



Two-dimensional NMR spectroscopy links structural moieties of soil organic matter to the temperature sensitivity of its decomposition

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Soil organic matter (SOM) represents a huge carbon pool, specifically in boreal ecosystems. Warming-induced release of large amounts of CO₂ from the soil carbon pool might become a significant exacerbating feedback to global warming, if decomposition rates of boreal soils were more sensitive to increased temperatures. Despite a large number of studies dedicated to the topic, it has proven difficult to elucidate how the organo-chemical composition of SOM influences its decomposition, or its quality as a substrate for microbial metabolism. A great part of this challenge results from our inability to achieve a detailed characterization of the complex composition of SOM on the level of molecular structural moieties.

¹³C nuclear magnetic resonance (NMR) spectroscopy is a common tool to characterize SOM. However, SOM is a very complex mixture and the chemical shift regions distinguished in the ¹³C NMR spectra often represent many different molecular fragments. For example, in the carbohydrates region, signals of all monosaccharides present in many different polymers overlap. This overlap thwarts attempts to identify molecular moieties, resulting in insufficient information to characterize SOM composition.

We applied two-dimensional (2D) NMR to characterize SOM with highly increased resolution. We directly dissolved finely ground litters and forest floors—fibric and humic horizons—of both coniferous and deciduous boreal forests in dimethyl sulfoxide and analyzed the resulting solution with a 2D ¹H-¹³C NMR experiment. In the 2D planes of these spectra, signals of CH groups can be resolved based on their ¹³C and ¹H chemical shifts, hence the resolving power and information content of these NMR spectra is hugely increased. The 2D spectra indeed resolved overlaps observed in 1D ¹³C spectra, so that hundreds of distinct CH groups could be observed and many molecular fragments could be identified. For instance, in the aromatics region, signals from individual lignin units could be recognized. It was hence possible to follow the fate of specific structural moieties in soils. We observed differences between litter and soil samples, and were able to relate them to the decomposition of identifiable moieties.

Using multivariate data analysis, we aimed at linking the detailed chemical fingerprints of SOM to turnover rates in a soil incubation experiment. With the multivariate models, we were able to relate signal patterns in the 2D spectra and intensities of identifiable molecular moieties to variability in the temperature response of organic matter decomposition, as assessed by Q₁₀.

In conclusion, the characterization of SOM composition at the molecular level by solution-state 2D NMR spectroscopy is highly promising; it offers unprecedented possibilities to link SOM molecular composition to ecosystem processes, and their responses to environmental changes.