

EGU2020-8131

<https://doi.org/10.5194/egusphere-egu2020-8131>

EGU General Assembly 2020

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The dramatic variability of cations impacts on Fe speciation in Fe-OM nanoaggregates

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Natural colloids composed of iron (Fe) and organic matter (OM) are a key factor controlling metallic pollutants mobility according to their high adsorption capacities, consequence of their high binding sites density. The physico-chemical condition in which the Fe-OM nanoaggregates are formed influences their structural organization, and more specifically the Fe speciation. In this study, we probe the influence of three major cations, present in high quantity in natural systems: Calcium (Ca), Aluminum (Al) and Silicon (Si). Ca is known to have a huge affinity toward OM, as well as Al which also easily get into Fe hydroxides structure. For its part, Si is known to restrain Fe oxides growth and crystallinity, despite mechanisms remain unknown. Ca, Al and Si are thus expected to modify Fe-OM nanoaggregates organization and impact Fe speciation.

Mimetic environmental Fe-OM-cation nanoaggregates were synthesized with different Fe/OM and cation/Fe ratios. They were observed by TEM. The Fe speciation was characterized by XAS as well as the cations interactions with the components of the Fe-OM colloids. The size and arrangement of Fe-nanoparticles were determined by SAXS. Results show that Fe speciation is complex and variable according to Fe and cation contents relative to OM. Fe phases appear to be composed of oligomers and ferrihydrite nanoparticles, both embedded in the OM matrix. The Fe-nanoparticles are forming a fractal network which organization is controlled by the OM. When the Fe/OM ratio increases, oligomers content decreases to the benefit of Fe-nanoparticles which size increases. Adding cations, this phenomenon is strongly modified, either increased, with the addition of Ca and Al, or decreased, with the addition of Si. These modifications result from the different interactions we could evidence between the cations and the different Fe-OM network components.

These results clearly highlight the dramatic effect of Al, Si and Ca cations on the Fe-OM colloidal network, impacting both Fe speciation and OM organization. These structural modifications directly impact the capabilities of Fe-OM nanoaggregates to trap and transport pollutants.