

Organic matter and Si - The guardians of Fe-rich colloid persistence in a redox-active floodplain

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Fe-rich colloids are important export agents of micronutrient, contaminant, and organic matter throughout terrestrial environments. Their persistence, redox-active and multielement content renders colloids key contributors to biogeochemical reactions. However, few studies have characterized such colloids at the μm – nm scale, nor have they documented the influence of seasonally-variable field hydrological and geochemical conditions on colloid dynamics.

We used an array of advanced analyses (cryo-TEM, TEM-EDS, Mössbauer spectroscopy, Fe-EXAFS, and XPS) to characterize Fe-rich colloids detected at our Slate River floodplain field site and linked the results to our field hydrological and chemical data. Fe-rich colloids are mixed-phase assemblages composed of Si-coated and organic matter enmeshed ferrihydrite nanoparticles. Fe(II) and Fe(III) co-existed in the colloids under both oxic and anoxic conditions, which is attributed to the passivating effects of the Si and organic matter matrix. We propose that this compositional stability supports the ferrihydrite foundation, as well as the occurrence of Fe(II), that is either complexed by the organic matter matrix or embedded in the ferrihydrite structure. Colloid composition and abundance demonstrated seasonal variability – snowmelt colloids sampled in the spring were more reduced and exhibited greater Si-organic matter protection compared to baseflow colloids sampled in summer and autumn. We hypothesize that longer residence times coupled with high porewater organic matter levels, contribute to the persistence of a more reduced colloid composition during snowmelt. In comparison, increased downward flow velocity with infiltrating oxygen is likely to promote transport of more oxidized colloids at baseflow. Our findings provide novel insights on the architecture and dynamics of natural Fe-rich colloids in floodplain systems, with implications to organic matter and nutrient cycling.