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Decomposition of Nitrogen-15 Labeled Hoop Pine Harvest Residues in Subtropical Australia

Timothy J. Blumfield,* Zhihong Xu, Nicole J. Mathers, and Paul G. Saffigna

ABSTRACT

Information on decomposition of harvest residues may assist in the maintenance of soil fertility in second rotation (2R) hoop pine plantations (*Araucaria cunninghamii* Aiton ex A. Cunn.) of subtropical Australia. The experiment was undertaken to determine the dynamics of residue decomposition and fate of residue-derived N. We used ^{15}N-labeled hoop pine foliage, branch, and stem material in microplots, over a 30-mo period following harvesting. We examined the decomposition of each component both singly and combined, and used ^{13}C cross-polarization and magic-angle spinning nuclear magnetic resonance (^{13}C CPMAS NMR) to chart C transformations in decomposing foliage. Residue-derived ^{15}N was immobilized in the 0- to 5-cm soil layer, with approximately 40% ^{15}N recovery in the soil from the combined residues by the end of the 30-mo period. Total recovery of ^{15}N in residues and soil varied between 60 and 80% for the combined-residue microplots, with 20 to 40% of the residue ^{15}N apparently lost. When residues were combined within microplots the rate of foliage decomposition decreased by 30% while the rate of branch and stem decomposition increased by 50 and 40% compared with rates for these components when decomposed separately. Residue decomposition studies should include a combined-residue treatment. Based on ^{13}C CPMAS NMR spectra for decomposing foliage, we obtained good correlations for methoxyl C, aryl C, carbohydrate C and phenolic C with residue mass, ^{15}N enrichment, and total N. The ratio of carbohydrate C to methoxyl C may be useful as an indicator of harvest residue decomposition in hoop pine plantations.

The effect of management practices on the sustainability of forest plantations becomes increasingly important as subsequent rotations are grown on the same land (Jones et al., 1999). In the southern hemisphere, following canopy closure, a plantation is essentially a closed system for nutrient cycling (Folster and Khanna, 1997) therefore major plantation disruption occurs at harvesting, and in the period between planting and canopy closure. It is during this period that forest practices, including the management of harvest residues, may critically affect future soil fertility and tree nutrient status and are therefore important in sustaining the plantation system.

A major management change within hoop pine plantations in Southeast Queensland, Australia, has been the retention of harvest residues on site, pushed into continuous mounds, or windrows, along the contour lines. While windrowed harvest residues have been shown to be effective barriers against erosion, little is known about their decomposition kinetics and how this affects nutrient conditions in following rotations. Successful plantation management strategies require detailed knowledge of the residue decomposition process and the fate of the nutrients subsequently released (Vanlauwe et al., 1997). In hoop pine plantations, litterfall occurs within a closed system and forms a reasonably constant part of the renewal process with a soil faunal and microbial community that is adapted to, and prepared for, litter utilization. Conversely, harvest residues form a massive influx to a highly disturbed system where the temperature and moisture regimes have been radically altered (Attiwill and Adams, 1993; Carlyle, 1994), and where the soil physical environment has also changed, with some areas subjected to compaction and soil disturbance (Greacen and Sands, 1980).

Microplots have been successfully used for the study of the decomposition of ^{15}N-labeled leucaena residues (Xu et al., 1993a, 1993b), allowing the fate of the residue-derived ^{15}N to be traced through the soil profile. A major problem associated with this technique is the potential for exclusion of invertebrates by microplot walls, however, the technique has better soil and microbe contact than the more commonly used litterbag method (Xu et al., 1993a, 1993b). By using ^{15}N-labeled harvest residues for this experiment, we expected to be able to trace the movement of residue-derived N through the soil profile and, by performing a mass balance of the ^{15}N remaining within the system, elucidate N losses and gains from residues and soils within the microplots. The use of single-component and combined-residue microplots was expected to yield data on the synergistic effects of mixing residues, a more realistic setting than single-component studies that have been undertaken (Parfitt et al., 2001).

The use of ^{15}N-labeled harvest materials to study residue decomposition and subsequent release of residue-derived N has been limited by the availability of adequately ^{15}N-labeled and representative material. Agricultural research has made use of ^{15}N-labeled clover (Wivstad, 1999), maize, and wheat (Thomsen et al., 2001). Nitrogen-15 enriched foliar material has been produced by spraying the leaves of trees with a ^{15}N-enriched nutrient solution (Cotrufo et al., 2000; Zeller et al., 2001). However, this method produces only ^{15}N-labeled foliage, not the ^{15}N-labeled stem and branch material required for a comprehensive study of harvest residues. In a study of residue decomposition in *Pinus radiata*

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Abbreviations: CC/MC, carbohydrate C to Methoxyl C ratio; CPMAS NMR, cross-polarization and magic-angle spinning nuclear magnetic resonance.

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plantations, Parfitt et al. (2001) used ^{15}N-labeled needle and fine branch material from previously ^{15}N-fertilized trees. The size of the material used (5- to 10-mm diam.) was substantially smaller than normally occurs in hoop pine harvest residues (with stem residues up to 200 mm in diameter), which has implications with respect to the area of the residue–soil interface. Soil contact, which may be considered a function of substrate size, can influence rates of residue decomposition (Henriksen and Breland, 2002) and N release (Carlyle et al., 1998). In the current study, we used ^{15}N-labeled foliage, branch, and stem material from whole 10-yr-old hoop pine trees that had been harvested about 2 yr after being fertilized with ^{15}N-labeled ammonium sulfate (Xu et al., 2000). This allowed us to examine the decomposition of individual residue components, singly and in combination. We were also able to use larger quantities than those normally used, approximately 100 g of foliage per microplot compared with the 2 to 5 g normally placed in litterbags (Huang et al., 1998; Kainulainen and Holopainen, 2002).

The objectives of this study were to quantify: (i) the decomposition dynamics of both individual residue components and combined components of harvest residues based on dry matter loss and ^{15}N mass loss; (ii) changes in foliage residue C functional groups, as revealed by ^{13}C CPMAS NMR, and the relationships between C functional groups and the foliage decomposition variables; and (iii) fate of ^{15}N-labeled residue components, both individual and combined, in the soil and residue system in the first 2 yr following residue application in a hoop pine plantation of subtropical Australia.

MATERIALS AND METHODS

Site Description

The study site was established immediately following clearfall harvesting of a first rotation (1R) hoop pine plantation in the Imbil State Forest (26°31′ S, 152°38′ E). The site, of approximately 1 ha, had a slight to moderate slope (10–15°) with an easterly aspect. The soils within the plantation area have been generally described by Webb and Tracey (1967) and are classed as Red Ferrosols (Isbell, 1996) approximating to the USDA classification of a Rhodic Paleudult (Soil Survey Staff, 1999). Soil chemical properties (Xu et al., 1995) are given in Table 1. The area lies within the subtropical zone, being approximately 150 km north of Brisbane. The predominating weather pattern is cool dry winters and hot wet summers. This pattern is subject to variation in response to an overlap between tropical and temperate weather systems. There is a wide variation in annual rainfall (495–1964 mm, mean 1188 mm). The average daily temperature ranges from 19.4 to 30.5°C (mean 25°C) in midsummer and from 6.9 to 21.5°C (mean 14.2°C) in winter (Bubb et al., 1998). Rainfall and temperature were measured daily at the Imbil Forestry Office situated within 5 km of the site and were considered to be representative of the area (Fig. 1). In situ soil temperature and moisture were measured using Monitor Sensors (Aust) Pty Ltd soil temperature and soil moisture (gypsum block) sensors (Monitor Sensors, Brendale, QLD, Australia) that were buried 5 cm below the soil surface underneath windrowed hoop pine residues and in an adjacent area that had been cleared of residues. Sensors were connected to a data logger recording at 15-min intervals.

Nitrogen-15 Labeled Residues

Three hoop pine trees, harvested at approximately 10 yr old, were used to investigate the uptake of ^{15}N-labeled ammonium sulfate (Xu et al., 2000). The trees were harvested about 2 yr following application of the ^{15}N-labeled fertilizer, applied at 300 kg N ha^{-1}. The ^{15}N-enriched tree biomass was stored in drying racks until stable moisture content had been achieved. Trees were sectioned and subsamples taken from each section. The average ^{15}N enrichment and total N (%) of the biomass were: stem, 0.1797 atm% ^{15}N excess, 0.21% total N; branch, 0.2265 atm% ^{15}N excess, 0.40% total N; and foliage, 0.2073 atm% ^{15}N excess, 1.20% total N. For the purposes of ^{15}N-enrichment, uniform labeling of the material was assumed. Subsamples of each residue type were oven dried at 70°C to a constant mass for moisture determination.

Microplots

Two hundred forty microplots were constructed from heavy duty polyvinyl chloride (PVC) pipe with a diameter of 25 cm, wall thickness approximately 3.5 mm and length 30 cm. The microplots were chamfered at one end to help insertion, had 3-mm holes drilled at the opposing end to tie down the covers, and numbers etched into the top outside edge for identification. Each was pushed 20 cm into the ground using the rear hydraulic arm of a backhoe pressing on to a large wooden block. This method minimized disturbance to the soil core that would have resulted from manual insertion and prevented the formation of preferential flow pathways down the inside of the tube.

The ^{15}N-labeled residues were weighed and stored in paper bags for transport to the experimental site. The treatments were assigned in a randomized complete block design, with three replications for each of the five treatments as: control (no residues), foliage-only, branch-only, stem-only, and combined. Branch material was generally 50 mm and stem material about 150 to 200 mm in diameter. In the control plots, branch and stem material were mixed together and the foliage cascaded over the top. The amount of residue allocated to each treat-

Table 1. Chemical properties of the 0- to 90-cm soil profile for the experimental area.†

Soil depth	CEC	Electrical conductivity	Total K	Total N	Organic C	Available P	Total P	pH
cm	cmol kg^{-1}	mS m^{-1}	mg kg^{-1}	g kg^{-1}		mg kg^{-1}		1:5 H_2O
0–5	36.1	8.84	5234	3.30	46.00	46.2	965	5.98
5–10	27.1	6.44	5666	2.20	29.70	24.9	911	5.55
10–20	23.4	4.63	5596	1.60	19.00	23.1	853	5.43
20–30	22.3	3.20	6318	1.10	12.90	18.6	706	5.44
30–60	29.4	3.78	6492	0.60	6.70	10.0	497	5.31
60–90	32.4	6.38	6020	0.30	3.20	6.5	302	5.41

† The soil properties were determined by the methods described in Xu et al. (1995). CEC, cation exchange capacity.

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ment was based on the area of each microplot using the average dry matter of hoop pine harvest residues. Residues were assigned randomly to each microplot on a dry matter basis as follows: control; foliage-only (102.5 g); branch-only (184 g); stem-only (90 g); and combined (foliage 102.5 g, branch 184 g, and stem 90 g). The surface layer of the soil within the microplot was picked clean of all debris and visible organic matter before residue placement. All microplots, including the control, had 9-mm galvanized mesh attached as a cover. The microplots were color coded to facilitate sampling. Weed control was performed around the microplots to prevent shading and within the microplots to prevent ^{15}N uptake.

Sampling had a higher frequency for the foliage-only and combined microplots with monthly sampling for the initial 6-mo period, three month for the next 6 mo and 6 mo thereafter. The branch- and stem-only microplots were sampled at three-month intervals during the first 12 mo and then at 12-mo intervals thereafter.

Sample Preparation and Analysis

Microplots were chosen at random for sampling from each of the three blocks. Residues within the microplots were carefully removed by hand and stored in plastic bags before removal of the microplot. The soil around the outside of the microplots was removed on the down-slope side and the microplot pushed over, this method gave a relatively clean break with the soil at the bottom of the microplot. The microplot was then sealed in a plastic bag for transportation and storage. Both residues and microplots were stored in a constant temperature environment at 4°C until sample preparation, which took place as soon as was practical following sampling.

The microplots were cut down opposite sides, and one side removed. This allowed precise division of the soil profile by depth. Soils were divided into 0- to 5-, 5- to 10-, and 10- to 20-cm layers. Each soil layer was thoroughly mixed by hand and subsampled for soil moisture determination and chemical analysis. The subsample was air dried and then passed through a 2-mm sieve before being stored in sterile airtight containers. Residue samples were dried at 60°C to a constant mass. The residues in the combined treatments were carefully separated by hand and then treated as individual samples. Foliar samples were crushed with a mortar and pestle as a preliminary preparation while branch and stem materials were cut up using a bandsaw, which was thoroughly cleaned between each operation. Before analysis, both residue and soil samples were ground to a fine homogenous powder in a planetary mill (Rocklabs, New Zealand).

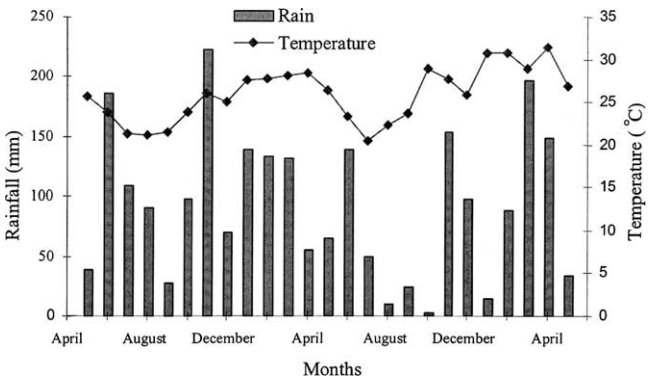

Fig. 1. Rainfall and temperature data for the first 24 mo of the decomposition period.

Total Nitrogen and Nitrogen-15 Analysis

Approximately 20 mg of soil and 6 mg of foliage, branch and stem of the homogenized powder were weighed into tin capsules for analysis to determine total N and ^{15}N enrichment using an Isoprime isotope ratio mass spectrometer (Micromass, UK Ltd., Manchester, UK) with a EuroEA3000 Elemental Analyzer (Eurovector, Milano, Italy). A minimum of 10% replication was used to verify the accuracy of the results. Internal standards were calibrated against AR grade acetanilide and cross-calibrated against N_2 reference gas. Stem samples, which were low in N, were spiked with 30 μg N, as ammonium sulfate, before analysis.

Carbon-13 CPMAS Nuclear Magnetic Resonance

Solid-state ^{13}C CPMAS NMR spectra of the foliage for each of the three replicates from the foliage-only microplots at 0, 3, 6, 12, 24, and 30 mo were obtained at a frequency of 100.6 MHz on a Varian Unity Inova400 spectrometer (Varian Inc., Palo Alto, CA). Samples were packed in a silicon nitride rotor (optical density [OD] = 7 mm) and spun at 5 kHz at the magic angle. Single contact times of 4 ms were applied, with an acquisition time of 14 ms, and a recycle delay of 2 s. Approximately 2500 transients were collected for each sample and a Lorentzian line broadening function of 50 Hz was applied to all spectra. Chemical shift values were referenced externally to hexamethylbenzene at 132.1 ppm, which is equivalent to tetramethylsilane at 0 ppm.

Relative intensities for the chemical shift regions were determined by integration using the Varian NMR software package (Version 6.1c, Varian Inc., Palo Alto, CA). No attempt was made to remove spinning sidebands during acquisition. However, the carboxyl C spectral region produces spinning sidebands, which appear at approximately 223 ppm. Because these are of equal intensity and are produced on either side of the originating center-band, the visible carboxyl spinning sideband was integrated, and the aromatic and carboxyl C spectral regions were corrected for their presence.

Statistical Analysis

Analysis of variance was performed using the SPSS Base 10 system (SPSS, 1999) and curve fitting was performed using the STATISTICA software program (Statsoft, 1999). Half-life ($t_{1/2}$) was estimated for variables with an exponential curve derived from the formula:

$$y(\text{g or \%}) = A\exp(-bt) \text{ thus } t_{1/2} = \ln 0.50/-b$$

where y equals residues remaining (g or %); A is the initial residue weight (g or %); b equals constant derived through curve fitting; and t is the time since residue placement.

RESULTS AND DISCUSSION

Residue Mass Loss

Residue mass loss has been the variable most commonly used when examining decomposition kinetics for both litter (Zimmer, 2002) and harvest residues (O'Connell, 1997; Parfitt et al., 2001). Decomposition rate of the single component residues in this experiment in descending order was: foliage (richest in N and finest material), branch (lower in N and larger in size than foliage), and stem (lowest in N and coarsest material). These components had an estimated decomposition half-life of 18, 64, and 78 mo, respectively (Table 2).

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Table 2. The remaining residue mass (% of initial mass) and remaining ^{15}N mass (% of initial ^{15}N mass) as a function of time for the single component and combined-residue microplots in the 30-mo decomposition period.

	Remaining residue mass (%) vs. decomposition period						Remaining ^{15}N mass (%) vs. decomposition period					
	a‡	b‡	R^2	n	sig	$t_{1/2}$§	a‡	b‡	R^2	n	sig	$t_{1/2}$§
						mo						mo
Foliage only	100.9	−0.0392	0.86	36	***	18	101.4	−0.039	0.69	28	***	7
Branch only	94.7	−0.0108	0.67	21	***	64	96.2	−0.1	0.83	17	***	18
Stem only	100.6	−0.0084	0.5	21	***	78	nd¶	nd	nd	18	ns†	nd
Combined residue (foliage)	101.8	−0.0274	0.71	36	***	26	105.9	−0.03	0.71	32	***	23
Combined residue (branch)	96.2	−0.0159	0.79	36	***	32	nd	nd	nd	36	ns	nd
Combined residue (stem)	103.1	−0.0215	0.71	35	***	44	nd	nd	nd	35	ns	nd
Combined residue	99.2	−0.0204	0.94	36	***	34	91.5	−0.039	0.94	34	***	17

* $p < 0.05$.
** $p < 0.01$.
*** $p < 0.001$.
† $p > 0.05$.
‡ $y = a\exp(bx)$.
§ Estimated half-life for decomposition.
¶ nd, not determined since the fitted equation is not statistically significant ($p > 0.05$).

However, this pattern of mass loss was changed when combined residues were studied, either as single components or collectively. While the rate of decomposition of the foliage was greater in the single-component than in the combined-residue microplots, the rate of the branch and stem decomposition was higher in the combined-residue than the single-component microplots. Mass loss of the separate components in the combined-residue microplots followed the order: foliage > stem > branch with an estimated half-life of 26, 32, and 44 mo, respectively. In combination, these residues had a half-life of 34 mo (Table 2).

Single-component microplots may be useful for clarifying the potential contribution of an individual component to overall decomposition and thus make a valuable contribution to an evaluation of the proportional significance of each component to the C and nutrient cycles.

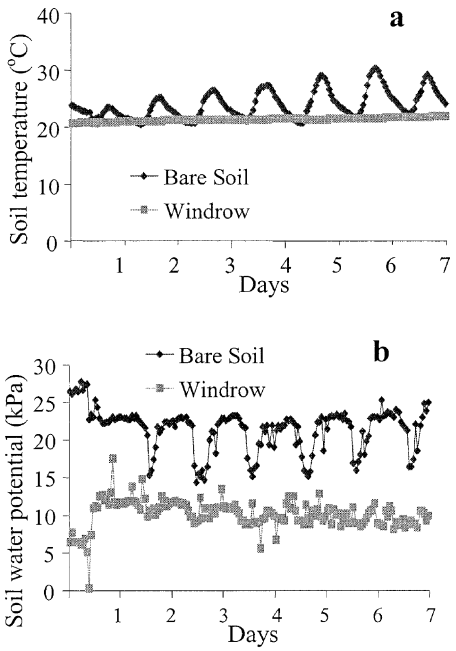

Fig. 2. Differences between bare soil and windrow-covered soil over a 7-d period in October 1999 for: (a) temperature at the 0- to 5-cm soil depth; and (b) soil moisture (shown as soil water potential) at the 0- to 5-cm soil depth.

However, observation of the mixtures within the combined residue microplots gave a clearer elucidation of the kinetics of hoop pine harvest residue decomposition. One of the major factors responsible for the altered rates of decomposition within the combined residue microplots was probably the change in microclimate, as the increased mass of the combined residues would have provided protection from extremes in temperature, insolation, and helped to retain moisture, thus providing the microbial community with optimal conditions for decomposition (Anthofer et al., 1997). In particular, the branch and stem materials in the single component microplots were laid on bare soil and fully exposed to the sun, an environment that is less than optimal for decomposition processes. Temperature and soil moisture probes that were placed into the 0- to 5-cm soil layer under a windrow and in an adjacent patch of bare earth clearly demonstrated the insulating effect of residues that leads to more stable temperatures (Fig. 2a) and higher and more stable soil moisture (Fig. 2b) than with bare earth. The use of mixed residues was also in agreement with Follett (2001) who stressed the need to conduct ^{15}N research under realistic management conditions. In addition, mixing of the foliage, branch, and stem materials in the combined-residue microplots would alter the substrate quality (such as C/N ratio) for microbial decomposition, which might also result in different decomposition kinetics of the mixed residue components than those of single component microplots (Xu et al., 1993b).

Residue Nitrogen-15 Enrichment and Recovery

In microplots containing single component residues the remaining ^{15}N enrichment of atom% ^{15}N excess (expressed as a percentage of the initial ^{15}N enrichment) declined exponentially for all components in the order of: stem = branch > foliage, with a 50% reduction in ^{15}N enrichment by 12, 15, and 35 mo, respectively (Fig. 3). When all residue components were combined within microplots, the ^{15}N enrichment for the individual components declined exponentially in the order: stem > foliage > branch (Fig. 4a,b,c), with a 50% reduction in ^{15}N enrichment by 21, 38, and 44 mo, respectively. In combi-

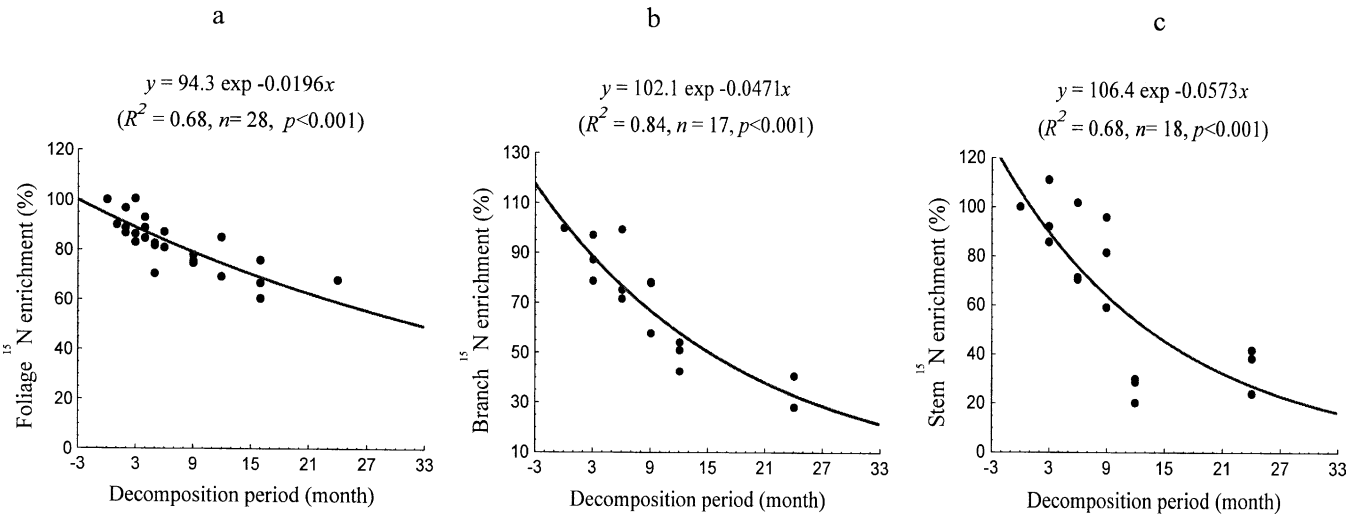

Fig. 3. Nitrogen-15 enrichment (% of initial ^{15}N enrichment) in the decomposing residues for the single-component microplots in the 30-mo period for: (a) foliage, (b) branch, and (c) stem.

nation, the residues had a 50% reduction in ^{15}N enrichment by 32 mo (Fig. 4d). The reduction in foliage ^{15}N enrichment was comparable in both single-component and combined-residue microplots.

This trend was mirrored by ^{15}N retention in the decomposing residues with ^{15}N mass losses generally faster in the stem and branch components than the foliage (Table 2). In the microplots containing single component residues, ^{15}N retention declined exponentially in the order: branch > foliage with a 50% loss by 7 and 18 mo, respectively. There was no significant relationship for ^{15}N retention in the stem materials ($p > 0.05$). In the microplots containing combined residues, curves could not be fitted to data for branch and stem. Nitrogen-15 retention of the foliage component declined exponentially by 50% in 23 mo. In combination, there was an exponential decline in ^{15}N retention with a 50% reduction by 17 mo. Some caution must be exercised when interpreting the data from the stem and branch components due to the low initial ^{15}N enrichment and consequently greater margin for error. The agreement in the ^{15}N enrichment and ^{15}N retention data between the single-component foliage, the combined-residue foliage, and the combined residues suggest that these were the more reliable data. These data suggest that approximately 50% of the ^{15}N mass may be lost within 18 to 24 mo from residue application. There were significant correlations between residue mass loss and ^{15}N mass loss for foliage-only and combined-residue microplots ($P < 0.001$, data not shown), which was similar to findings for ^{15}N-labeled beech litter (Zeller et al., 2000). It is interesting to note that the half-life based on ^{15}N mass loss for the single-component microplots is much shorter than that of the corresponding components based on dry matter loss, which has also been reported by Xu et al. (1993b).

Carbon-13 CPMAS NMR Spectra of Decomposing Foliage

The ^{13}C CPMAS NMR spectra for the decomposing residues from the foliage-only microplots at 0, 3, 6, 12, 24, and 30 mo following residue application are given in Fig. 5. While there are limitations in the use of ^{13}C CPMAS NMR spectra for quantitative analysis, it may be valid to compare the intensity of C functional groups among similar samples (Lorenz et al., 2000). Similarly, the measurement of the changes in C functional groups as revealed by ^{13}C CPMAS NMR over a period of decomposition is both useful and appropriate. For convenience, this type of spectra is often divided into the four common chemical shift regions, alkyl C (0–45 ppm), O-alkyl C (45–110 ppm), aromatic C (110–160 ppm), and carbonyl C (160–220 ppm) (Mathers et al., 2000; Parfitt and Newman, 2000). However, as shown in this study, subdividing some of these chemical shift regions: O-alkyl C into methoxyl C (45–60 ppm), carbohydrate C (60–94 ppm) and di-O-alkyl C (94–110 ppm); aromatic C into aryl C (110–142 ppm) and phenolic C (142–160 ppm); and carbonyl C into carboxyl C (160–185 ppm) and ketone/aldehyde C (185–220 ppm) can provide further structural information.

Of the eight chemical-shift regions, methoxyl C, carbohydrate C, aryl C, and phenolic C had significant correlations with the decomposition variables examined (Table 3). Methoxyl C, aryl C, and phenolic C demonstrated properties in the decomposing foliage that are associated with recalcitrant compounds showing an increase as residue mass was lost and as residue total N concentration increased as a result of the decomposition process. Methoxyl C and phenolic C were also significantly correlated with ^{15}N enrichment. The recalcitrant nature of methoxyl C, which had the highest correlations of the regions considered, would be disguised under common operating procedures, when it would be included with the O-alkyl C region, which consists mainly of cellulose and polysaccharides that are considered to decompose rapidly (Skjemstad et al., 1997). Carbohydrate C, which is also usually considered as part of the O-alkyl C chemical-shift region, demonstrated properties associated with the labile, readily decomposable C fractions. The relationship of carbohydrate C with residue mass was strongly bimodal, suggesting that following an initial decrease

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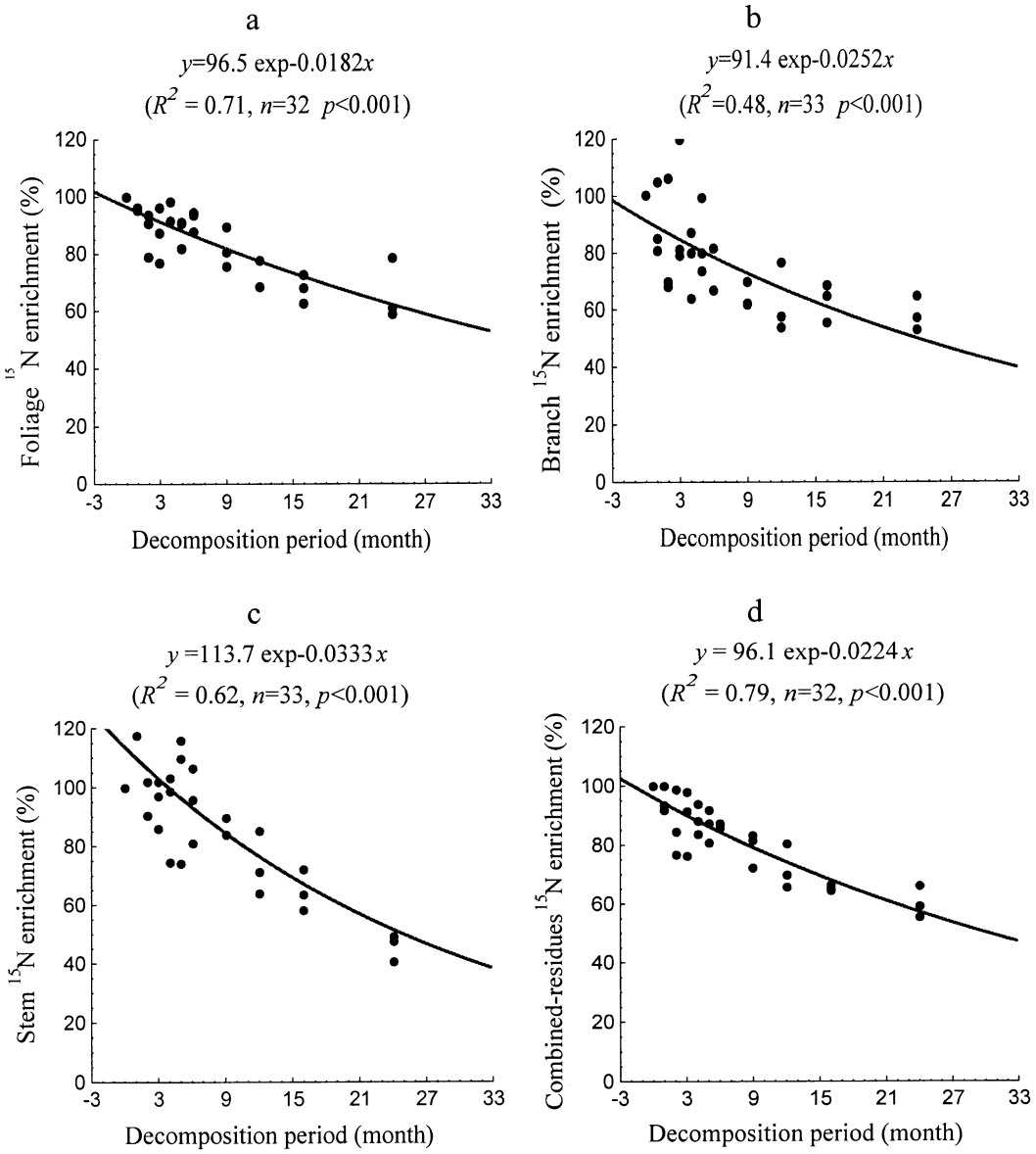

Fig. 4. Nitrogen-15 enrichment (% of initial ^{15}N enrichment) in the decomposing residues for the combined-residue microplots in the 30-mo period for: (a) foliage, (b) branch, (c) stem, and (d) combined residues.

due to the decomposition process, there may have been an increase in microbial biomass toward the end of the decomposition period and subsequently more secondary, microbially metabolized compounds such as carbohydrates.

The ratio of alkyl C to O-alkyl C has been suggested as an indicator of the extent of decomposition of the organic materials that are contained in forest litter (Baldock and Preston, 1995; Baldock et al., 1997). In a study of the decomposition of spruce litter, Lorenz et al. (2000) found an increase in the alkyl C to O-alkyl C ratio of decomposing litter and noted that the changes in the aromatic, phenolic, and carboxyl C regions were not significant. Quideau et al. (2000) found the alkyl C to O-alkyl C ratio under pine trees to be a good indicator of soil organic matter decomposition and of its susceptibility to further microbial degradation. However, despite adhering to the major constraint suggested by Baldock et al. (1997), that comparisons be limited to demonstrably comparable inputs under similar environmental conditions, we found no relationship between any of the variables we studied and the alkyl C/O-alkyl C ratio.

While both methoxyl C and carbohydrate C showed a strong relationship with all (methoxyl C) or most (carbohydrate C) of the variables under consideration, they moved in opposing directions. This indicated that a composite index of the two regions, the carbohydrate C/methoxyl C (CC/MC) ratio, might provide a robust index of decomposition in hoop pine foliage that encompassed both readily decomposable and recalcitrant materials. The CC/MC ratio was seen to decline steadily through all indicators of advancing decomposition. There was an exponential decline in the CC/MC ratio as residue mass (Fig. 6a), residue ^{15}N enrichment (Fig. 6b), residue ^{15}N mass (Fig. 6c), and residue N mass (Fig. 6d)

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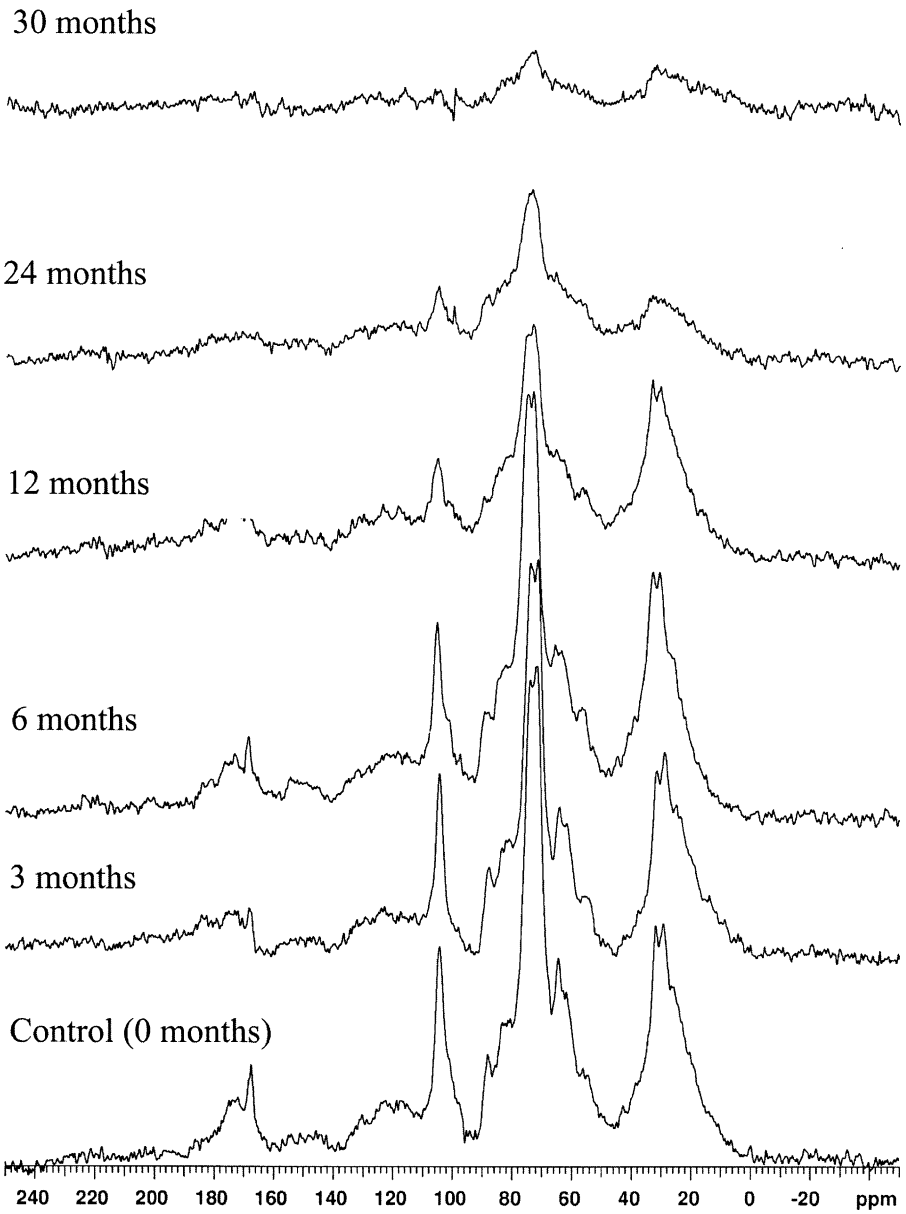

Fig. 5. Carbon-13 CPMAS NMR spectra for the decomposing foliage residues from the foliage-only microplots at 0, 3, 6, 12, 24, and 30 mo after residue application.

decreased. Residue total N concentration (g kg^{-1}) increased over the decomposition period and there was a corresponding exponential decline in the CC/MC ratio (Fig. 6e). Despite the fact that the carbohydrate C region was the dominant subgroup within the O-alkyl C chemical shift region, forming up to 40% of total C, the CC/MC

Table 3. Simple linear correlations of the C functional groups (methoxyl C, carbohydrate C, aryl C, and phenolic C) based on ^{13}C CPMAS NMR with decomposing foliage variables: (mass) foliage residue mass; (total N) foliage total N concentration; and (^{15}N) foliage ^{15}N enrichment (% of initial enrichment) in the 30-mo period.

	Mass	Total N	^{15}N	Methoxyl C	Carbohydrate C	Aryl C
	mg	g kg^{-1}	%			
Total N	−0.877***					
^{15}N	0.717**	−0.724**				
Methoxyl C	−0.826***	0.730**	−0.664*			
Carbohydrate C	0.273 ns†	−0.645*	0.795**	−0.719*		
Aryl C	−0.594**	0.830**	0.534 ns	0.753**	−0.593 ns	
Phenolic C	0.495*	0.672*	0.645*	0.875***	−0.781**	0.783**

* $p < 0.05$.
** $p < 0.01$.
*** $p < 0.001$.
† $p > 0.05$.

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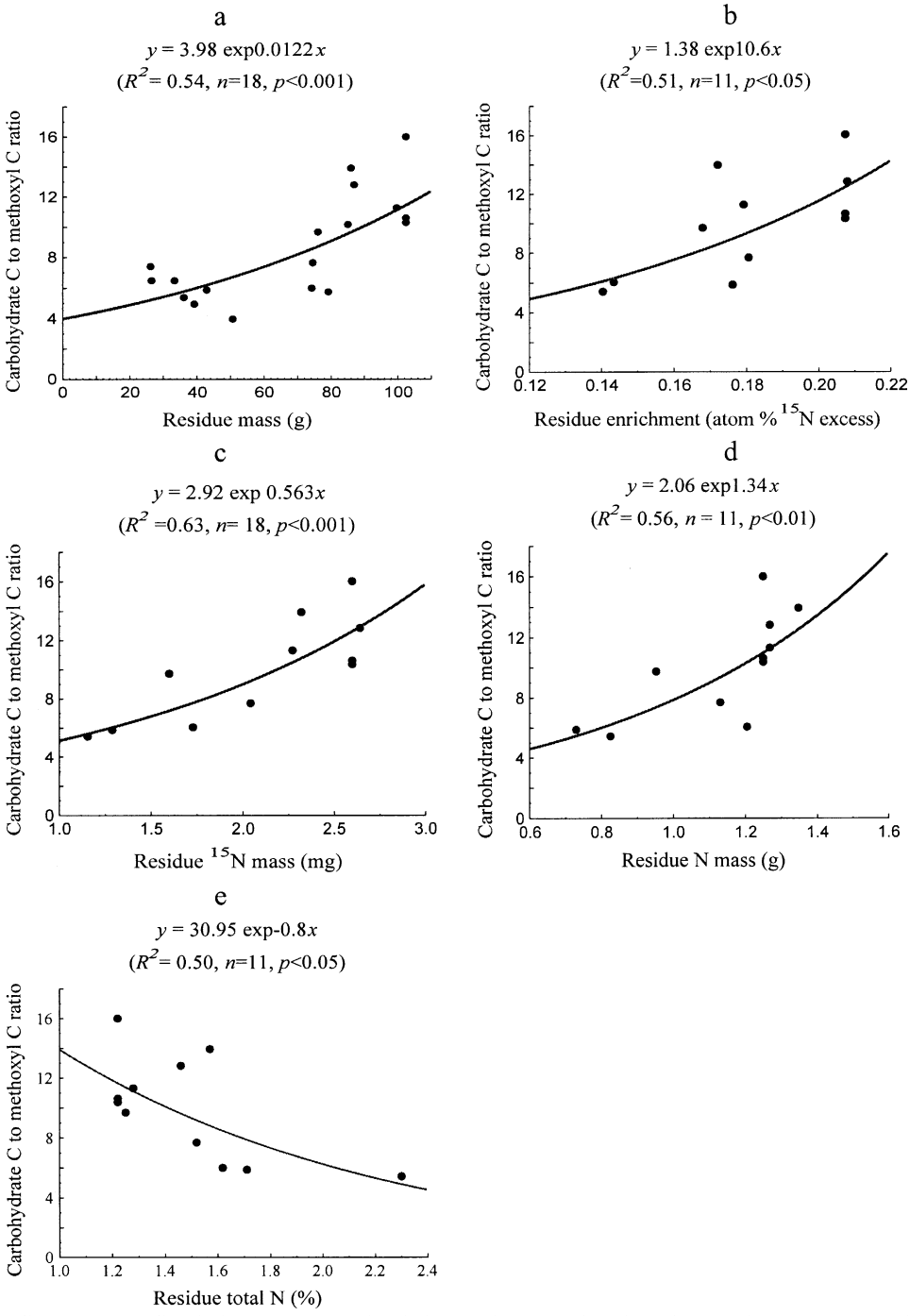

Fig. 6. Carbohydrate C to methoxyl C ratio in the decomposing foliage residue as a function of: (a) residue mass, (b) residue ^{15}N enrichment, (c) residue ^{15}N mass retained, (d) residue N mass retained, and (e) residue total N concentration (g kg^{-1}).

ratio proved a better indicator of decomposition than carbohydrate C alone. While it has been noted that the alkyl C to O-alkyl C ratio is not suitable to distinguish stages of decomposition in wood or woody residues (Baldock et al., 1997), further research would be required to examine whether the CC/MC ratio could be useful in distinguishing the stages of decomposition in hoop pine and possibly other types of woody debris. The potential for the CC/MC ratio to act as a composite indicator of residue decomposition warrants further investigation in the continuing stages of this experiment and for different types of decomposing residues under a range of environmental conditions, in forest and other ecosystems.

Soil Nitrogen-15 Recovery

In the foliage-only microplots, low recoveries of residue-derived ^{15}N (<10%) were present in the 0- to 5-cm depth for the initial 9 mo of decomposition, rising to 45% between 12 and 30 mo. Nitrogen-15 recoveries at the 5- to 10- and 10- to 20-cm depths were significantly

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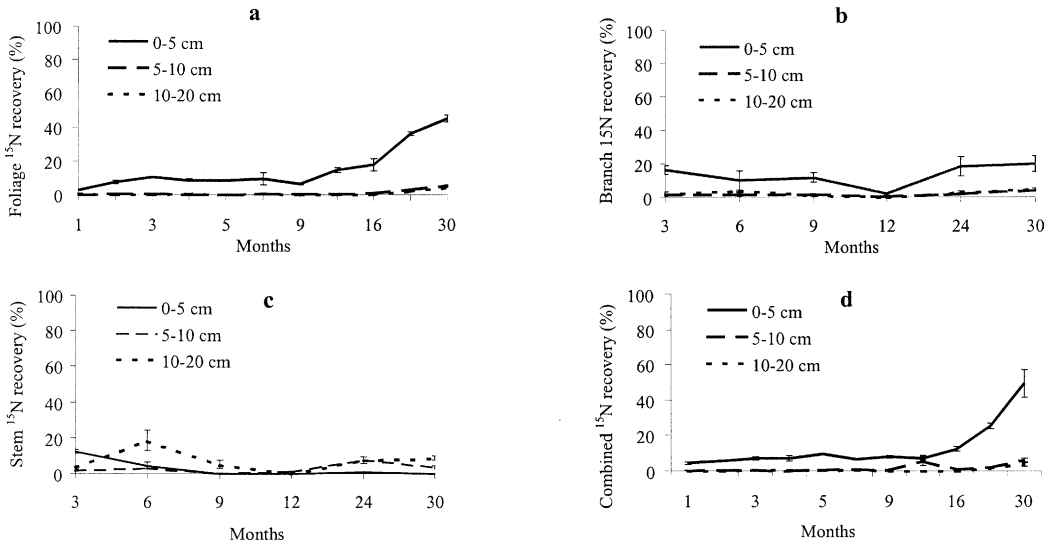

Fig. 7. Soil ^{15}N recovery (% of initial residue^{15}N added) at the 0- to 5-, 5- to 10-, and 10- to 20-cm depths in the 30-mo period for: (a) foliage-only, (b) branch-only, (c) stem-only, and (d) combined-residues microplots.

lower than the 0- to 5-cm depth ($p < 0.001$), with a mean around 5% by the end of the decomposition period (Fig. 7a). These findings were similar to that of Zeller et al. (2001) who found that after 3 yr, the ^{15}N released from decomposing litter remained at the soil surface. This suggests that residue-derived N would be immobilized in the organically rich, topsoil for considerable periods following ^{15}N release, a conclusion that is supported by previous work undertaken in hoop pine plantations showing that residue retention promotes N immobilization for at least 2 yr (Blumfield and Xu, 2003). It is also probable that a proportion of the fragmented residues within the organic layer would still have retained the ^{15}N, which had therefore been translocated rather than released.

In the branch-only microplots (Fig. 7b), ^{15}N recovery remained below 20% of added ^{15}N at the three soil depths throughout the decomposition period. Nitrogen-15 recovery was significantly greater at the 0- to 5-cm depth than at the other depths ($p < 0.001$). In the stem-only microplots (Fig. 7c), Nitrogen-15 recovery was low (<20%) throughout the decomposition period for the 0- to 5- and 5- to 10-cm depths though the 10- to 20-cm depth had a maximum ^{15}N recovery of 20%, which was sufficient to make the difference between the 5- to 10- and 10- to 20-cm depths significant ($p < 0.05$). Nitrogen-15 recovery in the combined residue microplots (Fig. 7d) was low at the 0- to 5-cm depth for the first 12 mo (around 10%) rising to a maximum of approximately 50% between Months 16 and 30. Nitrogen-15 recovery at the 5- to 10- and 10- to 20-cm depths in the combined-residue microplots remained below 10% throughout the decomposition period. The ^{15}N recovery at the 0- to 5-cm depth in the combined residue microplots was significantly different to the 5- to 10- and 10- to 20-cm depths ($p < 0.001$). The relatively high levels of ^{15}N recovery in the soil in the branch-only and stem-only microplots throughout the decomposition period, indicates that labile N may not be immobilized within lower quality substrates, that is, those with a high C/N ratio or which do not contain readily available C for microbial utilization. However the lower soil ^{15}N recovery in the combined-residue microplots suggests that, despite an increase in the rate of decomposition for stem and branch, the ^{15}N released was immobilized within the combined residues. Thus, it seems probable that the labile C, which was released during foliage decomposition, was utilized by the microbial community to immobilize the N that had been released from all of the residue components.

Total Nitrogen-15 Recovery

There was a rapid exponential decline in ^{15}N recovery within the soil-residue system in the branch-only microplots from around 100% at Month 3 to around 40 to 60% of added ^{15}N at Month 9 and thereafter (Fig. 8a). There was no clearly definable trend in the system ^{15}N recovery for the stem-only microplots over the decomposition period though it was around 80% in the first 3 mo and between 40 to 60% at the end of the period (data not shown). The low and quite variable ^{15}N recovery in branch-only and stem-only microplots must be considered to be the result of the low initial total N concentration of these materials and relatively low ^{15}N enrichment, that can result in significant experimental error.

The total ^{15}N recovery in the soil-residue system for the foliage-only microplots remained around 80 to 100% for the first 6 mo of the decomposition period (Fig. 8b), but declined linearly to around 60 to 80% of the ^{15}N added by the end of the sampling period. The combined residue microplots followed a similar pattern with system ^{15}N recovery around 80% for the first 6 mo declining exponentially to around 60% by the end of the sampling period (Fig. 8c). The total system ^{15}N recoveries in the foliage-only and combined-residue microplots, though lower than those reported by Zeller et al. (2001), were within the range reported by Xu et al. (1993a, 1993b) for a ^{15}N microplot experiment. The low ^{15}N recovery

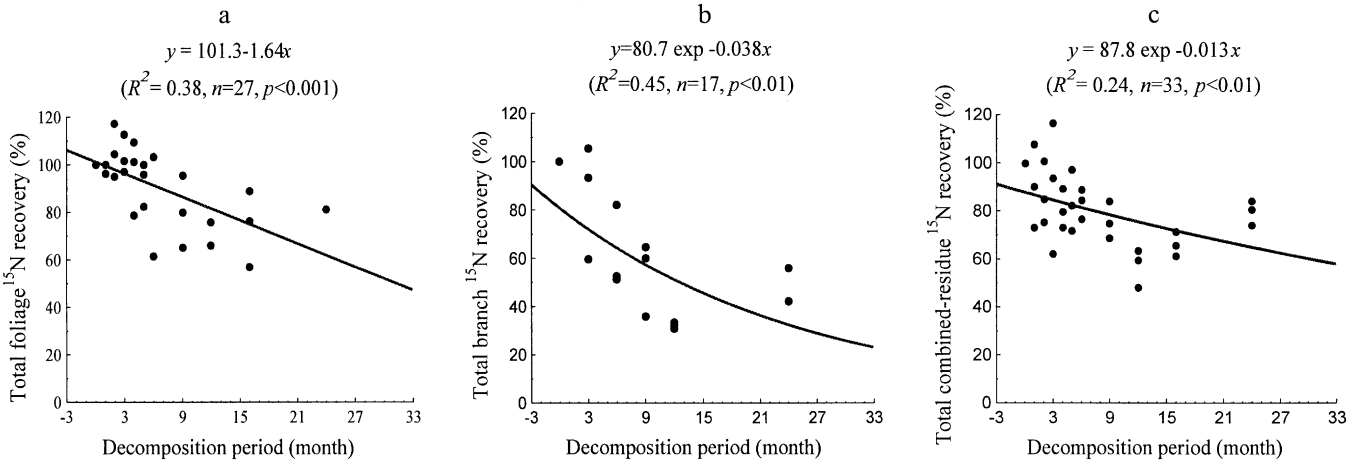

Fig. 8. Total ^{15}N recovery (% of the initial added residue^{15}N) in the decomposing residues and the top 20-cm soil within the microplots in the 30-mo period for: (a) foliage-only, (b) branch-only, and (c) combined residues; there was no significant relationship between total ^{15}N recovery and decomposition period in the stem-only microplots ($p > 0.05$).

in the 5- to 10- and 10- to 20-cm soil depths indicates that ^{15}N leaching may not have been a major factor in the ^{15}N losses. While ^{15}N leaching is possible, some evidence of the passage of ^{15}N through the lower soil depths would have been expected over the 2-yr sampling period, especially following the wet season.

Berg (1988) noted that a decrease in ^{15}N excess of decomposing ^{15}N-labeled pine needles may have been due to an increase in litter total N arising from an invasion of the litter by fungal mycelium and consequent transfer of N from the soil to the litter. In this experiment there was an increase in total N in foliage from both combined-residue and single-component microplots from 1.1 to about 1.4 g in Month 2 though levels subsequently declined to 0.9 g for combined-residue and 0.8 g for single-component microplots by Month 24 (data not shown) indicating that some N uptake had taken place. However, the recovery of about 45% of the mass of the applied ^{15}N in the soil of the single-residue and 50% in the soil of the combined-residue microplots clearly shows an actual loss of ^{15}N from the residues though it is possible that dilution of the ^{15}N excess by an increase in residue total N may account for some of the missing ^{15}N in the total ^{15}N recovery of the soil–residue system.

The potential for denitrification to occur under windrowed hoop pine residues has been reported to be high (Pu et al., 2001). The link between nitrous oxide emissions and soil water has been noted by Smith et al. (1998) while Zechmeister-Boltenstern et al. (2002) have reported that warm moist soils favored nitrous oxide flux. Nitrous oxide emission has also been strongly correlated with nitrification rates in the forest soils of tropical Australia (Breuer et al., 2002). Thus gaseous N losses within the soil–residue system might be a further potential mechanism for N loss under the decomposition conditions in hoop pine plantations.

CONCLUSIONS

While it was important to study the decomposition of the individual components that made up the harvest residues, this study has demonstrated that omission of at least one treatment of combined residues might have the potential to misrepresent the decomposition dynamics of harvest residues under operational conditions. This would be particularly true where residues were piled or windrowed. The use of ^{15}N-labeled residues demonstrated that N released during decomposition would be retained within the residues for a considerable period. Immobilization within the soil organic layer has the potential to prevent N loss through leaching. However, there was an apparent potential for gaseous N loss during residue decomposition. Carbon-13 CPMAS NMR was a useful tool in studying the decomposition process within hoop pine foliage and the finer resolution for the C functional groups employed in this experiment has shown that methoxyl C in particular was well correlated with the decomposition process.

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