Labile structures in organic matter under the incfluence of multivalent cations – an issue for dynamic interfaces?

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Soil organic matter (SOM) controls large part of the processes occurring at biogeochemical interfaces in soil and may contribute to sequestration of organic chemicals. In this contribution, the idea that sequestration of organic chemicals is driven by physicochemical SOM matrix aging, and its consequences for transport processes will be discussed. In contrast to chemical aging processes, physical matrix aging involves changes in the supramolecular arrangement of SOM molecules and molecule segments. Organic chemicals can be entrapped in nanovoids, which can tranform to a semi-persistent cage. Persistence of entrapment directly depends on the rigidity and stability of the cage. Water molecule bridges (WaMB) and cation bridges (CaB) between segments of soil organic matter (SOM) have been found to stabilize the supramolecular SOM matrix and are therefore suspected to control immobilization of organic chemicals in soil. Contaminants sequestered by WaMB or CaB can be immobilized or released suddenly upon changes in environmental conditions like moisture, temperature or melting. Understanding their dynamics is highly important to model the reaction of soil as well as release and transport of organic chemicals on changes in climatic conditions. While the idea of CaB in solid soil organic matter is more and more accepted, there is increasing evidence that such cross-links are not relevant in all types of soil organic matter, depending on the spatial distribution of charged functional groups in the OM. Only if distances between functional groups are sufficient, CaB can form. Larger distances can be bridged by CaB-WaMB associations. Also interfacial properties are dynamic. Soil wettability can with increasing involvement of functional groups in CaB-WaMB associations. In the extreme case, high concentrations of multivalent cations can hydrophobize surfaces of SOM. Associations of CaB and WaMB evolve slowly and form a supramolecular network in SOM. Those dynamic associations can fix molecular arrangements inducing water repellency and increase kinetic barriers for the release and uptake of water and sorption and transport of organic chemicals in soil.

The role of soil Cu in chelate mediated Fe acquisition by plants

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Iron is an essential micronutrient to plants. In soils with a neutral to alkaline pH, the solubility of Fe bearing minerals is very low and can become limiting for plant growth. To avoid Fe deficiency in plants grown on such soils, the solubility of Fe needs to be increased. This can be established by means of chelating agents, which strongly bind Fe and form a soluble Fe complex. These chelating agents can either have a natural or an antropogenic origin.

Grasses (including wheat, barley and rice) are very efficient in preventing Fe deficiency, because their Fe acquisition strategy includes the exudation of chelating agents called phytosiderophores (PS). These PS can dissolve soil Fe and the resulting FePS complex can be taken up by a high affinity membrane transporter. In agricultureal practice, plant species that are less efficient in acquiring Fe are commonly supplied with micronutrient fertilizers based ons synthetic chelating agents. For Fe fertilization on calcareous soils, FeEDDHA (iron ethylene diamine bis-N,N'- hydroxyphenyl acetic acid) is among the most effective.

Soils contain several metals that can compete with Fe for binding to chelating agents, thereby compromising the efficiency of the chelate mediated Fe uptake mechanism. Cu is among the stronger competitors and occurs in soil in quantities that could substantially compromise Fe uptake.

It will be shown and discussed that the extent to which Cu effectively competes with Fe for complexation under soil conditions is controlled by both thermodynamic and kinetic factors. These factors include the specific affinity of the chelating agent for Fe and Cu, the Fe and Cu activity in the soil, the extent to which metal complexes adsorb to reactive soil components, the mobilization rate of Fe and Cu, and the displacement rate of Fe from the Fe-chelate by Cu. Both with PS and synthetic Fe chelates, Cu may considerably limit the time-span the chelating agent remains effective as Fe transporter.

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