California Arsenic Bioaccessibility (CAB) Method:

Bench-Top Prediction of Relative Bioavailability in Contaminated Soils

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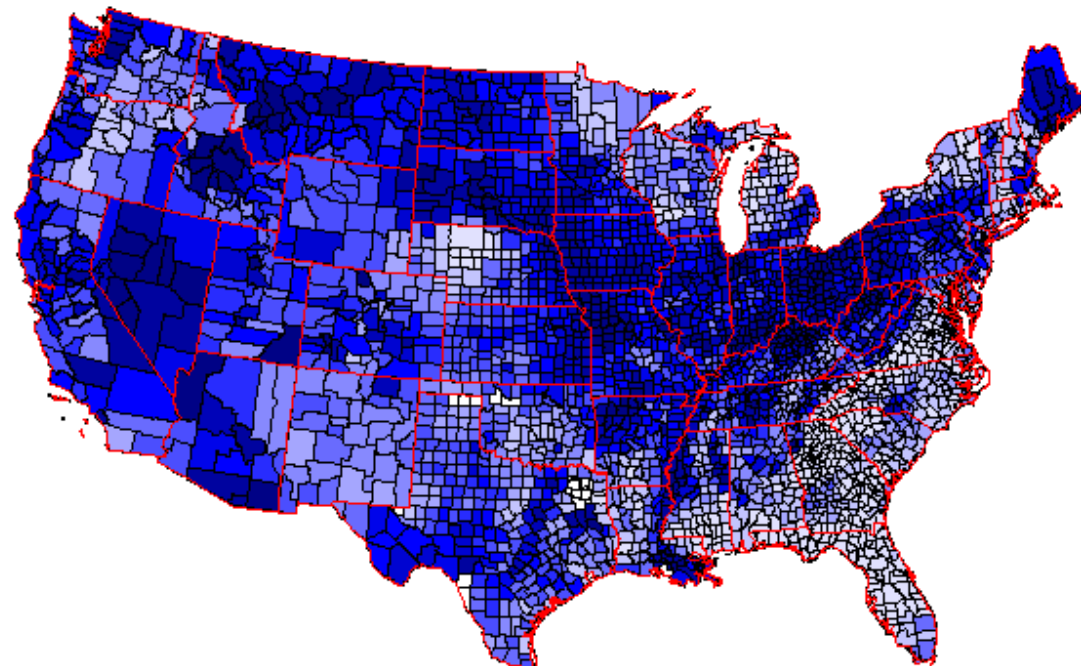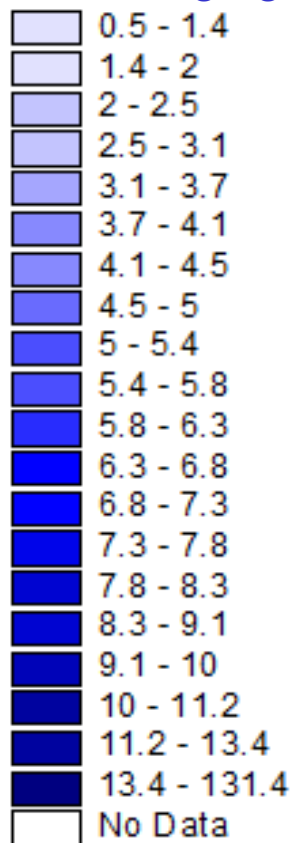
Background Arsenic in Soils

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Arsenic mg/kg

- 0.5 - 1.4
- 1.4 - 2
- 2 - 2.5
- 2.5 - 3.1
- 3.1 - 3.7
- 3.7 - 4.1
- 4.1 - 4.5
- 4.5 - 5
- 5 - 5.4
- 5.4 - 5.8
- 5.8 - 6.3
- 6.3 - 6.8
- 6.8 - 7.3
- 7.3 - 7.8
- 7.8 - 8.3
- 8.3 - 9.1
- 9.1 - 10
- 10 - 11.2
- 11.2 - 13.4
- 13.4 - 131.4
- No Data

US EPA Regional Screening Level: 0.68 mg/kg*
CA DTSC Screening Level: 0.11 mg/kg*
*Assume USEPA Default of 60% Bioavailability

https://mrdata.usgs.gov/geochem/doc/averages/as/usa.html

Why is Bioavailability Important?

- Improve Accuracy of Human Health Risk Assessments / Decrease Uncertainty

- Standard Toxicity Criteria is based on soluble forms of arsenic (e.g. Sodium Arsenate)

- Minerals in soil bind arsenic and can reduce bioavailability and toxicity

Bioaccessibility vs. Bioavailability

ITRC, Bioavailability in Contaminated Soils Guidance, 2017
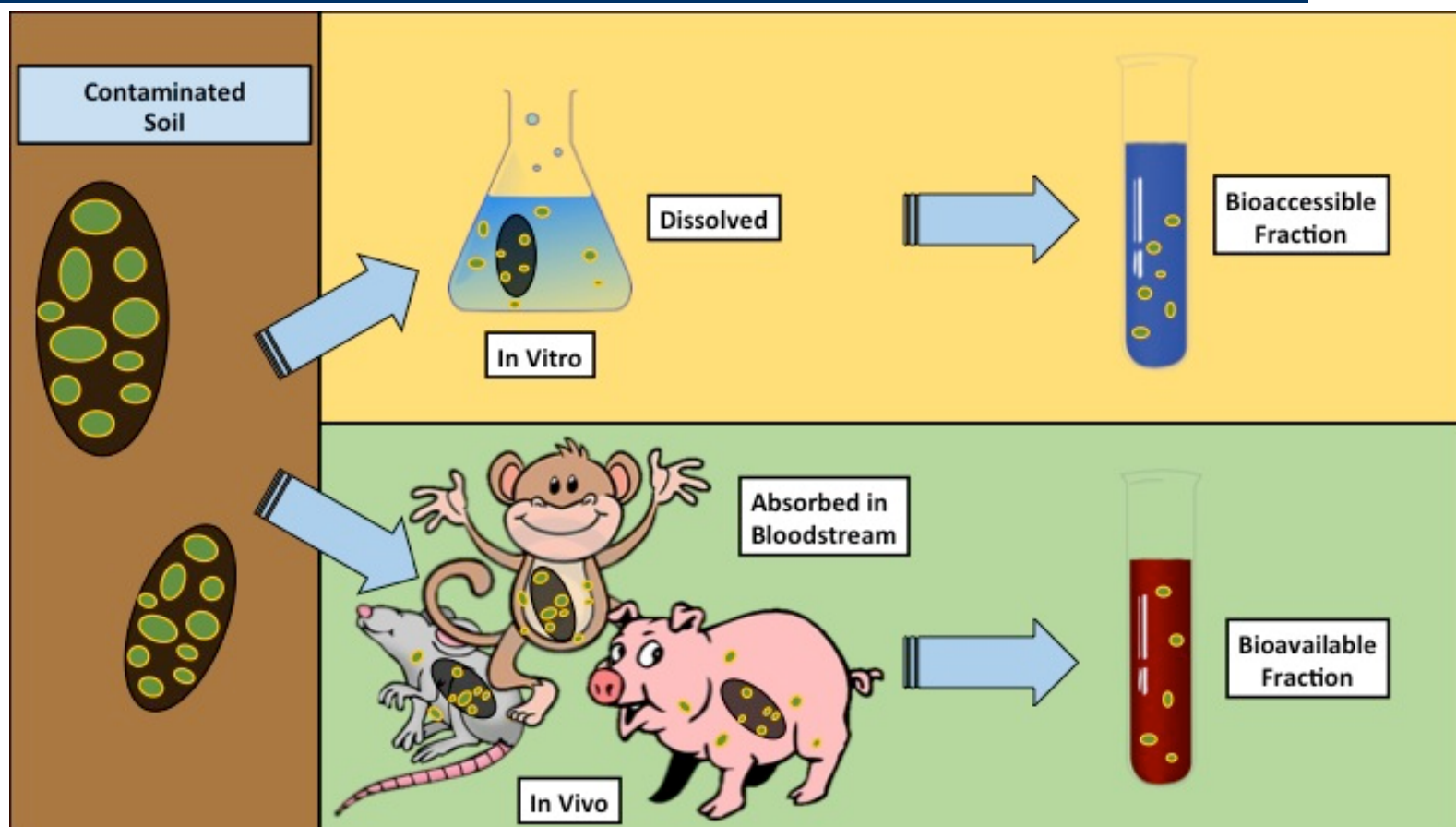
Qualities of *in vitro* Methods

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- Mimic how arsenic is released from soil particles
- Dissolved metals compared to total metals from soils of the same particle size used in the extraction
  - i.e If soils are sieved prior to extraction the total metals should be measured in those sieved soils.
  - IVBA (%)= dissolved As/Total As x 100
- IVIVC (*in vivo in vitro* correlation)
  - Model predicts *in vivo* RBA from *in vitro* IVBA

DTSC Arsenic Bioavailability Study*

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Objectives

- Improve correlation between in vitro and in vivo methods through improvement of the in vitro simulated gastro-intestinal assay.

- Establishing a methodology for implementation at sites throughout California.

# Methods Available at the Start of Study

- In Vivo Relative **Bioavailability** (RBA)
  - Swine, Mouse, Monkey
  - Expensive and Time Consuming

- In Vitro **Bioaccessibility** (IVBA)
  - Most Developed for Pb
  - Underpredicted Bioavailability in High-Iron Soils

Sample Collection

- 25 Soil Samples Collected from Empire Mine State Historic Park and Rattlesnake Gates

- 15 to 12,095 mg/kg As;

  median 2,980 mg/kg As
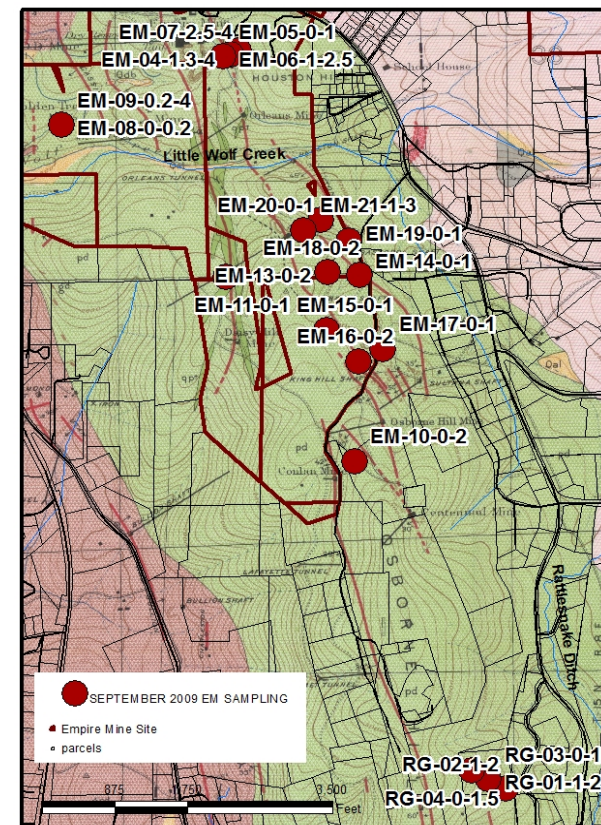
EMPIRE MINE STATE PARK
SEPTEMBER 2009
EM SAMPLE LOCATIONS

Materials and Methods
In vivo Bioavailability (RBA)

- Groups of 5 pigs dosed daily
- Absorbed As estimated by As excreted in urine over 48 hrs
- Urinary As excretion - a linear function of dose and independent of time after day 5

RBA Data Evaluation

- As excreted in urine = C x V (L/48 hrs)

- Plot As urine vs As dosed
  Urinary **E**xcretion **F**raction is slope of this line

- $RBA_{(x)} = UEF_{(x)}/UEF_{(Na\ arsenate)}$

- Note: Each RBA is a ratio of slopes
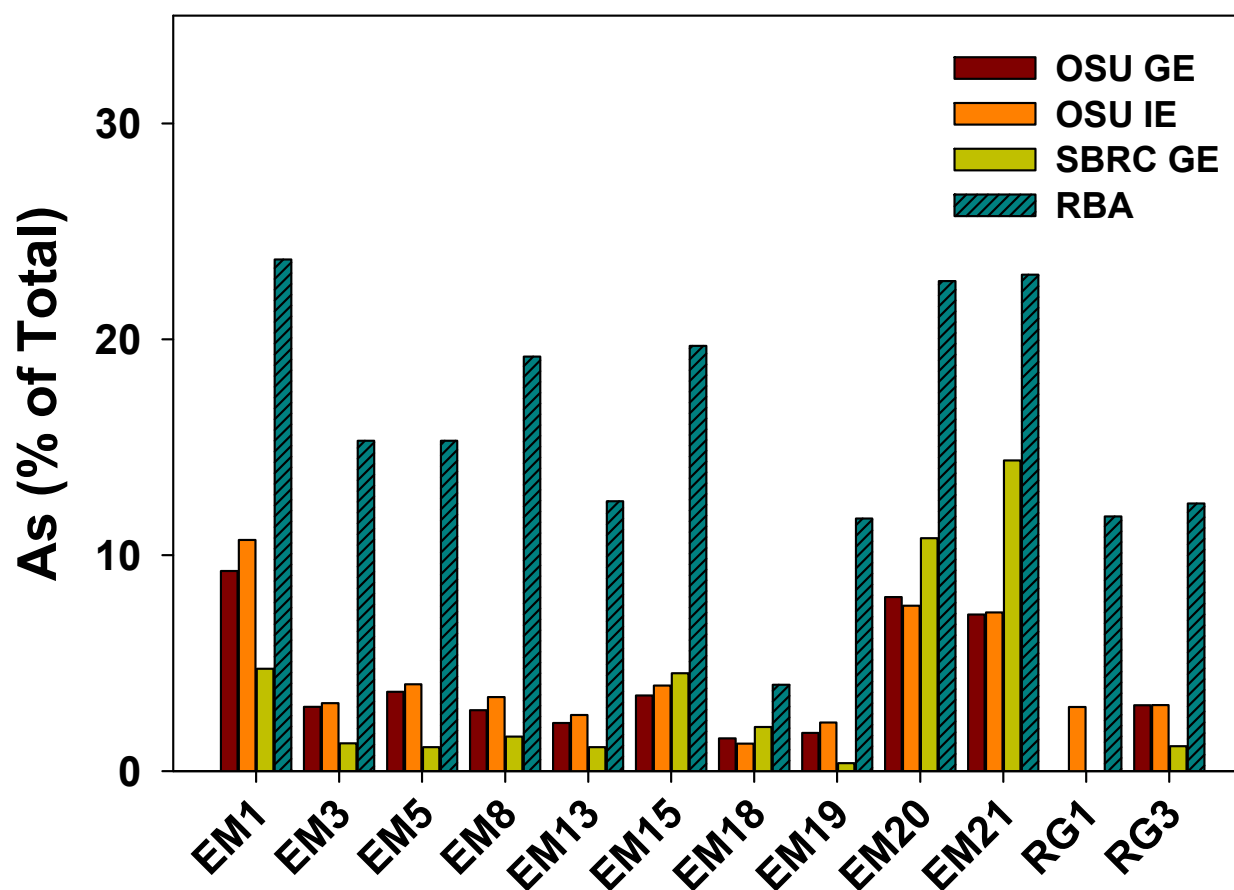
Study RBA Results 4% to 24%

In vitro Bioaccessibility

- Existing Methods Tested:
  - OSU In Vitro Gastric Extraction
  - OSU In Vitro Intestinal Extraction
  - SBRC/US EPA Method Extraction

- New Method Tested:
  - California Arsenic Bioaccessibility (CAB) Method

Existing In Vitro Methods Underestimate Bioaccessibility

Method Comparison
OSU-IVG vs. CAB

OSU-IVG

- 1g:150mL
- GE: 0.1M NaCl, 1%pepsin, pH 1.8, 1 hour
- IE: GE + bile & pancreatin, pH 6.5, 2 hours

CAB

- 1g:150mL
- GE: 0.1M NaCl, 1%pepsin, pH 1.5, **ascorbic acid**, 2 hour

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Development of CAB Method Regression to Predict RBA

Soil Sources Include:

- Mining
  - Gold, Silver, Zinc, Copper, and Lead
  - Tailings and Slag

- $PbAsO_4$ Orchard Pesticide

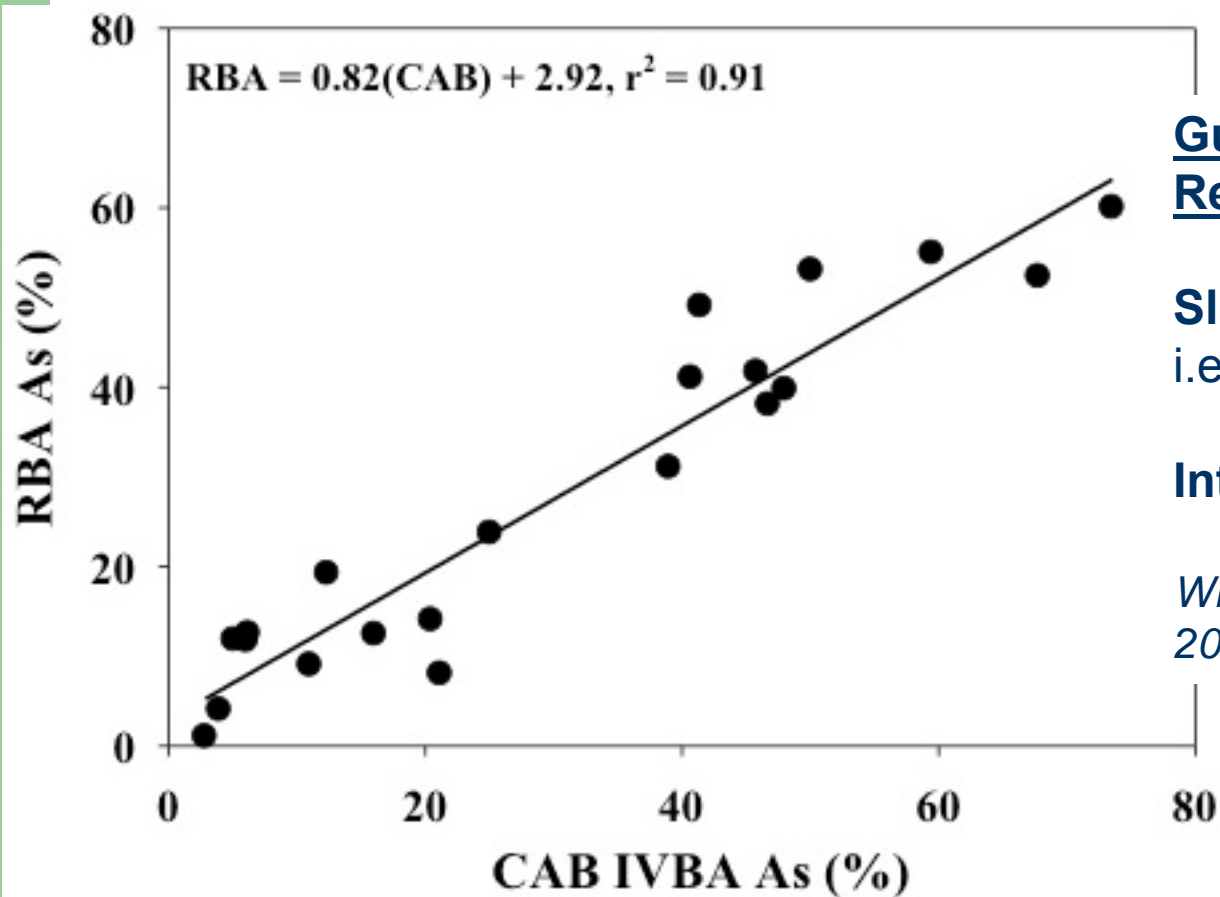## Wide Range of RBA:

- 1% to 60%

Robust Regression between CAB & RBA

$$RBA = 0.82(CAB) + 2.92, r^2 = 0.91$$

Guidelines for a Robust Regression:

Slope 0.8 - 1.2
i.e. in vitro ≈ in vivo $r^2 > 0.6$

Intercept ≠ zero

Wragg et al.
2011, Sci. Total Environ.
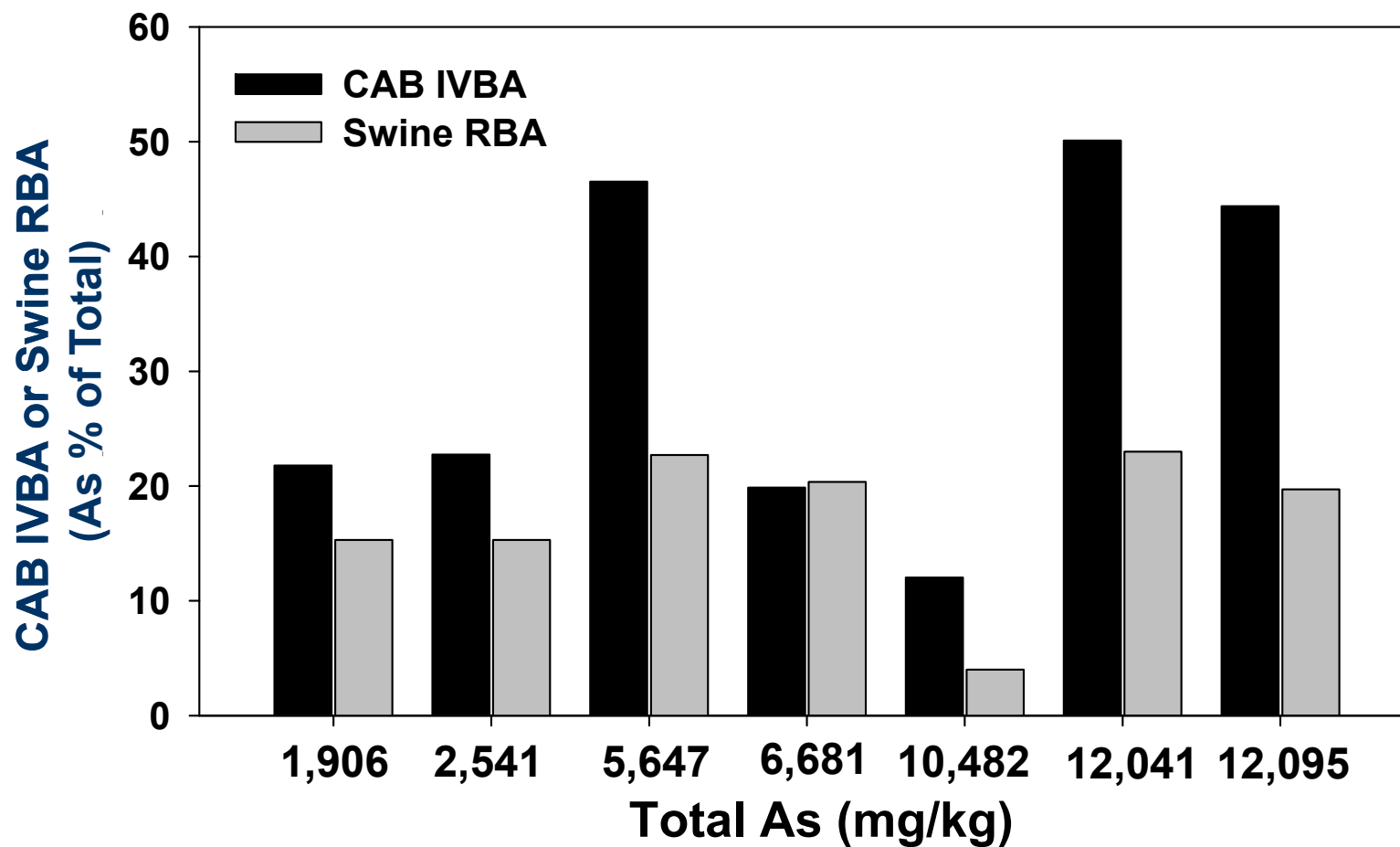
CAB Predicts RBA for Soils with Low to Moderate Total As
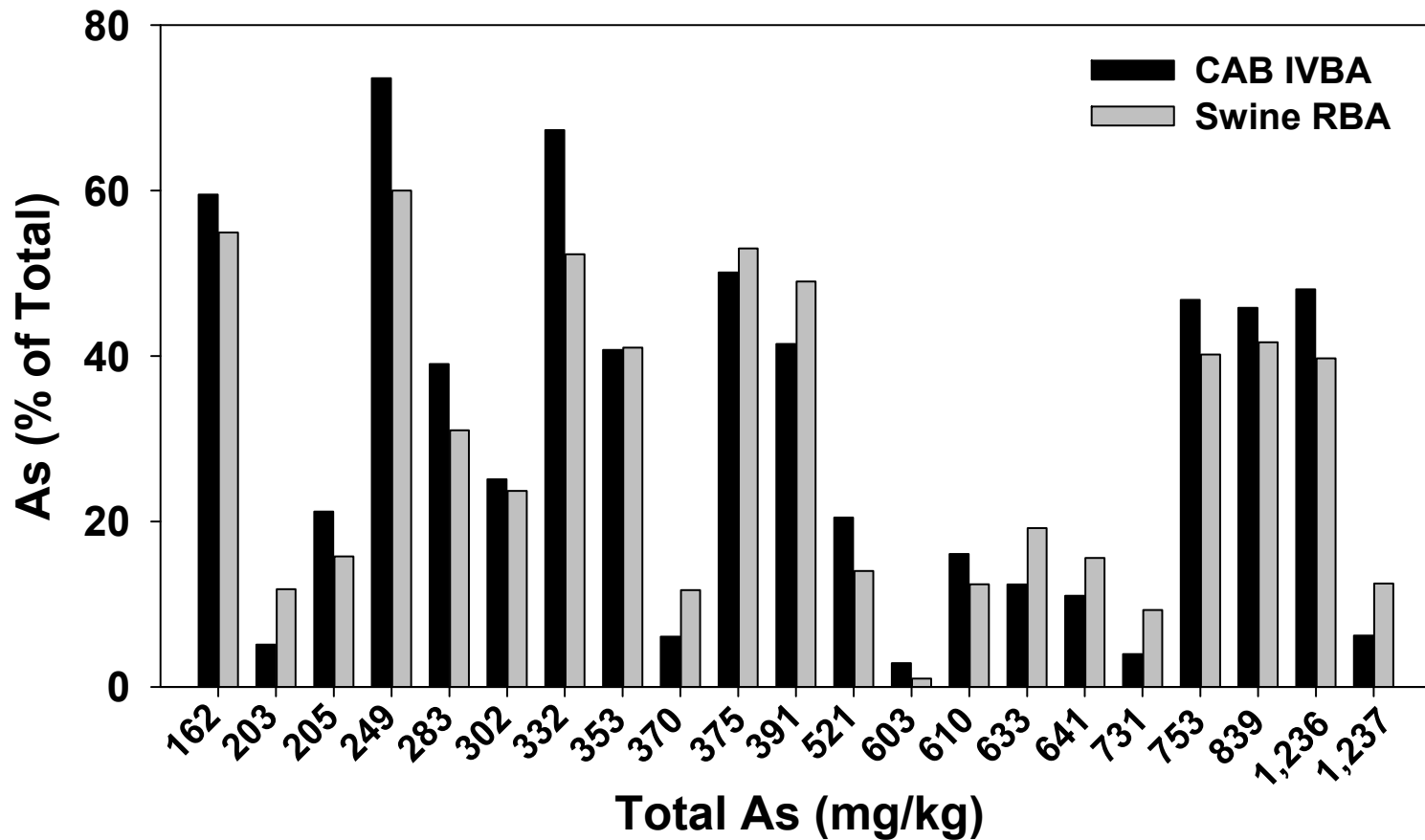
CAB not for Soils with Arsenic >1,500mg/kg

CAB Method is Reproducible

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- **Ohio State University**

- **Prima Environmental**
  - Intra-laboratory RSDs: Mean 3.8%, Median 3.9%
  - Inter-laboratory RSDs: Mean 8.5%, Median 4.5%

- **Brooke's Applied Sciences**
  - In Progress (preliminary results 👍)

Conclusions on CAB Method

- Accurately predicts swine RBA in various soil types when Arsenic is <1,500 mg/kg

- Inexpensive and Repeatable

- Improves remedial decisions without compromising health protection

New California Guidance

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

HUMAN HEALTH RISK ASSESSMENT (HHRA) NOTE

HERO HHRA NOTE NUMBER: 6

RELEASE DATE: AUGUST 22, 2016

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

https://www.dtsc.ca.gov/AssessingRisk/upload/HHRA-Note-6-CAB-Method-082216.pdf

Decision Matrix for Using CAB

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Exposure Scenario	Arsenic Concentration in Soil			
	Low (<100)	Medium (100-500)	High (500-1000)	Very High (>1000)
Residential	🟩	🟨	🟥	🟥
Commercial/ Industrial	🟩	🟩	🟨	🟥
Recreational	🟩	🟩	🟧	🟧

Likelihood that site specific RBA will change remedial decisions

🟩 high   🟩 medium high   🟨 medium low   🟥 low

Acknowledgements

http://www.dtsc.ca.gov/InformationResources/Arsenic_Relative_Study.cfm