Using the Bioavailability of Arsenic as a Risk Assessment Tool at Railroad Sites



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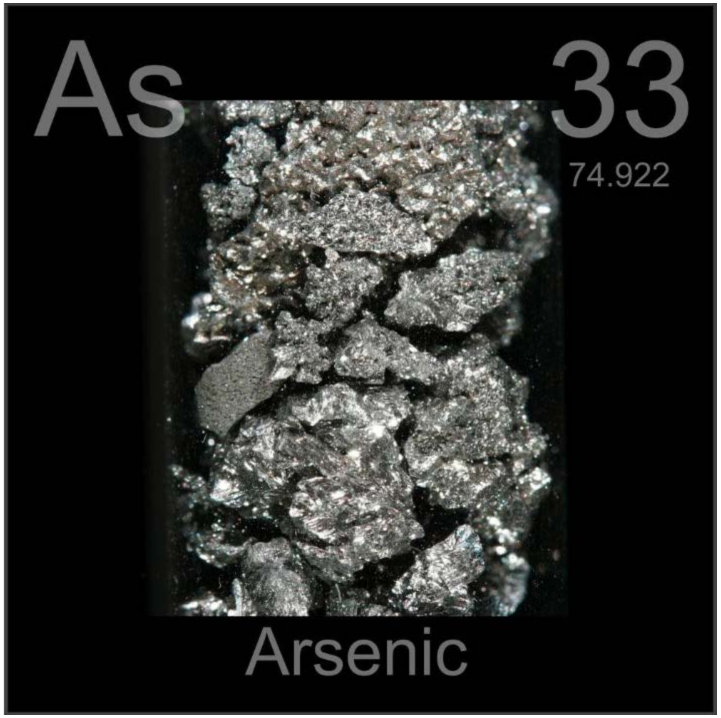
Background

- Arsenic (As) in groundwater and soil is a common constituent of concern at railroad sites nationwide.
- Recognized background concentrations vary significantly from region to region.
- The sources can derive from natural geogenic sources, such as bedrock, or anthropogenic sources such as pesticides, wood preservatives, and coal combustion.



Background

– Potential Sources of Arsenic at Railroad Sites:
  - Arsenic based herbicides and pesticides
  - Rail Tie Wood Preservatives
  - Nearby Industry
  - Coal Combustion Processes/ Coal Storage

Terminology

Bioavailability:

The fraction or percentage of an ingested dose of arsenic that is absorbed into the systemic circulation.

Absolute Bioavailability (ABA):

The ratio of the amount of arsenic absorbed to the amount ingested.

$$ABA\ (\%) = \frac{absorbed\ dose}{administered\ dose} \times 100$$

(USEPA, 2012)

Terminology

Relative Bioavailability (RBA):

The ratio of the ABA of arsenic present in the soil to the ABA of As in an appropriate reference material.

$$RBA(\%) = \frac{absorbed\ fraction\ from\ soil}{absorbed\ fraction\ from\ reference\ material} \times 100$$

(USEPA, 2012)

Terminology

Bioaccessibility:

The physiological solubility of arsenic in the gastrointestinal tract. Arsenic that enters the body must become bioaccessible in the gastrointestinal track in order to be absorbed.

The fraction of arsenic that is solubilized is referred to as the *in vitro* bioaccessibility (IVBA).

(USEPA, 2012)

In Vivo vs. *In Vitro* Methods

In Vivo Methods

Animal Models
- Swine, Monkey, Mice, etc.

Time Consuming
- Up to 6 months

Cost
- Up to $100,000 or more

Limited Data
- Relatively few samples analyzed per site

In Vitro Methods

Lab Simulated Gastrointestinal Model

Shorter Turnaround-Time
- Sampling time on the order of days
- Laboratory turnaround-time and report on the order of weeks

Cost
- ~$300/ sample and can analyze a lot of samples per site

Previous Studies and Application

Examples where As bioavailability adjustments have been included in remediation targets for contaminated sites in the USA

Site	Contaminant	Test	Bioavailability (%)	Clean up Target (μg g⁻¹)	Regulator Agency
National Zn Co. Bartlesville, OK	Pb	*In vivo*, rat	40	925[1] (500)[2]	Oklahoma DEQ
	Cd	*In vivo*, rat	33	100[1] (30)[2]	
	As	*In vitro*, PBET	25	60[1] (20)[2]	
Anaconda, MT	As (soil)	*In vivo*, monkey	18	250[2]	USEPA Region VIII
	As (dust)	*In vivo*, monkey	26		
Crego Park, MI	As	*In vitro*, PBET	10	68[1] (6.8)[2]	Michigan DEQ
Union Pacific Railroad Yard, Sacramento, CA	As	*In vivo*, pig	< 0.1	No clean up (up to 1,800 μg g⁻¹ As in slag)[1]	Cal-EPA

[1]Clean up target after site-specific bioavailability assessment.
[2]Clean up target prior to bioavailability adjustment.

(NFESC, 2000; Kelley et al, 2002; Juhasz et al. 2003)

Determining When to Use IVBA As

- Is remediation not feasible or cost prohibitive?
  - Excavations or soil blending, for example, can be costly or not feasible due to active infrastructure like rail lines, warehouses, and other structures.

- Cost of measuring IVBA over cost of remediation or other corrective action
  - The cost of IVBA sampling and analysis is relatively inexpensive when compared to the cost of an excavation of an entire impacted area.
  - IVBA assessment provides a tool to help reduce the size of the impacted area needing treatment.

Determining When to Use IVBA As

- Number of chemicals present on site
  - If multiple types of impacts drive risk, the cost of the IVBA study may outweigh the benefit.
- Are concentrations close to established state default cleanup criteria?
  - IVBA study can show that concentrations on site do not pose an unacceptable risk to human health.
- Size and type of the site
  - Is direct contact a risk pathway or is direct contact managed by current site conditions?
- Potential for regulatory acceptance
  - Work with regulatory agency on approval of work plan.

Example Sites

- Site 1: Former Manufactured Gas Plant
  - TRC performed IVBA As evaluation
- Site 2: Former Rail Yard
  - Candidate for IVBA As evaluation
- Site 3: Railroad Surplus Site
  - Possible candidate for IVBA As evaluation dependent on regulatory input and site objectives

Example Sites

	Site 1 Former Manufactured Gas Plant	Site 2 Former Rail Yard Site	Site 3 Railroad Surplus Site
State	Michigan	Michigan	Mississippi
Prior Land Use	Manufactured Gas Plant Processes	Foundry; Rail Yard	Coal Storage
Potential Source of Arsenic	MGP Processes	Foundry Sand	Coal Piles
Arsenic Background Level	10.6 mg/kg(1)	2.3 mg/kg(2)	6.8 to 13.76 mg/kg(3)
IVBA As Measured	Yes	No	No

1) As background level shown is the Huron-Erie Lobe 1 standard deviation background level from the MDEQ Michigan Background Soil Survey 2005 (Updated 2015).
2) As background level shown is the Michigan Lobe 1 standard deviation background level from the MDEQ Michigan Background Soil Survey 2005 (Updated 2015).
3) Background soil arsenic concentration for the Citronelle formation (range 6.80 mg/kg to 13.76 mg/kg, average 10.28 mg/kg) as reported in "Arsenic Concentrations in Selected Soils and Parent Materials in Mississippi", MAFES Bulletin 1104.

Former Manufactured Gas Plant

Analyte	Total Arsenic	SBRC gastric Total Bioaccessible Arsenic[(2)]	Percent SBRC gastric Bioaccessible Arsenic	Percent Relative Bioavailable Arsenic[(3)]
Residential DWP Criteria	4.6	NC	NC	NC
Non-Residential DWP Criteria	4.6	NC	NC	NC
GSI Protection Criteria	4.6	NC	NC	NC
Residential Direct Contact Criteria	7.6	NC	NC	NC
Particulate Soil Inhalation Criteria	9.10E+05	NC	NC	NC
Non-Residential Direct Contact Criteria	37	37[(4)]	NC	NC
Site Specific Non-Residential Direct Contact Criteria	153[(5)]	NC	NC	NC
Statewide Default Background Levels[(1)]	5.8	NC	NC	NC
Units	mg/kg	mg/kg	%	%
Minimum	3.1	1.2	2.0	3.6
Maximum	120.0	21.5	50.0	51.3
Mean	39.2	5.9	16.7	18.2
Geometric Mean	27.4	3.9	11.4	13.7
95% Upper Confidence Limit	--	--	22.7	24.2

NC = No Criteria; mg/kg = milligrams per kilogram

5) Site Specific Non-Residential Direct Contact Criteria is currently under review by the Michigan Department of Environmental Quality. Value shown is calculated value as presented to the agency.

Former Manufactured Gas Plant

Using IVBA to Calculate RBA:

$$\text{Arsenic RBA (\%)} = 0.992 \times \text{SBRC*}_{\text{gastric}}\ (\%) + 1.66$$

$$\text{Arsenic RBA (\%)} = 0.992 \times 22.7\% + 1.66 = 24.2\ \%$$

(Juhasz et. al. 2009)

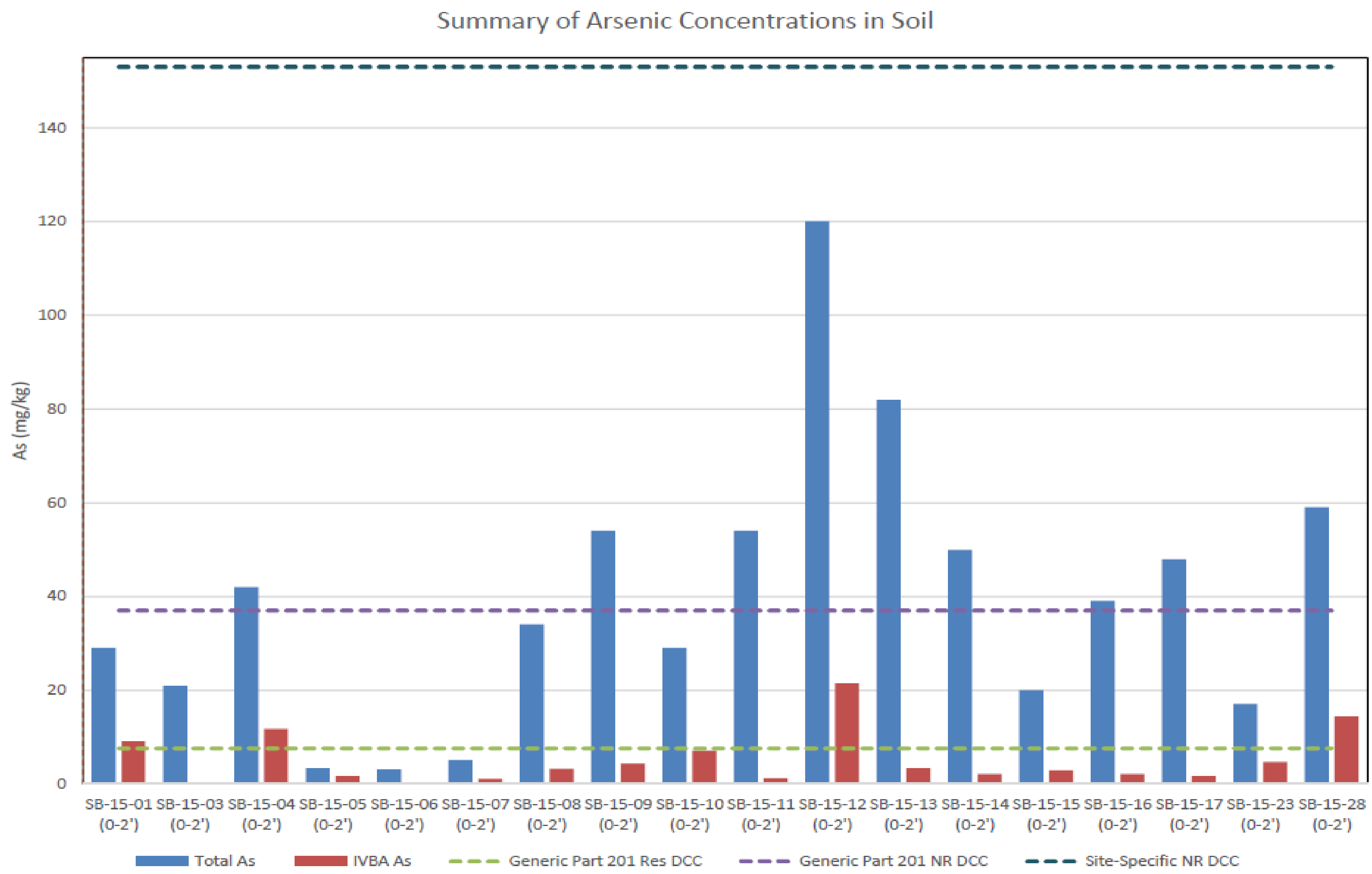
Calculating MI Soil Site Specific Non-Residential Direct Contact (NRDC) Criteria for Total As

MI Soil Site Specific NRDC Criteria = MI Soil NRDC Criteria / (RBA/100)

153 mg/kg = 37 mg/kg / 0.242

*SBRC = Solubility/ Bioavailability Research Consortium

Former Manufactured Gas Plant



Former Rail Yard

- 22 sample above Statewide Default Background Levels
- 9 samples above MDEQ Part 201 Non-Residential Direct Contact Criteria

Analyte	Total Arsenic
Non-Residential Drinking Water Protection Criteria	4.6
Non-Residential Direct Contact Criteria	37
Statewide Default Background Levels	5.8
Units	mg/kg
Min	2.6
Max	180
Mean	38
Geometric Mean	22
Total Samples	24

Former Rail Yard

- Using IVBA as a risk assessment tool to develop site specific clean up criteria has the potential to be used for:
  - Arsenic, Cadmium, Chromium*, Lead and Mercury.
- Other constituents of concern on site are limited in extent and typically located in separate areas from the arsenic contamination.
- Based on an estimate of Arsenic Relative Bioavailability at 50% or less, a reasonable MI Soil Site Specific NRDC Criteria for total As can be achieved.

*Speciation data is needed to develop site specific IVBA study for Chromium.

Former Rail Yard

Using IVBA to Calculate Potential RBA:

Low IVBA Estimate: Arsenic RBA (%) = 0.992 x 25.0% + 1.66 = 26.5 %

High IVBA Estimate: Arsenic RBA (%) = 0.992 x 50.0% + 1.66 = 51.3 %

(Juhasz et. al. 2009)

Calculating Potential MI Soil Site Specific NRDC Criteria for Total As:

Low IVBA Estimate: 72 mg/kg = 37 mg/kg / 0.265

High IVBA Estimate: 139 mg/kg = 37 mg/kg / 0.513

Railroad Surplus Site

- 8 samples collected at 4 boring locations
  - 4 samples were surface soil samples (0-2')
- All samples above Tier 1 Restricted Criteria
- 6 samples above Tier 1 Unrestricted Criteria

Analyte	Total Arsenic
Tier 1 Restricted	3.82
Tier 1 Unrestricted	0.426
Background Level(1)	10.28
Units	mg/kg

Minimum	3.6
Maximum	25.3
Mean	8.2
Geometric Mean	6.8
Number of Samples	8

- Only 1 sample above the background soil arsenic concentration for the Citronelle formation(1).

(1) Background soil arsenic concentration for the Citronelle formation (range 6.80 mg/kg to 13.76 mg/kg, average 10.28 mg/kg) as reported in "Arsenic Concentrations in Selected Soils and Parent Materials in Mississippi", MAFES Bulletin 1104.

Railroad Surplus Site

- Small investigation area- site is 3,200 square feet

- The As is found in association with cinders and coal/coke fines near the surface.
  - Previous studies show that As associated with coal typically has a low bioavailability.

- Other constituents found onsite that exceed criteria are not found in the same area as the As exceedance, with the exception of one semi-volatile organic compound.

Railroad Surplus Site

Regulatory Input and Objective Review:

- Bioavailable As would need to measure at or above 15% or 1.5% for Tier 1 Restricted/ Unrestricted criteria, respectively, to be adjusted over 25.3 mg/kg.
- Bioavailable As would need to measure at or below 40% for the bioavailable portion of As to fall below the background level.
- Acceptance of this method to assess risk at this site is largely dependent on cleanup objectives and support of the regulatory agency.

References:

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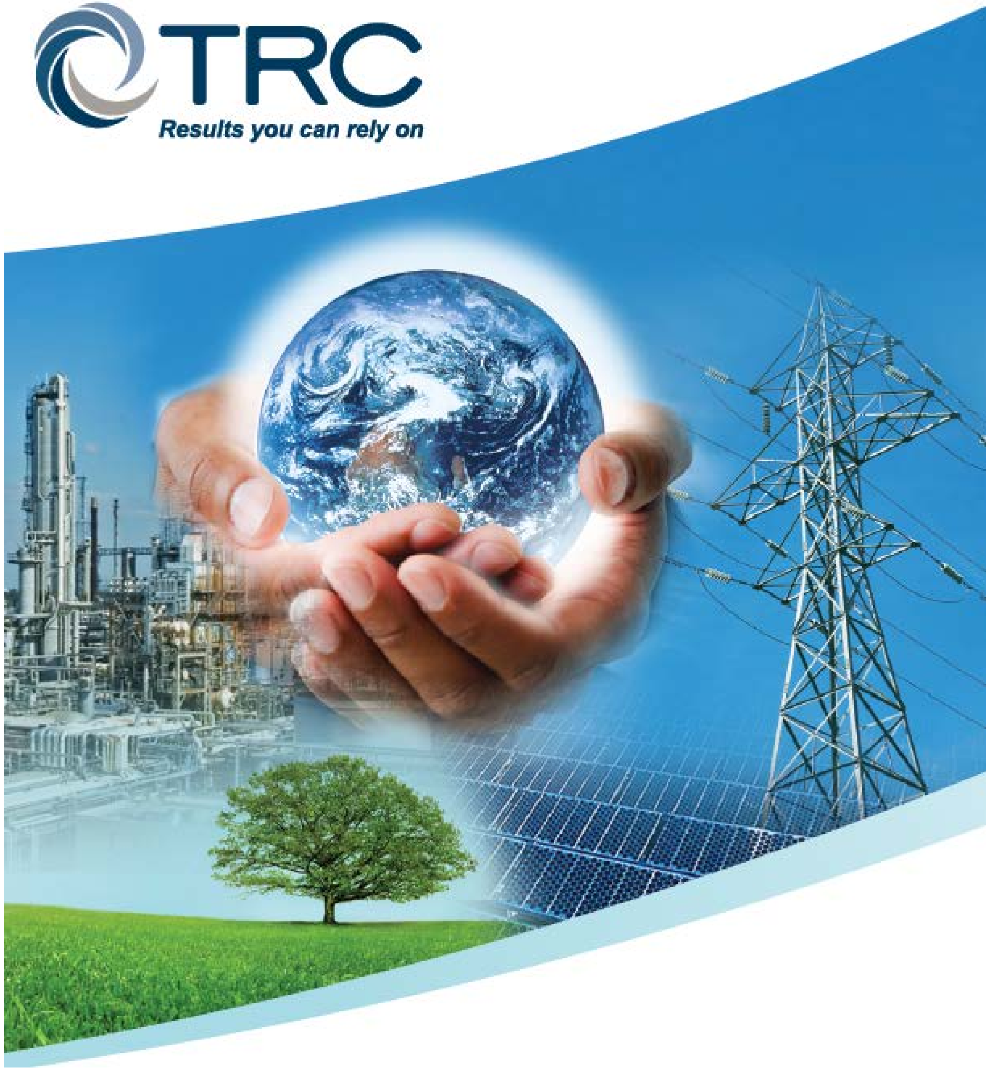
Questions?

TRC
Results you can rely on



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