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Organic speciation of (micro)nutrients in relation to overall dissolved organic matter composition in soil water extracts: New insights from ultrahigh resolution mass spectrometry

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The Kohala climate gradient in Hawaii is an established model system to study the effects of long-term precipitation trends on soil development and has a large range in soil organic matter (SOM) stocks. The amount and composition of SOM plays an important role in the biogeochemical cycling of (micro)nutrients (such as S, N, P and Se). Previous studies found a strong correlation between soil organic carbon (SOC) concentration, organic matter composition, and organic speciation of P, S and Se along the precipitation gradient (Helfenstein et al. 2018, Tolu et al. 2022). However, the identification of organic species remains limited to broad SOM fractions, including functionally or operationally defined pools, such as microbial, plant-available, or residual forms of an element (Helfenstein et al., 2018), and chemically separated fractions that are aligned with parallel reference materials of humic, fulvic, or hydrophilic organic acids to differentiate properties of the organic material, such as molecular size, complexation behavior or aromaticity (Tolu et al., 2022). Ultrahigh resolution mass spectrometry (UHR-MS) offers a possibility to directly reveal the molecular complexity of organic matter residing in soils and soil solution and can therefore assist in identification of organic species containing (micro) nutrients and of organic molecules that are indirectly related to (micro) nutrient mobility. We analyzed aqueous soil extracts, representing the most bioavailable soil pool, with size-exclusion chromatography (SEC) coupled to UHR-MS (Orbitrap). We will demonstrate here that molecular diversity of DOM in these extracts increased along the gradient with increasing SOC stocks (increasing precipitation), and relate this change to trends in molecular composition with soil depth. Furthermore, we will show how (micro)nutrients are present in these organic structures and how the presence of their anions and small metabolites is linked to the trends in main organic composition.

References:
Helfenstein et al. (2018) *Nat Commun* **9**: 3226.
Tolu et al. (2022) *Nat Commun* **13**: 6974.