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7.1 Fate and Transport

Arsenic occurs in mineral deposits of many elements including copper, silver, gold, zinc, mercury, uranium, tin, lead, molybdenum, tungsten, nickel, and cobalt (<u>Craw and Bowell 2014</u>). Mining operations for any of these minerals can results in soil contamination with arsenic. The most common mineral forms of arsenic associated with mining are arsenopyrite, marcasite, enargite, orpiment, realgar, and tennantite (<u>Craw and Bowell 2014</u>). These minerals weather to form many secondary arsenic minerals in soil. The occurrence and forms of arsenic contamination in soil from mining activities has been recently studied (<u>Bowell and Craw 2014</u>).

Arsenic fate and transport is complex because there are many valences and forms of arsenic that can occur naturally. Arsenic can change valence under different redox states and notably reduced As(III) is considerably more soluble than As(V). Arsenic also can change mineral forms as a result of weathering, generally becoming more stable and less available for solubilization and uptake over time.

Arsenicals were widely used as weed killer herbicides and insecticides. Lead arsenate use on fruit orchards has resulted in soil contamination. Water-soluble arsenates were used to prepare in-field cattle dips (baths used to immerse livestock) used to kill ticks and other insects. This practice has led to point-source arsenic soil contamination across historical cattle production areas.

Chromated copper arsenate (CCA) is a water-soluble inorganic pesticide used as a preservative to protect wood from biological deterioration. The preservative is forced into wood as an aqueous salt solution containing arsenate (As(V)),

chromate (Cr(VI)), and cupric (Cu²+) ions (<u>Hemond and Solo-Gabriele 2004</u>). CCA-treated wood was the most common wood preservation method used in the United States from the 1970s through 2004, representing 75% of the wood preservation industry (<u>Shalat et al. 2006</u>). In this process, the wood is dipped in a solution of CCA and subjected to vacuum pressure to force penetration of CCA into the wood. Average arsenic concentrations in surface soils immediately adjacent to CCA-treated utility poles in service ranged from 150 to 400 mg/kg but approached background levels (below 5 mg/kg) within 0.50 m from the poles. A positive correlation was found between surface soil arsenic content and total iron content. Arsenic(V) was the predominant arsenic species in surface and subsurface soils. (<u>Zagury et al. 2008</u>).

Arsenic from CCA-treated wood may be leached by rainwater and weathering, causing arsenic to accumulate in the soil beneath and adjacent to CCA-treated wood structures. The amount and rate of leaching varies and depends on factors such as climate, rain/soil acidity, and wood age. Arsenic leaching into the soil around CCA-treated wood is primarily in the form of As(V) for new wood, and As(V) and As(III) have been detected in weathered CCA-treated wood (Khan et al. 2004). Once released from the surface of the wood, by leaching or sloughing, the arsenic may enter surrounding soil, where it may remain in complexes with other components of the CCA mixture or form associations with minerals in the receiving soils (Shalat et al. 2006).

There are many less common sources of arsenic soil contamination. For example, arsenic was used in production of colored glass. Historical glass work waste may contain percent levels of arsenic and has resulted in significant contamination of surrounding areas.

The combination of various chemical species with different soil/solid matrices of arsenic produces a wide range of arsenic

solubility and speciation. For example, the solubility of mineral orpiment, As_2S_3 , in water is 0.005 g L⁻¹, while the solubility of

arsenic trioxide, As_2O_3 , is 37 g L⁻¹. These differences have a significant effect on bioavailability and human exposure to arsenic associated with ingestion of contaminated soil.

Inorganic As(V) and As(III) adsorb to many soil clays. Iron, aluminum, and manganese form oxide, oxyhydroxide, and hydroxide clays. These hydrous oxide clays react strongly with oxyanions, including arsenate and arsenite, and reduce solubility and bioavailability (Beak et al. 2006a; Rodriguez et al. 2003).