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Carbon-driven release of Mn into groundwater: Insight into the colloid formation and mobility of NOM-Mn complexes.

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Manganese (Mn) ranks as the 10th most abundant element metal in Earth's crust and is ubiquitous in soils and sediments [1]. Despite being an essential element for human health, Mn can cause adverse health effects, even at low concentrations naturally present in the environment [2]. Mn oxides participate in a range of redox and complexation reactions with natural organic matter (NOM), leading to the release of Mn from soils and sediments and impacting drinking water quality. Previous studies focus primarily on the reduction of Mn oxides to dissolved Mn phases and have often neglected the formation of Mn colloids, a key factor controlling Mn transport and environmental behavior. This study investigates the effect of NOM on Mn oxides in terms of Mn speciation, colloid formation, and aggregation. Batch experiments were conducted wherein varying concentrations of humic acid (HA) was reacted with 0.5 mM Mn oxide suspensions at molar C:Mn ratios ranging from 0 to 15. Size-fraction experiments were run to quantify colloids formation in reaction products. The colloids formed under different C:Mn ratios were characterized using XRD, XPS, TEM, and aggregation behavior was examined in natural water using DLS. The presence of carbon increased Mn release by hindering colloids aggregation and promoting reductive dissolution of Mn oxides. C-Mn colloid formation increased significantly with increasing molar C:Mn ratios, increasing from 1.1% (C:Mn=0) to 33.0% (C:Mn=15). C-Mn colloids (C:Mn=3) exhibited a hydrodynamic diameter of ca. 150 nm in both surface and groundwater over 30 days, while Mn oxides readily aggregated into much larger particles (>6000 nm) in groundwater. These findings provide insight into the mechanisms that govern the intricate cycling of Mn among particulate, colloidal, and truly dissolved phases in the environment. Examining the formation and aggregation of NOM-Mn colloidal complexes not only provides valuable insight into Mn's environmental fate, but also reveals its potential to sequester and mobilize contaminants.

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