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Characterizing Metallo-Organic Species Involved in Biological Metal Acquisition from Soils Using Advanced Mass Spectrometry

Rene Boiteau¹, Malak Tfaily¹, Jared Shaw¹, Lawrence Walker¹, Nikola Tolić¹, Yina Liu¹, Albert Rivas Ubach¹, Rosalie Chu¹, Matt Newburn¹, Ljiljana Paša-Tolić¹, Dave Koppenaar¹, Errol Robinson¹, and Nancy Hess¹

¹ Environmental Molecular Sciences Laboratory (EMSL), Pacific Northwest National Laboratory, Richland, WA

Contact: Nancy Hess [nancy.hess@pnl.gov]

Many elements are scarcely soluble in aqueous conditions found in soils unless complexed to strong binding organic ligands. To overcome this limitation, some plants and microbes produce chelators that solubilize micronutrient metals such as Fe, Ni, Cu, and Zn from mineral phases. These complexes are taken up by organisms via specific membrane receptors, thereby differentially impacting the bioavailability of these metals to the plant and microbial community. Although the importance of these chelation strategies for individual organisms has been well established, little is known about which pathways coexist in natural systems or how they interact and compete for metal binding. Identifying these metallo-organic species within environmental systems has remained a formidable analytical challenge due to the vast diversity of compounds and poorly defined metabolic processes in complex soil matrix. Fourier transform mass spectrometry (FTMS) offers the mass resolving power and accuracy required to resolve the unique isotopic signatures of many trace element containing compounds. In particular, the novel high magnetic field (21T) Fourier transform ion cyclotron resonance (FTICR) mass spectrometer at EMSL provides a unique combination of fast spectral acquisition rate, resolving power, accuracy and sensitivity needed to identify metal isotopologues on a liquid chromatography (LC) timescale. The same separation platform can also be combined with inductively coupled plasma mass spectrometry (ICPMS) to identify and quantify metal complexes. Herein, we employed recently developed LC-ICPMS-FTMS methods to characterize the speciation of water-soluble dissolved trace elements (e.g. Fe, Ni, Cu, and Zn) from soils. Samples were separated with reversed-phase (RP) LC and the eluent was analyzed by tandem quadrupole ICP-MS to detect and quantify metals associated with different organic species. The same RPLC platform was subsequently coupled with FTMS (Orbitrap and 21T ICRMS) to identify and quantify metalloorganic species by automated identification of chromatographically coherent features that match distinct metal isotopic patterns. Both plant and fungal metal binding metabolites were putatively identified, revealing compound-specific patterns of chelation to biologically essential metals. Numerous plant metabolites, including nicotianamines as well as phytosiderophores typically implicated in iron acquisition by grasses, dominated the speciation of divalent metals such as Ni, Cu, and Zn. In contrast, fungal siderophores bound comparatively more trivalent Fe. These results define direct biochemical pathways that underpin biological-mineral interactions in grassland soils. They also raise new questions about the competition of these compounds for metal binding and their bioavailability to different members of the rhizosphere population.