Prediction of iodine adsorption on oxides by surface complexation modeling with spectroscopic confirmation

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A deficiency in environmental iodine can cause a number of health problems. Understanding how iodine is sequestered by materials is helpful for evaluating and developing methods for minimizing human health effects related to iodine. In addition, ^{129}I is considered to be of strategically important for safety assessment of underground radioactive waste disposal. To assess the long-term stability of disposed radioactive waste, an understanding of ^{129}I adsorption on geologic materials is essential. Therefore, the adsorption of iodine (I^- and IO_3^-) on naturally occurring oxides is of environmental concern.

The surface charges of hydrous ferric oxide (HFO) in NaI electrolyte solutions were measured by potentiometric acid-base titration. The surface charge data were analyzed by means of an extended triple-layer model (ETLM) [1] for surface complexation modeling to obtain the I^- adsorption reaction and its equilibrium constant. 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 HFO. The adsorption equilibrium constants for I^- on β-TiO_2 and γ-Al_2O_3 were also evaluated by analyzing the surface charge data of these oxides in NaI solution as reported in the literature [2, 3]. Comparison of these adsorption equilibrium constants for HFO, β-TiO_2 and γ-Al_2O_3 based on site-occupancy standard states permitted prediction of I^- adsorption equilibrium constants for all oxides by means of the Born solvation theory. The batch adsorption data for I^- on HFO and amorphous aluminum oxide reported in the literature [4] were reasonably reproduced by ETLM with the predicted equilibrium constants, confirming the validity of the present approach. Using the predicted adsorption equilibrium constants, we calculated distribution coefficient (K_d) values for I^- adsorption on common soil minerals as a function of pH and ionic strength.

[1] Sverjensky (2005) *GCA* **69**, 225-257. [2] Sprycha (1984) *JCIS* **102**, 173-185. [3] Sprycha (1989) *JCIS* **127**, 12-25. [4] Whitehead (1974) *J. Sci. Food. Agric* **25**, 73-79.

Mercury(II)-sulfur binding in peat

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The bioavailability of mercury in aqueous systems depends on mercury(II) speciation which is influenced by natural organic matter (OM). Strong bonds between mercury(II) and reduced sulfur atoms are most important, but difficult to characterize because of the macromolecular nature of OM and the typically low concentrations of mercury(II). We report four binding environments, two of which are new, obtained using Extended X-ray Absorption Fine Structure spectroscopy performed at liquid He temperature on peats from the Florida Everglades with added mercury(II). The peats adsorbed Hg^{2+} at concentrations between 60 and 99,000 ppm from pH 6 $Hg(NO_3)_2$ solutions open to the atmosphere and exposed to light. One new environment appeared at 60 and 350 ppm as multinuclear clusters in which approximately each of four mercury atoms was bonded to two sulfurs at 2.34 Å and one at 2.54 Å, and mercury atoms in the tetramers were separated by 4.1 Å. The cluster structure is similar to those of metallothioneins, and does not match those of cinnabar or metacinnabar. Reduced sulfur, characterized using ambient X-ray Absorption Near Edge Structure spectroscopy, continued to be a dominant ligand at 4000 ppm, forming linear mercury(II)-disulfide bonds of length 2.34 Å. A three-part mixture of the linear units, five-membered chelate rings with oxygen/nitrogen, carbon, and sulfur, and five-membered rings without sulfur formed at 19,000 ppm. The first chelate ring with oxygen/nitrogen at 2.08 Å, sulfur at 2.40 Å, and a high number of carbon atoms at and just beyond 3 Å suggests an aromatic component. At 99,000 ppm, only the chelates could be discerned with at most 15% containing sulfur. The results provide new evidence for a continuum description of Hg(II)-complexation with natural organic matter.