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Competitive Adsorption of Humic Substances and Low Molecular Weight Organic Acids on Goethite Surfaces: Experiment and Modeling

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Humic substances (HS) are the major constituents of soil organic carbon, Earth's largest terrestrial carbon pool. Their stability and residence time in soils are strongly enhanced by association with soil minerals, particularly metal (oxyhydr)oxides like goethite. Low molecular weight organic acids (LMWOAs), exuded by plants and microorganisms, have been shown to also strongly interact with these minerals. Therefore, they compete with HS for adsorption onto soil metal (oxyhydr)oxide surfaces, potentially inducing desorption and enhanced microbial respiration of HS. Acceleration of HS decomposition, in turn, alters carbon storage dynamics in soils. Despite its significance, the geochemical mechanisms underlying HS-LMWOA interactions at metal (oxyhydr)oxide surfaces remain poorly understood.

This study quantitatively investigates the competitive adsorption of HS (using humic acid (HA), fulvic acid (FA) as analogues) and LMWOAs (citric acid, malic acid) at goethite surfaces across ranges in HS and LMWOA concentrations, pH, and ionic strength. Batch adsorption experiments and surface complexation modeling with the Charge Distribution model for Natural Organic Matter (NOM-CD), were used for elucidating these competitive interactions.

Results show that LMWOAs can strongly compete with HS for adsorption sites on the goethite surface, and that the extent of competition is highly pH-dependent: competition was strongest at pH 6, reducing HS adsorption by up to 50%. However, no competition was observed above pH 8. Ionic strength was found to have a minor influence on the competition. Citric acid was a stronger competitor than malic acid, and FA proved more sensitive to competition than HA.

The NOM-CD model with updated model parameters could effectively describe HS-LMWOA interactions. The greater competition effect from citric acid than from malic acid can be attributed to its larger number of carboxylic acid groups, forming inner- and outer-sphere complexes. FA is more sensitive to this competition because it is spatially bound closer to the goethite surface than HA.

Our results contribute to an improved understanding of the HS-LMWOA interactions at mineral surfaces in the context of soil carbon dynamics and highlights the need to consider plant and microbial exudates in carbon storage. Our results can provide a reference for sustainable agricultural management and climate change.