

## **Molecular insights into the coupled reactions of sorptive fractionation and oxidation of DOM on manganese oxide**

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Dissolved organic matter (DOM) is ubiquitous in soil and aquatic environments, and plays a crucial role in environmentally significant processes such as the global cycling of carbon, migration and transformation of contaminants, and dynamics of microbial communities. Manganese oxide, an important natural mineral commonly found in soils, sediments, and ocean floors, is known to strongly interact with DOM. However, the coupled sorptive fractionation and subsequent oxidation of DOM on manganese oxide are still poorly understood at molecular levels.

In this study, the coupled reactions of sorptive fractionation and oxidation of DOM on  $\delta$ -MnO<sub>2</sub> were investigated with batch experiments, electrospray ionization coupled with Fourier-transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR-MS), and gas chromatography-mass spectrometry (GC-MS). ESI-FT-ICR-MS results showed that DOM molecules with different chemical properties showed varying adsorptive fractionation. Compounds with high molecular weight and unsaturation, and low oxygen compounds were preferentially adsorbed on  $\delta$ -MnO<sub>2</sub>. Some of the high molecular weight DOM molecules can be oxidized into lower molecular weight molecules, leading to the formation of low unsaturation compounds. GC-MS was employed to characterize the typical oxidation products of DOM such as formaldehyde, acetone, etc. Our results help to gain a better understanding of the geochemical cycling of C in natural environments.