Study of the As-bearing byproducts of wetland reoxidation using μXAS

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Organic matter (OM)-rich areas that undergo alternating redox conditions in accordance with the water saturation, such as wetlands, can play a significant role in the groundwater contamination by arsenic (As) [1]. Under reduced conditions (high-water period), Fe-oxyhydroxides, OM and As are solubilised. However, there is a lack of data on the fate of As when the water level decreases, namely when wetland reduced soil solutions are reoxidized. Several hypotheses could be considered: (i) As is not totally oxidized and As(III) is bound to colloidal OM via sulfhydryl (SH-) groups or ii) As(III) and/or As(V) are bound to colloidal reoxidized Fe embedded within OM matrix.

We developed an experimental device able to collect the oxidation byproducts directly in wetland soils. To state about the As fate, we performed μXRF and μXAS analysis of these solids at the As, S and Fe K-edge.

The μXRF mapping highlighted the heterogeneous distribution of As, S and Fe. Despite the oxidized conditions, XANES showed that S occurred in different oxidation states including 21% as SH- OM functional group, and that 10 to 40% of As is AsIII (supporting the first hypothesis). Previous nanoSIMS data showed that As and S are colocalized in few spots. Unfortunately, EXAFS analysis did not reveal any distance related to As bound to OM (via C or S) but only As-Fe(III) distances. EXAFS revealed that Fe is as strongly amorphous iron oxides that are heterogeneously organized (one layer of octahedra to more). These results highlight the role of OM in conditioning the oxidation byproducts of wetland and their ability to trap As either as As(V) or As(III). The influence of S needs, however, to be assessed.