

## Prediction of iodine ( $I^-$ and $IO_3^-$ ) adsorption and surface speciation on oxides by surface complexation modeling

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Aqueous iodine species occur mainly as iodide ( $I^-$ ) and iodate ( $IO_3^-$ ), depending on the redox conditions. The adsorption of  $I^-$  and  $IO_3^-$  on naturally occurring oxides is of environmental concern. The adsorption behaviors of  $I^-$  and  $IO_3^-$  by iron and aluminum oxides were examined as a function of pH, ionic strength and solid concentration. The adsorption data were analyzed by means of an extended triple-layer model (ETLM) for surface complexation modeling to obtain the  $I^-$  and  $IO_3^-$  adsorption reactions and these equilibrium constants.

The adsorption of  $I^-$  was determined to be an outer-sphere process from ETLM analysis, which was consistent with independent X-ray absorption near edge structure (XANES) observation of  $I^-$  adsorbed on hydrous ferric oxide (HFO). The adsorption of  $IO_3^-$  was determined to be both an outer- and an inner-sphere process. The predicted model speciation of  $IO_3^-$  on oxides showed that the inner-sphere species increase with increasing ionic strength and solid concentration while outer-sphere species distribute on wide range of pH conditions under low ionic strength. Additionally, the outer-sphere species are dominant for  $\gamma$ - $Al_2O_3$ , whereas the inner-sphere species are dominant for HFO and goethite.

Comparison of adsorption equilibrium constants for iron and aluminum oxides based on site-occupancy standard states permitted prediction of  $I^-$  and  $IO_3^-$  adsorption equilibrium constants for all oxides by means of the Born solvation theory. The batch adsorption data from previous reports for  $I^-$  and  $IO_3^-$  on oxides were reasonably reproduced by ETLM with the predicted equilibrium constants, confirming the validity of the present approach.

## Interaction of Cu and Cd with organic matter and biogenic sulfide in periodically flooded soils

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The bioavailability and mobility of metal contaminants in periodically flooded soils such as freshwater floodplain soils or paddy soils may be of major concern with respect to ecosystem health, groundwater protection and food production. Reliable quantification of respective risks requires a sound mechanistic understanding of the processes controlling metal solubility at such sites, with special consideration of their periodic flooding and associated changes in soil redox-state and metal speciation.

Based on our earlier observation that chalcophile metals may compete for biogenic sulfide in periodically flooded sulfate-limited soils [1], we performed laboratory incubation experiments with a soil adjusted to variable levels of Cu (2 and 5 mmol/kg), Cd (0.2 mmol/kg) and sulfate (sulfate balanced, limited and excess). X-ray absorption spectra of soil samples after different incubation times showed that Cd and Cu became increasingly S-coordinated during sulfate reduction. The sequestration of Cd into CdS was slightly enhanced in the presence of excess sulfate and slightly delayed under sulfate-limitation, confirming that competitive metal sulfide formation under sulfate-limitation affected metal dynamics. However, the observation that 45-60% of the Cu became S-coordinated prior to sulfate-reduction pointed to metal complexation by organic thiol-groups as another possible sequestration mechanism. 35-40% of Cd was found to be partially thiol-bound even in the oxic soil prior to flooding. Metal complexation with thiol-groups of soil organic matter (SOM) has previously been reported for Cd [2], but not for Cu. We assume that the fast reduction of the borderline cation Cu (II) to the chalcophile Cu (I) prior to sulfate-reduction induces a shift in organic Cu-complexation from carboxyl- and/or amine- to thiol-groups. Our results suggest that complexation of chalcophile metals with thiol-groups in SOM may interfere with their competition for biogenic sulfide in sulfate-limited soils. Further studies are required to quantify Cu (I)-thiol complexation by soil organic matter and its importance in periodically flooded soils.

[1] Weber *et al.* (2009) *GCA*, **73**, 5513–5527 [2] Karlsson *et al.* (2005) *ES&T* **39**, 3048–3055