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Arsenic speciation driving risk based corrective action

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HIGHLIGHTS

- Arsenic speciation in aerated soils indicates a substantial bias for arsenate.
- Seasonal rainfall and short term flooding do not affect the ratio of arsenite to arsenate in well-drained soils.
- Remediation should be focused on arsenate instead of arsenite in well aerated soils.
- Increased arsenate in soils may increase effectiveness of phytoremediation.

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ABSTRACT

The toxicity of arsenic depends on a number of factors including its valence state. The more potent trivalent arsenic [arsenite (As^{3+})] inhibits a large number of cellular enzymatic pathways involved in energy production, while the less toxic pentavalent arsenic [arsenate (As^{5+})] interferes with phosphate metabolism, phosphoproteins and ATP formation (uncoupling of oxidative phosphorylation). Environmental risk based corrective action for arsenic contamination utilizes data derived from arsenite studies of toxicity to be conservative. However, depending upon environmental conditions, the arsenate species may predominate substantially, especially in well aerated surface soils. Analyses of soil concentrations of arsenic species at two sites in northeastern Texas historically contaminated with arsenical pesticides yielded mean arsenate concentrations above 90% of total arsenic with the majority of the remainder being the trivalent arsenite species. Ecological risk assessments based on the concentration of the trivalent arsenite species will lead to restrictive remediation requirements that do not adequately reflect the level of risk associated with the predominate species of arsenic found in the soil. The greater concentration of the pentavalent arsenate species in soils would be the more appropriate species to monitor remediation at sites that contain high arsenate to arsenite ratios.

1. Introduction

Arsenic contamination is an issue of concern worldwide and it is a considerable risk factor in various countries including Bangladesh, Taiwan, India, Mexico, China, Chile, Argentina, and the USA (Adriano, 2001; World Health Organization, 2001). As a natural element, arsenic is widespread and ranks twentieth in crustal abundance, fourteenth in seawater, and twelfth in the human body (ATSDR, Agency for Toxic Substances and Disease Registry, 2007; Ahuja, 2008). In the last century, arsenic based pesticides, herbicides, and insecticides were applied throughout the United States that subsequently led to considerable contamination of domestic and agricultural land (ATSDR, Agency for Toxic Substances and Disease Registry, 2007; Bhattacharya et al., 2007). Arsenic has been released into the environment in both organic and inorganic forms. The two arsenic species most important to toxicology are also the most commonly observed in natural environments, trivalent arsenic [arsenite (As^{3+})] and pentavalent arsenic [arsenate (As^{5+})]. Arsenite is considered to be the significantly more potent than arsenate due at least in part to the more rapid cellular uptake of the trivalent moiety (ATSDR, Agency for Toxic Substances and Disease Registry, 2007; Dopp et al., 2004; Jain and Loeppert, 2000).

Arsenic interferes with over 200 enzymes involved in cellular energy production and metabolism (ATSDR, Agency for Toxic Substances and Disease Registry, 2007; Dopp et al., 2004; Singh et al., 2011). Arsenite rapidly binds to sulfhydryl groups of proteins resulting in increases in reactive oxygen species and inhibiting enzyme functions, while the less acutely toxic pentavalent arsenate is more effective at perturbing phosphoproteins and ATP production.

In the U.S., more than 90% of total arsenic consumption is for agricultural purposes. These include production of wood preservatives (74% of total), herbicides, insecticides, algicides, fungicides, desiccants, antiparasitic medications and growth stimulants for plants and animals (Woolson, 1975; ATSDR, Agency for Toxic Substances and Disease Registry, 2007). The widespread agricultural use of arsenicals over

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several decades has left behind a legacy of highly contaminated soils in orchards and farmlands. Some old orchard fields contain up to 2500 mg/kg of total residual arsenic (average arsenic levels in soils range from 0.1 to 40 mg/kg (mean = 6 mg/kg)), raising concerns over the possibility of food chain and ground water contamination from residual arsenic in these soils (ATSDR, Agency for Toxic Substances and Disease Registry, 2007; Woolson, 1977; World Health Organization, 2001).

Different arsenic-containing compounds vary considerably in their toxicity to mammals (ATSDR, Agency for Toxic Substances and Disease Registry, 2007; Ng et al., 1998). While some compounds are highly toxic (AsH_3), others are considered essentially non-toxic (arsenobetaine and arsenocholine, also known as "fish arsenic") (ATSDR, Agency for Toxic Substances and Disease Registry, 2007; ATSDR, Agency for Toxic Substances and Disease Registry, 2009). A general ranking of arsenical toxicity, from highest to lowest, is as follows: Arsine gas > inorganic trivalent compounds > organic trivalent compounds > inorganic pentavalent compounds > organic pentavalent compounds > elemental arsenic (Woolson, 1977). Factors other than speciation may also influence toxicity. These include physical state, solubility, particle size, the rate of absorption into cells, the rate of elimination, fitness or health of the patient and an individual's genetic background (ATSDR, Agency for Toxic Substances and Disease Registry, 2007; ATSDR, Agency for Toxic Substances and Disease Registry, 2009; Dopp et al., 2004). Arsenate and arsenite are the most common forms of arsenic observed in most environments and to which humans are most commonly exposed (Adriano, 2001; ATSDR, Agency for Toxic Substances and Disease Registry, 2007; ATSDR, Agency for Toxic Substances and Disease Registry, 2009; Ahuja, 2008).

1.1. Arsenite

The toxicity of arsenite (As^{3+}) is based upon its high affinity for sulfhydryl (–SH) groups (ATSDR, Agency for Toxic Substances and Disease Registry, 2007; Davidson et al., 1986; Yan-Chu, 1994). Sulfhydryl groups (also known as thiol groups) are found in proteins that contain cysteine residues and in other important cellular compounds. The reaction between arsenite and enzymatic sulfhydryl groups leads to inactivation of a variety of enzymes, which is believed to be the cause of the overt toxicity of arsenite. Although numerous cellular enzymes are susceptible to arsenite-mediated deactivation, those enzymes involved in the tricarboxylic acid cycle (Kreb's cycle) are particularly sensitive (ATSDR, Agency for Toxic Substances and Disease Registry, 2007; ATSDR, Agency for Toxic Substances and Disease Registry, 2009; Momplaisir et al., 2001; Rochette et al., 1998). In most cases, enzyme activity can be restored by administration of mono- and dithiols. British anti-Lewisite (2,3-dimercaptopropanol), a widely used antidote for arsenic poisoning, effectively blocks the action of arsenite on sensitive enzyme systems (Adriano, 2001; ATSDR, Agency for Toxic Substances and Disease Registry, 2007; ATSDR, Agency for Toxic Substances and Disease Registry, 2009; Ahuja, 2008).

1.2. Arsenate

Arsenic, like phosphorous, is in Group V of the periodic table, and the pentavalent arsenate is an analog of inorganic phosphate (ATSDR, Agency for Toxic Substances and Disease Registry, 2007; Carbonell et al., 1998; Hughes et al., 2011). Arsenate (As^{5+}) is thought to be capable of uncoupling oxidative phosphorylation by a mechanism based upon the competitive substitution of arsenate for phosphate. This results in the formation of an unstable arsenate–phosphate ester that is rapidly hydrolyzed. The high-energy bonds of adenosine triphosphate (ATP) are not conserved due to this arsenolysis (Hughes et al., 2011; Jekel, 1994). The resulting substantial reductions in the formation of ATP may lead to significant toxicity with potentially lethal consequences. Additionally, absorbed arsenate is reduced metabolically to arsenite in human tissues (ATSDR, Agency for Toxic Substances and Disease Registry, 2007; ATSDR, Agency for Toxic Substances and Disease Registry, 2009; Hughes et al., 2011; Singh et al., 2011). Although the kinetics of the tissue based reduction of arsenate to arsenite have not been clearly established, the health impacts of exposure to arsenate may be compounded by the combined mechanisms of action of both arsenite and arsenate (Ouypornkochagorn and Feldmann, 2010). Human health and ecological risk assessments normally focus on the toxicity of total inorganic arsenic without considering the difference in toxicity of the two main species (TCEQ (Texas Commission on Environmental Quality), 2014a; TCEQ (Texas Commission on Environmental Quality), 2014b; USEPA (U.S. Environmental Protection Agency), 1998).

The present study focuses on two contaminated sites in Texas, in areas of historical industrial activity. These two sites are located in areas of upland soils with a high redox potential indicating the aerobic nature of the material. Chemical investigations revealed that both sites contained elevated levels of arsenic in the surface soil. Site one located in College Station, Texas was operated as a drilling service facility from 1952 to 1994 producing products and services for cementing and stimulating oil and gas production wells. Site two located northeast of Houston was used as a formulating facility for pesticides from the 1940s and 50s until the 1970s. Arsenic was the primary contaminant in surface soil for both properties.

The ecologic receptor group animal for the ecological risk assessment for this study was the Least Shrew (*Cryptotis parva*). The Least Shrew is abundant and has a high population density, thus making up a large portion of the diet of owls, hawks, and snakes (Otteni et al., 1972; Schmidly, 2004). The Least Shrew is the smallest mammal in Texas and occurs in grasslands in eastern and central portions of the state (like those found at the subject sites) (Schmidly, 2004). It feeds on snails, insects, sow bug, and other small invertebrates. The diets of these invertebrates and their burrowing behavior result in a high potential of direct and indirect exposures to arsenic in surface soils. The availability of natural history and toxicological information also supports selection of the Least Shrew as a measurement receptor (Otteni et al., 1972; Schmidly, 2004).

Both sites in Texas were assessed using arsenic speciation data to calculate a risk based remedial goal. Arsenic speciation analysis of soil provides insightful information associated with risk assessment, fate and transport, and chemical equilibrium within the substrate.

2. Methodology

The methodology for this research consisted of three parts. First, soil sampling and speciation analysis from two similar sites located in Texas. Then measures of arsenite and arsenate toxicity were reviewed and compared to the toxicity of total arsenic. Finally, an ecological remediation goal was calculated for arsenic based on the concentration of arsenite versus arsenate.

2.1. Site locations

Site one is comprised of an approximately 18.4-acre tract of vacant land in College Station, Texas. This subject property appears to have been first developed in the 1940s and 1950s, and was historically utilized as an arsenical pesticide formulation facility. Unfortunately, details regarding the composition of pesticides including arsenicals used at this facility were not recorded in the site history and are not available. The facility ceased operations sometime in the 1970s. Soils at the site are primarily upland and well drained. Contamination at the site has been weathered for over 50 years.

Site two is comprised of approximately 5 acres of currently vacant land in Texas northwest of College Station. The property was first developed in the 1950s, and was historically utilized as a drilling services facility. The facility was operated from 1954 to 1994 and offered services for cementing and stimulating oil and gas wells. The facility included a bulk cement plant, a dry chemicals storage building, an acid plant, truck wash facility and maintenance shop. Arsenic contamination at the site was most likely from oilfield equipment cleaning and sediment