	68	212	244.5

Note: Mean values (n = 15) ± confidence intervals. M_0, percentage of initial mass of material subject to loss; S_0, asymptote; k, decomposition rate; p, p value for individual parameters; a and b, parameters of polynomial regression model; $p(a, b)$, p value for a and b parameters; C_m, value of C remaining when N remaining is maximum in model; N_m, maximum of N remaining in model; C:N_m, C:N ratio when N remaining is maximum in model.

Fig. 1. Changes in residual mass with time of decomposition of foliar litters and wood blocks from (A) trembling aspen, (B) white spruce, and (C) balsam fir. Changes of nitrogen remaining with carbon remaining of foliar litters and wood blocks from (D) trembling aspen, (E) white spruce, and (F) balsam fir. Parameters of the models are described in Table 2.



significantly between aspen and spruce foliar litters and aspen wood blocks (Figs. 1A and 1B). The model for balsam fir wood was not significant because of the high variation in residual mass following 5 years of decay (Fig. 1C), but maximum decomposition limit was marginally significant (p = 0.084; Table 2*a*). After 5 to 6 years of decay, the observed amount of foliage residual mass ranged from 23.5% to 32.4% (Table 2*a*), indicating that foliar litters had almost reached their maximum decomposition limits. This was not the case for the wood blocks, especially for conifers as their residual masses were still between 39.7% and 66.7%.

Carbon and nitrogen dynamics

Initial C concentrations differed slightly between litter types (results not shown), and initial N concentrations were significantly ($p < 0.001$) higher in foliage than in wood (Tables 3 and 4). Increases in N concentrations with time were faster for wood than for foliage ($p = 0.003$). Wood N concentrations increased significantly ($p = 0.048$) faster for aspen than for fir and spruce, and by the end of the incubation period, concentrations were 9.1, 4.6, and 3 times higher than initial concentrations for aspen, spruce, and fir wood, respectively (Table 3). In terms of the foliage, the

Table 3. Carbon and nitrogen concentrations and C:N ratios of foliar litters and wood blocks from three boreal species at the start, after one year, and at the end of a field incubation experiment.

	C ($mg.g^{-1}$)			N ($mg.g^{-1}$)			C:N ratio		
Litter types	Initial	1st year	Final	Initial	1st year	Final	Initial	1st year	Final
Aspen leaves	479 (1)	474 (6)	433 (33)	8.0 (0.2)	13.0 (2.1)	19.6 (3.2)	60.2 (1.3)	37.2 (6.2)	22.3 (2.2)
Spruce needles	473 (5)	476 (14)	485 (3)	6.8 (0.4)	10.7 (0.6)	21.3 (0.4)	69.4 (3.9)	44.4 (2.4)	22.8 (0.3)
Fir needles	515 (3)	494 (7)	533 (2)	11.9 (0.1)	24.7 (0.6)	21.3 (0.7)	43.3 (0.3)	20.0 (0.3)	25.1 (0.9)
Aspen wood	480 (5)	478 (4)	493 (5)	0.6 (0.1)	1.5 (0.5)	5.5 (2.7)	806.0 (131.4)	347.6 (109.7)	105.3 (51.4)
Spruce wood	473 (11)	455 (35)	487 (4)	0.5 (0.3)	1.0 (0.2)	2.5 (0.7)	987.4 (298.2)	485.2 (98.3)	202.8 (63.2)
Fir wood	487 (11)	498 (1)	508 (20)	0.6 (0.05)	1.1 (0.4)	1.9 (0.4)	766.5 (61.6)	478.5 (132.5)	266.0 (40.9)

Note: Mean values are reported (n = 3, each from five pooled samples), and standard deviations are indicated in parentheses.

three species reached similar N concentrations (19.6–21.3 $mg \cdot g^{-1}$) by the end of the experiment. Initial C:N ratios were lower in foliar material than in wood (Tables 3 and 4). The decrease in C:N ratio with time was significantly (p = 0.020) faster for aspen than for coniferous species and significantly (p = 0.006) faster for wood than for foliar material (Table 4).

The N content in foliar litters increased during the first part of the experiment, until the N content reached between 123% and 132% of the initial amount (Figs. 1D, 1E, 1F); the critical C:N ratios after which there was a net loss of N were between 25.7 and 35.8 (Table 2*b*), which is higher than final C:N ratios in foliar litters (22.3–25.1; Table 3). For wood material, the data were highly variable, resulting in poor polynomial regressions (Figs. 1D, 1E, 1F). There was a net gain of N in wood followed by a net loss when C:N ratios reached values between 196 to 259 (Table 2*b*). These critical C:N ratios were reached by the end of the experiment by aspen and spruce wood litters, but not by fir wood (Table 3), in which the polynomial regression does not describe adequately changes of N content (Fig. 1F).

CPMAS NMR spectra

All ^{13}C CPMAS NMR spectra (Fig. 2; Appendix A, Table A1) were dominated by the *O*/*N*-alkyl region (46–111 ppm), which represented a higher proportion in wood (78%–83%) than in foliar litter (51%–66%). The most prominent signal at 73 ppm was characteristic of the C-2, C-3, and C-5 of pyranoside rings in cellulose and hemicelluloses (Preston et al. 2000). The di-*O*-alkyl peak at 105 ppm was assigned to anomeric C (C-1), whereas the peak at 65 ppm corresponded to the C-6 of these carbohydrates. The shoulders at 83 and 89 ppm may be due to C-4 of cellulose. The shoulder at 56 ppm was a signal for the methoxyl C characteristic of lignins. The *O*/*N*-alkyl region could also include some signals of condensed and hydrolysable tannins and contributions in the methoxyl region from *N*-alkyl C of proteins. The carbonyl region (166–222 ppm) was the least important on all spectra, although it was larger in foliar litter (4%–7%) than in wood (2%–3%) spectra. The peak at 173 ppm was attributed to carboxylic acids, amides, and esters (Fig. 2).

The alkyl region (0–46 ppm) represented a higher proportion of the spectra for foliar litter (16%–32%) than for wood material (5%–7%). Three peaks at 25–33 ppm arising from aliphatic compounds such as waxes, cutin, and lipids were present on the foliar litter spectra but not on the wood blocks spectra (Fig. 2). All spectra displayed a peak at 21 ppm corresponding to methyl C of the acetyl groups of hemicelluloses (Kolodziejski et al. 1982). Additionally, amino acids may contribute to the intensity of the alkyl and carbonyl regions (Almendros et al. 2000).

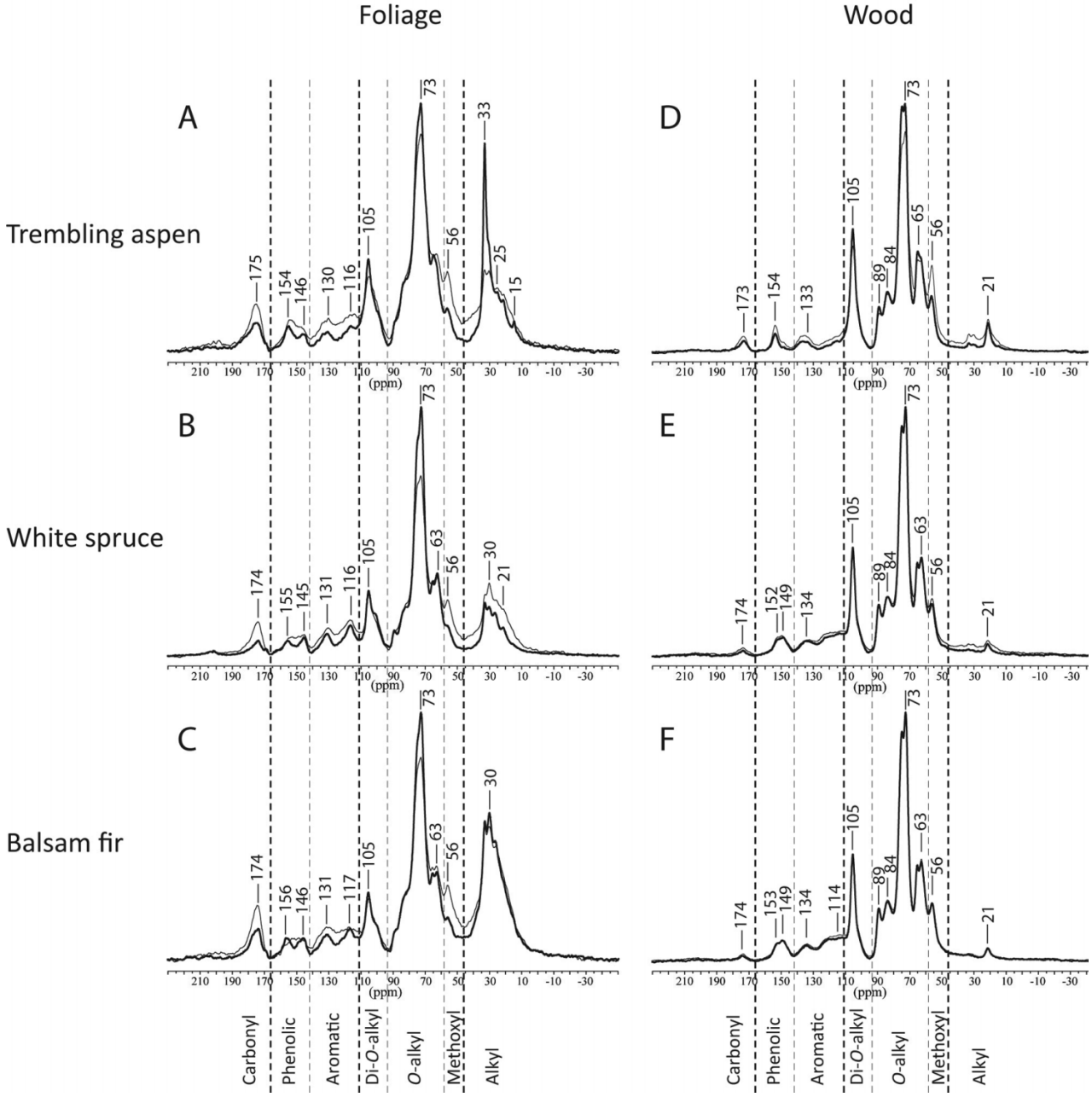
The aromatic and phenolic regions (111–166 ppm) were quite different among litter types (Fig. 2). On the spectra of the aspen wood blocks, there was a small peak at 154 ppm, produced by C-3 and C-5 of etherified structures in syringyl units of lignins, and a broad shoulder at 136 ppm from C-4 in syringyl units (Preston et al. 2000). The C-2 and C-6 of syringyl units likely contributed to the peak at 105 ppm. Coniferous wood blocks spectra displayed a large signal from 112 to 123 ppm, which may be derived from the C-2, C-5, and C-6 of guaiacyl units, whereas the shoulder around

Table 4. Effects of material (leaves vs. wood), tree species (aspen, spruce, and fir), and time of incubation on the chemical composition of litters assessed by means of mixed linear models.

	N (log)		C:N (log)		Alkyl:*O*/*N*-alkyl (sqrt)		Phenolic:*O*-alkyl	
Fixed factors	*E*	*p*	*E*	*p*	*E*	*p*	*E*	*p*
(Intercept)	–2.61	<0.001	6.48	<0.001	0.255	<0.001	0.0577	<0.001
Material (leaves)	2.65	<0.001	–2.63	<0.001	0.426	<0.001	0.0484	<0.001
C1 (aspen vs. conifers)	0.12	0.071	–0.10	0.089	0.011	0.129	–0.0094	0.008
C2 (fir vs. spruce)	–0.12	0.236	0.10	0.300	–0.002	0.878	–0.0032	0.493
Time	0.25	<0.001	–0.24	<0.001	0.008	0.005	0.0034	0.003
Material (leaves) × C1	–0.20	0.001	0.18	0.004	–0.001	0.873	0.0105	0.003
Material (leaves) × C2	–0.18	0.089	0.17	0.121	–0.154	<0.001	–0.0141	0.023
Time × C1	0.02	0.048	–0.02	0.020	0.002	0.180	0.0003	0.671
Time × C2	0.03	0.076	–0.03	0.072	0.001	0.722	–0.0027	0.051
Material (leaves) × time	–0.11	0.003	0.10	0.006	–0.005	0.193	0.0019	0.198
Material (leaves) × time × C1	(–)	(–)	(–)	(–)	–0.005	0.035	–0.0002	0.808
Material (leaves) × time × C2	(–)	(–)	(–)	(–)	0.010	0.027	0.0060	0.003
	V (log)		S:V (sqrt), in wood		Cn:V (sqrt)		Vac:Val	
Fixed factors	*E*	*p*	*E*	*p*	*E*	*p*	*E*	*p*
(Intercept)	2.493	<0.001	0.650	<0.001	0.147	<0.001	0.251	<0.001
Material (leaves)	–1.278	<0.001	(–)	(–)	0.586	<0.001	–0.081	<0.001
C1 (aspen vs. conifers)	–0.216	<0.001	0.487	<0.001	–0.008	0.518	0.191	<0.001
C2 (fir vs. spruce)	0.032	0.618	0.017	0.493	–0.032	0.199	0.009	0.672
Time	–0.045	0.008	–0.011	0.102	0.002	0.786	0.017	<0.001
Material (leaves) × C1	0.054	0.279	(–)	(–)	0.042	0.007	–0.220	<0.001
Material (leaves) × C2	–0.061	0.495	(–)	(–)	0.018	0.514	–0.016	0.586
Time × C1	–0.042	<0.001	–0.011	0.022	–0.007	0.029	(–)	(–)
Time × C2	–0.014	0.501	0.001	0.892	0.004	0.526	(–)	(–)
Material (leaves) × time	0.091	<0.001	(–)	(–)	–0.036	<0.001	(–)	(–)
Material (leaves) × time × C1	0.036	0.021	(–)	(–)	(–)	(–)	(–)	(–)
Material (leaves) × time × C2	0.024	0.384	(–)	(–)	(–)	(–)	(–)	(–)

Note: The reference level for material is wood. The first contrast (C1) is positive when the parameter is higher for aspen than for conifers; the second contrast (C2) is positive when the parameter is higher for spruce than for fir. Transformations realized to reach normality and homogeneity assumptions are indicated in parentheses. *E*, estimated value of the model; *p*, *p* value of *t* test for individual parameters; (–), nonsignificant interaction removed from model. Transformations: log, logarithmic; sqrt, square-root. N, nitrogen concentration; C, carbon concentration. NMR: alkyl, 0–46 ppm; *O*/*N*-alkyl, 46–111 ppm; phenolic, 142–166 ppm; *O*-alkyl, 58–93 ppm. V, vanillyl phenols; S, syringyl phenols; Cn, cinnamyl phenols; Vac, vanillic acid; Val, vanillin.

Fig. 2. CPMAS ^{13}C NMR spectra of fresh foliage and wood material (thick line) and spectra of material decayed for 5 to 6 years (thin line).

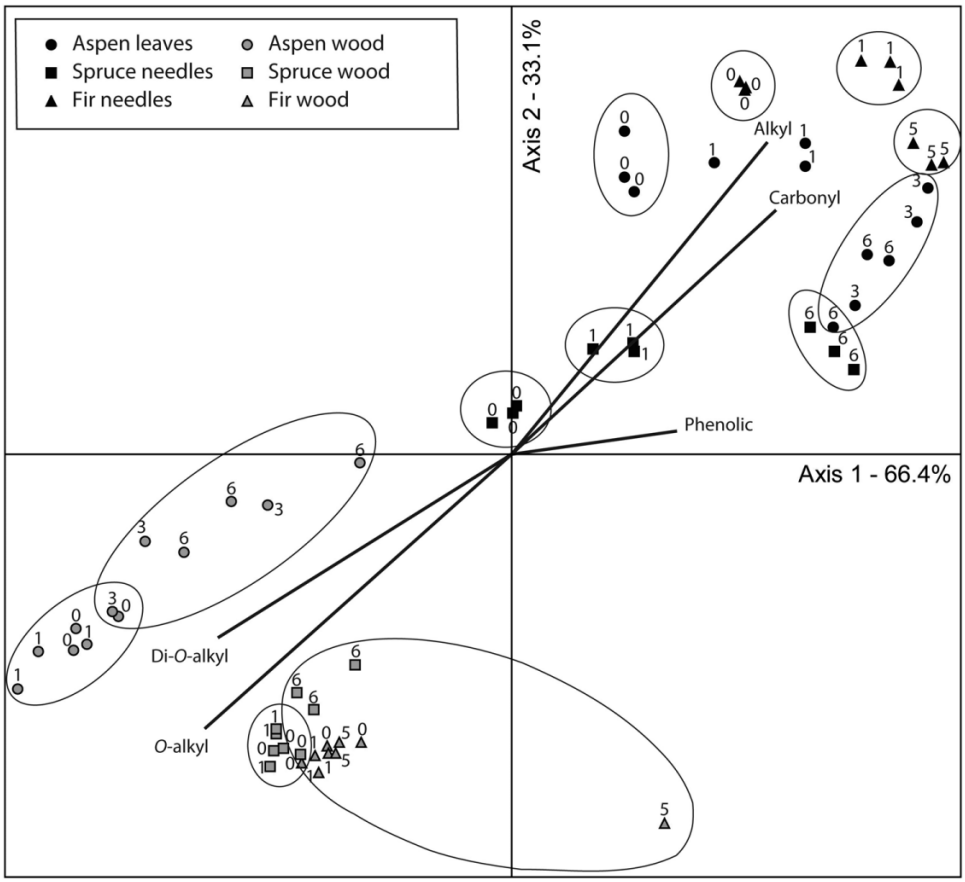


133 ppm resulted from the C-1, the shoulder at 149 ppm from the C-3, and the shoulder at 153 ppm from the C-4 of guaiacyl units. Signals from tannins were not detected on any wood spectra, which presented no characteristic split peak at 144 and 154 ppm. The foliar litter spectra indicated a mixture of lignins and tannins structures, with four broad peaks at 116, 131, 145–146, and 155–156 ppm. The DD spectra for wood blocks showed the predominance of lignin versus tannin structures, with an important peak at 56 ppm and a small one at 105 ppm (results not shown). The DD spectra for foliar litters had peaks at 105, 145, and 155 ppm (results not shown), supporting the presence of condensed tannins (Lorenz et al. 2000). The methoxyl peak at 56 ppm also indicated the presence of lignins.

In summary, fresh wood material was characterized by higher proportions of *O*/*N*-alkyl C, mainly arising from carbohydrate C, whereas foliar material contained a higher proportion of alkyl C resulting from cutin, waxes, and other lipids and a higher proportion of carbonyl C (Fig. 3). Furthermore, the aromatic and phenolic regions (Fig. 2) resulted from the presence of lignins in wood and from a mixture of lignins and tannins in foliage. Aspen wood had a higher proportion of carbohydrates and a lower proportion of lignins than coniferous species. Differences in foliage composition were linked to a higher proportion of alkyl C in fir, a higher proportion of *O*/*N*-alkyl C in spruce, and a higher proportion of carbonyl C in aspen.

During decomposition, shoulders appeared on foliar litter

Fig. 3. NMS ordination of CPMAS ^{13}C NMR integral areas from aspen, fir, and spruce foliar litter and wood blocks. Numbers on tops of symbols (circles, squares, and triangles) indicate time of decay (years). The spectral NMR areas to map the vectors are the alkyl (0–46 ppm), the methoxyl (46–58 ppm), the *O*-alkyl (58–93 ppm), the di-*O*-alkyl (93–111 ppm), the aromatic (111–142 ppm), the phenolic (142–166 ppm), and the carbonyl (166–222 ppm) regions. Groupings based on MRPP analysis are encircled. Cutoff for correlation vectors was set at $r^2 = 0.5$. NMS ordination produced a solution with a stress of 2.87, which was achieved after 73 iterations.



spectra in the aromatic region, mainly between 145 and 155 ppm and between 115 and 130 ppm (Figs. 2A, 2B, and 2C). Peaks at 157 and 154 ppm in decayed aspen leaf litter may be from syringyl units, and peaks at 146, 148, and 153 ppm in decayed coniferous foliar litters are characteristic of guaiacyl units (Preston et al. 2000). Following 5 or 6 years of decay, foliar litters had a chemical composition very different from initial compositions ($p < 0.001$; Table 5; Fig. 3). Differences among the three tree species had narrowed down compared with initial compositions, as indicated by the decrease in the *T* value of the MRPP analysis (Table 5; Fig. 3), but the three species still had distinct chemical compositions ($p = 0.003$; Table 5; Fig. 3), mainly arising from different alkyl C proportions. The decay of spruce needles was characterized by a decrease in the proportion of the *O*-alkyl C group and an increase of the proportions of alkyl, phenolic, and carbonyl C (Fig. 3). For aspen and fir leaf litters, the proportion of *O*-alkyl C initially decreased, while the proportions of alkyl, phenolic, and carbonyl C increased. Thereafter, the phenolic and *O*-alkyl C increased, while the proportion of the alkyl C group decreased (Fig. 3).

Decayed wood blocks kept a chemical composition clearly distinct from that of foliar litters ($p < 0.001$; Table 5; Fig. 3). Although the decrease of the *T* value indicated more similarity of chemical composition between wood blocks at the end of the experiment (Table 5), initial and final wood blocks were not significantly different ($p = 0.083$; Table 5). Little changes in composition appeared during the study period for coniferous wood, as revealed by the small differences between the initial and final spectra (Figs. 2E, 2F). Similarly, all observations representing initial and final composition stayed closely clustered on the NMS ordination, with the exception of one fir wood block that showed an increase in the proportion of alkyl, phenolic, and carbonyl C groups and a decrease in the percentage of *O*-alkyl C (Fig. 3). In aspen wood, few changes appeared during the first year of decomposition, except for a small increase in the concentration of *O*-alkyl C. After the first year, the proportion of *O*-alkyl C group decreased and the proportion of alkyl, phenolic, and carbonyl C increased (Fig. 3). Species kept distinct wood compositions at the end of the experiment ($p = 0.010$; Table 5), differing by their proportions of alkyl, *O*-alkyl, phenolic, and carbonyl C.

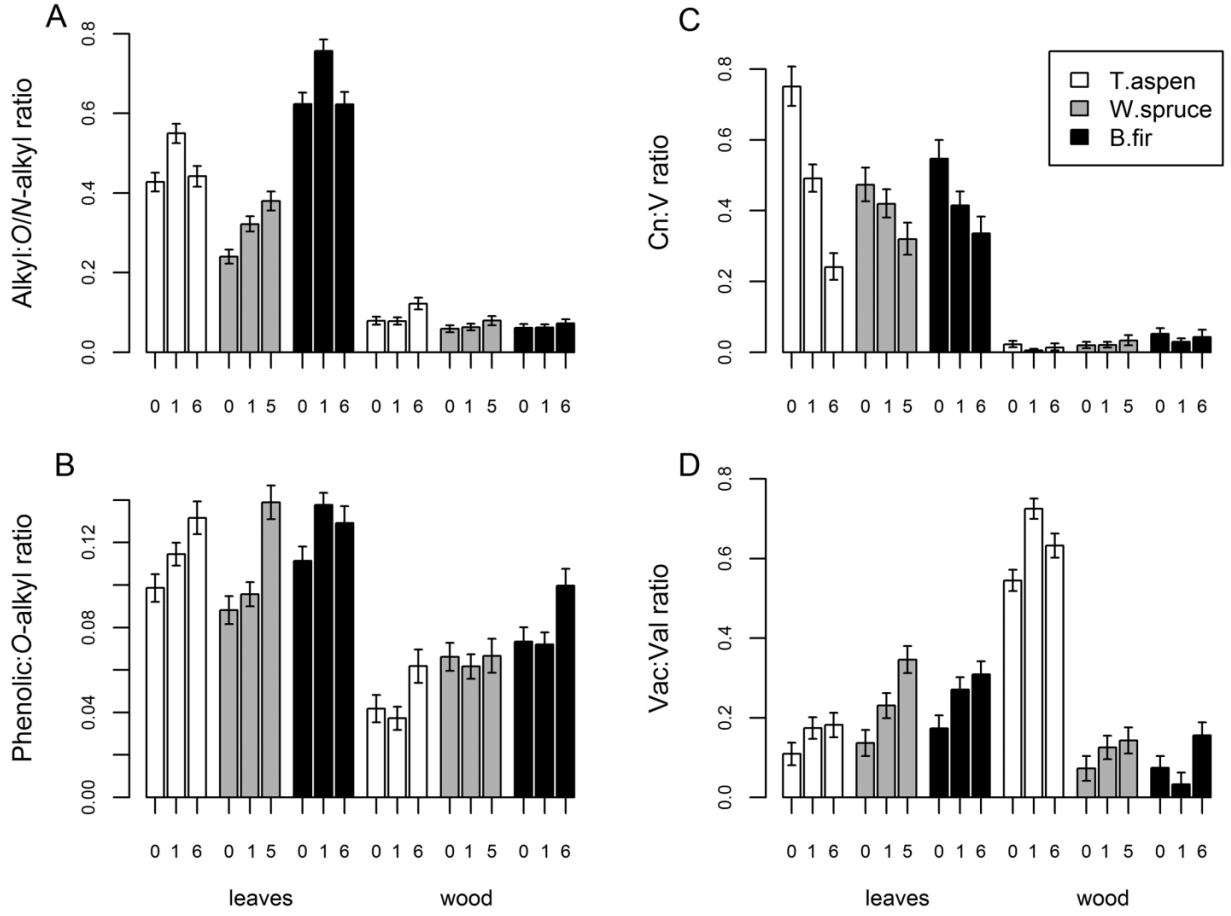
Changes in the alkyl:*O*/*N*-alkyl ratio differed significantly ($p = 0.035$) between the aspen leaf litter and the other litter types (Table 4) for which the ratio increased ($p = 0.005$). The alkyl:*O*/*N*-alkyl ratio increased faster for spruce foliar litter than for the other coniferous litters ($p = 0.027$), as the

Table 5. Distances in the NMS ordination space between litter types at the start and at the end of a field incubation experiment, obtained by MRPP analysis with the Sorensen distance.

	T	*A*	*p*
Distances between leaf litters and wood blocks			
Initial	–10.25	0.531	<0.001
Final	–10.94	0.566	<0.001
Distances between species and time of decay (leaf litters)			
Initial distance between species	–4.68	0.850	<0.001
Final distance between species	–3.92	0.593	0.003
Distance between initial and final leaf litters	–7.74	0.292	<0.001
Distances between species and time of decay (wood blocks)			
Initial distance between species	–3.82	0.708	0.003
Final distance between species	–2.87	0.280	0.010
Distance between initial and final wood blocks	–1.49	0.050	0.083

Note: *T* value, separation among groups; *A* value, within group heterogeneity; *p* value, significance of the difference.

Fig. 4. Integrated spectral CPMAS ^{13}C NMR area and lignins phenolic ratios in foliar litter and wood blocks from three boreal species of northwestern Quebec at initial time (0), after 1 year of decay, and after either 5 or 6 years of decay: (A) alkyl:*O*/*N*-alkyl ratio; (B) phenolic:*O*-alkyl ratio; (C) Cn:V ratio; and (D) Vac:Val ratio. V, vanillyl phenols; Cn, cinnamyl phenols; Vac, vanillic acid; Val, vanillin.



fir foliar litter showed little changes (Fig. 4). The phenolic:*O*-alkyl ratio increased significantly ($p = 0.003$) for aspen and coniferous litters over the 5- to 6-year period (Table 4; Fig. 4B), but this increase was very little for spruce wood and larger for spruce than for fir foliar litter.

Lignin monomers

The V phenols were significantly ($p < 0.001$) higher in coniferous litters than in aspen litters and remained significantly higher in wood than in foliar material throughout the incubation period (Tables 4 and 6), whereas the Cn phenols did not differ between species and were higher in foliage than in wood. Initial Cn:V ratios in foliage ranged from 0.47 to 0.75 and were significantly ($p < 0.001$) higher than in wood (Fig. 4D). Initially, the P phenols constituted a high amount of the phenols in spruce foliar litter, contrary to other

Table 6. Initial and final concentrations of phenolic degradation products obtained from the CuO oxidation of foliar litters and wood blocks of three boreal species.

		CuO oxidation products (mg.g^{-1} dry mass)				
Litter type	Time of decay (years)	V	S	Cn	P	TPC
Aspen leaves	0	2.52 (0.96)	n.d.	1.70 (0.52)	0.41 (0.23)	n.d.
	6	3.29 (1.46)	n.d.	0.74 (0.12)	0.35 (0.16)	n.d.
Spruce needles	0	3.64 (1.39)	n.d.	1.72 (1.32)	4.35 (0.25)	n.d.
	6	5.69 (0.88)	n.d.	1.81 (0.27)	0.57 (0.04)	n.d.
Fir needles	0	4.21 (1.33)	n.d.	2.50 (1.99)	0.70 (0.32)	n.d.
	5	5.09 (0.84)	n.d.	1.68 (0.04)	0.29 (0.07)	n.d.
Aspen wood	0	8.15 (2.07)	21.73 (5.71)	0.16 (0.09)	0.68 (0.47)	30.73 (8.19)
	6	3.95 (0.61)	8.65 (2.79)	0.06 (0.05)	0.35 (0.20)	13.02 (3.65)
Spruce wood	0	15.71 (1.77)	0.65 (0.46)	0.31 (0.06)	0.13 (0.12)	16.80 (2.20)
	6	16.07 (3.80)	0.62 (0.06)	0.56 (0.19)	0.42 (0.42)	17.67 (4.48)
Fir wood	0	14.81 (5.28)	0.47 (0.15)	0.76 (0.31)	0.06 (0.02)	16.09 (5.63)
	5	15.40 (0.40)	0.36 (0.03)	0.66 (0.09)	0.19 (0.07)	16.62 (0.46)

Note: Mean values ($n = 3$), with standard deviations in parentheses; n.d., no data; TPC, total phenolic constituents (sum of vanillyl phenols (V), syringyl phenols (S), cinnamyl phenols (Cn), and *p*-hydroxy phenols (P)).

litters (Table 6). The main phenol in all litters was vanillin. The S:V ratio was higher in aspen than in coniferous wood ($p < 0.001$). The results yielded initial V:S:Cn ratios of 51:136:1 for aspen, 51:2:1 for spruce, and 63:2:3 for fir wood blocks. The Vac:Val ratio was higher in wood blocks than in foliar litters ($p < 0.001$) and higher in aspen than in coniferous wood ($p < 0.001$) but lower ($p < 0.001$) in aspen leaves than in coniferous needles (Fig. 4D; Table 4). The P:V, Pac:Pal, and Sac:Sal ratios did not show any trend except for a higher P:V ratio in spruce foliar litter (results not shown).

The amount of V phenols decreased significantly ($p < 0.001$) in aspen wood compared with coniferous wood (Table 4) and increased significantly in foliar litters ($p < 0.001$). Amounts of TPC decreased with time in aspen wood but not in coniferous wood. Decreases of Cn:V ratios with time were significant ($p < 0.001$) in foliar litters (Table 4; Fig. 4C) and higher in aspen than in coniferous litters ($p = 0.029$), and decreases of the S:V ratio were significant ($p = 0.022$) in aspen wood. The Vac:Val ratio increased significantly ($p < 0.001$) with time in all litters (Fig. 4D; Table 4). Lignins from the aspen wood had a high proportion of syringyl phenols, but the Sac:Sal ratio remained low throughout the decomposition study (results not presented).

Discussion

Our results underline the differences in biochemical composition between foliage and wood material during the first 5 to 6 years of decomposition. Similar predicted maximum decomposition limits were found for foliage and wood. However, decomposition of aspen, fir, and spruce foliar litters generated organic matter rich in alkyl, phenolic, and carbonyl C, whereas little changes appeared in wood of all three species as their cellulose content remained high.

Maximum decomposition limit

The exponential model with an asymptote used to estimate maximum decomposition limits gave satisfactory results (Fig. 1), except for balsam fir wood, which was characterized by low mass losses. Slow decomposition of balsam fir wood has been reported for logs or branches (Edmonds 1987). Losses of mass of other litters were within the range reported after 6 years of decay by the study of Preston et al. (2009*a*). The maximum decomposition limit of foliar litters was in the same range as what has been reported by Berg et al. (1996). To our knowledge, our study is the first one reporting maximum decomposition limit values for wood. Aspen wood differed from coniferous wood by decomposing faster, and similarly to the foliar litters, aspen wood was close to reaching its maximum decomposition limit at the end of the experiment.

Previous studies (Berg 2000; Prescott 2010) have indicated that low-molecular-mass N compounds such as ammonium and amino acids influence decomposition by repressing the formation of lignolytic enzymes in white-rot fungi and by reacting with products of degradation forming recalcitrant compounds. Despite lower initial N concentrations, the maximum decomposition limit in wood was similar to that of foliar litters, indicating that other factors were coming into play. Berg (2000) found a negative correlation between lignin concentrations and maximum decomposition limit in Norway spruce needle litter. Although lignins can have a rapid turnover (Lorenz et al. 2007), they have been shown to react during decay with N or residual carbohydrates to form a recalcitrant matrix (Berg 2000). Hence, they could impede the completeness of decay in wood, mainly composed of cellulose, hemicelluloses, and lignins, as reflected on the ^{13}C CPMAS NMR spectra dominated by *O*/*N*-alkyl, aromatic, and phenolic C groups (Figs. 2 and 4). Moreover, low nutrient content in wood (Laiho and Prescott 2004) and extractives (Cornwell et al. 2009) could influence decomposition (Berg 2000; Hättenschwiler and Vitousek 2000), although these were not studied here. Regardless of the underlying processes responsible for this phenomenon, it was interesting to note that for the boreal tree species that we studied, maximum decomposition limit values for wood were similar to those for foliage, contrary to our first hypothesis.

Foliar litter decomposition patterns

The gain of N in all litters during the early phase of decay is mainly due to immobilization by saprotrophic fungi that can overcome local nutrient deficiency through mycelial translocation (Boberg et al. 2010; Schimel and Hättenschwiler 2007). Carbon and nitrogen concentrations were in the same range as other published data for aspen (Moore et al. 2006) and white spruce (Trofymow et al. 1995) foliar litters. However, N concentration in balsam fir foliar litter was higher in this study (11.9 $mg \cdot g^{-1}$) than in Trofymow et al. (1995). Balsam fir is a tree species demanding high levels of nutrients (Paré et al. 2002) that can accumulate a high level of nitrogen, depending on soil richness. The critical C:N ratios in which N is released found in this experiment were lower than those of aspen (54) and black spruce (63) found in the study of Moore et al. (2006), which may result from differences between sites. The N concentration reached an asymptote in foliar litters (results not shown), with the C:N ratio of the decayed material stabilizing between 22.3 and 25.1. Soil fungi and bacteria typically have lower C:N ratios of 10 and 4, respectively (Vance and Chapin 2001), whereas the C:N ratio of the forest floor for the same stands was higher, around 29 (Brais et al. 2004), which suggests litter inputs having higher C:N ratios such as wood material.

Contrary to wood, leaves and needles contained a high proportion of alkyl C (Fig. 3) from cutin, waxes, and other lipids located in the cuticle surrounding their epidermis (Kögel-Knabner 2002). These biopolymers are considered highly recalcitrant to decomposition (Lorenz et al. 2007), and the alkyl:*O*/*N*-alkyl ratio is often reported as a sensitive index of the extent of decomposition, as decomposition is often associated with an increased content of alkyl C and a decreased content of *O*/*N*-alkyl C (Baldock and Preston 1995). The alkyl:*O*/*N*-alkyl ratio and the concentration of alkyl C increased in spruce foliar litter (Fig. 4). However, in aspen and fir foliar litters where the initial alkyl C proportion was high, the alkyl:*O*/*N*-alkyl ratio remained stable, indicating a concomitant decrease of the content in alkyl C and *O*/*N*-alkyl C compounds resulting from concomitant decomposition of celluloses and aliphatic compounds initially present and also from degradation of microbial products such as proteins and lipids that resonate in the alkyl region (Quideau et al. 2005). Because only a small proportion of the initial alkyl C was preserved after 5 or 6 years of decay for aspen and fir foliage, we conclude that the enrichment in alkyl C expected during decomposition of foliar litters is not universal but instead is species-dependant.

However, all foliar litters were enriched in phenolic C during decomposition (Fig. 3). The aromatic and phenolic regions in spectra of initial foliar litters were dominated by peaks characteristic of tannins, but these peaks disappeared during decomposition, whereas peaks characteristic of guaiacyl or syringyl phenols of lignins appeared. This can result from a loss of the soluble tannins from the foliar litters, likely by leaching (Lorenz et al. 2000; Preston et al. 2009*b*), that left a residue in which the majority of aromatic C was part of lignin moieties. The observed increase in phenolic C of foliar litters likely resulted from a relative increase in lignin concentrations compared with more labile litter biomolecules, but also from the formation of aromatic by-products of decomposition such as aromatic humus precursors (Berg et al. 1996; Prescott 2010). Moreover, the significant increase in the amount of V phenols with decomposition as obtained by CuO oxidation clearly indicated their recalcitrance. The significant decrease of the Cn:V ratio in foliar litters (Fig. 4C) was more important in aspen than in coniferous foliar litters and indicated a preferential degradation of the cinnamyl phenols over the vanillyl phenols, which has been documented previously (Otto and Simpson 2006). The Cn:V ratios of initial foliar litters was consistent with those in other studies (Hedges and Mann 1979; Kögel and Bochter 1985; Otto and Simpson 2006). The high level of P phenols in spruce leaf litter was very close to the value reported for black spruce by Williams et al. (1998). The Vac:Val ratio was higher in coniferous foliar litters than in aspen throughout the incubation period, as found for Norway spruce and European beech in the study of Klotzbücher et al. (2011).

Therefore, our third hypothesis was not confirmed in this study, as the Cn phenols were more degraded in aspen foliage, whereas the P phenols were more degraded in spruce foliage. However, the P phenols can also be derived from proteins and tannins (Otto and Simpson 2006), and the S phenols characteristic of deciduous lignins are thought to be preferentially degraded over the V phenols (Otto and Simpson 2006). Contrary to what our second hypothesis suggested, there was no enrichment in alkyl C in all foliar litters. However, despite large initial differences in chemical composition (Fig. 3; Table 5), foliar litters of aspen, spruce, and fir converged to a chemical composition similarly rich in alkyl, phenolic, and carbonyl C. Preston et al. (2009*a*, 2009*b*) found a similar convergence for white birch, jack pine, aspen, black spruce, and other species of western Canada over a 6-year period. Although Berg (2000) postulated that it should be possible to distinguish differences in humus buildup among tree species, our results suggest that all foliar litters had comparable maximum decomposition limits and an increasing similarity in composition, which would lead to an equivalent contribution to long-term C sequestration and similar humus composition.

Wood decomposition patterns

Nitrogen concentrations in deadwood were similar to those in other studies (Laiho and Prescott 1999; Lambert et al. 1980). Nitrogen gain during wood decomposition was important relative to its low N content, and N concentration reached more than twice the initial values. The critical C:N ratio at which N is lost was far higher than in leaf litter. Hart (1999) suggested that N release in decaying wood occurs at ratios higher than those of the microbial biomass due to a decrease in C availability.

Our findings for lignin oxidation products (V, S, and Cn) (16–30.7 $mg \cdot g^{-1}$) are within the range of other studies, extending from 5.1 $mg \cdot g^{-1}$ for brown leaves of quaking aspen (Otto and Simpson 2006) to 102.9 $mg \cdot g^{-1}$ for wood of silver maple (Hedges and Mann 1979). The CuO oxidation method is a semiquantitative method that can release between 25% and 75% of the outer part of lignin in the form of monomers (Hedges and Ertel 1982; Otto and Simpson 2006), which explains the large variation between studies. However, CuO oxidation is indicative of lignin composition and content. The V:S:Cn ratios of initial wood blocks were consistent with those in other studies, with a predominance of vanillyl phe-

nols in gymnosperms and a predominance of syringyl in angiosperms (Hedges and Mann 1979; Otto and Simpson 2006). Aspen wood had lower initial concentrations of aromatic and phenolic C from lignins than coniferous species and its S:V ratio was higher, indicating that lignins from aspen wood were more susceptible to degradation than those of coniferous wood. Little changes were observed during the first year of aspen wood decomposition, but lignin concentrations increased thereafter (Fig. 3). Nonetheless, aspen wood composition remained distinct from both coniferous species to the end of the study period, i.e., aspen wood contained a lower proportion of lignins but higher proportions of alkyl and carbonyl C. Other studies (Fukasawa et al. 2009; Preston et al. 1990) have documented a third phase of wood decomposition in which chemical composition remains stable in well-decomposed logs. In our study, aspen wood had almost reached its maximum decomposition limit and would probably undergo small transformations in chemical composition with further decay.

Coniferous wood underwent only minor changes in composition during our study, which is consistent with results obtained by Preston et al. (2009*a*) for western hemlock wood. The amount of total phenolic constituents remained stable in coniferous wood, suggesting preservation of the chemical structure of lignins (Table 6) mainly composed of recalcitrant vanillyl phenols. The phenolic:*O*-alkyl ratio increased slightly, arising from an increase of the concentration of lignins and lignin-like by-products (Baldock and Preston 1995; Berg et al. 1996). The Vac:Val ratio increased with time, accompanied by an increase of the carbonyl C group, which arise from side-chain oxidation of lignins by the oxidative enzymes secreted by microorganisms (Otto and Simpson 2006). The Vac:Val ratio of coniferous wood blocks after 6 years of decay reached low values from 0.14 to 0.16 and would probably increase with further decay. Coniferous wood would require additional time to enter a stable state. Further changes in composition would depend on the microorganisms involved (Baldock and Preston 1995). Although white-rot fungi can degrade both lignins and carbohydrates, brown-rot and soft-rot fungi degrade mainly carbohydrates (Baldock and Preston 1995; Fukasawa et al. 2009). Differences in decomposition patterns between aspen and the coniferous species could have resulted from differences in environmental forest stand characteristics as litterbags from each species were placed in different stand types (e.g., aspen litter was left to decompose in aspen stands, etc). However, a parallel study conducted in the same stands compared the composition of fungal communities on decaying aspen and balsam fir wood blocks and found no differences in these communities between stand types, with most differences in fungal communities being linked to wood species (H. Kebli, personal communication).

In summary, our second hypothesis was not verified in wood material. Although wood chemical composition became enriched in phenolic C, as well as slightly enriched in alkyl C, little changes appeared overall during decomposition. As we expected in our third hypothesis, lignins of coniferous wood were more recalcitrant than those of aspen, which could explain the slower decomposition of coniferous wood. Although wood has the potential to create a higher diversity in the residual organic matter composition than foliar litters, its importance in C sequestration will depend on its final composition once it reaches its maximum decomposition limit.

Conclusions

The maximum decomposition limit constitutes an important parameter of the C cycle, and our results indicate that foliar litter and decomposing wood reach similar limits. The chemical composition of organic matter resulting from foliage decomposition was rich in alkyl, phenolic, and carbonyl C, whereas the residual material from decomposing wood was still rich in celluloses. Once litters have reached their maximum decomposition limit, the residual organic matter is assumed to be composed of fairly stabilized fractions. Hence, organic matter resulting from foliage decomposition may be more stable compared with wood due to its relatively high proportion of aliphatic compounds. However, wood takes more time to reach its maximum decomposition limit and generates a more diverse composition for the resulting organic matter, contributing to the chemical and physical complexity of the forest floor. Further study is necessary to determine the specific factors and mechanisms involved in the formation of organic matter until the maximum decomposition limit in wood is reached. This study considered decomposition of small heartwood blocks during a 6-year experiment, without sapwood and bark. Understanding longer term decay patterns for whole coarse woody debris is necessary to assess precisely the contribution of deadwood to C sequestration.

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Appendix A

Table A1 follows.

Table A1. Integration values of the major C types (% of total area) in the ^{13}C NMR spectra of original and decayed foliar litters and wood blocks

Litter type	Time of decay (years)	Alkyl (0–46 ppm)	Methoxyl (46–58 ppm)	*O*-alkyl (58–93 ppm)	Di-*O*-alkyl (93–111 ppm)	Aromatic (111–142 ppm)	Phenolic (142–166 ppm)	Carbonyl (166–222 ppm)
Aspen leaves	0	24.61 (1.61)	3.67 (0.06)	43.49 (0.49)	10.44 (0.24)	6.89 (0.36)	4.29 (0.27)	6.60 (0.22)
	1	28.47 (1.09)	4.92 (0.26)	37.89 (1.81)	9.08 (0.4)	7.88 (0.42)	4.33 (0.26)	7.44 (0.49)
	3	25.40 (3.08)	6.47 (0.19)	35.40 (2.06)	8.62 (0.63)	9.65 (0.32)	5.05 (0.41)	9.42 (0.34)
	6	23.36 (2.05)	7.02 (0.08)	37.12 (1.22)	8.79 (0.55)	9.99 (0.13)	4.89 (0.45)	8.82 (0.23)
Spruce needles	0	15.91 (0.23)	3.91 (0.25)	52.06 (0.32)	10.34 (0.07)	9.03 (0.16)	4.59 (0.20)	4.16 (0.31)
	1	19.69 (0.18)	4.48 (0.12)	46.99 (0.66)	9.69 (0.15)	9.41 (0.39)	4.49 (0.14)	5.25 (0.32)
	6	20.69 (0.85)	6.22 (0.43)	39.76 (0.34)	8.50 (0.20)	11.74 (0.51)	5.52 (0.26)	7.58 (0.40)
Fir needles	0	31.53 (0.23)	4.56 (0.05)	38.66 (0.04)	7.39 (0.08)	7.83 (0.04)	4.31 (0.05)	5.72 (0.08)
	1	34.23 (0.49)	5.82 (0.25)	32.84 (0.44)	6.60 (0.05)	9.45 (0.44)	4.52 (0.12)	6.55 (0.33)
	5	29.53 (0.53)	6.70 (0.22)	33.91 (0.41)	6.82 (0.09)	10.02 (0.43)	4.38 (0.27)	8.63 (0.33)
Aspen wood	0	6.57 (0.57)	5.97 (0.26)	62.92 (0.74)	14.15 (0.15)	4.83 (0.35)	2.63 (0.17)	2.95 (0.20)
	1	6.58 (0.45)	6.25 (0.23)	63.84 (0.96)	14.15 (0.17)	4.29 (0.40)	2.37 (0.24)	2.52 (0.31)
	3	8.11 (0.85)	7.39 (0.70)	59.00 (2.85)	13.35 (0.32)	5.68 (1.01)	3.20 (0.52)	3.25 (0.63)
	6	9.36 (1.14)	7.33 (1.04)	56.62 (3.63)	12.96 (0.49)	6.49 (1.04)	3.46 (0.57)	3.77 (0.45)
Spruce wood	0	4.67 (0.11)	6.06 (0.05)	61.93 (0.43)	11.72 (0.07)	9.62 (0.28)	4.10 (0.17)	1.91 (0.11)
	1	5.01 (0.45)	6.13 (0.06)	62.03 (0.28)	11.69 (0.09)	9.43 (0.16)	3.82 (0.09)	1.88 (0.15)
	6	6.15 (1.07)	6.44 (0.50)	59.87 (1.33)	11.29 (0.36)	9.92 (0.38)	3.99 (0.28)	2.36 (0.32)
Fir wood	0	4.81 (0.33)	6.63 (0.18)	60.34 (1.06)	11.24 (0.25)	10.47 (0.56)	4.43 (0.24)	2.08 (0.21)
	1	4.84 (0.41)	6.64 (0.12)	60.64 (0.32)	11.29 (0.14)	10.38 (0.21)	4.37 (0.16)	1.84 (0.08)
	5	5.26 (1.12)	7.20 (1.32)	56.36 (6.82)	10.53 (1.41)	12.57 (3.36)	5.40 (1.76)	2.67 (0.68)

Note: Mean values ($n = 3$), with standard deviations in parentheses.

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