# When iron and silver nanoparticles meet natural organic matter: Probing NP-NOM interactions with molecular spectroscopy and quartz crystal microgravimetry

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As natural organic matter (NOM) is ubiquitous in natural waters and known to complex with nanoparticle (NP) surfaces, it is important to study NP-NOM dynamics to better understand the fate and transport of NPs. This work combines molecular spectroscopy and quartz crystal microgravimetry (QCM) to determine the mechanisms and kinetics of NOM interaction with the surfaces of NP and silica. Hematite NPs (FeNPs) and silver NPs (AgNPs) were used to represent natural and engineered NPs in this study.

The identity and affinity of NOM on NP surfaces can affect the way NPs behave in aquatic systems. $^1$H NMR and Raman spectroscopy were used to identify the reactive organic functional groups in Suwanee River NOM and probe the mechanism of covalent and non-covalent bonding. FeNPs was observed to expedite the spin-lattice relaxation time ($T_1$) of aromatic and heteroatom-substituted aliphatic groups, which suggests a decrease in molecular motion (intra- and inter-molecular) upon interaction with the NPs. Raman spectroscopy was used to probe the interatctions of NOM with AgNPs having a polyvinyl pyrrolidone (PVP) capping agent. Raman spectroscopy suggested that O-substituted alkyl groups in the NOM interacts with both the polyvinyl domain of (PVP) and the oxygen atom of the PVP-capped AgNPs. These spectroscopy results have important implications for the fate of NPs in aqueous suspensions, as NOM may change the stability of NPs.

While NP's interactions with "free" NOM in the bulk solution is critical in predicting their mobility, NP's associations with "immobilized" NOM on mineral or other environmental surfaces are equally important in controlling their transport in natural waters. With high sensitivity (ng/cm$^2$) to quantify mass deposition on substrate surfaces, QCM was used as a tool in determining the extent and kinetics of NP adsorption in real-time. Preliminary QCM experiments revealed observable differences in the adsorption dynamics of FeNPs and AgNPs on silica substrate when NOM is coated on either the particle surface or substrate surface or both. For example, at pH 6, deposition of FeNPs on silica substrate was found to be at least two order of magnitude slower in the presence of NOM. QCM results also suggested that humic and fulvic fractions of the NOM exert differing degrees of influence on the adsorption of AgNPs.

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# Mobility of antimony in soils under changing redox conditions

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Human activities have led to highly elevated antimony (Sb) concentrations in many soils and, consequently, to increased exposure of biota to this toxic element. Knowledge about the risks of Sb leaching from such soils is, however, very limited.

A key factor regarding the mobility of Sb in soils is the water regime. Many soils are subject to permanent or periodic water-logging. Under aerobic conditions, Sb is stable as the pentavalent $Sb(OH)_6^-$ in soil solution. Under reducing conditions, the trivalent $Sb(OH)_3$ becomes dominant [1]. Both species strongly differ in their affinity to iron (Fe) and manganese (Mn) (hydr)oxides. The interplay of Sb redox transformations, differential sorption and reductive dissolution of Mn and Fe (hydr)oxides during water-logging and its effect on Sb mobility has received little attention though.

Here, we investigated changes in Sb speciation and solubility over a reduction-reoxidation period in Sb-contaminated shooting range soil (pH 7.8). Lactate was used as carbon source to stimulate microbial activity. Antimony(V) concentrations strongly decreased with the development of reducing conditions (Figure 1), while dissolved Sb(III) concentrations remained low. During further reduction, soluble Sb(III) increased together with dissolved Fe(II) concentrations. Reoxidation of the soil batches caused Sb(III) to decrease and soluble Sb(V) to increase again.

The results indicate that water logging conditions at first led to the immobilization of Sb by reduction of Sb(V) to Sb(III), since the latter has a higher binding affinity to metal hydroxides. When reducing conditions continued, the previously bound Sb(III) was released into the solution again due to reductive dissolution of the (hydr)oxides, resulting in increased mobility.

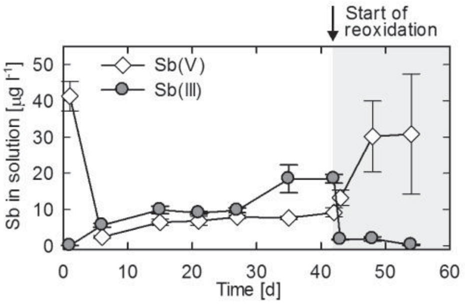

**Figure 1**: Antimony(III) and Sb(V) concentrations during varying redox conditions. Error bars are the standard deviation of triplicates.

[1] Filella, Belzile & Chen (2002) *Earth-Sci. Rev.* **57**, 125 - 176.