



Binding of Cd by ferrihydrite organo-mineral composites: Implications for Cd mobility and fate in natural and contaminated environments

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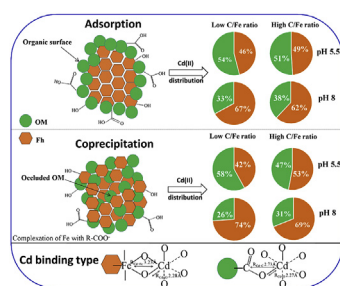
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HIGHLIGHTS

- First investigation of Cd sorption by adsorbed and coprecipitated Fe-OC composite.
- Cd sorption is independent of composite type but is a function of C content and pH.
- Inner-sphere Cd complexes are formed on the Fe-OC composite.

GRAPHICAL ABSTRACT



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ABSTRACT

Adsorption and coprecipitation of organic matter with iron (hydr)oxides can alter iron (hydr)oxide surface properties and their reactivity towards nutrient elements and heavy metals. Organo-mineral composites were synthesized using humic acid (HA) and iron oxide, during coprecipitation with ferrihydrite (Fh) and adsorption to pre-formed Fh with two C loadings. The Fh–HA coprecipitated composites have a higher C content and smaller surface area compared to the equivalent adsorbed composites. NanoSIMS shows there is a high degree of spatial correlation between Fe and C for both composites, but C distribution is more uniform in the coprecipitated composites. The C 1s NEXAFS reveals a similar C composition between the Fh–HA coprecipitated and adsorbed composites. However composites at high carbon loading are more enriched in aromatic C, likely due to preferential binding of carboxyl functional groups on aromatic rings in the HA. The amount of Cd sorbed is independent of the composite type, either coprecipitated or adsorbed, but is a function of the C loading. Composites with low C loading show Cd sorption that is almost identical to pure Fh, while composites with high C loading show Cd sorption that is intermediate between pure Fh and pure HA, with sorption significantly enhanced over pure Fh at pH < 6.5. A bidentate edge-sharing binding was identified for Cd on pure Fh and Cd-carboxyl binding on

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pure HA. These findings have significant implications not only for the sequestration of Cd in contaminated environments but also the coupled biogeochemical cycling of Cd, Fe and C in the critical zone.

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1. Introduction

The geochemical cycles of iron and organic carbon (OC) are closely linked in soils and sediments. In soils iron (hydr)oxides are found coprecipitated with and coated in sorbed OC (Mikutta et al., 2014), while in marine sediments recent work estimates that ~21% of the total OC present in sediments is intimately associated with reactive iron phases (Lalonde et al., 2012). Iron–organic association may protect OC against degradation and thus promote its preservation (Mikutta et al., 2007), but the intimate association of OC with iron (hydr)oxides can also affect the crystal structure, surface properties, reductive dissolution and transformation of the iron (hydr)oxides (Schwertmann et al., 2005; Shimizu et al., 2013). It is well known that pure iron (hydr)oxides are extremely efficient sorbents of nutrients and heavy metals due to their large surface areas and abundant reactive functional groups (Schultz et al., 1987), but because of their association with OC, iron (hydr)oxide–organic composites can have significantly different reactivity towards nutrients and contaminant metals compared to their pure iron (hydr)oxide counterparts (Chen et al., 2009; Moon and Peacock, 2012, 2013; Ding et al., 2015; Wang et al., 2016a). Understanding the sorption of nutrients and heavy metals with iron (hydr)oxide–organic composites is important because in natural and contaminated environments iron (hydr)oxides are typically found coprecipitated with and coated in sorbed OC (Schwertmann et al., 2005; Shimizu et al., 2013; Mikutta et al., 2014), and elemental sequestration by these iron–OC composites is a key process in the biogeochemical cycling of trace elements in the critical zone.

Ferrihydrite (Fh) is a poorly crystalline iron (hydr)oxide that is ubiquitous in geologic systems (Michel et al., 2007), occurring as the precursor to other stabilized ferric oxides such as haematite and goethite. Ferrihydrite plays a substantial role in the sequestration of trace elements in its pure and Fh–organic composite forms. Earlier reports show that 2-line Fh can sorb up to 500, 366, 250 and 62.5 mg/g Zn^{2+} , Pb^{2+} , Cd^{2+} and Cu^{2+} from aqueous solution, respectively (Rout et al., 2012). Spectroscopy evidence and modelling results indicate that trace metals such as Cu and Pb are bound to the Fh surface via inner-sphere sorption complexes (Scheinost et al., 2001; Dyer et al., 2003; Trivedi et al., 2003; Tiberg et al., 2012). Ferrihydrite–organic composites are also potent scavengers of trace metals, and often show enhanced sorption capacities compared to the isolated pure mineral end-member. For example, when Fh is coprecipitated with abiotic organic components such as fulvic acid (14.7 wt% C), the maximum sorption capacity for Pb^{2+} is 62.7% higher (at 19.26 mg/g) and there is a higher Pb binding affinity, compared to the pure Fh (Wei and Xiang, 2013). Similarly, when Fh is adsorbed with a simple organic ligand such as phthalate, the sorption of Cd is increased at pH 4–7 due to the formation of a surface ternary complex (Song et al., 2009). In particular however, Fh–organic composites often show enhanced sorption of metals in the mid-low pH regime compared to their pure Fh counterpart (Moon and Peacock, 2012, 2013). Work to date attributes this phenomenon to the presence of additional binding sites associated with the organic fraction and/or new high-affinity sites created when the organics adsorb to the (hydr)oxide surfaces (Ali and Dzombak, 1996; Alcacio et al., 2001; Christl and Kretzschmar, 2001). For example, for Fh coprecipitated with

biotic organic matter (OM) in the form of bacterial cells, Moon and Peacock (2012) show that Cu sorption is enhanced in the mid-low pH regime (~pH 4–5.5) compared to pure Fh, because Cu sorbs onto the bacterial fraction of the composites in addition to the mineral fraction. Furthermore, the intimate association of *Bacillus subtilis* with Fh fundamentally changes the Fh and OM physicochemical properties, compared to the isolated pure counterparts, resulting in so-called ‘non-additive’ sorption behaviour, where the sum of the sorptivities on the pure end-member Fh and OM does not equal the sorptivity on the Fh–OM composite. Specifically this non-additive behaviour is attributed to a surface charge effect, where in the mid-low pH regime the negative charge of the OM is reduced in the presence of the positive charge Fh, such that Cu sorption to the OM fraction of the composite is less than would be predicted according to additivity (Moon and Peacock, 2013). This non-additivity feature is also found in Cd^{2+} –ferrihydrite–*Comamonas* spp (Song et al., 2009), Pb^{2+} –ferrihydrite–*Bacillus subtilis* (Kulczycki et al., 2005), Sr^{2+} –ferrihydrite–*Shewanella alga* (Small et al., 1999) and Cu^{2+} –ferrihydrite–*Anoxybacillus flavithermus* (Franzblau et al., 2016) systems. Moreover, additivity metal sorption behaviour is also found in Cd^{2+} –kaolinite–*Bacillus subtilis* (Alessi and Fein, 2010) and Cd^{2+} –montmorillonite–*Pseudomonas putida* (Du et al., 2016b) systems. Overall the intimate association of Fh with OM, and the resulting changes in the Fh–OM composite physicochemistry mean that it is difficult to predict metal sorption onto Fh–OM composites in natural and contaminated environments (Moon and Peacock, 2013).

Work to date shows that careful investigation of metal sorption to Fh–OM composites is essential to understand and predict both nutrient trace-metal cycling and heavy-metal contamination in soils and sediments. Interaction of OM with iron (hydr)oxides can occur via coprecipitation, where iron (hydr)oxide is precipitated in the presence of OM, or via sorption of OM onto the iron (hydr)oxide surface (Kleber et al., 2015). The physicochemical properties of these two different kinds of iron–OM composites have received increasing attention recently (Eusterhues et al., 2011; Chen et al., 2014; Mikutta et al., 2014), however, their environmental reactivity and especially their sorption behaviour towards trace elements, still remains poorly understood. Cadmium occurs naturally in the Earth's crust, and therefore is found in virtually all components of terrestrial and marine ecosystems. Cadmium accumulation in drinking water and food (e.g., *Oryza sativa* L.) poses severe human health issues (Järup and Akesson, 2009). For example, Cd is emerging as the most serious metal pollutant in China, where around 7% of total soil exceeds the environmental standard limit (Du et al., 2016a).

In this work we investigate Cd sorption on two different kinds of Fh–OM composites, namely those formed via coprecipitation with OM versus adsorption of OM onto preformed Fh surfaces. Humic acid (HA) was chosen as a model organic fraction to represent OM found in soils and sediments. For each composite type, coprecipitated or adsorbed, we synthesise two different composites, one with low C loading (~5 wt% C; ~0.5 C/Fe molar ratio) and another with high C loading (~15 wt% C; ~2 C/Fe molar ratio). We characterise the Fh–HA composites in terms of C content, specific surface area (SSA), mineralogy and crystallinity, organic C composition and

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