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Cooperative water-SOM interactions derived from the organic compound effect on SOM hydration

Mikhail Borisover

Institute of Soil, Water and Environmental Sciences, Agricultural Research Organization, The Volcani Center, Bet Dagan, Israel (vwmichel@volcani.agri.gov.il).

Interactions of water molecules with soil organic matter (SOM) may affect the ability of SOM to participate in multiple physical, chemical and biological processes. Specifically, water-SOM interactions may have a profound effect on interactions of organic compounds with SOM which is often considered as a major natural sorbent controlling the environmental fate of organic pollutants in the soil environment. Quantification of water - SOM interactions may be carried out by using water vapor sorption isotherms. However, water sorption isotherms providing macroscopic thermodynamic data do not allow examining water-SOM interactions on a microenvironment scale. The examination of water-SOM interactions in a local SOM environment may be carried out by determining the response of the SOM hydration to sorption of probe organic compounds. Recently, the model-free approach was proposed which allows quantifying effects of sorbing organic molecules on water - SOM interactions, by using relatively more available data on the effect of water activity on organic compound - SOM interactions. Therefore, this thermodynamic approach was applied to the experimental data describing sorption of organic compounds by SOM, both from the vapor and liquid phases, at various water activities. Hence, the response of water interactions with the model SOM materials such as a humic acid and an organic matter-rich peat soil to the presence of various organic sorbates was evaluated. Depending on a molecular structure of organic sorbates probing various molecular environments in SOM, the SOM-bound water may be driven in or out of the SOM sorbents. Organic compounds containing the atoms of oxygen, nitrogen or sulfur and preferring a relatively "polar" SOM microenvironment demonstrate the distinct enhancing effect on water-SOM interactions. In contrast, the "low-polarity" organic compounds, e.g., hydrocarbons or their halogen-substituted derivatives, produce a weakening effect on water-SOM interactions. Importantly, the changes in water-SOM interactions induced by the presence of organic compounds may demonstrate the cooperative behavior: (1) several water molecules may be involved in an enhanced hydration of SOM, (2) at the presence of an organic sorbate, interactions of water molecules with SOM enhance the uptake of the following water molecules. The proposed cooperative water-SOM interactions may result from a perturbation of the SOM matrix due to a sorption of organic and water molecules where a partial disrupting of molecular contacts in SOM makes easier the following SOM-water interactions thus promoting the enhanced SOM hydration.