In situ decomposition of northern hardwood boles: A $^{13}$C NMR study of tissue chemistry changes

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Abstract: In temperate forest ecosystems, coarse woody debris (CWD) is an important pool of carbon and a habitat for fauna ranging from microbes to birds, reptiles, and small mammals. Decomposition of this C pool releases CO$_2$ to the atmosphere, with a small fraction remaining as recalcitrant soil organic matter. How our changing climate is likely to alter CWD decomposition is unclear because little is known about the chemistry of intermediate and end products of the process. We studied the changes in nutrient content (N, P, K, Ca, Mg, Zn) and tissue chemistry in bark and wood of boles of sugar maple (Acer saccharum), American beech (Fagus grandifolia), and yellow birch (Betula alleghaniensis) over 11 years in situ decomposition in a northern hardwood forest in New Hampshire, USA. Decomposition resulted in the relative accumulation of N, Ca, and Zn, whereas K was rapidly lost from tissues. Results from solid-state $^{13}$C nuclear magnetic resonance (NMR) spectroscopy indicated that there were few changes in the structural chemistry of wood, even in samples exhibiting more than 75% loss in mass. Changes in bark chemistry varied by species. In general, the aryl C content of bark increased during decomposition, while other fractions (alkyl C, O-alkyl C, and carbonyl C) showed few consistent patterns.

Introduction: Coarse woody debris (CWD) is comprised of the fallen material from trees and other woody plants in terrestrial ecosystems. In temperate forests, CWD supports a complex food chain spanning trophic levels from bacteria to soil arthropods and their predators. The decomposition of CWD releases CO$_2$ to the atmosphere and contributes to the accumulation of soil organic matter. Understanding the transformations of woody tissues during decomposition is useful for assessing the possible effects of climate change on forest C cycling processes. Unfortunately, few long-term studies have monitored chemical change in woody tissues in situ (e.g., Preston et al. 1998). Here, we report the results of an 11-year experiment in which hardwood boles were allowed to decompose in situ and monitored for mass loss, nutrient content, and tissue chemistry using nuclear magnetic resonance (NMR) spectroscopy.

Materials and Methods: Wood and bark samples were collected at the Hubbard Brook Experimental Forest (HBEF) in central New Hampshire, USA (43° 56'N, 71° 45'W). In July 1990 and May 1991, we collected samples of tissues from freshly filled trees of these three dominant species that were approximately 70 years old. A segment of the bole, approximately 1 m long, was isolated with a chain saw. Half of each bole was sampled fresh and the other half was left in the field to rot. After subsampling, bark was separated from wood, both were dried at 80°C to constant weight and ground. Elemental analysis was conducted using a Carlo Erba EA 1108 elemental analyzer for C, H, and N. O content was determined using difference from total ash-free weight.

Total concentrations of K, Ca, Mg, P, and Zn were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) on HNO$_3$ digests. Subsamples were ashed overnight at 450°C, and the ash was dissolved in concentrated HNO$_3$. The digest solution was then diluted with DI water to 10% HNO$_3$ prior to ICP analysis.

The $^{13}$C NMR analyses were performed on a Bruker AVANCE 300 spectrometer, operating at 75.47 MHz for $^{13}$C and with cross-polarization with magic-angle spinning (CPMAS). We used a 1-ms contact time, acquisition time of 17.5 ms, and a recycle delay of 3 s. The samples were spun in zirconia rotors with Kel-F caps. Chemical shift values were internally referenced to the anomeric C peak at 105 ppm. Assignments of resonance regions and corrections for spinning sidebands (which were trivial) are described in Johnson et al. (2005).

Results and Discussion: After more than 10 yr of decomposition, mass loss of wood and bark ranged from 37-78%. Concentrations of N, Ca, and Zn increased in wood and bark during decomposition, whereas the K concentration declined. The C:N ratio declined exponentially during decomposition in both wood and bark, due to the increase in N concentration (Fig 1).

Figure 1: Effect of decomposition on the molar C:N ratio of wood and bark.
Results from NMR spectroscopy indicated that decomposition of wood was approximately homogeneous. Even after 10 years of decomposition and mass loss of 37-78%, the spectra of decomposed samples were often indistinguishable from fresh wood from the same bole (Fig. 2). This pattern is consistent with the action of white-rot fungi.

Figure 2. $^{13}$C NMR spectra for fresh and decomposed American beech wood from the same log. Lower panel shows the integrated intensities for major spectral regions.

Unlike the wood samples, bark showed noticeable changes in tissue chemistry during decomposition. For example, sugar maple bark from a log experiencing 78% mass loss after 10.5 yr of decomposition showed increased alkyl and aryl C signals, largely at the expense of O-alkyl C (Fig. 3). This indicates the preferential loss of carbohydrates (O-alkyl) compared to aliphatic C structures such as suberin, waxes, and resins in the bark. However, the changes in bark chemistry were not uniform for all samples. There was a general pattern of increasing aryl C signal intensity with length of decomposition time. Changes in other C families varied among samples. Our results suggest that major changes in the chemistry of decomposing tissues at Hubbard Brook probably occur in the very late stages of decomposition.

Figure 3. $^{13}$C NMR spectra for fresh and decomposed sugar maple bark from the same log. Lower panel shows the integrated intensities for major spectral regions.

Conclusions
Decomposition of northern hardwood boles resulted in striking changes in the elemental composition of CWD. However, there were fewer changes in the tissue chemistry, as revealed by $^{13}$C NMR spectroscopy. Wood appears to decompose approximately homogeneously. In contrast, bark exhibited highly variable changes in tissue composition during decomposition.

References
