HUMAN HEALTH RISK ASSESSMENT (HHRA) NOTE NUMBER 6

CALIFORNIA DEPARTMENT OF TOXIC SUBSTANCES CONTROL (DTSC)
HUMAN AND ECOLOGICAL RISK OFFICE (HERO)

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ISSUE: Recommended Methodology for Evaluating Site-Specific Arsenic Bioavailability in California Soils

SUMMARY:
Arsenic (As) contamination in soil is a frequent risk-driver at Cleanup Sites in California. Typical human health risk assessments assume that As in soil is 100% bioavailable, likely leading to an overestimation of risk. When As is present in soils, it associates with other minerals. These associations reduce the solubility of As thereby reducing the bioavailability of As and the resulting toxicity. The actual bioavailability of As in soils can span the entire range from 0-100%. Relative Bioavailability (RBA) is a ratio that compares the bioavailability of As in soil to that of As in water. Site-specific RBA can then replace the default assumption in the risk assessment equations resulting in a more refined estimate of risk. Historically, regulatory agencies have required *in vivo* animal studies in order to make site-specific adjustments to RBA. These studies are often cost prohibitive and time consuming. In 2008, DTSC obtained a US EPA grant to develop and evaluate new cost-effective methodologies for estimating the bioavailability of As in soils. We partnered with investigators from the US Geological Survey, The Ohio State University, The University of Missouri, and Chapman University to achieve these goals. This HHRA Note Number 6 is one of the outcomes of this work. This study was funded by a Brownfields Training, Research and Technical Assistance Grant from the US EPA (Brownfields Research Cooperative Agreement TR - 83415101).

The California Arsenic Bioaccessibility (CAB) method (Whitacre et al 2017) is a reliable, simple, and inexpensive tool to estimate site-specific RBA of As in soils. The use of site-specific RBA decreases the uncertainty of the risk assessment, improves remedial decisions, and often leads to significant savings of the resources available for remediation without compromising the level of health protectiveness.

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Decision Matrix: When to Evaluate Site-Specific Bioavailability?

A. Considerations: There are multiple considerations that must be evaluated prior to making the decision to proceed with a site-specific evaluation of As RBA. These considerations include:

1) Background Concentrations of Arsenic in Soil: Prior to considering an evaluation of As RBA, the background concentration of As in site soils should be determined. If As in site soils does not exceed background, no further evaluation is necessary. Table 1 lists the risk-based screening levels for As in California, which are typically well below background levels. If RBA will be applied to a site where the clean-up goals are set to background, the RBA of As in the background soils must also be evaluated (See Attachment 1).

Table 1: Risk-Based Screening Levels for Arsenic in Soil:

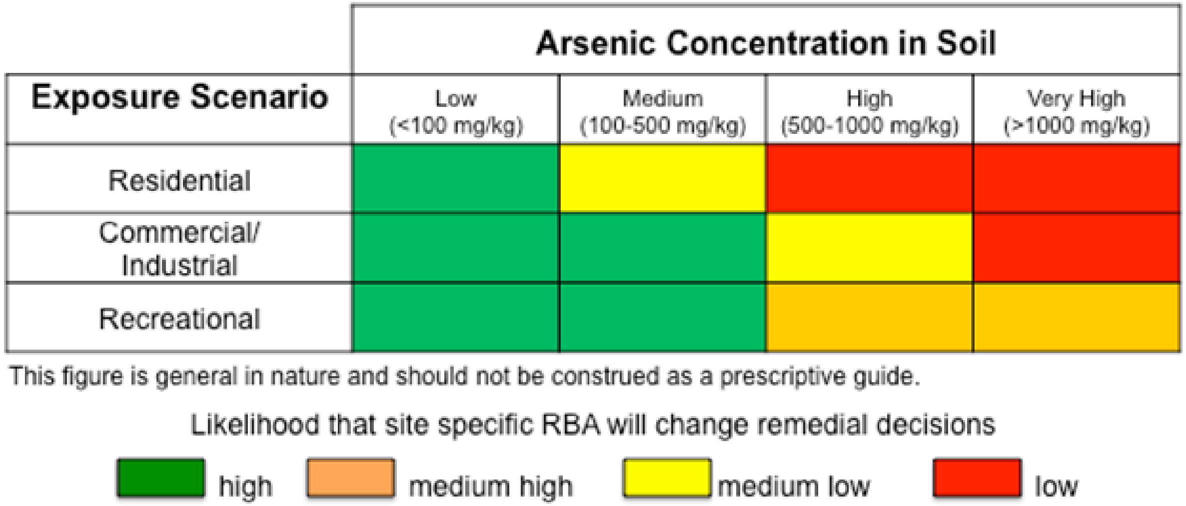
SCREENING LEVEL	CALIFORNIA DTSC RESIDENTIAL SCREENING LEVEL MG/KG ARSENIC [1]	CALIFORNIA DTSC INDUSTRIAL SCREENING LEVEL MG/KG ARSENIC [1]
CANCER (RISK OF ONE IN A MILLION)	0.11	0.36
NON-CANCER (HAZARD INDEX 1)	0.41	4.2

[1]Human Health Risk Assessment Note 3- DTSC-Modified Screening Levels, April 2019, https://dtsc.ca.gov/wp-content/uploads/sites/31/2019/04/HHRA-Note-3-2019-04.pdf

2) Total Arsenic in Contaminated Soils: The use of site-specific bioavailability is most beneficial at sites with As at low to moderate concentrations (See Figure 1).

3) Anticipated Future Land Use: Total As concentrations and future land use are interconnected considerations for a potential evaluation of bioavailability. As illustrated in Figure 1, the likelihood of site-specific RBA having a significant impact on remedial decisions is dependent on the relationship between total arsenic concentration and future land use.

Figure 1: Likelihood that Evaluating Bioavailability will Change Remedial Decisions



4) Soil Type: Arsenic bioavailability is greatly affected by the mineralogy of the soils in which it is bound. While it is not possible to predict bioavailability based solely on mineralogy, some basic associations which affect RBA are well known. For example, As bioavailability is lower in soils high in iron oxides (typically red or orange in appearance) whereas it is typically higher in sandy soils.

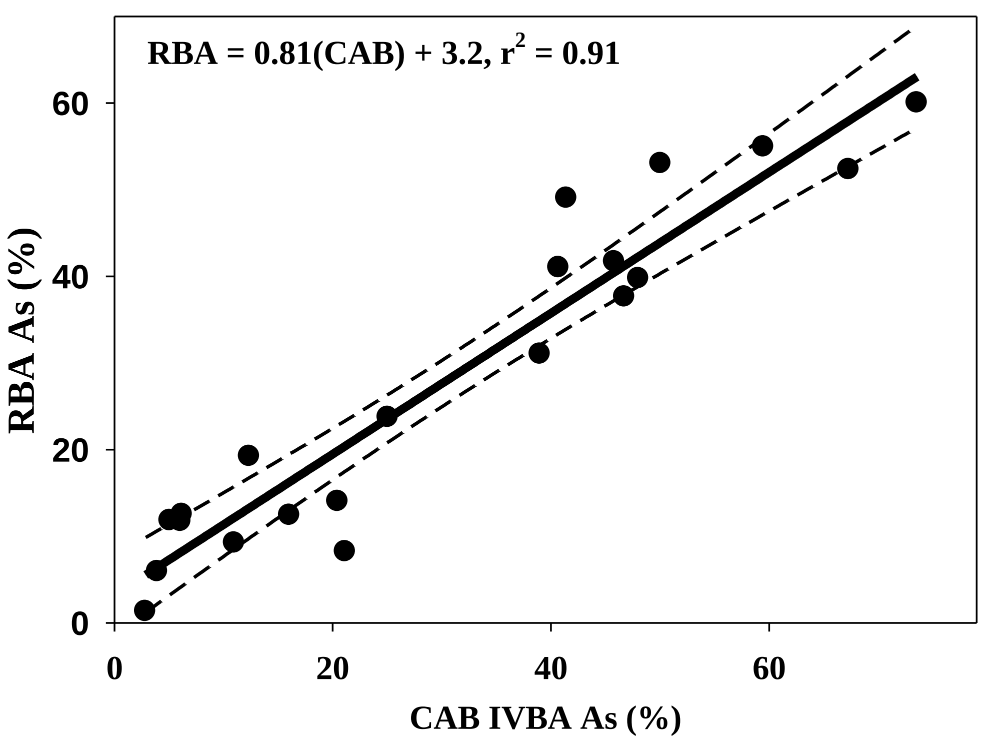
5) Arsenic Source Type: The source of the As contamination should also be considered prior to conducting a Bioavailability study. Arsenic associated with mining waste typically has a much lower associated RBA than As from pesticide applications, for example.

B. Regulatory Involvement: It is critical that regulatory involvement occur early on when a site-specific bioavailability evaluation is being considered. This involvement should include all parties with decision-making power (DTSC, US EPA, State and Regional Water Resources Control Boards, etc.). The entire team should discuss the considerations listed above, sampling strategies, and possible methodologies for determining site-specific RBA.

California Arsenic Bioaccessibility (CAB) Method: DTSC Recommended Methodology for Estimating Site-Specific Arsenic Bioavailability

A. **Method Development**: DTSC partnered with The Ohio State University to develop a new *in vitro* bioaccessibility (IVBA) method that can accurately predict *in vivo* RBA (Whitacre et al 2017 and DTSC 2015). In order to use an IVBA method to predict RBA the data must be compared to an established regression equation; this is known as in vivo in vitro correlation (IVIVC). An IVIVC was established for this method by combining datasets from California mining soils and an existing Strategic Environmental Research and Development Program (SERDP, Project ER-1742) study for soils containing less than 1,500 mg/kg As. The regression equation for the CAB method is RBA= 0.81*(CAB)+3.2 and has an associated r^2 of 0.91 (Figure 2). The results of the IVIVC demonstrate that the CAB method is highly predictive of RBA As, meeting the criteria of; an r^2 > 0.6, a slope between 0.8 and 1.2 (Denys et al. 2012; Wragg et al., 2011) and a y-intercept that does not deviate significantly from zero (Juhasz et al. 2014). In addition, this regression equation includes soils with widely varying As sources, indicating that the CAB method may be applicable to both goldmining and non-gold mining sites.

Figure 2: In Vivo In Vitro Correlation for the CAB Method IVBA and Juvenile Swine RBA



Arsenic sources for samples used in the IVIVC include various mining sources (gold, silver, zinc, copper, and lead) from both tailings and slag as well as pesticide applications.

B. **Method Limitations:** There may be some scenarios where the CAB Method is not appropriate or sufficient to help characterize site-specific As Bioavailability. In some cases, regulators may require in vivo RBA to make site-specific determinations. These scenarios could include, but are not limited to the following:
    1. Total As in soils greater than 1,500 mg/kg
    2. Unique Soil Characteristics (e.g. high or low pH)
    3. Arsenic Source that differs from those included in the IVIVC
    4. CAB only evaluates the incidental ingestion pathway. It is not for making adjustments to the dermal or inhalation exposure pathways.

C. **Laboratories Capable of Performing CAB Method:** As of August 22, 2016, only the two laboratories listed below have access to the Standard Operating Procedure (SOP) for the CAB Method to perform this analysis: 1) the method developer; and, 2) the repeatability study laboratory. More information regarding the repeatability study is currently available in Attachment 2 of DTSC's final report to US EPA (DTSC 2015), available at http://www.dtsc.ca.gov/InformationResources/upload/Arsenic_Study.pdf. For current information on the list of laboratories or if you are a laboratory interested in offering this method, please refer to the HERO contact person listed above.
    a. **Ohio State University, Dr. Nicholas Basta, Email: basta.4@osu.edu**
    b. **Prima Environmental, http://primaenvironmental.com/**

Applying Bioavailability to Human Health Risk Assessments

A. **Incorporating RBA into Risk Equations**

Example Risk Equation:

$$Risk_{soil} = SF_{oral} \times C_{soil} \times RBA \times IR \times EF \times ED \times 10^{-6} / BW \times AT$$

Where:

$Risk_{soil}$	=	Risk in Soil (unitless)
SF_{oral}	=	Slope Factor ($[mg/kg\text{-}day]^{-1}$)
C_{soil}	=	Concentration in Soil (mg/kg)
RBA	=	Relative Bioavailability (unitless, 0 to 1.00)
IR	=	Ingestion Rate (mg/day)
EF	=	Exposure Frequency (day/year)
ED	=	Exposure Duration (year)
BW	=	Bodyweight (kg)
AT	=	Averaging Time (days)

RBA is a part of every risk assessment equation; in the absence of site-specific information, it is conservatively assumed to be 100% or unity. US EPA released a default RBA recommendation of 60% for arsenic in soils (US EPA 2012); within this recommendation it is stated that not more than 5% of site soils are expected to have an As RBA exceeding 60%. Inclusion of site-specific RBA in the risk calculation allows for a refinement of the evaluation of risk and reduces uncertainty. RBA can be applied similarly to non-cancer estimates of hazard. It is important to note that RBA is applied only to the oral/ incidental ingestion pathway.

Comparison to Bioavailable Arsenic in Background Soils

1. Required if the site is to be cleaned up to background. This is typical of residential land use where naturally occurring concentrations of arsenic in soil often exceed risk-based screening levels. How the bioavailability of As in contaminated soil will be compared to that of background As should be discussed and agreed upon before the start of any bioavailability study. See Attachment 1 for examples of how bioavailable As in background soils can be incorporated into the risk assessment and remedial decision-making.

2. Under certain land use scenarios (e.g. recreational) when exposure is limited and risk-based clean-up goals are greater than background As concentrations, there is no need to consider the bioavailability in background soils.

Conclusions and Recommendations

The California Arsenic Bioaccessibility (CAB) method can accurately predict *in vivo* relative bioavailability of arsenic in California soils as measured in a juvenile swine model. An *in vitro in vivo* correlation was developed for this method using a variety of mineralogical regimes and arsenic sources.
The Human and Ecological Risk Office (HERO) recommends the use of the CAB method for estimating arsenic RBA in soils when arsenic contamination is below 1500 mg/kg. While CAB is DTSC's preferred methodology, HERO does recognize that other methods exist and may be allowed following discussion and proof of adequacy for the specific site being evaluated. Site-specific RBAs can be used in place of the default US EPA RBA of 60%. HERO highlights the importance that all parties (stakeholders, consultants, regulatory agencies) reach consensus regarding the use of site-specific RBA prior to commencing any such evaluation. HERO further encourages community involvement early on to help ensure public support of selected remedies.

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Attachment 1: Applying IVBA to a Hypothetical Site with Desired Unrestricted Land Use: Incorporating Bioavailable Arsenic in Background Soils

<u>Hypothetical Site with Soils Contaminated with Arsenic</u>
Future Land Use: Unrestricted Residential; therefore, background is clean-up goal
Background As in Soils: 30 mg/kg
Arsenic due to contamination: 100 mg/kg
IVBA is evaluated using the CAB Method:
IVBA must be evaluated in both background soils as well as contaminated soils

<u>Scenario 1:</u>
IVBA is greater in background than contaminated soils
IVBA Background: 50%
IVBA Contaminated Soils: 30%

Available As in Background: C_{soil} x IVBA= 30 mg/kg x 0.5 = **15 mg/kg**
Available As in Contaminated Soils: C_{soil} x IVBA= 100 mg/kg x 0.3= 30 mg/kg
Potential site-specific clean up goal for As in contaminated Soils: **50 mg/kg**

Whereas 50 mg/kg x 0.3= 15 mg/kg available Arsenic, which is comparable to the available As in background soils.

<u>Scenario 2:</u>
IVBA is the same in both background and contaminated Soils:
IVBA: 50%

Available As in Background: C_{soil} x IVBA= 30 mg/kg x 0.5 = **15 mg/kg**
Available As in Contaminated Soils: C_{soil} x IVBA= 100 mg/kg x 0.5= 50 mg/kg
Potential site-specific clean up goal for contaminated Soils: **30 mg/kg**

Whereas 30 mg/kg x 0.5= 15 mg/kg available Arsenic, which is comparable to the available As in background soils.
If IVBA is the same in both background and contaminated soils; clean-up goals do not change

<u>Scenario 3:</u>
IVBA is less in background than in contaminated soils:
IVBA Background: 30%
IVBA Contaminated Soils: 50%

Available As in Background: C_{soil} x IVBA= 30 mg/kg x 0.3 = **9 mg/kg**
Available As in Contaminated Soils: C_{soil} x IVBA= 100 mg/kg x 0.5= 50 mg/kg
To achieve the same bioavailable As as in background, contaminated soils would have to be cleaned up to less than 18 mg/kg; however:

DTSC does not require clean-up to below background concentrations, so **30 mg/kg** would remain the potential site-specific clean-up goal.
If IVBA is less in background than in contaminated soils; clean-up goals do not change