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Broadband molecular composition of dissolved organic matter in grassland soil as a function of depth

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We tested the application of electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR-MS) on dissolved organic matter (DOM) from four different soil depths (10 - 60 cm) of a large-scale grassland experiment ("The Jena Experiment").
DOM is a key component of the global carbon cycle and links terrestrial and aquatic ecosystems Thus, it is of special interest to understand its origin and fate. In soil profiles, DOM is assumed to change rapidly from surface- and plant-derived to microbial-derived compounds in deeper soil layers. Composition changes have been observed with various analytical techniques but the applied techniques were restricted either by molecular resolution or the number of analytes. To widen the understanding of processes along the soil profile, it is necessary to apply methods that capture the broadband molecular composition.
We used ESI-FT-ICR-MS to measure the molecular composition of DOM from four depths down to 60 cm of grassland soil at 18 plots of "The Jena Experiment". We focused on the shared depth trend of all plots leading to robust site trends. Molecular formulae assignment to detected masses gave access to the chemical composition of several thousand compounds. We applied statistical analyses to highlight the changes of DOM composition with depth for the complete spectra but also for N, S or P formulae separately. By analyzing Bray-Curtis distances of the spectras' molecular composition (relative intensities) we examined the general dissimilarity between depths. We used differential spectra of samples from 10 and 60 cm to identify formula with higher detected intensity in the respective depths. Considering only formulae of differential spectra that occurred in 90 % of the plots ensured the focus on the general depth trend for the whole site.
Analyzing Bray-Curtis distances revealed increasing differences of the molecular composition with increasing distance of sampling depth. Bimodal MS spectra shapes observed in the topmost sampling depths deviated the most from the "classical" unimodal shape known from riverine or marine DOM. With increasing soil depth, the bimodal shape changed to a rather unimodal shape while the intensity of masses in the middle molecular mass range (300 to 450 g/mol) gained intensity in relation to low molecular weight (LMW) molecules (150 to 300 g/mol). This depletion of small molecules with depth was highlighted by differential spectra and was accompanied by an increase in saturation. Formulae with higher detected intensity in 60 cm were characterized by remarkably narrow and H/C and O/C ranges.
Our data suggest that the abundance of small molecules and a bimodal peak distribution in topsoil might indicate a terrestrial "freshness signal" in the LMW range. Higher unsaturation and higher H/C and O/C ranges in the topsoil might reflect less microbial processing of DOM compared to deeper depths. Our findings support the view of sorption and desorption processes along the soil profile accompanied by increasing microbial processing.