Geochemical controls on the formation of U(IV)-bearing colloids in a mining-impacted natural wetland

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Uranium can accumulate in wetland soils via U(VI) sorption on soil components and/or precipitation of U(IV)-containing minerals under reducing conditions. In a natural wetland located near a former U mine, we observed a slight U release into a stream flowing through. This was evidenced by an increase in the U content in the stream (by ~ 0.13 μM) as a function of distance from the wetland inlet to the outlet[1]. To understand this phenomenon, depth-dependent soil and porewater samples were collected and preserved under anoxic conditions. Some of the cores obtained included a Fe-bearing clay-rich layer in the soil, while others were clay-poor. At these spots, the porewater and microbial community indicated the onset of microbial Fe(III) and SO_4^{2-} reduction. Under reducing conditions in the wetland, 99% of U is bound to soil. However, unexpectedly significant soluble U concentrations (~ 1 μM) were found at clay-rich locations, whereas much lower ones (~ 0.1 μM) were observed at a clay-poor location. Using laser fluorescence spectroscopy and X-ray absorption spectroscopy, we showed that U was mainly tetravalent in both porewater and soil and that U(IV) in the soil was non-crystalline. Electron microscopy and ultrafiltration analysis demonstrated that U in the porewater at clay-bearing locations was associated with $Fe(OH)_2$-organic matter colloids, whereas colloids at clay-poor locations contained little Fe and U. We conclude that the Fe-containing colloids at clay-rich locations are responsible for slight U release from the wetland and that the low U(IV) mobility at clay-poor locations is due to the limited association of Fe(II) to colloids in porewater. This limited availability of Fe(II) for colloid association results from pyrite precipitation.

[1] Wang, Y. *et al* 2013, Mobile uranium(IV)-bearing colloids in a mining-impacted wetland. *Nat Commun* **4**.