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Chapter 2

ASSESSING THE BIOAVAILABILITY OF ARSENIC IN SEDIMENTS FOR USE IN HUMAN HEALTH RISK ASSESSMENT

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ABSTRACT

Arsenic concentrations in sediments in a wetlands located downgradient from a landfill in northeastern Massachusetts were found to be over 1,000 mg/kg in several locations with a maximum detected concentration of 4,500 mg/kg. The elevated arsenic in sediment is likely the result of the dissolution of iron and arsenic in the underlying rock under reducing conditions mobilized with the groundwater and co-precipitating out into the sediments when groundwater reaches the oxidizing surface water, producing an iron and arsenic bearing floc. Approximately 15 acres of wetlands appear to be impacted from elevated arsenic concentrations. To assess the potential impacts to human health and to determine the extent of acreage requiring remedial action, a site-specific bioavailability factor was developed using an *in vitro* laboratory assessment. While *in vivo* (live animal) studies are considered to be the most accurate measures of bioavailability for assessing absorption of contaminants by humans, the *in vivo* studies are expensive and lengthy. The *in vitro* approach undertaken for this assessment simulates digestive activity in the stomach, including residence time, pH, temperature, agitation, and solid to liquid ratio. This *in vitro* laboratory approach coupled with an adjustment based on *in vivo* data, along with a mineralogical characterization of the impacted sediments, served to develop a site-specific bioavailability factor that resulted in more accurate human health risk characterization results.

Keywords: arsenic, bioavailability, sediment, risk assessment

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1. INTRODUCTION

Arsenic concentrations in sediments in a wetlands located downgradient from a landfill in northeastern Massachusetts, where arsenic occurs naturally in high concentrations in bedrock were found to be over 1,000 mg/kg in several locations with a maximum detected concentration of 4,500 mg/kg. The elevated arsenic in sediment is likely the result of the dissolution of arsenic and iron in the underlying rock under reducing conditions mobilized with the groundwater and co-precipitating out into the sediments when groundwater reaches the oxidizing surface water, producing an iron and arsenic bearing floc. Approximately 15 acres of wetlands sediments appear to be impacted from elevated arsenic concentrations. To assess the potential impacts to human health, and to determine the extent of acreage requiring remedial action, a site-specific arsenic bioavailability factor was developed using an *in vitro* laboratory assessment supported by other lines of evidence of reduced bioavailability.

2. SITE HISTORY

The landfill began operating shortly after the end of World War II. Historical mapping of the landfill area shows that the site operated as a gravel pit around this same period of time. Dumping was conducted in an "open face" manner by filling in old gravel pits until the early 1960s. Open burning in these pits was the primary method of waste disposal. The landfill was used for disposal of residential, commercial, industrial, and construction demolition wastes. Leachate from the landfill impacted a series of streams in a wetland area adjacent to the landfill. In 1973, an underdrain system was constructed as a pollution control measure to limit the amount of leachate entering the adjacent wetlands, and the landfill was closed to further solid waste disposal. The landfill site continued to be used as a recycling center and for the controlled disposal of leaves, brush and grass cuttings. In the 1980s, soils were used to cover the northern section of the site and ballfields were constructed.

3. CONCEPTUAL SITE MODEL

Typically, organic matter contained within landfills produces a deoxygenated (reducing) environment in groundwater beneath and directly downgradient of the landfill. This removal of oxygen is caused by the degradation of the organic matter by native microorganisms, a process that requires oxygen. Under reducing conditions, metals such as arsenic and iron in the solid phase aquifer materials

dissolve into the aqueous phase and become mobilized in groundwater. The source of metals may be natural (i.e., contained within soil and rock formations or as coatings on the surface of aquifer materials), landfilled waste, or some other unknown source. In general, when groundwater conditions become oxidizing, mobilized metals will typically be removed from solution as a solid precipitate.

At this site, reduced groundwater upwells into the wetland located downgradient of the landfill (i.e., the wetland serves as a point of groundwater discharge). When groundwater reaches the oxidizing surface water environment, iron and arsenic in solution precipitate as solid phase iron oxyhydroxides containing arsenic. The presence of iron and arsenic at concentrations below the laboratory method detection limits in downgradient surface water samples appears to indicate that the iron and arsenic are removed from solution via precipitation. Once the iron and arsenic have been removed from solution, the resulting solid phase particles may be transported further downstream via surface water flow. As a result there are depositional locations with elevated concentrations of iron and arsenic, as shown in Figure 1 below.

Figure 1. Example of iron/arsenic floc in sediment streams downgradient of the landfill.

4. DEFINITION OF BIOAVAILABILITY

Bioavailability is the extent to which a substance can be absorbed by a living organism and can cause an adverse physiological or toxicological response. Bioavailability is particularly relevant for metals, which may exist in a variety of chemical and physical forms, not all of which are readily absorbed by the body when ingested. However, most oral reference doses (RfDs) and cancer slope factors (CSF) used in risk assessment are based on studies in which dose is reported as the amount of chemical ingested rather than absorbed (USEPA, 1989).

Such studies make no assumptions concerning bioavailability. If the form of a chemical in the environment is less than that of the form relevant to toxicology or human epidemiological studies, these toxicity criteria may overestimate the risk. An adjustment for reduced bioavailability of some environmental forms of chemicals is needed in such cases to appropriately evaluate risks (USEPA, 2007).

Oral bioavailability of a substance can be expressed as either absolute bioavailability (ABA), or as relative bioavailability (RBA). ABA is the ratio of the amount of chemical absorbed to the amount ingested. RBA is the ratio of the amount of a test material, such as arsenic in soil, that is absorbed to the amount of an appropriate reference material, such as sodium arsenate. Sodium arsenate is considered an appropriate reference material for arsenic because it is a useful surrogate for the form(s) of arsenic on which oral toxicity criteria for arsenic are based. Sodium arsenate is soluble and available information suggests that it is also almost completely absorbed. Typically both ABA and RBA are expressed as a percent. An ABA is useful for characterizing risk when a RfD and/or CSF are based on an absorbed dose. However, since most toxicity criteria are based on an administered dose rather than an absorbed dose, the ABA of a substance is generally not used in the human health risk assessment process. RBA is useful when the bioavailability of a chemical form relative to the form relevant to critical toxicological or epidemiological studies can be estimated (USEPA, 2007).

5. PROCESS FOR DEVELOPING A SITE-SPECIFIC ARSENIC BIOAVAILABILITY FACTOR

5.1 *In Vitro* Analysis for Estimating RBA

Historically the RBA for arsenic has been determined using *in vivo*, (animal-based) studies. Typically the *in vivo* studies for arsenic have utilized young swine or primates, and have determined RBA coefficients through the comparison of the amount of arsenic ingested versus amount of arsenic excreted or retained in the animal. The *in vivo* studies are very expensive and can take many months to complete, but are generally accepted as the best means of assessing bioavailability. Because of the expense and time requirements of the animal-based studies, researchers have developed an *in vitro*, or laboratory-based method to determine RBA coefficients. The efficacy of the method has been tested via comparisons of results with those of animal studies, mainly studies where young swine were fed arsenic containing soil.

Generally, the *in vitro* method consists of placing the sample medium, such as arsenic impacted soil, into a fluid bath that simulates the human stomach. The amount of arsenic in the bulk sample is then compared to the amount of arsenic

that has dissolved into solution and an *in vitro* bioavailability (IVBA) coefficient is calculated. The raw results from the *in vitro* tests are then empirically adjusted to an *in vivo* RBA that is used in the risk assessment. In the *in vivo* studies the amount of arsenic excreted in the urine is plotted as a function of the amount of arsenic administered and a best fit linear regression line through the data is determined. Using the regression slope of 0.6966, the following equation is used to calculate the RBA (University of Colorado, 2011):

$$\textit{in vivo}\ \text{RBA} = 0.6966 \times \textit{in vitro}\ \text{RBA} + 3.2482$$

Several studies, including one on arsenic impacted sediments from the Aberjona River located in northeastern Massachusetts, have been conducted to assess the correlation between *in vivo* and *in vitro* bioavailability results. These studies suggest that the calculated IVBA is an appropriate screening tool for estimating the relative *in vivo* bioavailability (Brattin and Wahlquist, 2002). For the assessment of this site, results from 12 site samples and two reference (background) samples submitted to the University of Colorado Laboratory for Environmental and Geological Studies (LEGS) for *in vitro* analysis indicated low RBA of arsenic in downgradient wetlands sediments, with reported values ranging from 0.02% to 12.35% as presented in Table 1. The regression was applied to the raw *in vitro* results to approximate an equivalent *in vivo* arsenic RBA coefficient. The regression extrapolated *in vivo* RBA ranged from 3.26% to 9.94% with a 95% UCL value of 7.51%. The regression adjusted results, however, were not accepted by MassDEP. Therefore, a maximum value of raw *in vitro* value of 12.35% was selected, adjusted based on the EPA oral cancer slope factor assuming 98% absorption (USEPA, 2011) (0.1235 / 0.98 = 0.126) and a value of 12.6% RBA was selected for the landfill site as recommended by MassDEP.

The correlation between the *in vivo* and *in vitro* studies for arsenic are not strong enough to warrant using the *in vitro* method as a standalone means for the determination of a site-specific arsenic bioavailability coefficient. Therefore, additional information, such as soil mineralogy and forms of arsenic present in this matrix, is required to demonstrate correlations between the samples analyzed via the *in vitro* method and samples previously analyzed via *in vivo* methods. These soil mineralogy and geochemistry characteristics are typically determined using an electron microprobe (EMP) equipped with various spectrophotometers to identify specific elements and mineral forms.

Table 1. In Vitro Arsenic Bioavailability Analysis Results

Sample	Arsenic Concentration in Soil Sample (µg/kg)	*In Vitro* Bioavailability Coefficient (%)	Equivalent *In Vivo* Bioavailability Coefficient (%)
1	271,318	0.02	3.26
2	56,242	0.10	3.32
3	493,450	1.53	4.32
4	764,705	2.09	4.70
5	650,003	2.58	5.05
6	223,853	2.60	5.06
7	85,347	3.51	5.70
8	870,951	4.34	6.27
9	445,282	4.57	6.43
10	1,779,206	6.81	7.99
11	2,573,631	9.61	9.94
12	144,046	12.35	11.85
reference	4,781	53.64	40.61
reference	7,929	54.42	41.16

5.2 Geophysical Data Analysis

The three geochemical properties most commonly considered in relation to metals bioavailability evaluated using EMP are mineral phase, matrix association, and particle size.

- ***Mineral Phase:*** Refers to the chemical form, or species, in which the metal occurs in minerals composing site soil or sediment. Examples for arsenic include iron oxides, iron and zinc sulfates, iron sulfides, and arsenic bearing phosphates. In general, less soluble mineral phases are associated with low RBA values. Results from the EMP work indicated that 100% of the arsenic in all of the samples was present in a low solubility iron oxyhydroxide phase.
- ***Matrix Association:*** Refers to the physical association of the metal bearing grains with other mineral phases or matrices that may limit contact of the metal bearing grain with gastrointestinal fluids. Metal bearing grains that are entirely free in the soil are referred to as "liberated,"

whereas grains that are bound together are referred to as "cemented." Particles that exist in a secondary phase coating are referred to as "rimming." Metal bearing grains that are fully encased or cemented are essentially isolated from gastrointestinal fluid, are not believed to be available for dissolution and adsorption, and thus are typically associated with lower RBA. The most common matrix association of the arsenic containing particles at this site was liberated.

- ***Particle Size:*** Metals bearing particles occur in a large variety of sizes. Because dissolution of the particles in gastrointestinal fluid only occurs on a particle's surface, large particles are more likely associated with lower RBA values than smaller ones, because the ratio of particle surface area to volume tends to decrease as size increases. Average arsenic bearing particle sizes, measured at the longest dimension, ranged from 27.58 microns to 61.51 microns. The average arsenic bearing particle size for all samples was 40.8 microns.

As with any scientific research, not all lines of evidence are going to provide the same level of support. The matrix association indicating that the arsenic containing particles were liberated does not support the findings as strongly as the remaining lines of evidence. While all three of the geochemical properties are considered in the development of a site-specific RBA coefficient, mineral phase shows the strongest correlation to bioavailability, and thus is considered more heavily. Data collected from the Aberjona River study (Brattin and Wahlquist, 2002) suggested that the RBA of the arsenic is likely to be determined primarily by mineral phase and/or particle size rather than by matrix association.

5.3 National Arsenic Bioavailability Library

Dr. Drexler of the University of Colorado LEGS noted that the results of the *in vitro* and EMP analysis for the site sediment samples most closely resembled soil samples collected from Keaau Hawaii as part of an arsenic bioavailability study conducted for the State of Hawaii Department of Health. Similar to the landfill wetland sediment samples, the Keaau samples exhibited high concentrations of iron oxides. The soil samples collected as part of the Keaau study were analyzed for arsenic bioavailability via the *in vitro* and *in vivo* methods. Similar to the landfill samples, the Keaau soils exhibited low arsenic bioavailability (AMEC, 2007). The Keaau study concluded that there was a correlation between decreasing arsenic bioavailability with increasing iron oxide concentrations.

6. CONCLUSION

The cleanup value for arsenic in sediment at this site would be 150 mg/kg if the default value of 100% bioavailability for arsenic was used for a child trespasser scenario. This would result in approximately 15 acres of sediment requiring excavation and removal. Alternatively, a site-specific cleanup value for arsenic in sediment of 900 mg/kg was derived using a 12.6% bioavailability factor using a child trespasser scenario. This results in five hot spot areas requiring excavation and removal totaling approximately one half (0.5) acre of the wetlands area. This results in a considerable reduction in the amount of wetlands that would be disturbed/destroyed if the default value of 100% bioavailabilty was used to assess site health risks and a substantial cost savings to the affected town.

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