Podzolisation and exportation of organic matter in black waters of the Rio Negro (upper Amazon basin, Brazil)

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In the Rio Negro basin, podzols develop at the expense of clay-depleted laterites through localised and spectacular weathering fronts. This natural process leads to the remobilization of previously accumulated organic matter (OM) and elements (Al, Fe, Si). OM is thus redistributed within soil profiles and exported towards rivers, giving them their typical black coloration. In soils, this redistribution leads to a strong vertical variation of OM characteristics in podzols. However, little is known about the structure of OM transferred to rivers, and about the relative contributions of the different soil horizons to this exportation.

To investigate the fate of OM in the soil – water continuum in the Rio Negro basin, we have water-extracted OM from seven key soil samples collected in a soil sequence representative for the transition between latosol and podzol on the low-elevation plateaux of the Rio Negro basin. These samples enable following both vertical and lateral differentiations and they were compared with OM from the water-tables and rivers draining the soil sequence.

Specific UV Absorbance, pH and conductivity of aqueous samples were measured. OM chemical structure was investigated through solid-state ^{13}C nuclear magnetic resonance (NMR) and thermally assisted hydrolysis and methylation (THM).

OM water-extracted from different soil horizons was thus shown to exhibit contrasting features and we could identify compounds released upon THM specific to OM water-extracted from the different soil horizons investigated. Comparison with water from the drainage network suggests that, in the early rainy season, OM is mainly remobilised in deep horizons of well-developed podzols. This study opens new perspectives to trace the origin and evolution of OM in black rivers of the Rio Negro basin.

Structure, composition, size and reactivity of biogenic nano-uraninite

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Nanoparticulate biogenic uraninite is formed from the bacterial reduction of uranium(VI) and is of great importance to planned bioremediation strategies at uranium-contaminated sites in the U.S. The primary barrier to uranium release from this material in the subsurface is the material itself. A better understanding the chemical and physical properties of the material is therefore critical. Biogenic uraninite is fascinating from the standpoint that particle size (typically 2 to 5 nm), molecular-scale structure, and unit cell composition all have been posited to strongly moderate its stability in the subsurface. In particular, there has been concern that the nano-size of this material induces strain that destabilizes the material.

We have used EXAFS, *in situ* synchrotron powder diffraction, TEM, XPS, and continuous-flow dissolution measurements to assess the impacts of size, structure, and composition on the stability of biogenic uraninite. In the absence of cation dopants, biogenic uraninite was found to be unstrained and structurally homologous to stoichiometric UO_2, and this similarity persists in the solubility and kinetics of this material. These results suggest that size does not intrinsically impact reactivity. In contrast, unit cell composition, and in particular the presence of structural impurity cations, was found to have a pronounced impact on stability (as predicted from sedimentary uraninites), as well as on structure and particle size. These findings indicate that ground water solute chemistry is an important moderator of biogenic uraninite stability and raise intriguing questions about the role of size in the reactivity of nanoparticles in aquatic environments.