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Appendix B: Chemical Reactions of Metals

The principal factors that control **bioavailability** are discussed in greater detail in the Lead, Arsenic, and Polycyclic Aromatic Hydrocarbons (PAHs) chapters. More detailed discussion and references are provided here to direct readers interested in the details of soil chemistry and its effects on bioavailability of metals in soils.

Metals and metalloids, such as arsenic, undergo a wide variety of chemical reactions in soil, and these reactions in turn relate (in possibly complex ways) to bioavailability. For simplicity, "metals" is used here to refer to both metals and metalloids. Several representative reactions that affect metals availability in soil are presented in this section (Basta, Ryan, and Chaney 2005).

B.1 Metals Reaction with Iron and Manganese Oxides

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Sorption is a chemical process that regulates partitioning of metals between solution and solid phases in soils. Iron and manganese oxides act as sinks for metals in soil (McBride 1994; Sposito 1986; Essington 2004; Hettiarachchi et al. 2003; Lake, Kirk, and Lester 1984; Lombi et al. 2002; Scheckel and Ryan 2004). Metals sorption onto anoxide surface is a pH and charge dependent process described by the following chemical reactions:

Cation adsorption: $Fe\text{-}OH + M^{+} = Fe\text{-}OM + H^{+}$

Oxyanion adsorption: $Fe\text{-}OH + H_2L = FeH^{(x-i)}L^{(1-i)} + (i\text{-}1)H^{+} + H_2O$

Where:

Fe-OH is an iron oxide surface,

M is a metal cation, and

L is an oxyanion ligand.

For most metals adsorption by oxide surfaces increases with increasing pH. A review of metals sorption by oxides (Brown and Parks 2001) shows that iron and manganese oxides have a much greater adsorption capacity than aluminum oxides or clay minerals. Sorption by metal oxides is a major mechanism for removal of metals as cations (lead, cadmium, copper, chromium, mercury, nickel, and zinc) and metals as oxyanions (AsO_4^{3-}, AsO_2^{-}, SeO_4^{2-}, SeO_3^{2-}, MoO_4^{2-}, WO_4^{2-}, VO_4^{2-}, CrO_4^{2-}) from soil solution to soil solids (Sparks 2003; Stumm 1992).

B.2 Metal Reaction with Organic Matter

▼*Read more*

Metal cations also sorb to soil organic matter. Strong adsorption to organic matter reduces the solubility of several metals in soil (Adriano 2001). Sorption of metals to organic matter increases with pH because metals preferentially bind with ionized functional groups. Metal sorption to organic matter is less affected by decreasing pH than by metal sorption on oxides.

B.3 Metal Precipitation with Specific Anions

▼*Read more*

Metals form sparingly soluble precipitates with phosphate, sulfides, and other anions (Lindsay 2001). Metals precipitation is highly pH-dependent and increases with pH for many cations. Arsenate and other oxyanions can form insoluble precipitates with multivalent cations including iron, aluminum, and calcium. The mineral (precipitate) formed may control availability and mobility of the metal.

B.4 The Effect of Soil Chemical Reactions on Bioaccessibility

▼*Read more*

Lead and arsenic react with soil components to form insoluble sorbed or mineral phases ranging from weakly bound and

potentially bioavailable (bioaccessible) forms to strongly bound and largely unavailable forms (Chaney, Basta, and Ryan 2008). Bioaccessible arsenic was correlated with its bioavailability in swine (Rodriguez et al. 2003; Basta, Foster and Scheckel 2007) and inversely correlated with arsenic as iron minerals or sorbed to iron oxide surfaces (Basta, Foster, and Scheckel 2007). Reactive iron and aluminum oxide clays and soil pH have been shown to be the dominant soil properties that control arsenic bioaccessibility (Whitacre, Basta, and Dayton 2013; Yang et al. 2002). Additionally, many organic compounds (including PAHs) have a strong affinity for black carbon in soil (Cornelissen et al. 2005; Koelmans et al. 2006; Semple et al. 2013).