



Functional effects of manganese and iron oxides on the dynamics of trace elements in soils with a special focus on arsenic and cadmium: A review



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ABSTRACT

The dynamics and availability of arsenic (As), cadmium (Cd), and other trace elements in soils are of great concern to soil scientists. Owing to the human toxicity of As and Cd, the Codex Alimentarius Commission set maximum permissible concentrations of these elements in foodstuffs, including rice which is a major source of human intake of As and Cd, especially in Asia. Therefore, attenuation of As and Cd concentrations in crops, especially rice, is important for both human health and agroindustry.

Manganese (Mn) and iron (Fe) oxides have great capacity to sorb trace elements. Adsorption of cationic elements increases with increasing pH, whereas adsorption of arsenate [As(V)] shows the opposite trend. Adsorption of cationic elements by Mn oxides is generally much greater than adsorption by Fe oxides, whereas Fe oxides have a much higher adsorption capacity for As than Mn oxides do. Trace elements can co-precipitate with Mn/Fe oxides and are subsequently released from or incorporated into solid phases with aging depending on the natures of elements and on the surrounding conditions. Moreover, Mn/Fe oxides, especially Mn oxides, oxidize arsenite [As(III)] to As(V), which is less soluble. Sorbed elements solubilize under reducing conditions through reductive dissolution of Mn/Fe oxides. In addition to the transformation of As from As(V) to As(III), the release of As from Fe oxides is responsible for the increase in dissolved As concentration that accompanies flooding. In contrast, Cd precipitates as barely soluble sulfides under strong reducing conditions. This difference may explain why the concentrations of As and Cd in rice grown with different water management show opposite trends. Iron plaque, an Fe oxide precipitate that forms on rice roots, may attenuate As concentrations in rice tissues by fixing and sequestering As, although some studies have questioned this possibility.

There have been many attempts to use Mn/Fe oxides (or materials containing them) to attenuate the soil solubility of trace elements and/or reduce their uptake by crops. Application of Mn/Fe oxides has useful effects in most cases; in particular, application of Fe oxides or Fe oxide-containing materials immobilizes As in soils. Therefore, application of Mn/Fe oxides combined with flooded cultivation may attenuate the concentrations of both As and Cd in rice. However, additional studies are required because only a few studies have focused on the effects of application of Mn/Fe oxides on As mobility in anaerobic soils and consequent uptake by rice plants.

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1. Introduction

The dynamics of trace elements, especially arsenic (As) and cadmium (Cd), are of great concern owing to their toxicity to organisms. Long-term exposure to As can cause skin lesions, skin cancer, and various internal cancers (Smith et al., 1992; Tondel et al., 1999). Cadmium, which is well-known to cause Itai-Itai disease, can induce kidney failure and cancer (Huff et al., 2007). People for whom rice is a dietary staple obtain a substantial proportion of their total uptake of As and Cd through rice consumption. For example, Japanese people obtain 6.3% of their total As (MAFF, 2014), 60% of their inorganic As (Oguri et al., 2014), and about one-half of their Cd (MAFF, 2007) from rice. The Codex Alimentarius Commission has set maximum permissible

concentrations of As and Cd in various foodstuffs, including polished rice (0.2 mg kg^{-1} as inorganic As for As; 0.4 mg kg^{-1} for Cd). Therefore, reduction of As and Cd concentrations in crops, especially in rice, is important for both human health and agroindustry.

Manganese (Mn) and iron (Fe) are relatively abundant in soils. They exist predominantly as oxides, hydroxides, and oxyhydroxides (referred to hereafter as oxides) in aerobic environments, and these oxides sorb trace elements at high concentrations (Hall et al., 1996a; Tessier et al., 1979). The sorbed elements can be solubilized by reductive dissolution of the Mn/Fe oxides (Hindersmann and Mansfeldt, 2014). Mn and Fe have multiple redox states and can therefore function as both electron donors and electron acceptors in soils. Mn/Fe oxides oxidize arsenite, As(III), to arsenate, As(V), which is less toxic than As(III) (Amstaetter et al., 2010; Scott and Morgan, 1995). This fact suggests that Mn/Fe oxides affect the dynamics of trace elements in soils, especially paddy soils, which undergo drastic changes in redox conditions.

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Here we review (1) the effects of Mn/Fe oxides on the dynamics of As, Cd, and other trace elements in soils, (2) methods for extraction of trace elements occluded in Mn/Fe oxides in soils, and (3) attempts to use Mn/Fe oxides to immobilize trace elements in soils and to attenuate uptake of these trace elements by crops.

2. Occurrence of Mn/Fe oxides in soils

Table 1 shows some examples of Mn/Fe oxides present in soils. Manganese oxides in soils often reported to be amorphous form (e.g. Childs, 1975), but various crystalline forms were identified. Birnessite and vernadite are by far the most common Mn oxides, although lithiophorite is also common in Australian soils (McKenzie, 1989). Fe oxides such as ferrihydrite, goethite, hematite, and lithogenic magnetite occur in many soils (Schwertmann and Taylor, 1989). Although ferrihydrite has been referred to as “amorphous Fe hydroxide”, it has short-range-ordered structure and is not a true hydroxide (Schwertmann and Taylor, 1989). Both abiotic and biotic oxidations contribute to the formation of Mn/Fe oxides (Fortin and Langley, 2005; Tebo et al., 2004). Localization of Mn/Fe oxides frequently results in Mn/Fe-rich structures in soil profiles. The roots of rice plants and other aquatic plants are commonly coated with an Fe oxide precipitate referred to as Fe plaque (Chen et al., 1980; Otte et al., 1989). Mn/Fe nodules or mottles often exist in soils, especially in soils with imperfect drainage (Szymański et al., 2014), and are believed to result from migration of Mn(II) and Fe(II) within the soil profile and subsequent local re-oxidation and co-precipitation.

3. Reactions between trace elements and Mn/Fe oxides

3.1. Adsorption

Adsorption of arsenate, As(V), on Fe oxides decreases substantially with increasing pH, whereas adsorption of arsenite, As(III), slightly increases with increasing pH up to 8 to 9 and then begins to decrease (Dixit and Hering, 2003; Raven et al., 1998). Because As(V) species are more acidic ($pK_{a1} = 2.19$; $pK_{a2} = 6.94$) than As(III) species ($pK_a = 9.1$), the substantial decrease in As(V) adsorption with increasing pH is likely attributable to increased repulsion between negatively charged As(V) species and the negatively charged surface of Fe oxides. The repulsion between As(III) species and the Fe oxide surface

is weaker than that between As(V) species and the surface, and therefore increasing pH has less effect on adsorption of As(III). Bowell (1994) reported that at $pH < 7$, the amounts of four kinds of As adsorbed on goethite, hematite, and lepidocrocite decreased in the order As(V) > dimethylarsinic acid = monomethylarsonic acid > As(III), whereas at $pH > 7$, the order was As(V) > As(III) > monomethylarsonic acid = dimethylarsinic acid; and the affinities of the oxides for As decreased in the order goethite > lepidocrocite > hematite. Lafferty and Loepfert (2005) reported that goethite and ferrihydrite have high adsorption affinities for monomethylarsonic acid and As(V) from pH 3 to 10, whereas dimethylarsinic acid is not adsorbed by ferrihydrite at $pH > 8$ or by goethite at $pH > 7$. Arsenate adsorption on birnessite decreases with increasing pH, and the magnitude of adsorption is greater than that on phyllosilicates (Violante and Pigna, 2002). However, the amount of arsenate sorbed on birnessite is substantially less than that sorbed on goethite, allophane, and gibbsite. Considering the relatively small amount of Mn oxides in soil, they are unlikely to be as important for As(V) adsorption as Fe oxides.

In Table 2, cationic trace elements are listed in order according to the strength with which they bind to the surfaces of various Mn/Fe oxides. In most cases, Pb binds the most strongly, followed by Cu. In general, the order of the first hydrolysis constants of cationic ions and the solubility products of the metal hydroxides are useful indicators of binding strength (Kinniburgh et al., 1976). For example, Tan et al. (2005) showed that for divalent trace elements, the maximum amounts adsorbed by Fe–Mn nodules were $Pb \approx Cu > zinc (Zn) > cobalt (Co) > nickel (Ni) > Cd$, and this order completely corresponded to the order of the first hydrolysis constants of the elements. This fact indicates that Mn/Fe oxides have relatively lower affinity for Cd than for other trace elements. According to Backes et al. (1995), greater amounts of Cd and Co adsorb on Mn oxides (hausmannite and cryptomelane) than on Fe oxides (ferrihydrite and goethite). Among Mn oxides, the adsorption capacities for Cd, Co, Cu, Pb, and Zn decrease in the order birnessite \gg todorokite \approx cryptomelane > hausmannite (Feng et al., 2007). Retention of cationic trace elements by Mn/Fe oxides increases with increasing pH, and retention by Fe oxides increases rapidly with increasing pH in a narrow range (~ 2 pH units; Kinniburgh et al., 1976; McKenzie, 1980).

With time, adsorbed trace elements are gradually transformed into less desorbable forms, possibly by means of lattice penetration, recrystallization, and diffusion into pores (Ainsworth et al., 1994; Wang and Xing, 2002). Long aging and high temperature decrease Cd desorption from goethite (Mustafa et al., 2006). Ainsworth et al. (1994) reported that, unlike Cd and Co, adsorbed Pb on a hydrous ferric oxide (HFO) is completely reversible with time, at least for 16 weeks of aging, indicating that Pb is not incorporated into the solid phase. These investigators also showed a clear inverse correlation between ionic radius and rate of formation of the irreversibly adsorbed form, strongly indicating that ionic radius is closely related to ease of incorporation into the solid phase.

The adsorption of trace elements on Mn/Fe oxides is influenced by co-existing materials, which can compete for adsorption sites (Violante and Pigna, 2002; Waltham and Eick, 2002), change surface charge, and form ternary complexes (Swedlund et al., 2003; Zaman et al., 2009). For instance, Brechbühl et al. (2012) reported that carbonate species inhibit adsorption of As, especially As(III), on hematite, particularly at neutral to alkaline pH. Moreover, silicate ions block As adsorption by polymerizing on hematite surfaces, in addition to competing for adsorption sites (Christl et al., 2012). Grafe et al. (2001) reported that As(III) and As(V) adsorption on goethite is inhibited by co-existing humic, fulvic, and citric acids, whereas Cd adsorption on hematite is enhanced by humic acids but inhibited by ethylenediaminetetraacetate (Davis and Bhatnagar, 1995). Wang and Xing (2002) reported that pre-adsorption of phosphate ions on goethite shifts the Cd adsorption edge to lower pH (i.e., increases Cd adsorption at a given pH), by increasing surface negative charge and reducing electrostatic potential

Table 1
Examples of Mn and Fe oxides observed in soils.

Type	Mineral	Formula ^a	Reference	
Mn	Birnessite	Mn ₇ O ₁₃ ·5H ₂ O etc.	Arachchi et al. (2004); Manceau et al. (2005)	
	Hollandite	Ba ₂ Mn ₈ O ₁₆	Taylor et al. (1964)	
	Lithiophorite	(Al,Li)MnO ₂ (OH) ₂	Liu et al. (2002); Manceau et al. (2005); Taylor et al. (1964)	
	Manganite	γ-MnOOH	Szymański et al. (2014)	
	Pyrolusite	β-MnO ₂	Taylor et al. (1964)	
	Todorokite	(Na,Ca,K,Ba,Mn ²⁺) 2Mn ₄ O ₁₂ ·3H ₂ O	Szymański et al. (2014); Taylor et al. (1964)	
	Vernadite	δ-MnO ₂	Liu et al. (2002)	
	Fe	Ferrihydrite	Fe ₅ (O ₄ H ₃) ₃ etc.	Liu et al. (2002)
		Goethite	α-FeOOH	Arachchi et al. (2004); Liu et al. (2002); Manceau et al. (2005); Singh and Gilkes (1991)
		Hematite	α-Fe ₂ O ₃	Manceau et al. (2005); Ozcan and Ozaytekin (2011); Singh and Gilkes (1991)
Lepidocrocite		γ-FeOOH	Manceau et al. (2005)	
Maghemite		γ-Fe ₂ O ₃	Singh and Gilkes (1991)	
Magnetite		Fe ₃ O ₄	Ozcan and Ozaytekin (2011)	

^a The Mn oxide formulas are from McKenzie (1989), and those of the Fe oxides are from Schwertmann and Taylor (1989).

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