Mercury methylation, pore water geochemistry and legacy mercury contamination along the floodplain of the Connecticut River

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Mercury has long been stored in the fine-grained sediment along the various tributaries, ponds, lakes, and coves connected to the Connecticut River. Concentrations rose above background (<80 ppb) by the dawn of the Industrial Revolution and have, for the most part, mirrored the rise and fall of atmospheric mercury concentrations[1]. Total mercury concentrations in the sediment peak upstream in the Oxbow at approximately 500 ppb and near the mouth of the river, in Hamburg Cove, increase to nearly 3000 ppb. This sixfold rise is further exacerbated by the changing sedimentation rate from a low at the Oxbow (~1.5 cm/yr) to extremely high values for Hamburg Cove (~4.1 cm/yr)[1]. The rise in sedimentation rates towards the Long Island Sound are due to the influence of tidal pumping, allowing significant quantities of sediment fines to accumulate in these depocenters. In comparing mass accumulation rates (as $\mu g/m^2/yr$), Hamburg Cove accumulates mercury at nearly an order of magnitude greater than at the upriver Oxbow. In both locations, organic content ranges from 4 to 14%, but does not correlate well with mercury concentrations ($R^2 = 0.2664$). Although mercury readily adsorbs onto organic matter, the peaks in mercury concentration are more correlative with atmospheric loading and local mercury inputs than simply TOC. Methylmercury concentrations are also quite distinct in each location, with Hamburg containing over 1.5 ppb in its uppermost sediments while Oxbow concentrations never rise above 0.5 ppb. Variations in MeHg concentrations do not, however, correspond to those of total inorganic mercury, but instead suggest that SO_4 in pore water and the actions of SRB are needed to methylate the stored inorganic mercury. qPCR results also indicate the presence of sulfate reducers in these environments, just below the sediment interface. For Hamburg Cove this suggests that significant introduction of the bioavailable form of mercury is controlled by the occasional influx of salt water (with its high SO_4 concentration). With sealevel rise, it is likely that the magnitude of re-introduction of legacy mercury will increase and will eventually effect other floodplain waterbodies further up the Connecticut River Channel.

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Computational study of the most stable pyrophyllite edge surfaces for metal adsorption

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Abstract

Metal adsorption on mineral surfaces is a topic extensively pursued by researchers to improve the understanding of the environmental fate of metals, and provide natural low-cost adsorbents for remediation as this is an active mechanism in controlling the fate of metal ions in natural waters. Despite the wealth of available information focused mostly with basal surfaces, because edge surfaces are difficult to model, few studies were devoted to edge surfaces of clays.[1-3]

Pyrophyllite was chosen as a model because it is a non expanding phyllosilicate with neutral layers that do not require encapsulation of couter-ions, making it the best candidate for calculations that intend to discern such an important and complex problem.

The work presented herein follows on from experimental work done in our group,[4] and aims at interplaying with such results *via* the investigation of the metal adsorption mechanisms at the edge surface sites of pyrophyllite. Having been started with a non biased and systematic approach using atomistic simulation techniques, initially, the static simulation code METADISE[5] was used to cleave and hydroxylate low Miller index surfaces, and explore their structure and stability. Subsequent to ranking the cuts, classical modeling of the hydrated clay-edge surfaces showed that from the large set of Miller index planes cut, the (110), (-110), (010), and (100) surfaces are the most stable leading to a pseudo-hexagonal crystal shape generated with the first three surface planes, as documented for phyllosilicates. These edge surfaces were further optimised using DFT within the VASP code,[6] to calculate the energy of the diferent hydroxylated ensembles in oder to ascertain the most stable and hence the most likely for metal surface complex formation.

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