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Change in physical structure of a phenol-spiked sapric histosol observed by Differential Scanning Calorimetry

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Interactions of pollutants with soil organic matter (SOM), their fate and transformation are crucial for understanding of soil functions and properties. In past, many papers dealing with sorption of organic and inorganic compounds have been published. However, their aim was almost exceptionally fo-cused on the pollutants themselves, determination of sorption isotherms and influence of external factors, while the change in SOM supramolecular structure was usually ignored. The SOM structure is, however, very important, since the adsorbed pollutant might have a significant influence on soil stability and functions.
Differential scanning calorimetry (DSC) represents a technique, which has been successfully used to analyze the physical structure and physico-chemical aging of SOM. It has been found out that water molecules progressively stabilize SOM (water molecule bridge (WaMB)) (Schaumann & Bertmer 2008). Those bridges connect and stabilize SOM and can be disrupted at higher temperature (WaMB transition; (Kunhi Mouvenchery et al. 2013; Schaumann et al. 2013). In the same temperature region melting of aliphatic moieties can be observed (Hu et al. 2000; Chilom & Rice 2005; Kucerik et al. submitted 2013).
In this work, we studied the effect of phenol on the physical structure of sapric histosol. Phenol was dissolved in various solvents (water, acetone, hexane, methanol) and added to soils. After the evaporation of solvents by air drying, the sample was equilibrated at 76% relative humidity for 3 weeks. Using DSC, we investigated the influence of phenol on histosol structure and time dependence of melting temperature of aliphatic moieties and WaMB transition.
While addition of pure organic solvent only resulted in slightly increased transition temperatures, both melting temperature and WaMB transition temperature were significantly reduced in most cases if phenol was dissolved in these solvents. Water treatment caused a decrease in WaMB transition temperature but increased melting temperature. During the 150 days of physico-chemical aging, an increase in WaMB transition and melting temperature of aliphatic crystallites was was observed. Several types of treatments contrasting with this development were attributed to specific solvent –phenol interactions and will be discussed in this contribution.
The results indicate that after introduction of phenol and during the consequent relaxation of the SOM structure, the re-formation of water molecule bridges is significantly reduced and decelerated. WaMB has been suggested as one SOM stabilizing mechanism (Schaumann & Bertmer 2008); the incorporation of phenol destabilizes the physical structure of SOM. It is assumed that phenol can penetrate into the WaMB hotspots, competes with water and/or disrupts WaMB or participate in WaMB formation. Simultaneously, phenol can penetrate and irreversibly change also the aliphatic crystallites, which are traditionally not considered being actively involved in sorption processes. It furthermore could compete with the organic matter for the hydration water. In this contribution, we will discuss these mechanisms.
The results clearly demonstrate the potential of DSC to probe labile (physical) structures in soil organic matter and to elucidate interaction of organic chemicals with SOM moieties.

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