Method Comparison for Bioaccessible Lead and Arsenic in Soils

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Introduction

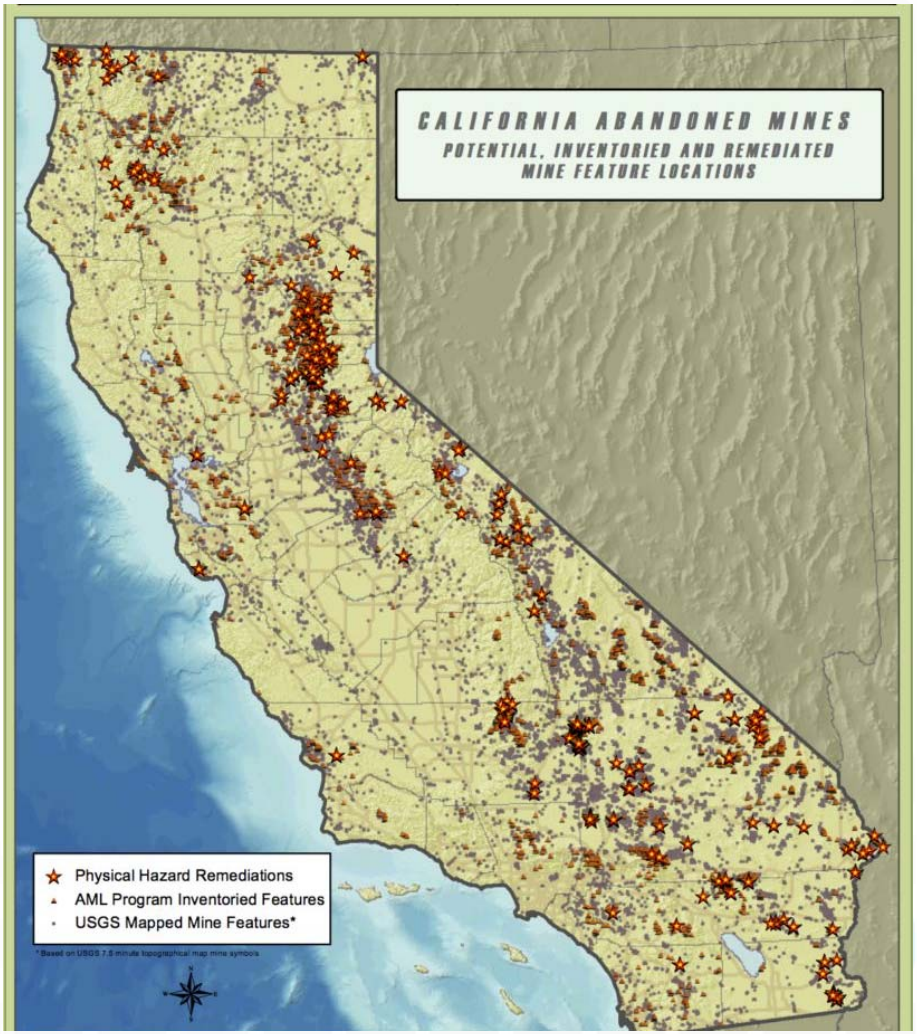
- Bioaccessibility extraction methods comparison
- Arsenic Speciation
- Analytical issues and resolutions

Problem – High Metals in Soils…a lot of Soils

- Multiple sites with high lead and/or arsenic levels
- Which sites to address first?
- Decisions based on total concentration vs bioaccessible

California's Gold Problem

- High Arsenic common in gold mines
- California has tens of thousands of abandoned or inactive gold mines



Health & Environmental Hazards of Arsenic & Lead

- Possible ingestion by small children
- Possible contaminated crops grown in soils with high arsenic or lead

How to measure metal concentration?

- Total Concentration
- Bioaccessible vs bioavailable
  - *In vitro* vs. *In vivo*
  - *In vitro* bioaccessible (IVBA)
  - IVBA = bioaccessible ÷ Total

Testing for Bioavailable Metals

- *In vivo* – swine studies
  - Time consuming
  - Expensive
  - Plus…. Gross (Poor pigs) ☹

Testing for Bioaccessible Metal

- Arsenic (As) – California Arsenic Bioaccessibility (CAB) Method
- Lead (Pb) – EPA Method 1340 "*In Vitro* Bioaccessibility Assay for Lead in Soil"

Bioaccessible to Bioavailable

- Lead: RBA = (0.878 × IVBA) – 0.028
- Arsenic: RBA = (0.81 × IVBA) + 3.2

- RBA – Relative bioavailable
- IVBA - *In vitro* bioaccessible

Bioaccessible Extraction Methods

- Soil Samples
  - Dried
  - Sieved
  - Acid extraction
  - Filtered
  - Extraction fluid analyzed for total As & Pb
  - Separate digestion by EPA 3050B for total concentration results

CAB vs EPA 1340 Extraction

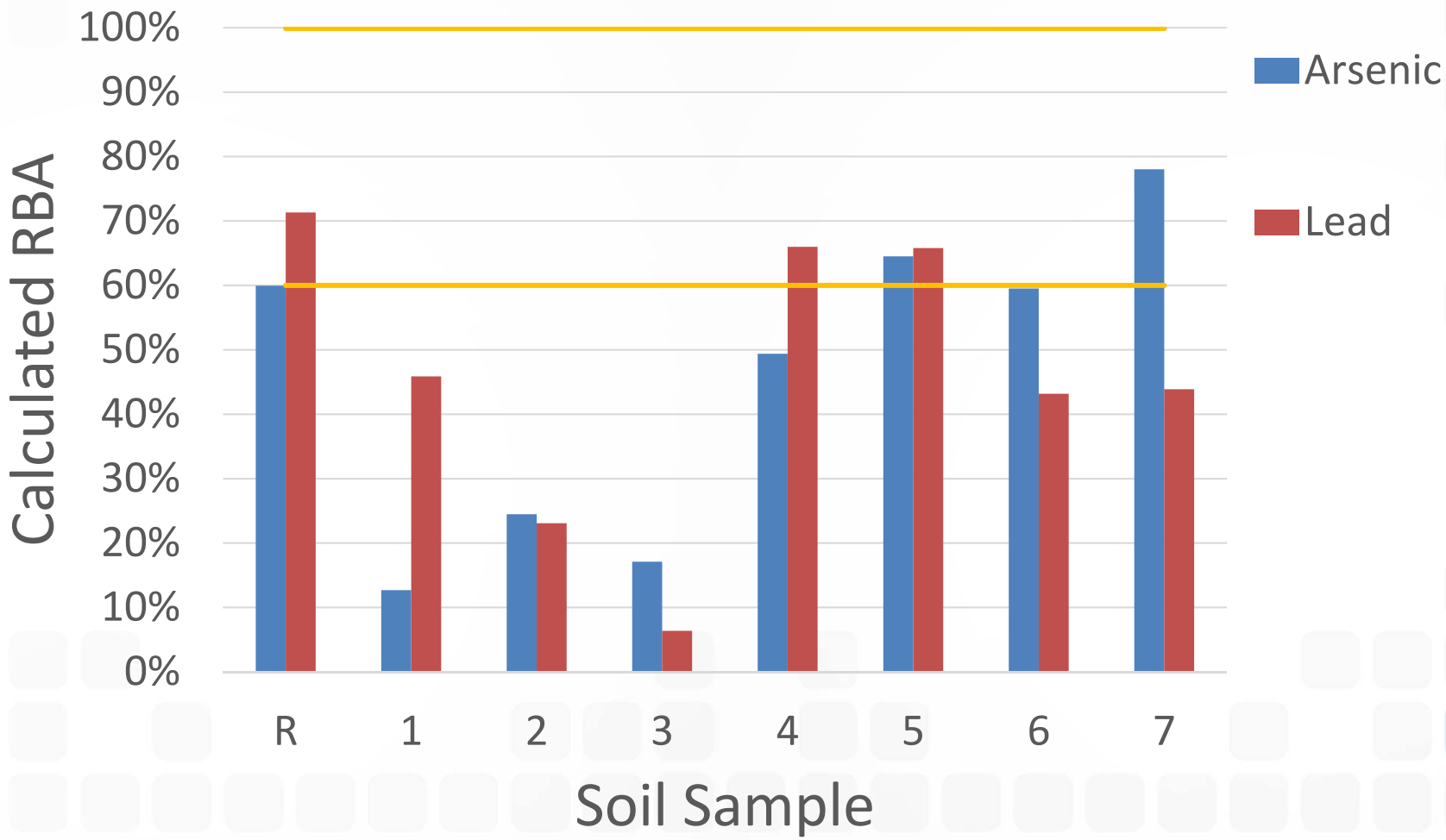
Comparison of CAB and EPA 1340 Extraction Methods		
	EPA 1340	CAB
Initial Sample Mass	1.0 grams	1.0 grams
Extraction Solution Volume	100 mL	150 mL
Incubation Temp	37 ± 2 °C	37 ± 2 °C
Rotation Speed	30 ± 2 rpm	30 ± 2 rpm
Incubation Time	60 minutes	120 minutes
Extraction Time	60-90 minutes	120-145 minutes
Extraction Fluid	Glycine Hydrochloric Acid	Pepsin NaCl Ascorbic Acid Hydrochloric Acid
Extraction pH	1.5 ± 0.5 pH units	1.50 ± 0.01 pH units
Number of pH adjustments	1	2
Number of pH checks	2	3

Extraction Materials

Analysis of Extraction Solution

- Extraction fluid analyzed for total As and Pb concentration

Calculated Relative Bioavailability (RBA)



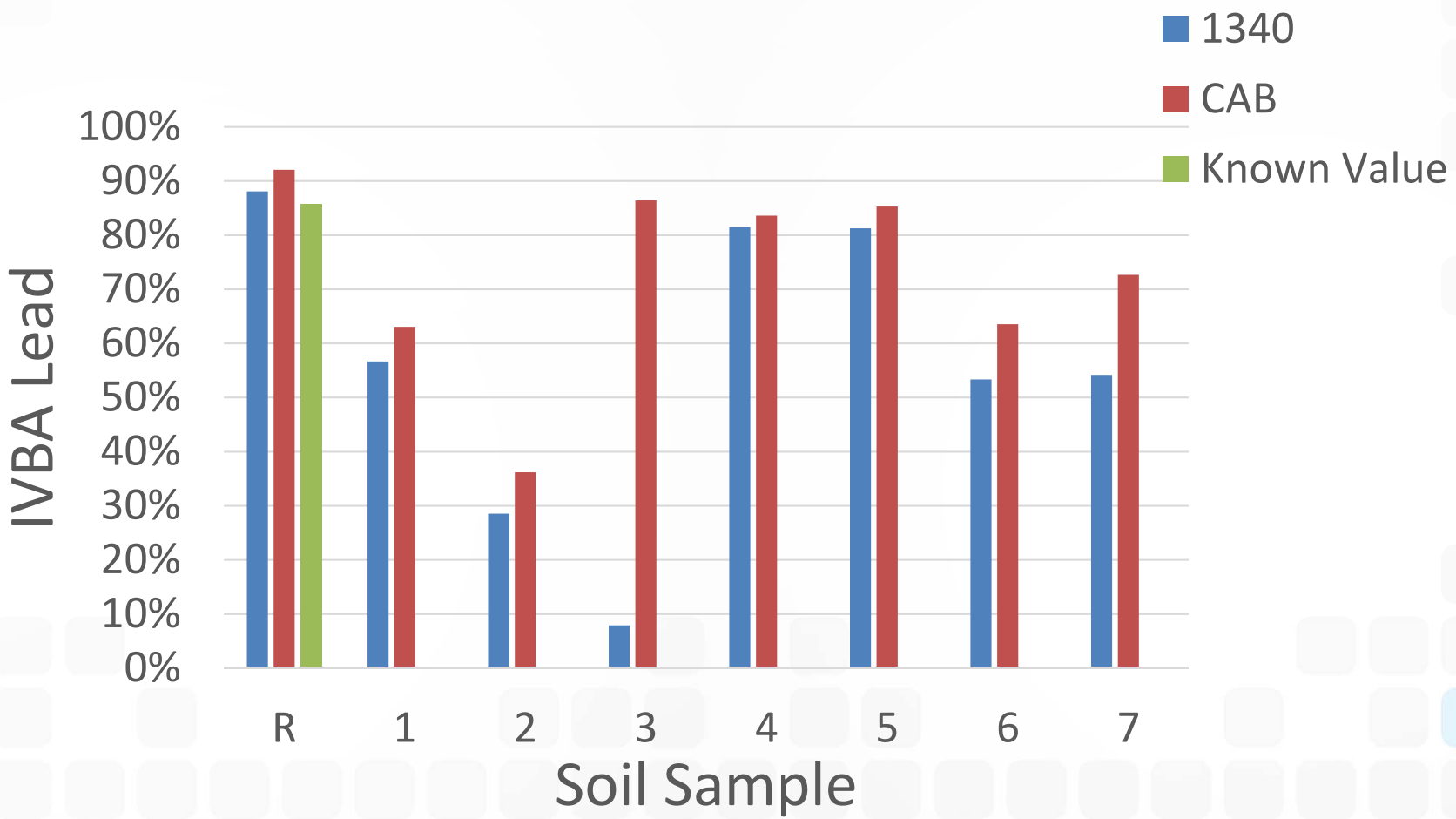
What if....

- CAB & EPA 1340 methods very similar
- Could we use CAB for both arsenic & lead?
- Could we use EPA 1340 for both lead & arsenic?

California Soil Samples

- CAB Round Robin Study
- Soils extracted by both methods
- Extracts analyzed for both As & Pb by ICP-MS
  - Agilent 8800 Triple Quad (QQQ)

EPA 1340 & CAB Results for Lead



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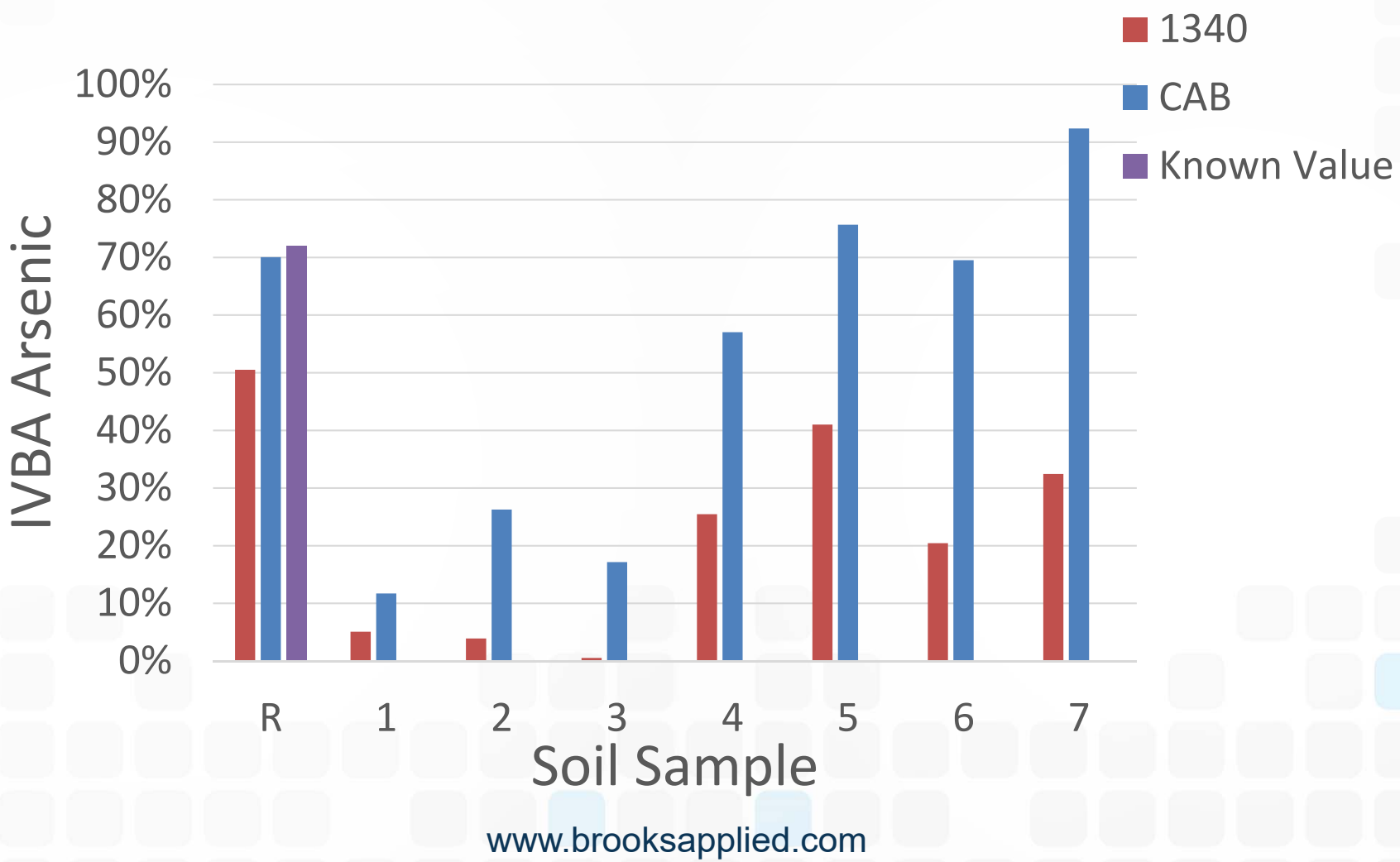
EPA 1340 & CAB Results for Arsenic



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So…

- Can you use CAB or EPA 1340 for both As & Pb???
- CAB over-predicts bioaccessible Pb
- EPA 1340 under-predicts bioaccessible As

Quality Control – EPA 1340

EPA 1340 Extraction Quality Control Sample Recoveries						
	As (mg/kg)	Percent Recovery	Relative Percent Difference	Pb (mg/kg)	Percent Recovery	Relative Percent Difference
Method Blank 1	0.002			0.01		
Method Blank 2	0.0004			0.004		
Method Blank 3	U*			0.007		
Blank Spike	9.96	100%		1.04	104%	
Reference Material	54.1	70.0%		1220	111%	
Source - Duplicate	123			1820		
Duplicate	121		1.00%	1760		3.00%
Source - Matrix Spikes	467			3230		
Matrix Spike**	475	79.0%**		3170	-6230%**	
Matrix Spike Duplicate**	472	57.0%**	33.0%**	3200	-3200%**	64.0%**

*U designates recovers below detect limit that could not be quantified

**due to high As & Pb concentrations in source sample Matrix Spikes and Matrix Spike Duplicates are not expected

Quality Control - CAB

CAB Extraction Quality Control Sample Recoveries						
	As (mg/kg)	Percent Recovery	Relative Percent Difference	Pb (mg/kg)	Percent Recovery	Relative Percent Difference
Method Blank 1	0.215			0.213		
Method Blank 2	0.214			0.111		
Method Blank 3	0.181			0.114		
Blank Spike	10.8	108%		1.06	106%	
Reference Material	74.9			1290	116%	
Source - Duplicate	227			1910		
Duplicate	234		3.00%	1850		3.00%
Source - Matrix Spikes	195			1580		
Matrix Spike**	200	46.0%**		1600	2190%**	
Matrix Spike Duplicate**	203	78.0%**	52.0%**	1610	2740%**	61.0%**

**Note: due to high As & Pb concentrations in source sample Matrix Spikes and Matrix Spike Duplicates are not expected

….and your point is?

- Important to use extraction proceed for designed target analyte
- CAB developed for bioaccessible arsenic
  - OK for Arsenic
  - NOT OK for Lead
- EPA 1340 developed for bioaccessible Lead
  - OK for Lead
  - NOT OK for Arsenic

I wonder if.... Arsenic Speciation

- Forms of Arsenic
  - Arsenite – As(III)
  - Arsenate – As(V)
  - Monomethyl arsenic acid (MMA)
  - Dimethylarsenic acid (DMA)
  - Plus many others

Arsenic Speciation Extraction & Analysis

- Soils exposed to extraction solution
  - Varying depending on target arsenic species

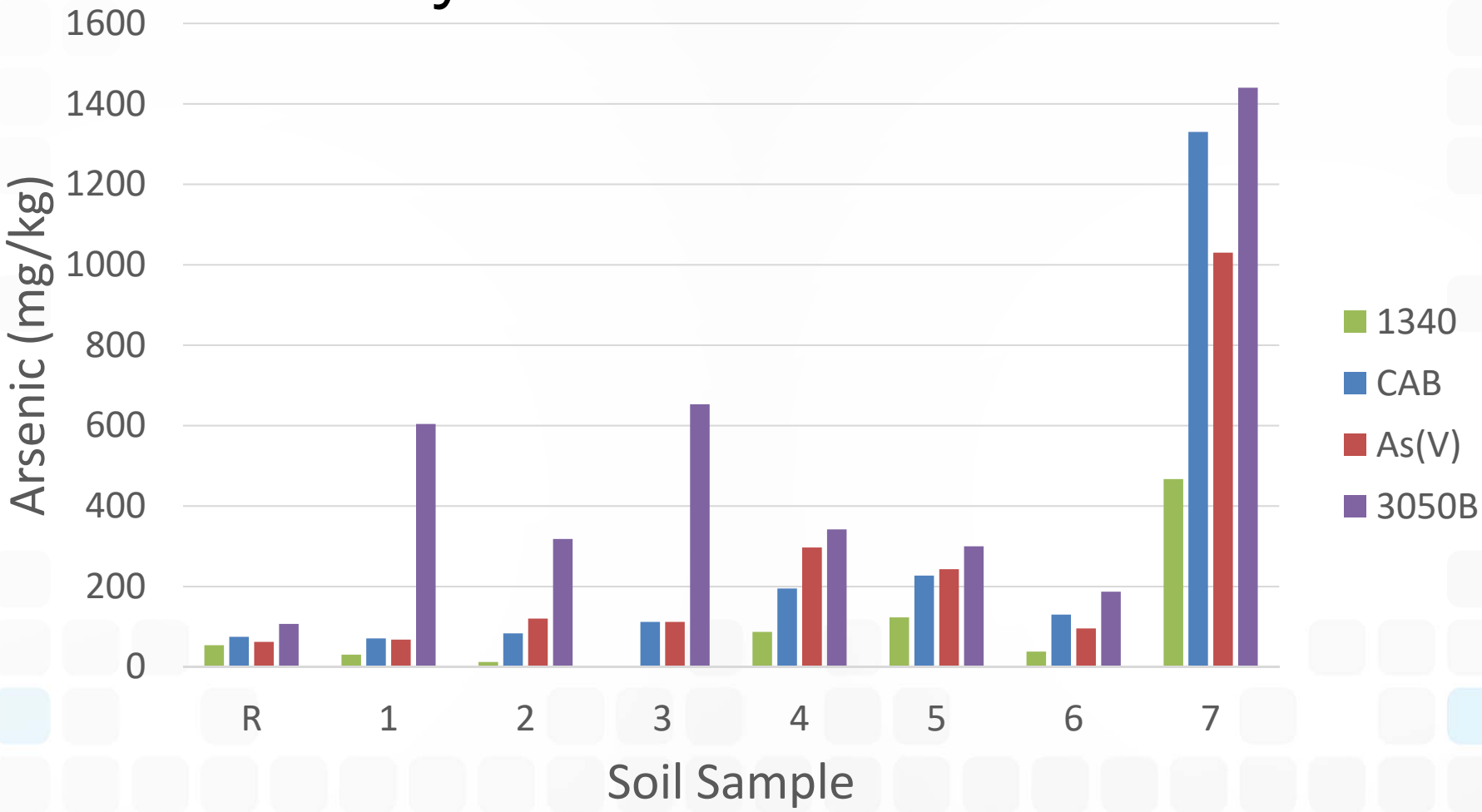
- Speciation extraction soils analyzed by IC-ICP-MS
  - Agilent 7700

As Speciation Results

Comparison of Arsenic, Bioaccessible Arsenic, and Arsenic Species (mg/kg)						
Sample	3050B	CAB	As(III)	As(V)	DMA	MMA
R	92.7	74.9	0.159	62.2	U	U
1	604	70.7	U	67.9	U	U
2	318	83.5	0.250	120	U	U
3	653	112	U	112	U	U
4	342	195	U	297	0.170	U
5	300	227	U	243	0.100	U
6	187	130	0.204	95.6	U	U
7	1440	1330	1.59	1030	0.950	U

*U designates recovers below detect limit that could not be quantified

Arsenic Concentration (mg/kg) by Extraction Method



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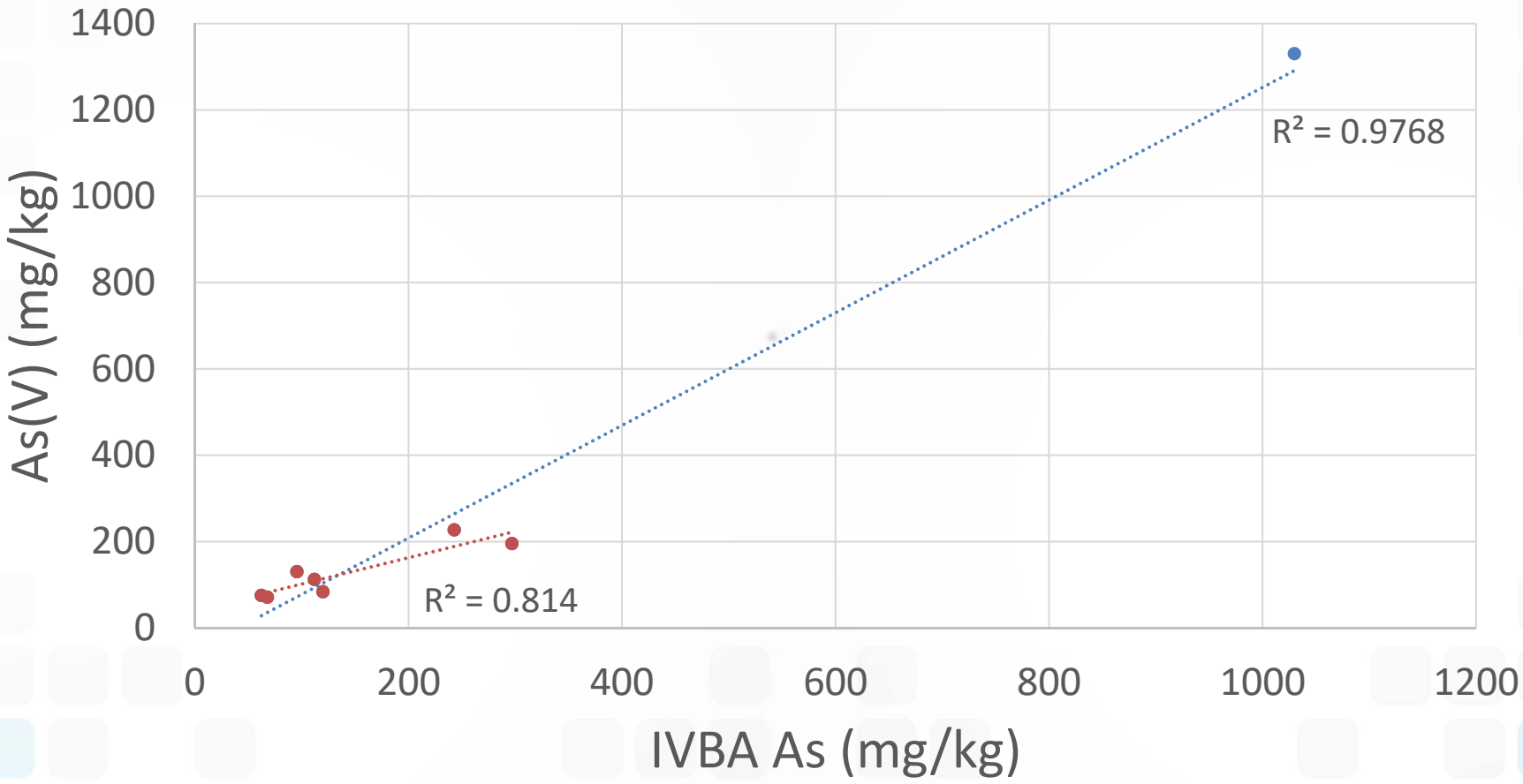
As(V) vs. IVBA As



Arsenic Speciation

- Most commonly found form As(V)
- As(V) and IVBA As show some correlation
  - More data points needed

Analytical Problems & Resolutions

- Extraction solutions analyzed for total As and Pb concentration
- Instrumentation for trace metals analysis
  - Atomic Absorption (AA)
  - Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)
  - Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
    - lowest detection limits

ICP-MS Overview

- Inductively Coupled Plasma Mass Spectrometry
  - Sample aerosolized
  - Introduced to argon plasma
    - Atomized & ionized
  - Ions separated by mass to charge ratio
  - Ions with correct mass to charge ratio reach detector and are measured

Analytical Issues

- High potential for interferences
- Complex Matrix
  - High total dissolved solids (TDS)

Mitigating Issues - Interferences

- Single Quadrupole vs QQQ (Triple Quad)
- Reaction/Collision Cell

Mitigating Issues - Interferences

- Reaction Gas vs Collision Gas Modes

Arsenic Analysis of EPA 1340 Extraction Solution				
Sample	Dilution Factor	Concentration (mg/kg)		
		As 75 [HEHe]	As 91 [O2]	As 91 [NH3]
Soil #3	1000	7.97	4.05	3.76
Soil #3	25	8.25	3.64	3.47

Mitigating Issues – Complex Matrices

- High dilution
  - Lower detection limit
- HMI Mode
- Matrix matching calibration
- Correct internal standard selection
  - Atomic mass vs ionization potential

Internal Standard Selection

- Atomic Mass
  - Space-charging
- Ionization Potential
  - How many atoms are ionized in the plasma?

Analyte	Isotope Mass	First Ionization Potential (eV)
Arsenic	75	9.81
Lead	208	7.416
Rhodium	103	7.46
Indium	115	5.786
Tellurium	125	9.009

Concluding

- Bioaccessibility Extractions
  - Use appropriate method for target analyte
- Arsenic Speciation
  - As(V) & IVBA As
- Analysis can be problematic, but remedied with new instrumentation improvement and correction analysis techniques

Thanks & Acknowledgement

- Ariana Dionisio - Brooks Applied Labs
- Shane Whitacre - The Ohio State University
- Nicholas Basta - The Ohio State University
- Valerie Hanley - The California Department of Toxic Substance Control

References

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