Update on Acute Copper SCTL and Arsenic Metabolism in Soil

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Acute Copper Alternative SCTL

Calculating an Updated Acute Copper SCTL

Acute toxicity-based SCTLs were updated using the following equation and assumptions:

$$SCTL_{acute} = \frac{BW}{\frac{1}{RfD_{acute}} \times IR \times CF}$$

All of the assumptions in the equation were updated to reflect current scientific knowledge.

Body Weight Update

$$SCTL_{acute} = \frac{BW}{\frac{1}{RfD_{acute}} \times IR \times CF}$$

Where:
BW = body weight (15.0 kg)

- Child body weight was updated to the current USEPA recommendation of 15 kg from 16.8 kg utilized in Chapter 24, M.D.C.C.

- The updated value is based on more recent body weight data and a slightly different method of averaging body weight.

- The change in body weight has a very small effect on the acute SCTL.

Acute Reference Dose Update

$$SCTL_{acute} = \frac{BW}{\frac{1}{RfD_{acute}} \times IR \times CF}$$

Where:
RfD_{acute} = 0.04 (mg/kg)

- The acute reference dose was updated from 0.09 mg/kg to 0.04 mg/kg.
- The previous reference dose was based on the WHO-recommended upper intake limit of copper for small children.
- The current ATSDR acute oral minimum risk level for copper is 0.01 mg/kg. Therefore, the chronic reference dose was used for the acute scenario.
- This estimate increases the estimated acute toxicity of copper.

Acute Soil Ingestion Rate Update

$$SCTL_{acute} = \frac{BW}{\frac{1}{RfD_{acute}} \times IR \times CF}$$

Where:
IR = soil ingestion rate (1 g)

- The ingestion rate for a pica event was updated from 10 g to 1 g based on recommendations in the 2011 USEPA Exposure Factors Handbook.
- This update decreases the estimated soil ingestion by a factor of 10 and increases the amount of copper allowable in soil for the protection of children.
- This change has the largest effect and increases the acute SCTL.

Updated Acute Copper SCTL

Acute toxicity-based SCTLs were updated using the following equation and assumptions:

$$SCTL_{acute} = \frac{BW}{\frac{1}{RfD_{acute}} \times IR \times CF}$$

Where:

BW = body weight (15.0 kg)

RfD_{acute} = 0.04 (mg/kg)

IR = soil ingestion rate (1 g)

CF = conversion factor (0.001 kg/g)

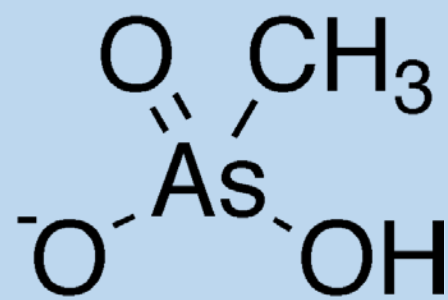
$SCTL_{acute}$ = 600 mg/kg copper

Arsenic Metabolism in Soil

Introduction

- Arsenic is a metalloid present naturally in soil.
- Arsenic exists in both inorganic (metal) and organic (metal attached to a carbon) forms.
- Historical use of arsenic as herbicides in agriculture (and other commercial/industrial activities) has resulted in accumulation in soil.
- Sites with elevated arsenic concentrations present a concern to human health. Chronic low level exposure in drinking water has been associated with cancer of the skin, bladder, lung, liver, kidney, and prostate.

Inorganic



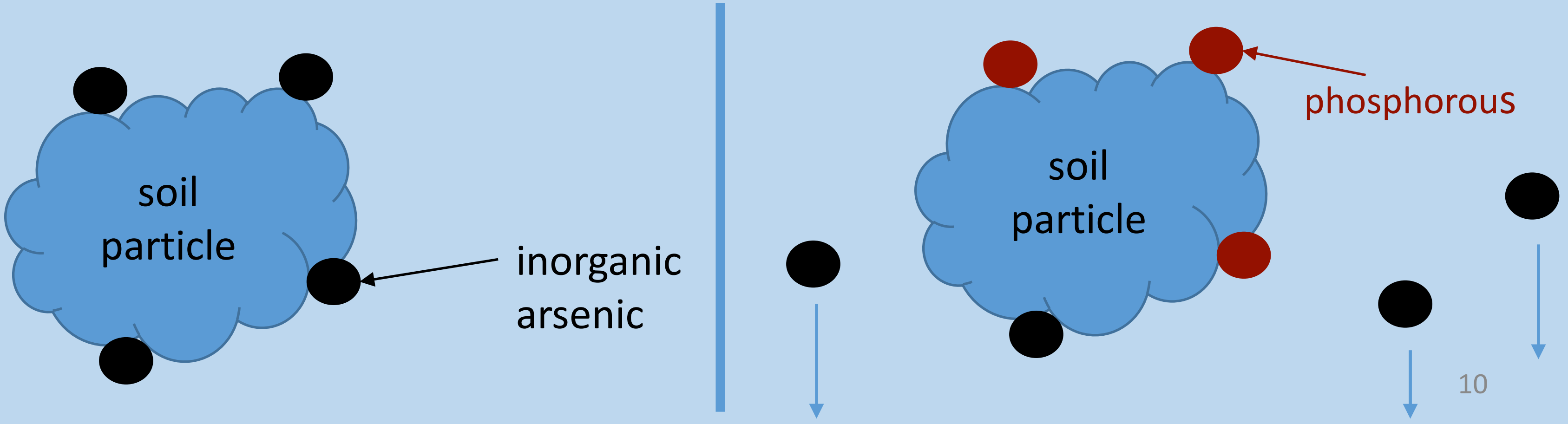
Organic

Inorganic Arsenic

- Most commonly exist in the environment in the +3 and +5 valence states – As^{III} (arsenite) and As^{V} (arsenate), respectively. Arsenate is the most prevalent form found in soil. Arsenite is the most prevalent form under anoxic and wet conditions.

- Inorganic arsenic binds to the negative surface charge commonly seen in soil (especially clay and soil rich in organic matter) and form arsenic-soil complexes. This soil binding prevents leaching so inorganic arsenic tends to persist in soil.

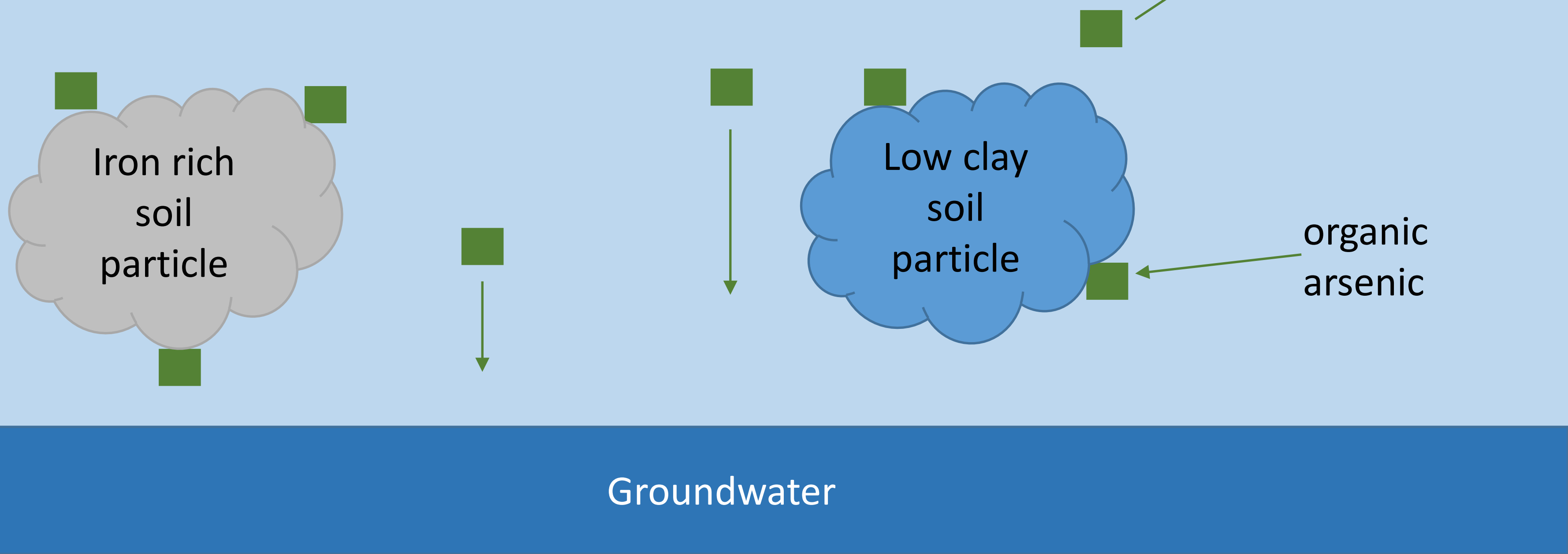
- In the presence of phosphorous, inorganic arsenic competes for binding sites and becomes more mobile.



Organic Arsenic

- Organic arsenicals are also primarily bound to soil, especially soil rich with iron and aluminum particles. However, they are more mobile than inorganic arsenic.
- Can be significantly mobile in soil with low organic carbon or clay content.
- More readily taken up by plants than inorganic arsenic.

uptake by roots



Species-specific SCTLs

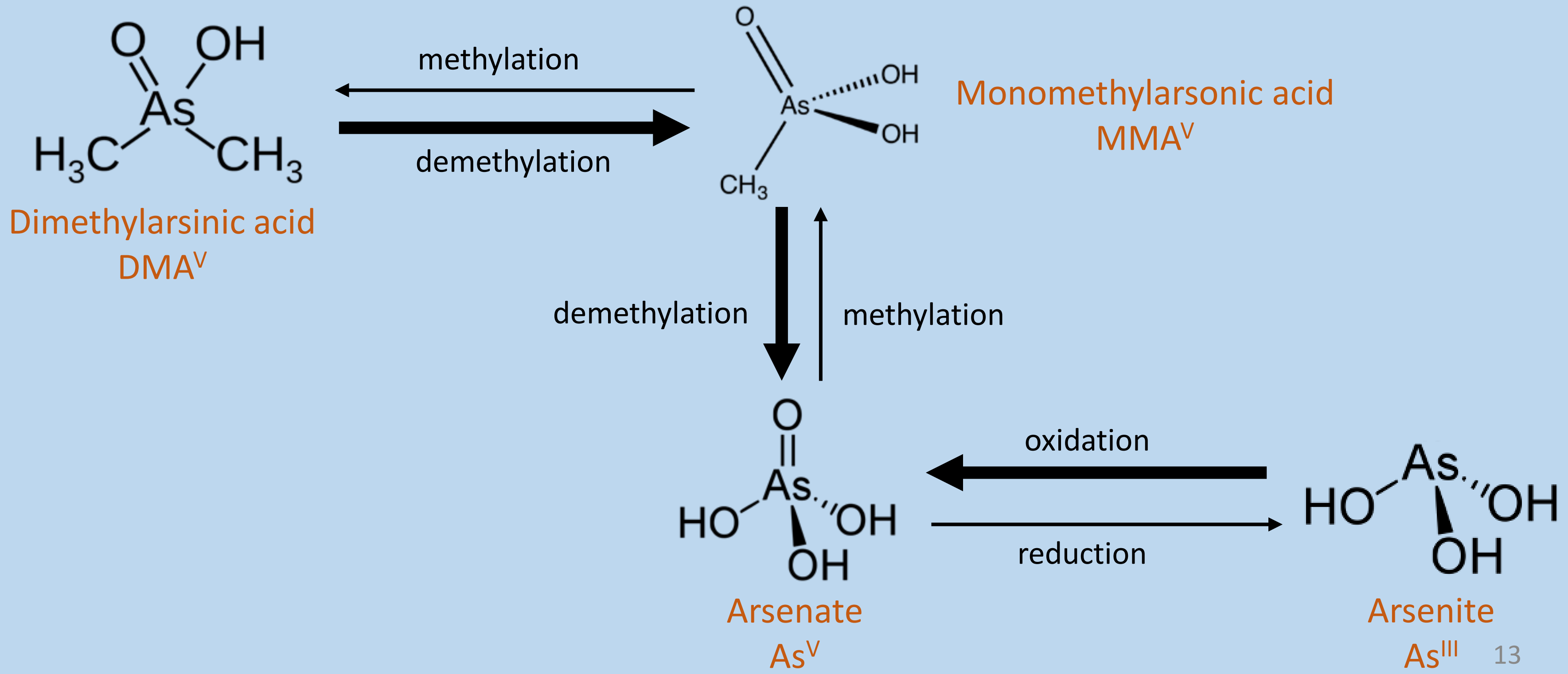
- Current regulatory practice does not distinguish between forms and compares total arsenic concentration to the cleanup target levels.

- This may overestimate toxicity at sites where organic arsenicals were used and are the primary source of arsenic contamination (e.g., agriculture, golf courses) because organic arsenicals are less toxic than inorganic arsenic.

- It has been questioned whether separate soil cleanup target levels (SCTLs) should be developed for different forms of arsenic.

Arsenic Transformation

- Like most metals, arsenic can change form in the environment
- Mediated by soil microorganisms (e.g., bacteria and fungi) and iron and aluminum oxides
- Predominant form differs based on soil type



Arsenic cycle

- The arsenic cycle within and between media (sediment/soil/water/biota/air) is not straightforward due to the variety of biotic and abiotic processes influencing the speciation of arsenic.

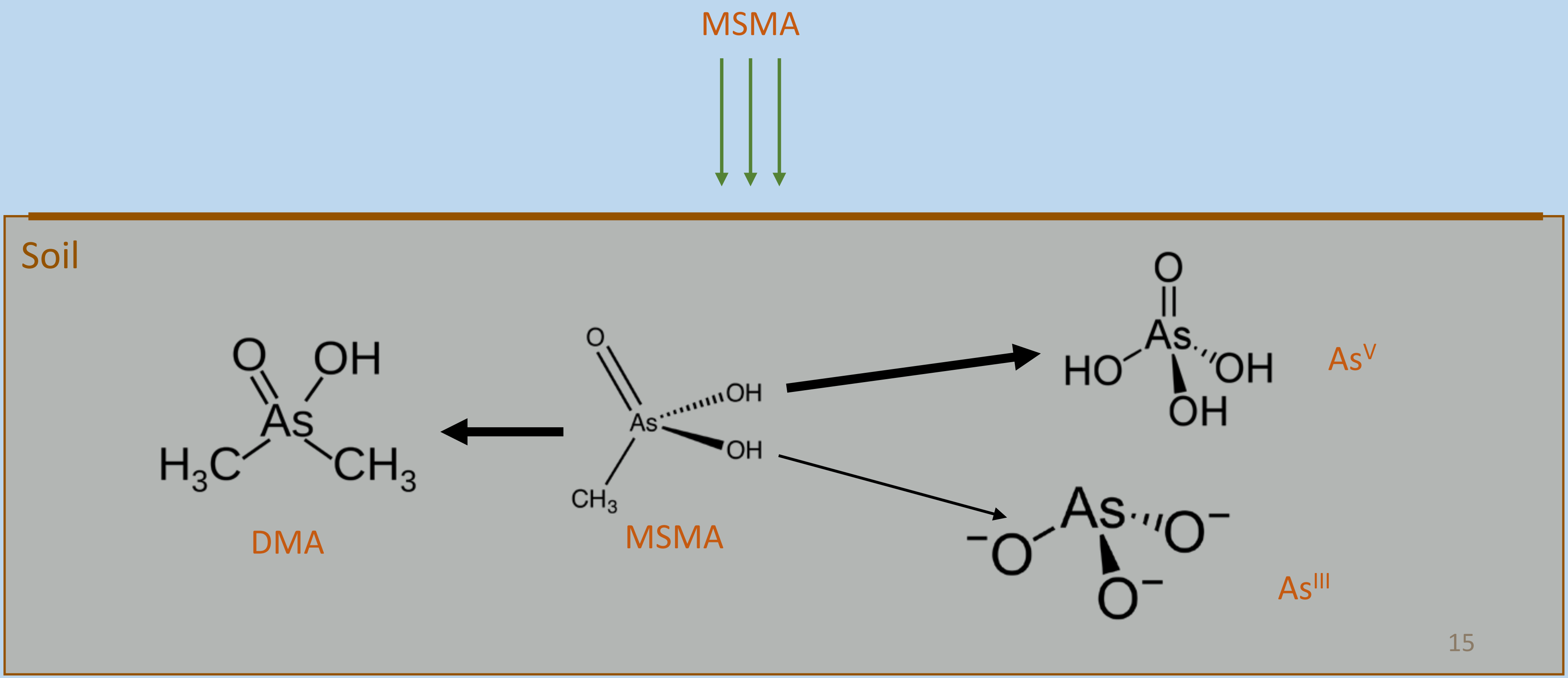
- Quantifying the change between arsenical species is also difficult due to the complex exchange of arsenic in the environment.

- Processes that affect the fate of arsenic include:

  1. Absorption and desorption to soil and sediments
  2. Transformation by microorganisms
  3. Precipitation and dissolution
  4. Accumulation in biological organisms (removal from soil)

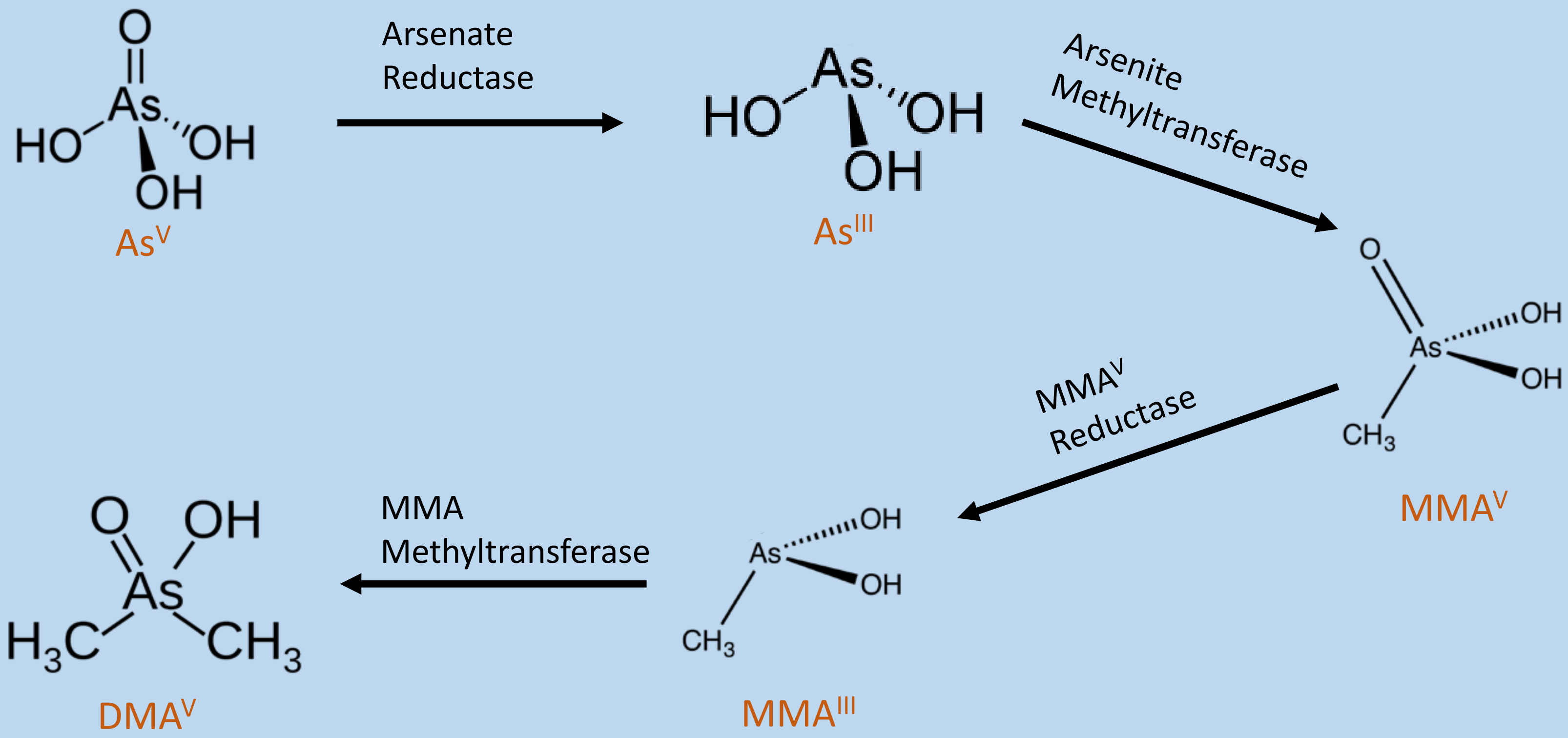
MSMA application study

- A study by Feng et al. in 2005 applied MSMA to constructed soil in an effort to replicate MSMA application at golf courses. All four arsenic species were detected in percolate water.



Arsenic metabolism in humans

- Humans convert inorganic arsenic to organic arsenic, which is more water soluble and more readily excreted in the urine.



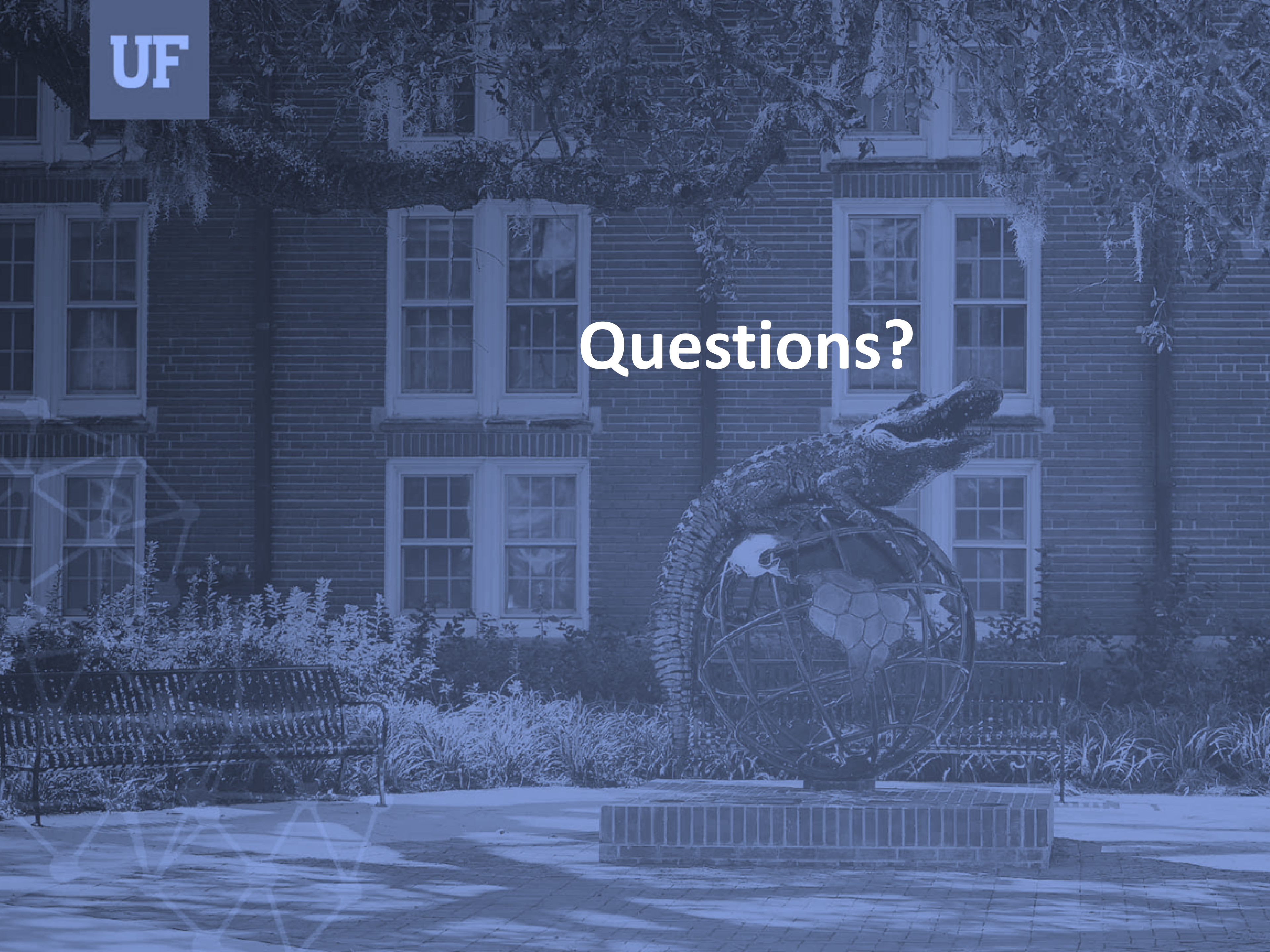
Arsenic regulation

- In order to support a decision to assess the organic and inorganic arsenicals separately, they would need to be stable in the environment.

- Current research suggests these forms are not stable.

- Inorganic arsenic is also transformed to organic arsenic in humans and animals.

- Therefore, the most prudent regulatory approach is to evaluate arsenic contamination in soil without distinguishing between inorganic and organic forms (i.e., in terms of total arsenic).


Questions?

Soil Ingestion and Bioavailability of Contaminants from Soil

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Soil Ingestion

Kids eat dirt? Really?

- Scenario 1: Daily incidental ingestion of soil
  - Small soil particles deposit on skin, get transferred to the mouth during eating or other hand-to-mouth activities, and swallowed.
- Scenario 2: Occasional intentional ingestion of soil.
  - Small children at play
- Scenario 3: Repeated intentional ingestion of soil.
  - Practiced in some cultures as a nutritional supplement or to ease minor stomach ailments.

How much soil is ingested?

- Three primary types of study designs are:
  - Tracer element method – uses excretion of trace elements by subjects and their concentrations in food, soil and other elements of their environment to estimate soil ingestion rate.
  - Biokinetic model comparison – compares predicted blood lead concentrations based on assumed soil ingestion rate with actual blood lead concentrations in subject.
  - Activity pattern method – uses data on hand-to-mouth and object-to-mouth rates to model estimated soil ingestion rate.

- Each of the study designs has strengths and weaknesses.

- The U.S. EPA periodically critically evaluates the literature and develops recommended ingestion rates for human health risk assessment.

- The most recent EPA Exposure Factors Handbook update (2017) recommends 200 mg/day for ages 6 months to <12 yrs and 100 mg/day for 12 yrs through adulthood as upper percentile values for chronic exposure. The recommended rate for soil pica in a child is 1 g/day, and 50 g/day for geophagia in all age groups.

Bioavailability of Arsenic from Soil

Basic Bioavailability Concepts

- Toxicity values for chemicals are based on the doses of chemical received by animal or human subjects and the effects observed. Most toxicities are produced after absorption of the chemical into the body, and oral exposure in toxicity studies is therefore generally to a form of the chemical that is well absorbed from the GI tract.
- The extent of absorption from the GI tract is its oral bioavailability and can theoretically be anywhere between 0 and 100%.
- Every oral toxicity value has an oral bioavailability associated with it.
- It is generally assumed that the oral bioavailability with environmental exposure is the same, i.e., the **relative** bioavailability is 1.0 (100%)
- Relative oral bioavailability (RBA) is the oral bioavailability with environmental exposure divided by the oral bioavailability in the study(ies) used to derive the toxicity values (safe limits of exposure).
- If reliable data indicate that the oral bioavailability is different with environmental exposure (e.g., exposure to the chemical in soil), the risk calculations or risk-based cleanup number can be adjusted using the relative oral bioavailability.

Determining Arsenic Relative Oral Bioavailability from Soil

- For determination of a relative oral bioavailability from soil, regulatory agencies generally require an in vivo (i.e., animal model) study. For arsenic, relative oral bioavailability studies have primarily been conducted in non-human primates, swine, and mice.

- A relative oral bioavailability study requires a determination of arsenic absorption from soil and water (water because the arsenic cancer slope factor is based on studies of people exposed to arsenic in drinking water).

- Literature values for relative oral bioavailability from samples from various arsenic-contaminated sites range from <10% to about 80%.

- A relative oral bioavailability study for a site costs in the hundreds of thousands of dollars. Consequently, they are not routinely performed.

- FDEP funded a study of arsenic relative oral bioavailability in five soil samples from different types of sites in Florida (Roberts et al., Tox. Sci., 2002). From this study, FDEP adopted a default relative oral bioavailability of 0.33 for arsenic.

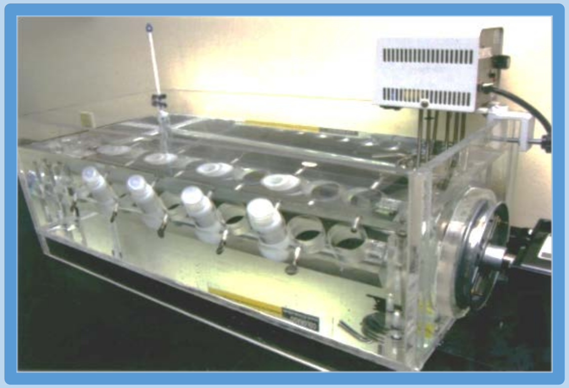
A Less Expensive Way to Estimate As Relative Oral Bioavailability

- Considerable effort has been expended to develop a more rapid and less expensive way to determine arsenic relative oral bioavailability on a site-specific basis.

- In vitro methods based upon arsenic bioaccessibility from soil have been developed to estimate bioavailability.
  - In this context, bioaccessibility refers to the fraction of chemical in soil that can be extracted under simulated gastrointestinal conditions.

- EPA Method 1340 has recently been adapted and approved by the US EPA for estimating the relative oral bioavailability of arsenic from soil.

- The state of California has also developed and approved a method with a similar approach, but somewhat different extraction conditions (California Arsenic Bioaccessibility method).



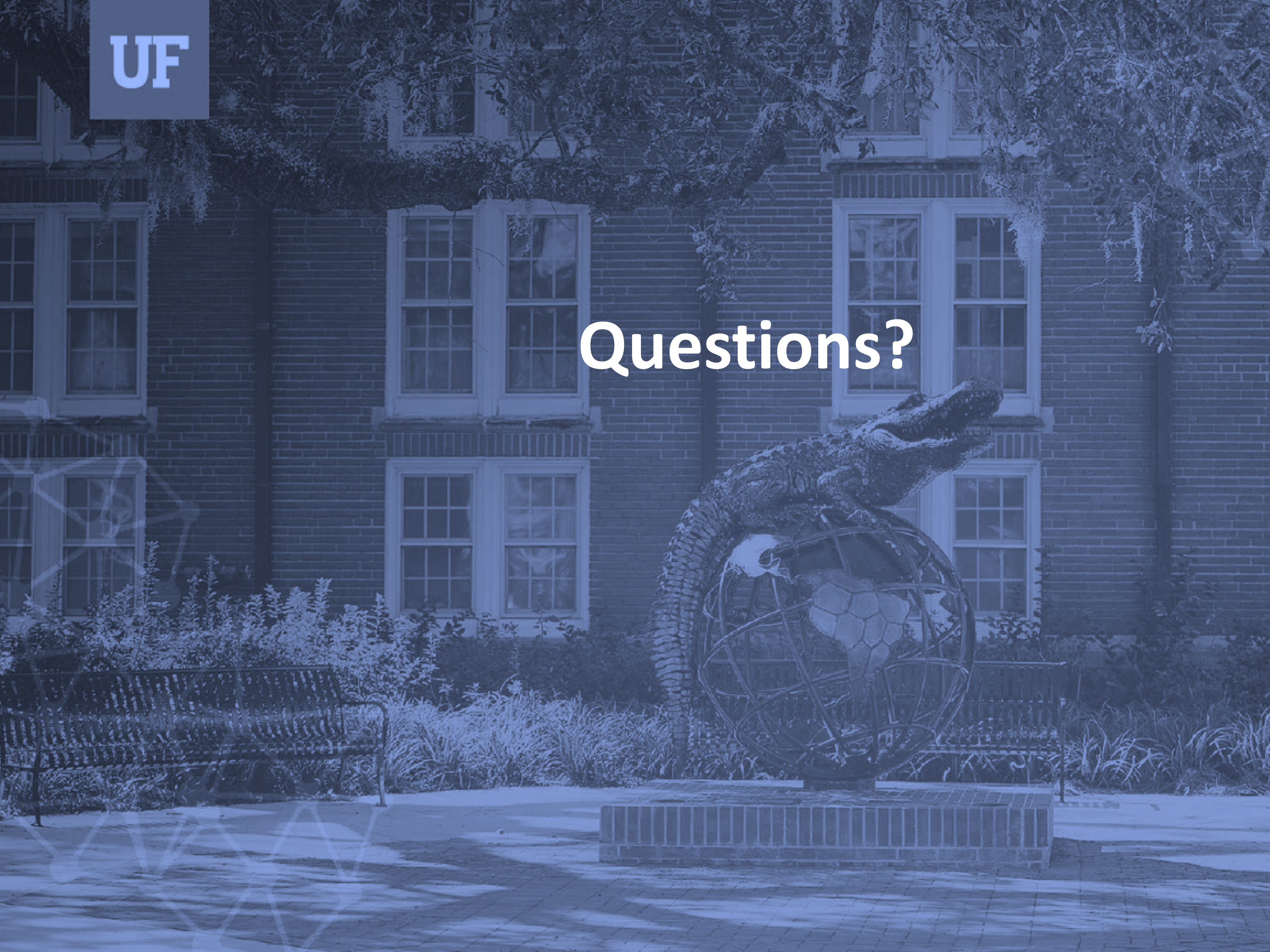
Important Considerations

- A bioavailability adjustment applies only to a risk-based cleanup goal. If the applicable cleanup goal is a background arsenic concentration, the relative oral bioavailability is irrelevant.

- The Miami-Dade County DERM Anthropogenic Background Study (published April 3, 2014) indicates an arsenic background of 7 ppm for surficial soil for the area South of SW 88th street. Elsewhere in the state, the background concentration is determined on a site-specific basis.

- The risk-based residential and commercial-industrial cleanup goals for arsenic are based upon a default relative oral bioavailability of 0.33. A site-specific arsenic relative oral bioavailability determination could cause the risk-based cleanup goal to go up (if the relative oral bioavailability is less than 0.33) or down (if it is more than 0.33).

- For sites in Miami-Dade County, a site-specific arsenic relative oral bioavailability would have to be very low (less than 10%) to increase the default residential risk-based cleanup goal (2.1 ppm) higher than 7 ppm.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