

Investigations of Carbon and Nitrogen Chemistry in Forest Ecosystems

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Understanding how soil carbon and nitrogen dynamics change with secondary succession and how they function in low-productivity sites requires knowledge of the chemical identity of the material in the various pools and their transformations. Thus, our chemistry investigations aim to characterize the C and N in the various pools identified in the ecological studies, and to understand the factors controlling the rate constants and fluxes that characterize the ecosystem. We focus on two areas: characterizing the nature of organic C, and using N-15 tracers to elucidate the movement and transformations of N.

Nuclear magnetic resonance (NMR) spectroscopy is the primary technique used to characterize organic C (Preston and Rusk 1990). The NMR facility at the Pacific Forestry Centre—still a first for forest ecology research—is equipped with a Bruker WM 250 MHz NMR spectrometer with multinuclear capability. It is a medium field instrument for solutions only, and spectra of solid-state samples are obtained through a network of collaborators and contractors. Our NMR studies of organic matter have included litterfall, woody debris, forest floor, organic horizons, and humified and poorly decomposed organic residues in mineral soil horizons. Work on the dissolved organic carbon pool should begin in 1993. Phosphorous-31 NMR is also used to determine the forms of extractable P; much of this P is in organic form, and thus closely tied to the organic C pool.

Large-diameter decaying fallen logs are a prominent feature of the forest floor in the Coastal Western Hemlock biogeoclimatic zone. The information available on changes in the major organic components, however, is still very limited, the traditional analytical procedures ("proximate analysis") are laborious, and the interpretation of the operationally defined chemical types often unclear, especially for highly decomposed samples. However, major organic components can be determined from a solid-state C-13 CPMAS NMR spectrum (i.e., NMR with cross-polarization and magic-angle spinning), which is obtained non-destructively in a few hours on about 300 mg of dry, powdered sample.

A study of heartwood in fallen logs of three species decomposing for up to 200 years in old-growth forests (Preston *et al.* 1990) showed that the main progress of decay was loss of carbohydrate C, with accumulation of a dark red, crumbly or pasty residue of virtually unaltered guaiacyl lignin. Signals from alkyl and carbonyl C were weak, but tended to increase slightly with decomposition, most likely due to the selective preservation of waxes and resins (alkyl C), and to oxidation of lignin. Accumulation of chitin was not observed, and there was little evidence for lignin decomposition or for formation of humic polymers. The pattern was consistent with attack by brown-rot fungi and very slow chemical hydrolysis, especially in the later stages.

We are now examining decomposition of small-diameter thinnings (<25 cm) after up to 20 years residence time in a second-growth Douglas-fir forest (the Shawnigan Lake site) which forms one of the immature plots of the chronosequence. In addition to solid-state C-13 NMR, chemical analysis of hydrolysable monosaccharides is being used to look at relative losses of cellulose and hemicellulose. Preliminary results (Preston 1993) show that with a drier site and smaller diameters, decomposition appears to proceed in a non-selective manner, characteristic of white-rot fungi. Despite a huge loss of mass and C, there is little change in overall composition up to 11 years after felling, but at 19 years, the relative proportion of lignin has started to increase. By this time, approximately the end of the first stage of decay in the old-growth study, these small diameter logs have lost structural integrity and are collapsing into the forest floor. These studies will be extended to selected samples from other sites of the chronosequences, to develop an overall model of decomposition of large woody debris.

We are also using NMR to characterize litterfall and the changes due to decomposition in the forest floor. We characterized deep organic horizons (Folisols) in the CWH zone of northern Vancouver Island. These develop due to limited decomposition and lack of disturbance, and are a factor in poor growth of young plantations (deMontigny *et al.* 1993). The studies of litterfall and organic horizons demonstrated the presence

of tannins (Preston and Sayer 1992), a component which is often missed or poorly quantified in ecological studies. Tannins sometimes indicate plant stress, discourage herbivory, and inhibit decomposition and N availability. From their detection via solid-state spectra, we have developed appropriate protocols to extract, purify, and quantify tannins in ecological investigations. Again, while these investigations have been carried out on a limited number of sites, they do represent both zones of the chronosequence and appear to have general validity. They will be extended to selected suites of samples from the chronosequences.

While levels of C are lower in the mineral horizons (typically <3%), they can also be characterized by NMR, by using a combination of physical and chemical fractionation. In addition to conventional humic fractions, two important pools appear to be "particulate organic C" (POC), a light fraction floatable in water and dissolved organic C (DOC). For example, using NMR, the effects of fertilization at Shawnigan Lake were reflected in a greater degree of decomposition in both the POC and humin fractions (Preston 1993). We now plan a more general investigation of successional changes in the quality of soil organic matter, using selected suites of samples from the chronosequences.

The focus has been on C-13 NMR, but some preliminary studies are under way to characterize forms of extractable P (orthophosphate, monoesters and diesters, pyrophosphate, polyphosphate, and phosphonate) in selected sites and chronosequences (Preston, in press). It is also possible to use N-15 NMR of enriched samples, and we hope to develop this area in future, to complement our conventional and tracer N techniques.

Soil N analysis and the use of N-15 tracers have been carried out at the Pacific Forest Centre for many years. We have two independent techniques for N-15 analysis: mass spectrometry and optical emission (Preston 1992). This allows analysis of samples down to a few μg of total N, and over the whole range of abundances, including investigations using variations in natural abundance. Conventional techniques include Kjeldahl digestion and distillation, specific-ion electrodes, and combustion analysis for total N. Thus, it is possible to tailor analytical protocols for the widest possible range of sample types. Two studies in progress are discussed elsewhere (Chang *et al.*, in these proceedings; Aarnio *et al.*, in these proceedings).

References

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