



Depth trends revisited: Source-induced fragmentation of soil dissolved organic matter

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Although representing only a small portion of all the organic matter being present in soils, dissolved organic matter (DOM) is its most mobile and reactive fraction. Along its transport down the soil profile, DOM interacts with minerals via sorption and aggregation phenomena, and with organisms via uptake, exudation or internal recycling. During this downward passage DOM composition changes too, shifting from a dominant plant/ plant decomposition product character to a more decomposer-driven signature. Such trends have been documented well by ultrahigh resolution mass spectrometry (FT-MS) which reveals thousands of molecular compositions (formulas) in one DOM sample (Roth et al. 2019). However, complementary properties of the molecules that constitute these signatures are largely missing. To test if the downward trend in molecular composition would also affect DOM's fragmentation sensitivity, and if these effects could obscure the final ecological interpretation, we obtained direct injection FT-MS data with and without source-induced fragmentation (SID) at 45 eV. As a test dataset, we used samples from suction plates installed in three soil profiles (at 5, 10, 20, 30 and 60 cm depth) developed on aeolian sand deposits (podzols, cambisols) in Linde, Brandenburg (Germany). These three sites vary mainly in vegetation cover (grassland, oak, pine). All sites showed a clear depth trend as reported earlier, especially without SID turned on. SID clearly decreased the ion abundance of signals in the molecular weight range 300-500 Da (center ~350), while signals in the range 150-400 Da (center ~ 225) increased; more formulas were detected with SID on. With depth, the population of molecules decreasing/ increasing changed significantly, especially between 30 and 60 cm depth, across all sites. At 60 cm depth, decreasing formulas were more aliphatic while increasing formulas were more confined to a narrow area in the center of the van Krevelen space ("island of stability"). Interestingly, the formulas decreasing significantly across all sites were largely CHO (no other heteroatoms, at all depths), S-containing (at 5, 10, 20 and 30 cm) or P-containing (30 and 60 cm), while formulas increasing were CHO (at all depths) and N-containing ones (at all depths, but mainly at 20 and 30 cm), thereby indicating depth-dependent differences and ionization of new N-containing molecules. In ordination space, sites were clearly differentiated according to SID status, depth and site (in this order), but SID did not affect the separation in terms of depth or site, i.e., the ecological interpretation of DOM fingerprints remained similar independent of the SID status. This means that trends in soil DOM studies are likely not obscured by differences in fragmentation during the electrospray ionization process.

Reference: Roth, V.-N., Lange, M., Simon, C., Hertkorn, N., Bucher, S., Goodall, T., Griffiths, R. I., Mellado-Vázquez, P. G., Mommer, L., Oram, N. J., Weigelt, A., Dittmar, T., Gleixner, G. (2019):

Persistence of dissolved organic matter explained by molecular changes during its passage through soil. *Nat. Geosci.* **12**: 755–761.