

Calcium as a booster of Fe-OM nanoaggregate sorption capacities: insights from a multiscale investigation

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Iron-Organic Matter (Fe-OM) nanoaggregates produced by redox alternation in wetlands are a key factor in the control of metallic pollutants mobility. Their ability to adsorb metal(loid)s depends on the size, morphology and structural arrangement between Fe and OM phases, which is mainly controlled by the OM occurrence. The physical, chemical and morphological organization of the nanoaggregates is influenced by the physico-chemical conditions prevailing in the environment that has to be explored to better understand and predict their reactivity towards pollutants. Calcium (Ca) is a common major ion in natural waters and exhibits high affinity for OM. Its impact on the size and structural organization of Fe-OM nanoaggregates could thus be major.

Mimetic natural Fe-OM nanoaggregates were synthesized at various Fe/OM and Ca/Fe ratios. Their surface reactivity was investigated by As sorption experiments. The global size of the aggregates was studied with A4F-UV-MALS-ICPMS and TEM observations. OM morphological organization was studied by SANS. The Fe phase was studied by SAXS and XAS at Fe K-edge. Ca interactions with Fe-OM nanoaggregates were investigated with XAS at Ca K-edge.

The morphological study of the nanoaggregates showed a size rise of both Fe and OM compounds with the increasing Ca/Fe ratios. By contrast, the Fe(III) nanooxide specific area decreased with the increasing Ca/Fe ratio, suggesting a subsequent decrease of their sorption capacities. However, surprisingly sorption experiments demonstrated the opposite. We evidenced that Ca was not bound to Fe but, to OM as an outersphere complex, allowing the formation of an extended OM molecules network. Iron phases are thus less recovered by OM molecules leading to an increase of the Fe nanooxides binding sites availability.