



Two-dimensional NMR spectroscopy as a tool to link soil organic matter composition to ecosystem processes

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Environmental factors (e.g. temperature and moisture) and the size and composition of soil microbial populations are often considered the main drivers of soil organic matter (SOM) mineralization. Less consideration is given to the role of SOM as a substrate for microbial metabolism and the importance of the organo-chemical composition of SOM on decomposition. In addition, a fraction of the SOM is often considered as recalcitrant to mineralization leading to accumulation of SOM. However, recently the concept of intrinsic recalcitrance of SOM to mineralization has been questioned. The challenge in investigating the role of SOM composition on its mineralization to a large extent stems from the difficulties in obtaining high resolution characterization of a very complex matrix.

^{13}C nuclear magnetic resonance (NMR) spectroscopy is a widely used tool to characterize SOM. However, SOM is a very complex mixture and in the resulting ^{13}C NMR spectra, the identified functional groups may represent different molecular fragments that appear in the same spectral region leading to broad peaks. These overlaps defy attempts to identify molecular moieties, and this makes it impossible to derive information at a resolution needed for evaluating e.g. recalcitrance of SOM. Here we applied a method, developed in wood science for the pulp paper industry, to achieve a better characterization of SOM. We directly dissolved finely ground organic layers of boreal forest floors—litters, fibric and humic horizons of both coniferous and broadleaved stands—in dimethyl sulfoxide and analyzed the resulting solution with a two-dimensional (2D) ^1H - ^{13}C NMR experiment. We will discuss methodological aspects related to the ability to identify and quantify individual molecular moieties in SOM. We will demonstrate how the spectra resolve signals of CH groups in a 2D plane determined by the ^{13}C and ^1H chemical shifts, thereby vastly increasing the resolving power and information content of NMR spectra. The obtained 2D spectra resolve overlaps observed in 1D ^{13}C spectra, so that hundreds of distinct CH moieties can be observed and many individual molecular fragments can be identified. For instance, in the aromatic spectral region, signals originating from various lignin monomers and unsaturated compounds can be resolved. This yields a detailed chemical fingerprint of the SOM samples, and valuable insights on molecular structures.

We observed differences in the respective aromatic region of the 2D spectra of the litter layers and the fibric and humic horizons, in relation with humification processes. We were also able to relate the cross-peak complexity and abundance patterns of identifiable molecular moieties to variability in the temperature response of organic matter degradation, as assessed by Q_{10} . To conclude, solution-state 2D NMR spectroscopy is a highly promising new tool to characterize SOM composition at the molecular level, which opens completely new possibilities to link SOM molecular composition to ecosystem processes, and their responses to environmental changes.