

Characterization of the network organization of iron-organic matter nano-aggregates and its impact on arsenic uptake

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Organo-mineral colloids play an important role in controlling the mobility and (bio)availability of pollutants such as arsenic (As) in natural aquatic systems. As an example, in wetlands the biogeochemical cycle of As strongly depends on iron (Fe) oxyhydroxides. More specifically are the riparian wetland soils that are periodically flooded. This leads to the establishment of reducing conditions and the solubilization of As(III), subsequently to the reductive dissolution of Fe(III)-oxyhydroxides. When the water level decreases, the wetland is reoxidized and the main As-carrying phases are nano-aggregates of organic matter (OM) associated with Fe-oxyhydroxides in which As is sorbed onto the Fe(III)-phases.

The physicochemistry of those systems appears to be highly complex and is not yet fully understood. In a previous work we have evidenced that As(III) is oxidized into As(V) by Fe(III)-oxyhydroxides with a persistence of As(III) explained by the presence of OM that limits the size of the Fe-phase which leads to an increase of As sorption on specific sites that are not active for As(III) oxidation. Furthermore, different Fe-OM-As complexes are observed in a very large size fraction range, i.e. from 5 kDa to 5 μ m.

Thus, it appears clearly that the fate of As in the environment (transport and speciation thus toxicity) is strongly related to the network organization of Fe-OM aggregates. However, up to now, little is known on this structure, especially on the components morphology and the consequences for As uptake.

In order to solve this question, we have synthesized models of nano-aggregates varying the Fe/organic carbon (OC) ratio. We have then successfully combined neutron and X-ray scattering (SANS and SAXS) with X-ray Absorption Spectroscopy (XAS), chemiometric XAS data analysis, dynamic light scattering (DLS) and transmission electron microscopy (TEM) to investigate their structure.

A fractal model has been applied to the Fe part characterization. Three distinct sizes were observed: i) primary beads of diameter $D = 1.6$ nm which are distributed as individual beads bound to OM or ii) forming intermediate nanometric aggregates of $D = 5$ to 10 nm, which are

distributed as isolated aggregates bound to OM or iii) as secondary Fe-aggregates of which $D = 0.2$ to $1.4 \mu\text{m}$, associated with a dense OM structure.

Before reaching the solubility limit of the Fe(III)-oxyhydroxides, Fe(III) is complexed to OM as small oligomers such as trimers. When the solubility limit is locally reached, Fe(III) precipitates as ferrihydrite nanoparticles embedded in OM. With the Fe content increase, the ferrihydrite intermediate aggregates combine to form secondary aggregates in which OM forms a spherical dense structure. The large secondary aggregates size increases and the Fe structure increasingly ramifies with the Fe/OC ratio increase.

A direct impact of this increase is that more As binding sites are available and thus the As adsorption rate increases with Fe/OC, for a constant As/Fe ratio.

In natural waters, Fe-OM colloids play an important role in the fate of pollutants such as As. Our investigations highlight the importance of their network structure on the availability of As adsorption sites of Fe-nanoparticles and thus on their adsorption capacity. Those results could be a key element to explain some metal/metalloid sorption variations observed in natural systems according to variations in Fe/OC ratios.

References

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