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Adsorption of cadmium to iron and manganese oxides during estuarine mixing

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Abstract

The adsorption of Cd to aged hydrous oxides (FeOOH and MnO_2) and to fractionated (<63 μm) sediment has been studied along an estuarine gradient created by mixing filtered river and marine end-members from the Beaulieu, southern England. In all cases, adsorption decreased logarithmically with increasing salinity but, for a given salinity, the conditional particle–water distribution coefficient, K_D, was two orders of magnitude greater on the Mn oxide than either the Fe oxide or fractionated sediment. The reversibility of Cd adsorption, evaluated by extraction of particles in NH_4OAc, decreased in the order: FeOOH > sediment ≫ MnO_2. The aqueous equilibrium speciation of Cd along the estuarine gradient was computed by WHAM 6, with organic complexation modelled using either the default settings for fulvic substances or measurements of the hydrophobic (C_{18}-retained) fraction of Cd. Free ion concentrations predicted from the latter approach correlated well with conditional distribution coefficients for each particulate phase, and slopes of the relationships yielded estimates of distribution coefficients normalised with respect to the free ion activity, K_D', of about 7×10^4, 4×10^4 and 5×10^6 mL g^{-1} for sediment, FeOOH and MnO_2, respectively. The results and model fits suggest that (i) Mn oxides exert an impact on the retention, mobilisation and availability of Cd in estuaries that is disproportional to their abundance, and (ii) the degree of organic complexation of Cd in estuaries may be overestimated using published, generic binding constants.

Keywords: Cadmium; Estuary; Iron oxide; Manganese oxide; Speciation; Complexation

1. Introduction

Cadmium is a highly toxic metal whose environmental behaviour has received considerable attention (Steinnes, 1989; Flyhammer, 1995; Porter et al., 2004). The geochemical behaviour of Cd in the estuarine mixing zone is reasonably well understood and results of various laboratory and field studies paint a broadly consistent picture. This, in part, is a reflection of the rather distinctive aqueous speciation of Cd. Thus, compared with many other trace metals, Cd has a low affinity for organic ligands but a high affinity for the chloride ion (Bilinski et al., 1991; Tipping et al., 1998). Consequently, organic complexes appear to be restricted to the low salinity reaches of many estuaries, and increasing salinity is accompanied by an increasing proportion of various chlorocomplexes and a concomitant reduction in the activity of the free ion (Paalman et al., 1994; Thouvenin et al., 1997; Lemaire et al.,

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2006). Since adsorption of Cd to suspended particles is largely limited to the free ion, distribution coefficients also undergo a reduction in magnitude across the freshwater–sea water interface (Turner, 1996) and, given that adsorption is partly reversible, salinity-induced desorption or mobilisation of the metal is generally observed *in situ* (Comans and van Dijk, 1988; Garnier and Guieu, 2003; Waeles et al., 2004).

Aside the activity of the free ion, the extent of Cd adsorption and mobilisation in estuaries will be dependent on the nature of the suspended particles. Several studies have focused on the interactions between Cd and calcite in estuaries, partly because of the importance of this mineral in the marine environment and the distribution of Cd in biogenic carbonates (Kozar et al., 1992; van der Weijden et al., 1994). Given their ubiquity and reactivity in the estuarine environment, however, it is perhaps surprising that equivalent studies have not been conducted with respect to hydrous oxides of Fe and Mn. The potential significance of these oxides was recently demonstrated, albeit indirectly and in combination, by comparing Cd sorption to untreated and chemically reduced estuarine particles along a salinity gradient (Turner et al., 2004a). In an earlier investigation of Cd adsorption to estuarine particles whose Mn oxides and Fe oxides had been selectively and sequentially removed, it was shown that the former were more significant than the latter, despite being considerably lower in abundance (Lead et al., 1998). This observation is consistent with the relatively high specific surface area and low pH of zero point charge of Mn oxides (Catts and Langmuir, 1986), and concurs with a variety of independent measures of Cd adsorption conducted in different types of environments (e.g. Oakley et al., 1981; Balistrieri and Murray, 1986; Ferreira et al., 1998; Dong et al., 2003; Covelo et al., 2007).

In order to evaluate, more directly, the relative significance of hydrous Fe and Mn oxides to particle–water interactions of Cd in estuaries, we investigate its adsorption to natural particles and to an aged Fe oxide and Mn oxide (FeOOH and MnO_2, respectively) added to an estuarine gradient created by the mixing of natural, filtered end-member waters. For a more mechanistic interpretation of the results, we also perform equilibrium speciation calculations for aqueous Cd along the estuarine gradient. The principal hypothesis is that hydrous oxides of Mn are able to exert an impact on the behaviour and fluxes of Cd in estuaries, both in the water column and, presumably, at the sediment–water interface, that is considerably greater than their abundance would imply.

2. Methods

2.1. Preparation and characteristics of the oxides

The aged oxides used in this study were selected to represent characteristics of sedimentary oxides that are either advected or resuspended into the estuarine water column, and were prepared by established techniques outlined below. All reagents used for the preparation of the oxides were of BDH/Merck AnalaR or Aristar grade, and were made up in ultra-pure Milli-Q water.

Preparation of the Fe oxide involved the accelerated aging of ferrihydrite. The latter was precipitated by agitating 5 mL of 1M $Fe(NO_3)_3$ with 18 mL of 2.5 M NaOH (Balistrieri and Murray, 1982) and, after washing and dilution to 100 mL, was aged by heating at 70 °C for 60 h in a stoppered bottle. The resulting solid was divided into sterilised 20 mL centrifuge tubes, and the contents of each tube were washed and centrifuged (20 min at 3000 rpm) ten times before being stored at 4 °C in the dark as 20 g L^{-1} suspensions. The oxide had characteristics typical of goethite (α-FeOOH); namely, a specific surface area (SSA, by BET nitrogen adsorption) of 18.0 m^2 g^{-1}, and component crystals (characterised by scanning electron microscopy; SEM) with dimensions of about 1 to 2.5 μm by 0.1 to 0.4 μm arranged in a “star-like” fashion (Nowack and Sigg, 1996).

The manganese oxide was prepared according to the following reaction (Davies-Colley et al., 1984):

$$3Mn^{2+} + 2MnO_4^- + 4OH^- \rightarrow 5MnO_2 + 2H_2O$$

by adding 1.452 g of $KMnO_4$, 3.766 g of $Mn(NO_3)_2.2H_2O$ and 5.32 mL of 2.5 M NaOH to a polyethylene flask. The resulting precipitate was diluted to 100 mL and the suspension was divided in to 20 mL sterilised centrifuge tubes. The contents of the tubes were centrifuged and washed as above, and the resulting 17 g L^{-1} suspensions were aged at 4 °C in the dark for a month before being used in the adsorption experiments.

Manganese oxide prepared in this way is sometimes referred to as birnessite (Davies-Colley et al., 1984) but mixtures of different oxides are often reported (Stone and Morgan, 1984) with an overall non-integral stoichiometry. Specific forms of oxide were not distinguished by our crystallographic analysis (either before or after aging) and, for the purposes of this paper, the precipitate is referred to as Mn oxide or MnO_2. The freshly prepared oxide had an SSA of 73.0 m^2 g^{-1}, similar to that for MnO_2 reported by Balistrieri and Murray (1982), but this was reduced to 49.0 m^2 g^{-1} after aging. SEM analysis revealed aggregates of spherical particles, with diameters ranging from about 0.1 to 1 μm, in both the fresh and aged precipitates.

2.2. Sample collection and characterisation

Sediment and water samples used in the adsorption experiments were collected from a river-estuary draining low-lying, protected heathland and woodland (Beaulieu, southern England). Detailed hydrographic and geochemical