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3 Technical Background

In this section is presented for soil and the properties of soil that influence bioavailability. The bioavailability of a contaminant in soil can vary widely depending on soil- or site-specific factors. Depending on the contaminant and site conditions, a variety of soil characteristics influence bioavailability, such as mineralogy, grain size, and soil organic matter. For metals, bioavailability is affected by mineralogy (form of the metal in the soil), soil particle size, and other factors that influence solubility. For organic chemicals, bioavailability is primarily influenced by sources of contamination and soil organic matter. Other important, site-specific factors include co-contaminants, historical site usage, and weathering of contaminants. Details of the specific source and soil characteristics that affect bioavailability are discussed in the chemical-specific chapters on lead, arsenic, and PAHs.

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The bioavailability of a contaminant in soil can vary widely depending on soil- or site-specific factors. These factors include the contaminant considered and site conditions such as mineralogy, grain size, soil properties (for example, soil pH, organic carbon, reactive clay oxides), and duration of weathering. For metals, bioavailability is affected by mineralogy, speciation (form of the metal in the soil), soil particle size, soil properties and other factors that influence solubility. For organic chemicals, bioavailability is primarily influenced by soil organic matter and the source of contamination (Roberts et al. 2016; Xia, Gomez-Eyles, and Ghosh 2016). These factors are described, briefly, below, and more information is included in the chemical-specific chapters.

3.1 Soil Mineral Phases

Metals are often present within or adsorbed to mineral phases in soil. These minerals may be the initial source of elevated metals in the soil or may have formed within the soil from other metals sources.

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The solubility of the mineral phases is a key factor controlling bioavailability. Solubility is influenced by the mineral structure, crystallinity, grain size, formation of weathering or precipitation rinds around the mineral grains, and other mineral phases that may be present in the grain. Reactive iron oxy-hydroxides (and in some cases manganese oxides) are also a key mineral phase for the availability of several metals, most notably arsenic, because they provide many strong adsorption sites for the most common arsenic ions (arsenate and arsenite). Additional metals adsorption and uptake into mineral structures occurs with clay minerals (hydrated sheet silicates with abundant adsorption and ion exchange sites). Site conditions, including soil saturation, soil pH, and soil oxidation-reduction potential influence the stability of existing metal phases, weathering, and incorporation of metals into mineral phases, as well as the degree and strength of adsorption of metals to clays and iron oxy-hydroxides. Clay minerals have also been reported to adsorb organic contaminants, thus potentially limiting bioavailability (Karimi-Lotfabad, Pickard, and Gray 1996).

3.2 Soil pH, Organic Matter, and Reactive Clay Minerals

Soil pH, organic matter and reactive clay minerals affect the bioavailability of contaminants in soil.

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Soil pH affects many biogeochemical processes in soil, including metal bioaccessibility and bioavailability, mineral dissolution rate, and solubility of metal solid phases in soil (<u>Basta, Ryan, and Chaney 2005</u>). In general, metal mineral dissolution and solubility increases as soil pH decreases. Soil organic matter decreases metal solubility in soil by chelation reactions and sorption of metal cations to negatively charged ion exchange sites. Soil organic matter varies in abundance and composition, and may include partially degraded plant matter as well as black carbon (partially combusted organic

matter). Black carbon originates from anthropogenic sources such as fossil fuel combustion or natural sources such as wildfires.

Organic matter abundance and type play a key role in bioavailability of organic chemicals such as PAHs. For example, black carbon is effective at limiting extraction of organic compounds from soil (<u>Alexander 2000</u>; <u>Brändli et al. 2008</u>). Black carbon may also limit bioavailability of metals in soil (<u>Houben, Evrard, and Sonnet 2013</u>). Reactive iron, aluminum, and manganese oxides in soil strongly sorb metals in soil and decrease their solubility and bioavailability (<u>Basta, Ryan, and Chaney 2005</u>). Detailed discussion of the effect of soil properties is included in <u>chemical reactions of metals</u>.

3.3 Soil Particle Size

Soil particle size also can affect the solubility of chemicals such as metals from soil, and thus their bioavailability.

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Smaller soil particle size ranges also contribute to ingestion exposures (USEPA 2016e; Ruby and Lowney 2012; Yamamoto et al. 2006; Siciliano et al. 2009; Choate et al. 2006; Kissel, Richter, and Fenske 1996; Duggan and Inskip 1985). USEPA's bioavailability test methods for lead specify testing of the <250µm particle size fraction (USEPA 2007b; USEPA 2012e). More recent analyses have indicated that an even smaller particle size fraction may be the primary contributor to incidental ingestion exposures (Ruby and Lowney 2012) or to dermal absorption of chemicals from soil (Spalt et al. 2009; Kissel 2011). Consequently, these smaller particle size fractions frequently drive human exposures to chemicals in soils at contaminated sites. USEPA recently revised its guidelines, recommending "moving...to <150 µm particle size" for characterizing the soil fraction that adheres to hands and contributes to incidental soil ingestion (USEPA 2016e).

Because smaller particles have larger surface area to mass ratios, they tend to demonstrate higher levels of solubility for metals (Ruby et al. 1996; Ruby et al. 1999). Figure 3-1 illustrates how mineralogy, grain size, encapsulation, and select soil properties may affect the bioavailability of lead and arsenic in soils. The solubility of a metal depends on its chemical form, which in turn may relate to contamination sources or environmental weathering with soil. For example, lead oxide resulting from combustion of leaded-gasoline has a greater solubility than lead sulfide, which might have originated from ore processing, or lead oxide emissions that have been present in soil for a number of years may have weathered to less soluble forms (Birkefeld, R., and Nowack 2007). Decreased grain size increases the effective surface area and therefore can affect the bioavailability of metals from soil particles. Reactive clay aluminum, iron and manganese oxides absorb lead and arsenic thereby decreasing their bioavailability in soil. Encapsulation in a different mineral matrix can reduce bioavailability by physically preventing reactions. Although Figure 3-1 is specific to lead and arsenic, the general principles are applicable for other metals as well.

FACTORS AFFECTING LEAD AND ARSENIC BIOAVAILABILITY

BIOAVAILABILITY/BIOACCESSIBILITY



High



Figure 3-1. Schematic of how different chemical species, particle sizes, and morphologies affect arsenic and lead bioavailability.

For organic chemicals, the relationship between bioavailability and particle size is more complex. While the larger surface area of smaller particles should enhance chemical dissolution, there is little research specific to the effect of particle size on bioavailability of bioaccessibility of organic chemicals (for example, <u>Rozett et al. 1996</u> and <u>Siciliano</u>, <u>Laird</u>, <u>and Lemeieux</u> 2010) and the available information is contradictory (<u>Ruby and Lowney 2012</u>). Most likely, the source of contamination and the content and nature of organic carbon in soils dominate the bioavailability for organic chemicals (see <u>Xia</u>, <u>Gomez-Eyles</u>, <u>and Ghosh 2016</u>).

Regardless of the contaminant, it is important that exposure estimates and the basis for RBA calculations be based on analytical data (contaminant concentration) for the same particle size fraction that is assumed to contribute to ingestion exposures. Do not rely on analytical data from bulk soil analysis that may be used for other site decisions.

The soil chemistry and soil-chemical interactions that affect bioavailability vary depending on the specific contaminants of interest. Additional details on these considerations are provided in the chemical-specific sections (lead, arsenic, and PAHs). Additional information is also provided about <u>chemical reactions of metals</u>.