

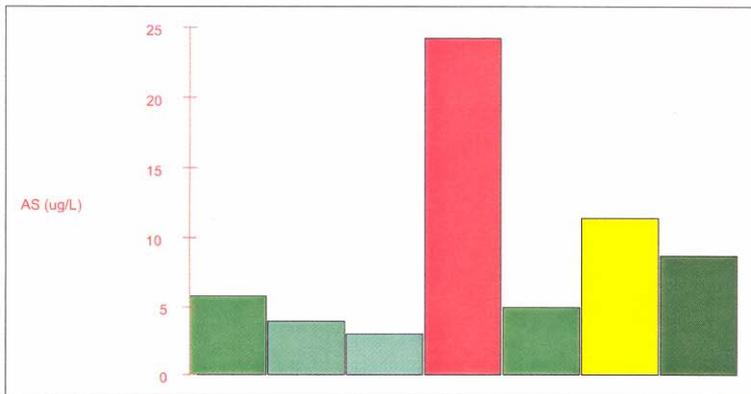
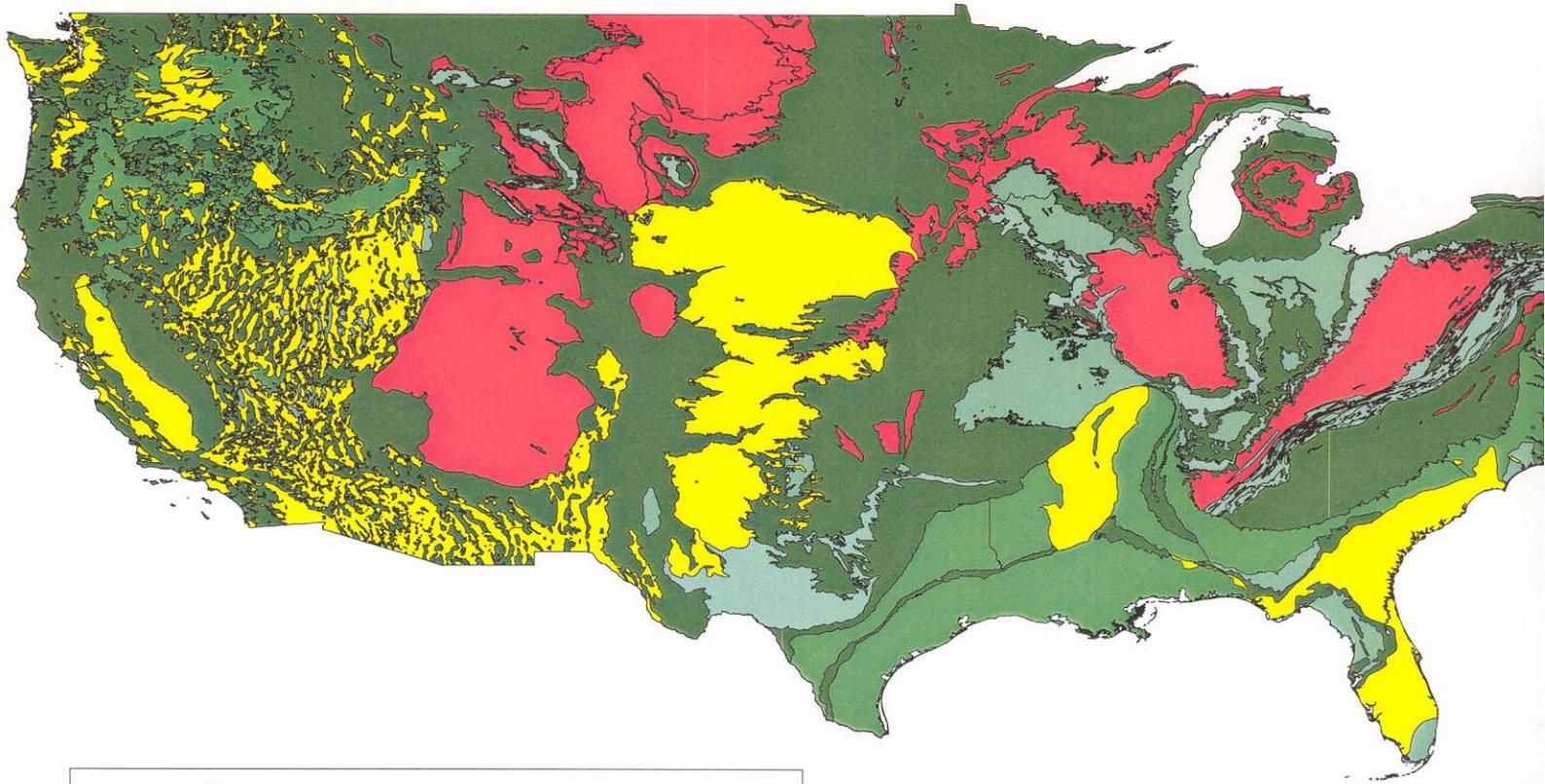
Applications for Laboratory Column Tests in Evaluating Arsenic Adsorption Media

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Outline

- **To column test, or to batch test, that is an interesting question**
- **Rapid small scale column tests**
- **Incipient breakthrough column tests**
- **Dynamic modeling of column tests – a new AwwaRF project**
- **Arsenic sensing needs for column tests**



AVERAGE AS

6 ug/L

4

3

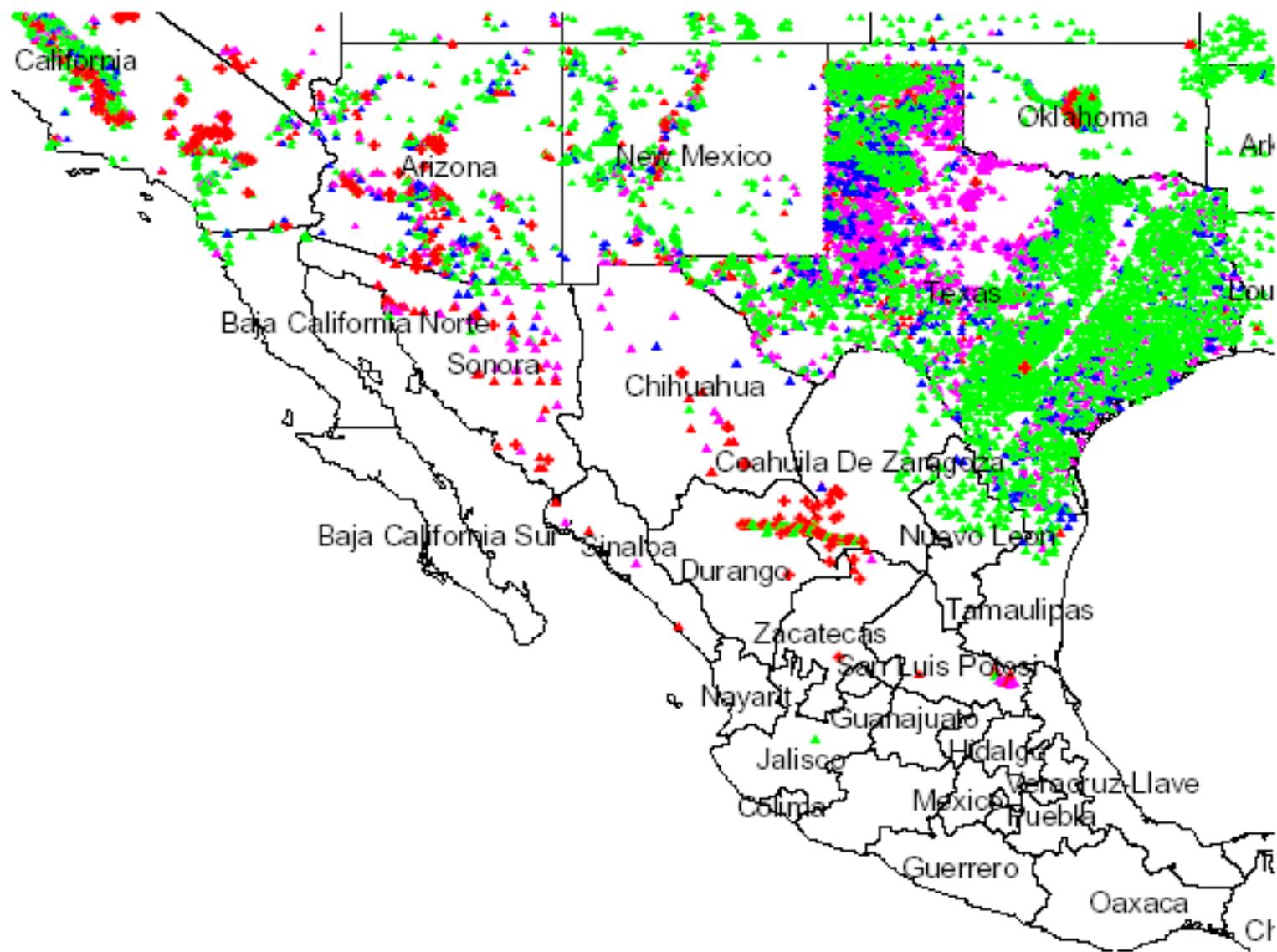
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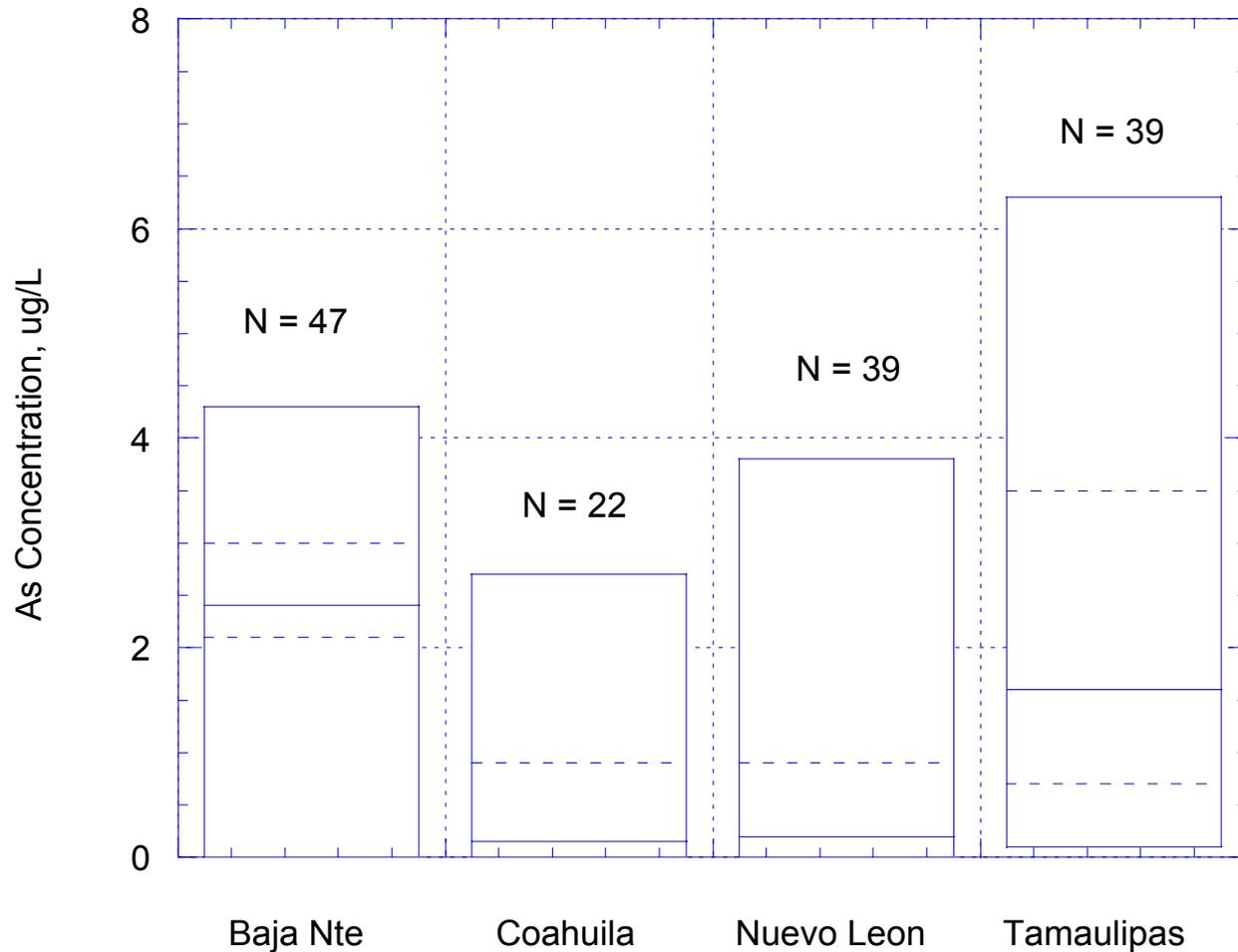
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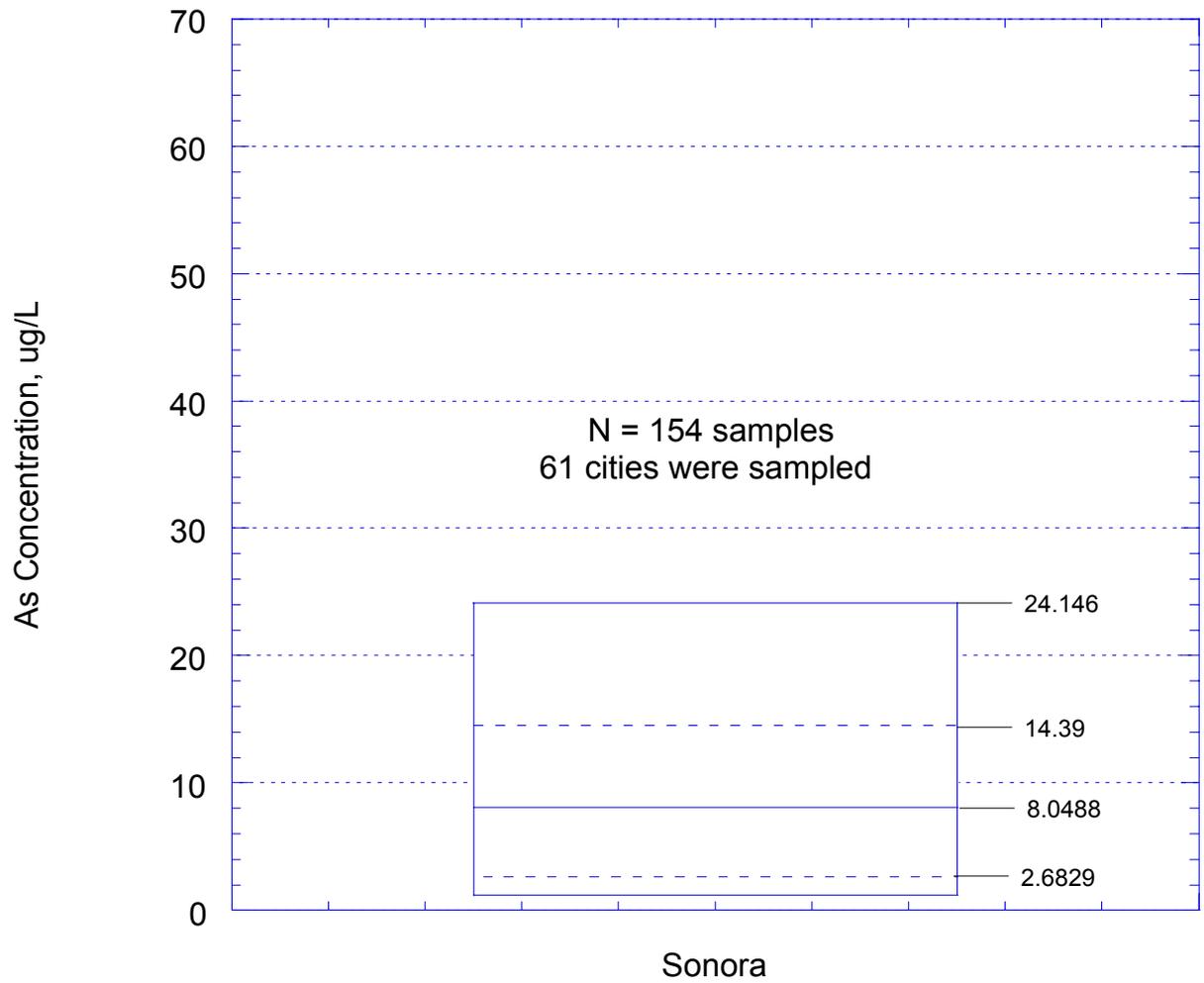
Rock_name	Count
Basalt and other volcanic-rock	659
Carbonate-rock aquifers	2518
Sandstone and carbonate-rock aquifers	2199
Sandstone aquifers	4414
Semiconsolidated sand aquifers	5393
Unconsolidated sand and gravel	8695
others	8219



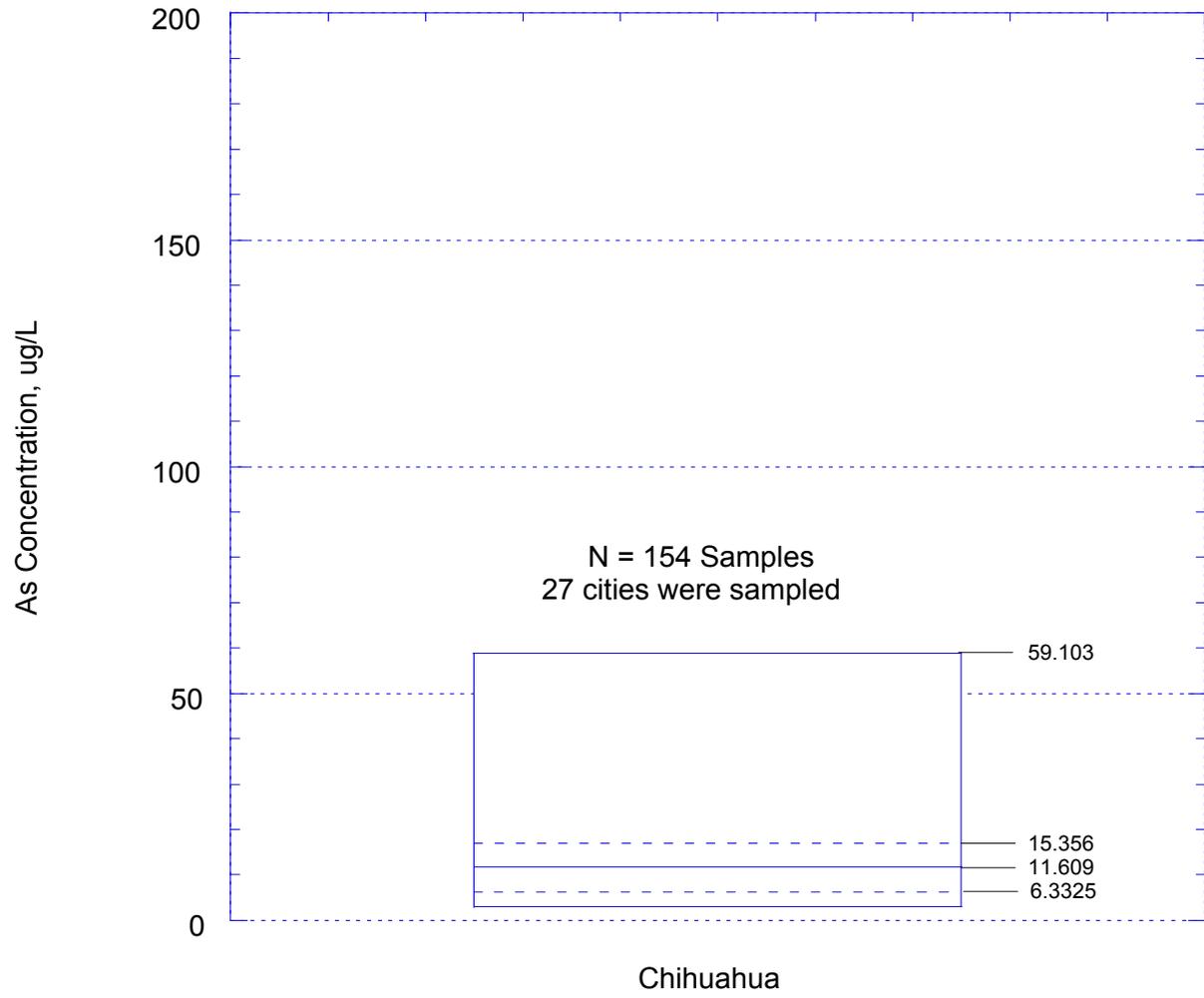
Arsenic Concentrations in 4 states are well below accepted health risk levels



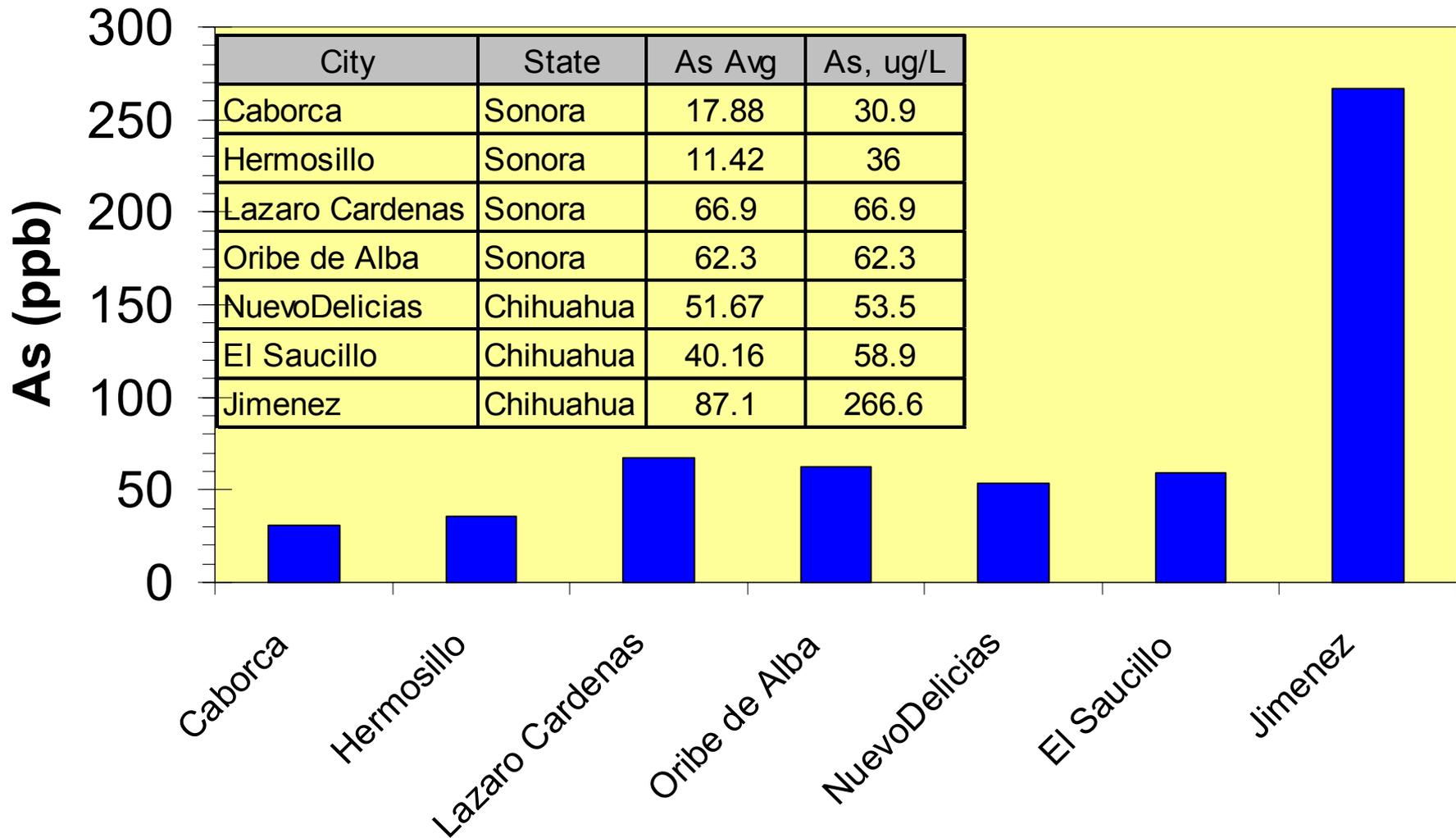
Arsenic concentrations in Sonora above US & WHO standards but below Mexican Standards



Arsenic Concentrations high in Chihuahua



Locations of Highest Arsenic Occurrence



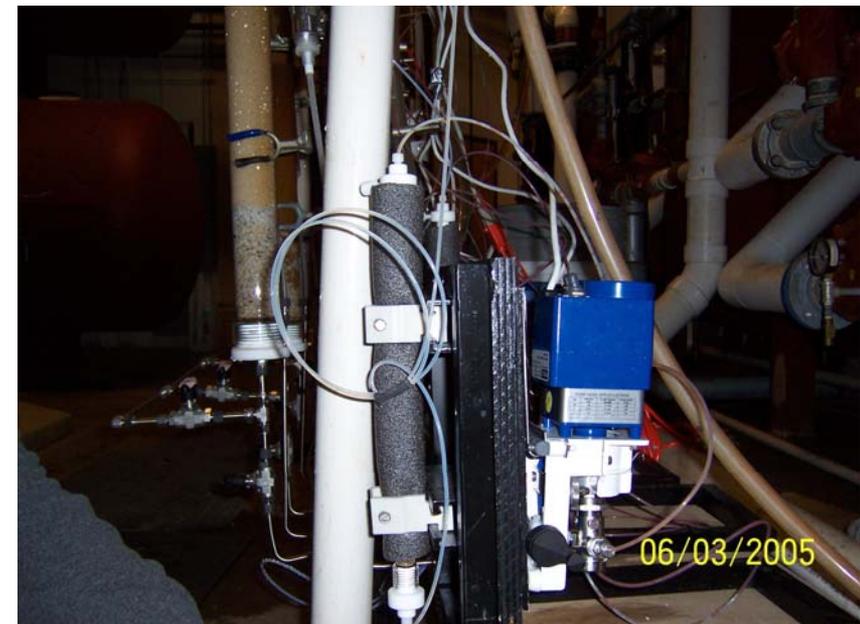
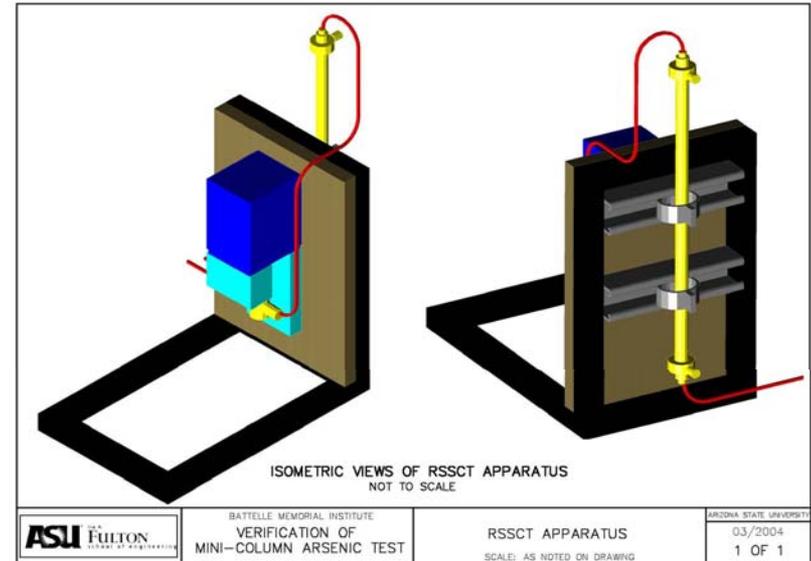
To column test, or to batch test, that is an interesting question



- **When are batch tests useful:**
 - Mechanistic understanding of arsenic removal
 - Validating quality control during media production
 - When enough batch tests are conducted in parallel with column tests, rough correlations of full-scale performance can be estimated from batch tests
- **What do laboratory column tests provide that batch tests do not:**
 - Kinetic effects of particle size
 - Preloading effects from competing ions
 - Used material for leaching tests
 - More “realistic” estimates of full-scale design life
- **What do pilot tests provide that lab column tests can not provide:**
 - Information of media attrition over time & backwashing
 - Exposure to media under variable influent groundwater conditions and air/water temperatures
 - Pressure build-up
 - Ability to handle wastestreams
 - Operator education

What is a Rapid Small Scale Column Test (RSSCT)?

- Rapid Small Scale Column Tests (RSSCTs) were initially developed by Crittenden and others for evaluating organic compound removal on activated carbon
- Fundamentally, the concept is to scale the hydrodynamics and mass transport from full-sized media in a pilot or full scale reactor *down* to smaller test media in a small-scale bench-top continuous flow test



Advantages of RSSCT

- RSSCTs can be conducted in a fraction of the time required of pilot tests (1% to 10% of the time)
- RSSCTs require less water than pilot tests, and can be conducted under controlled laboratory conditions
- RSSCTs are generally cheaper than pilot tests
- RSSCTs are continuous flow tests and allow evaluation of dynamic behavior and competition reactions that are more representative than batch tests
- RSSCTs were used during the USEPA ICR for organic carbon removal by GAC
- RSSCTs facilitate comparison of media and water quality effects

RSSCT Scaling Equations

1. Empty bed contact time (EBCT) of the small scale (sc) RSSCT column is proportional to that of a larger column (LC) based upon the ratio of the adsorbent media radius (R)
2. We have demonstrated that diffusivities are proportional to media radius
3. Loading rates (V) should be adjusted to minimize pressure loss and bed compaction. We recommend $Re_{SC} \times Sc$ of 2000

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left(\frac{R_{SC}}{R_{LC}} \right)^{2-x}$$

$$x = \frac{\text{Log} \left(\frac{R_{SC}}{R_{LC}} \right)}{\text{Log} \left(\frac{D_{s,SC}}{D_{s,LC}} \right)} \approx 1$$

$$\frac{V_{SC}}{V_{LC}} = \left[\frac{R_{LC}}{R_{SC}} \right] \times \frac{Re_{SC} \times Sc}{Re_{LC} \times Sc}$$

Supporting Publications:

Badruzzaman et. al (2004), Water Research, 38 (18)

Westerhoff et. al. (2005), J of Env Engg-ASCE, 131(2)

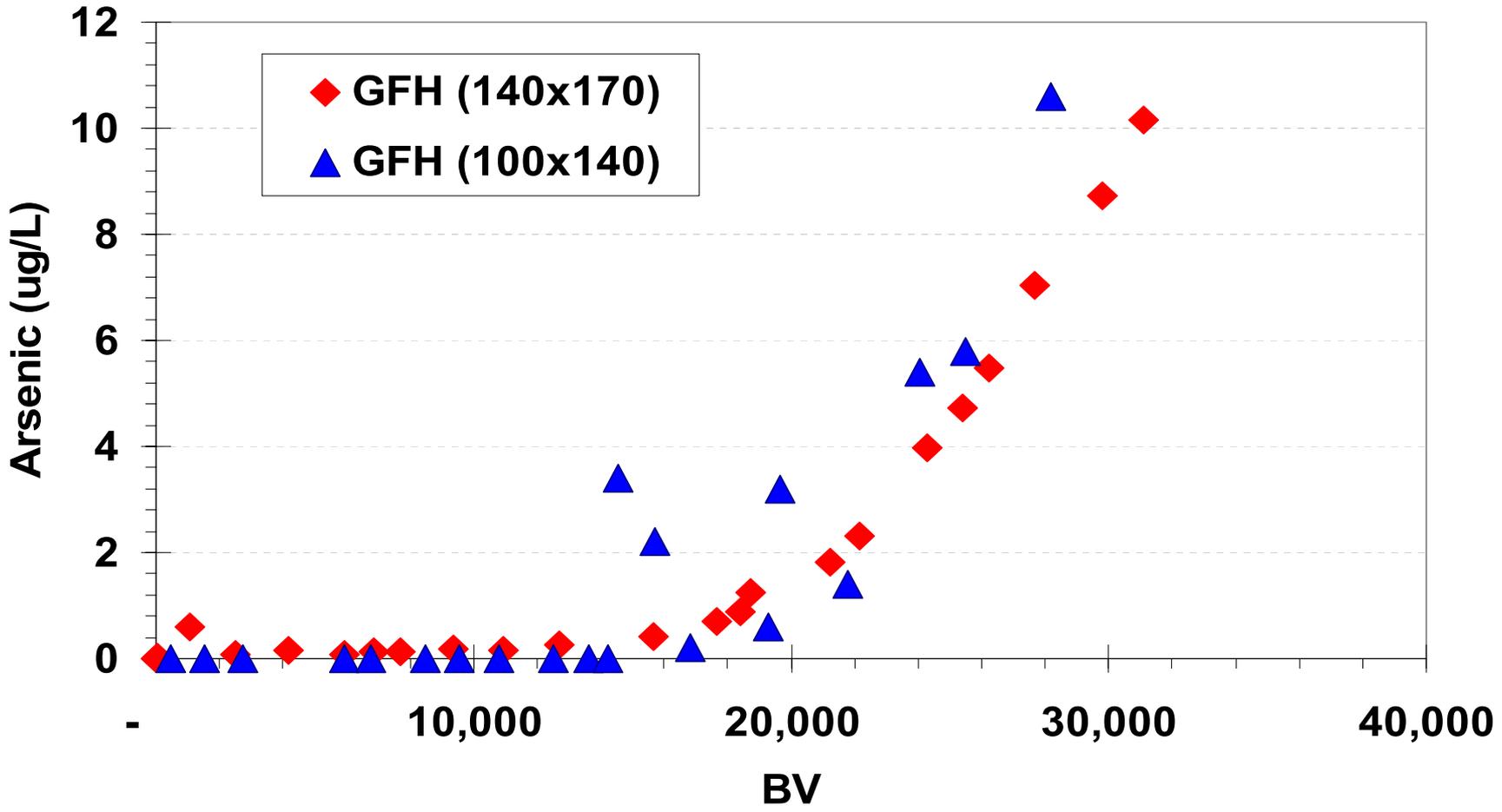
Badruzzaman et al (2005), ACS Symposium Series, Vol-915

RSSCT Column Preparation

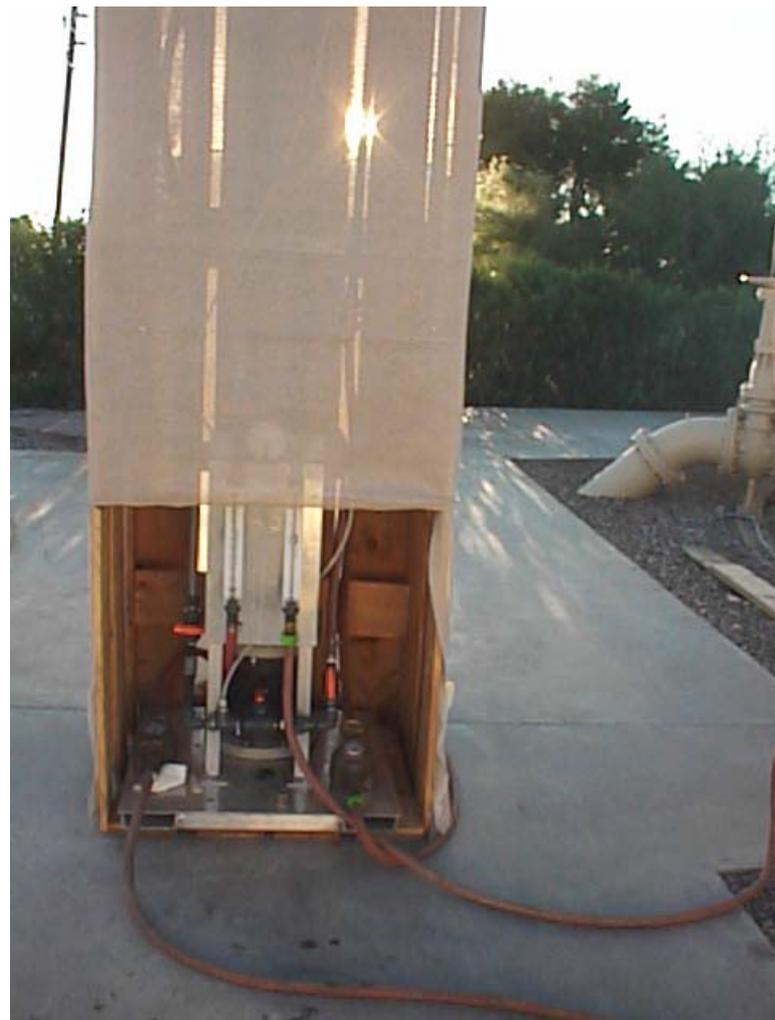
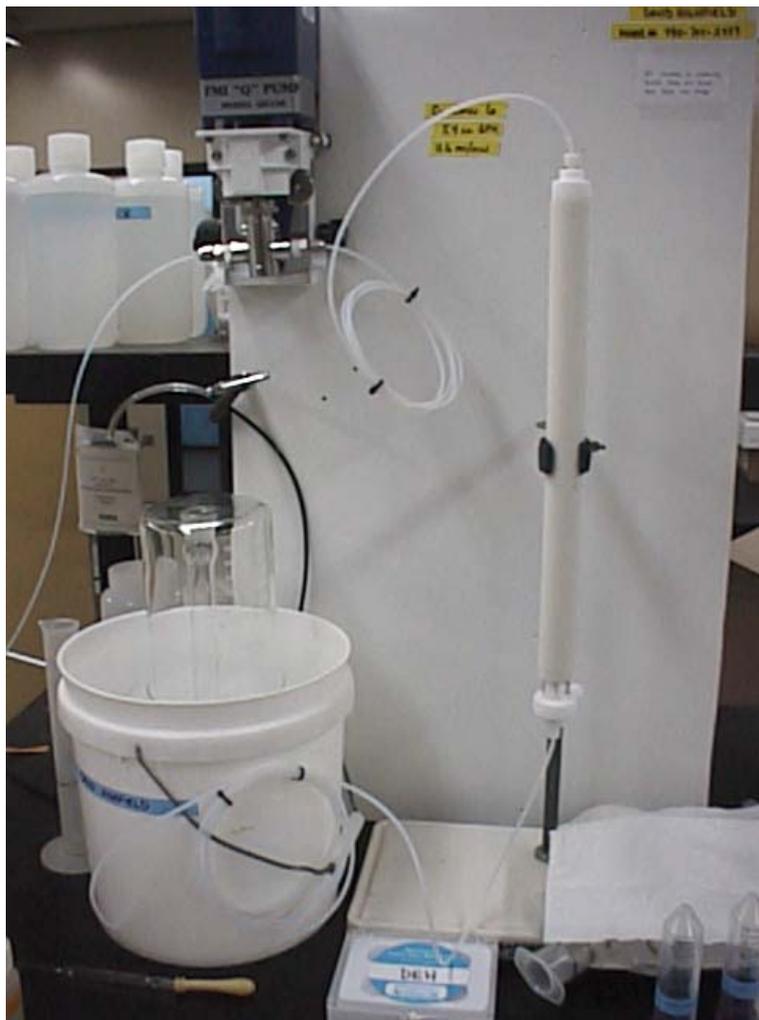
- Crush full-scale media
- Weight sieve media – usually to 100x140 mesh
- Weigh prescribed mass and add to column
- Backwash column to remove fines
- Tap column to compress bed
- Add more media as needed to get to prescribed mass and packed bed length
- Place effluent tube above media elevation to prevent air entrainment
- Condition with DI water
- Start test



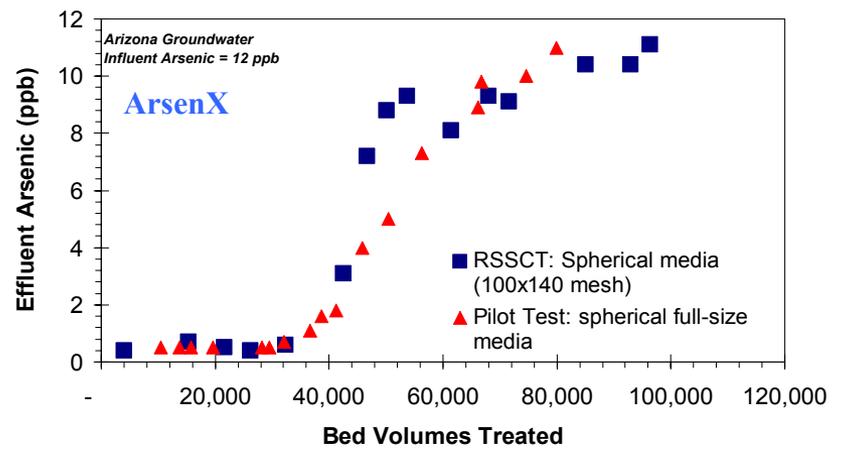
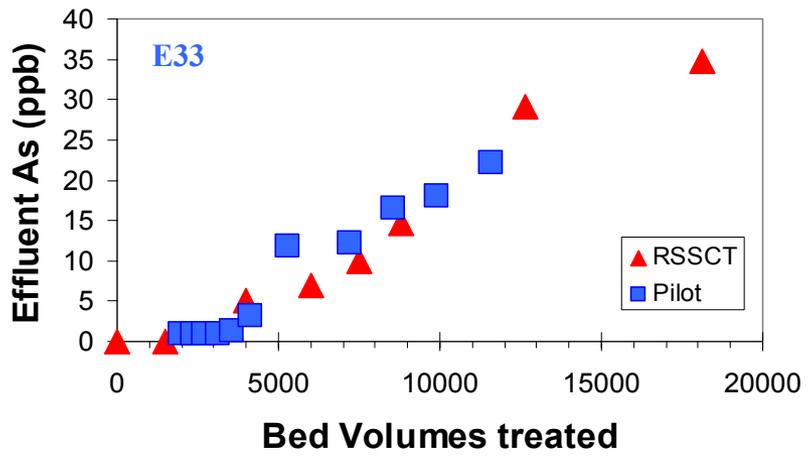
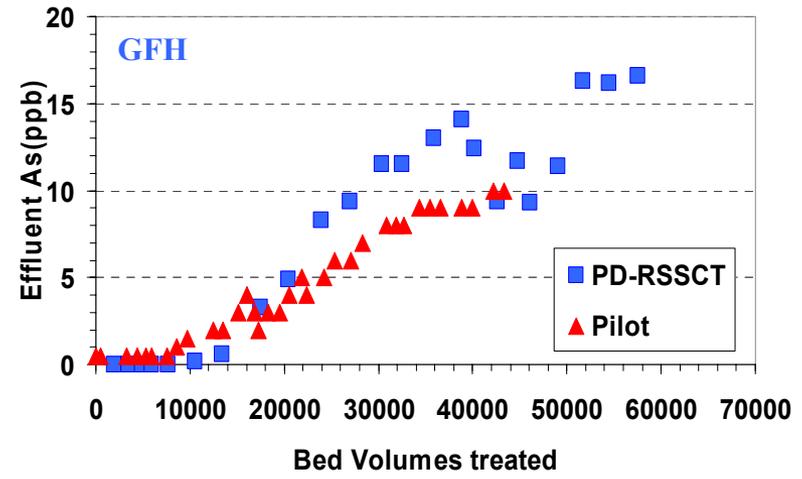
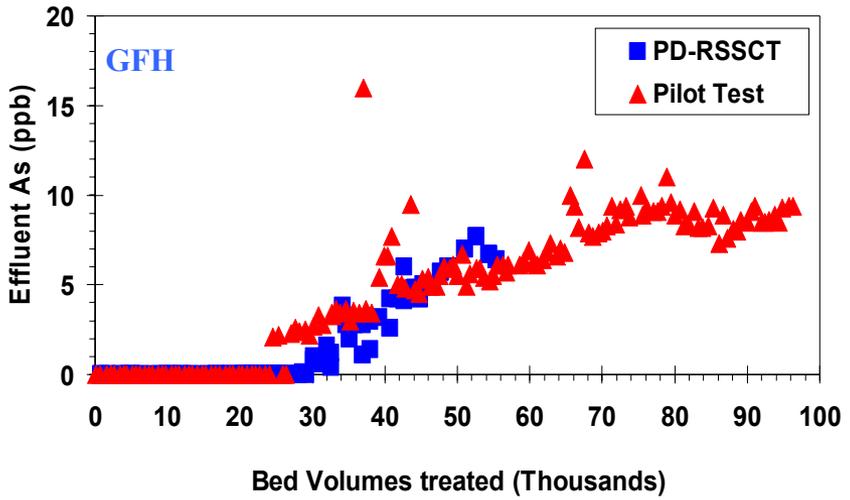
PD Scaling “works” with different GFH Mesh Sizes



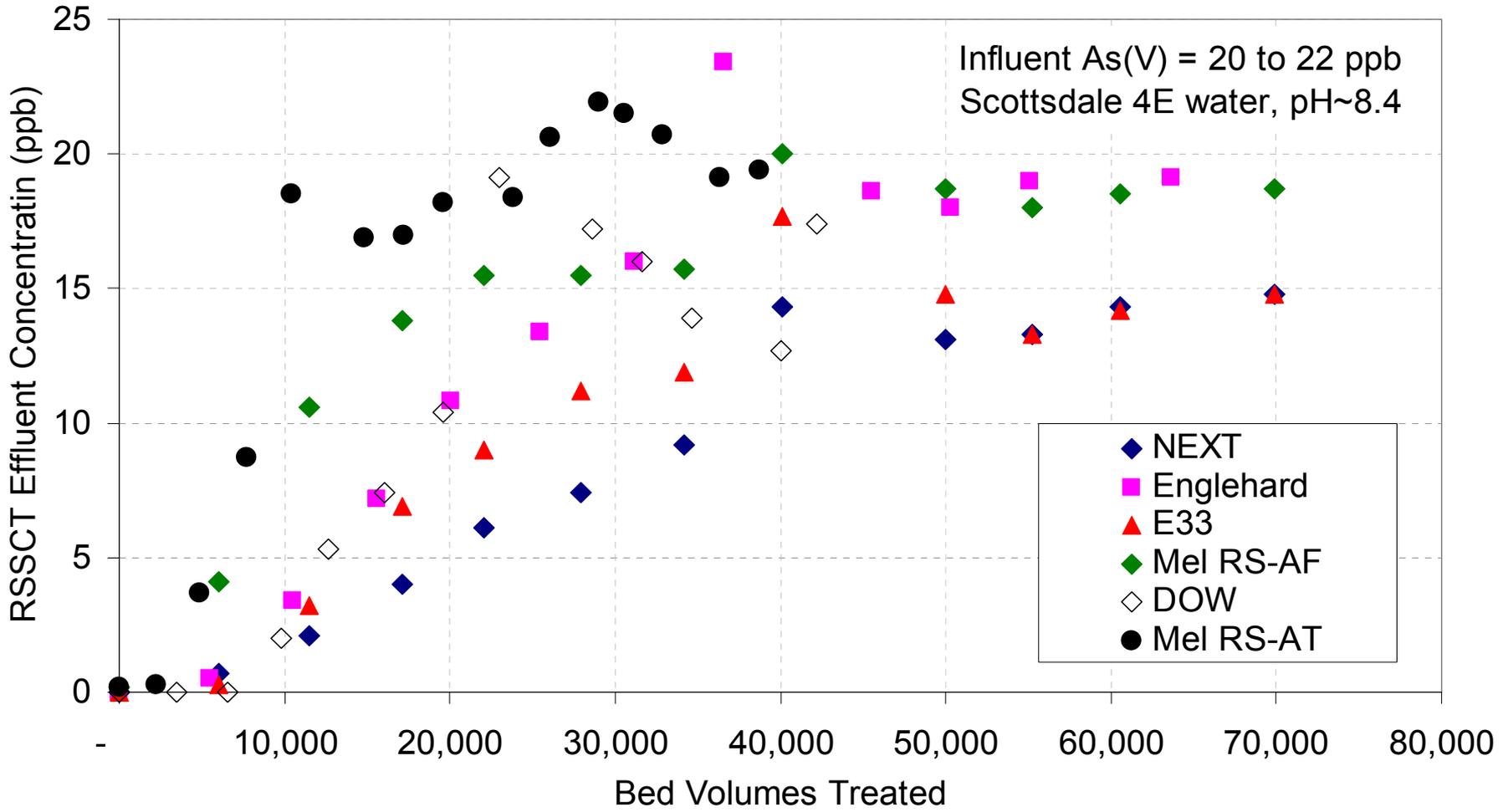
RSSCT-PD vs Pilot



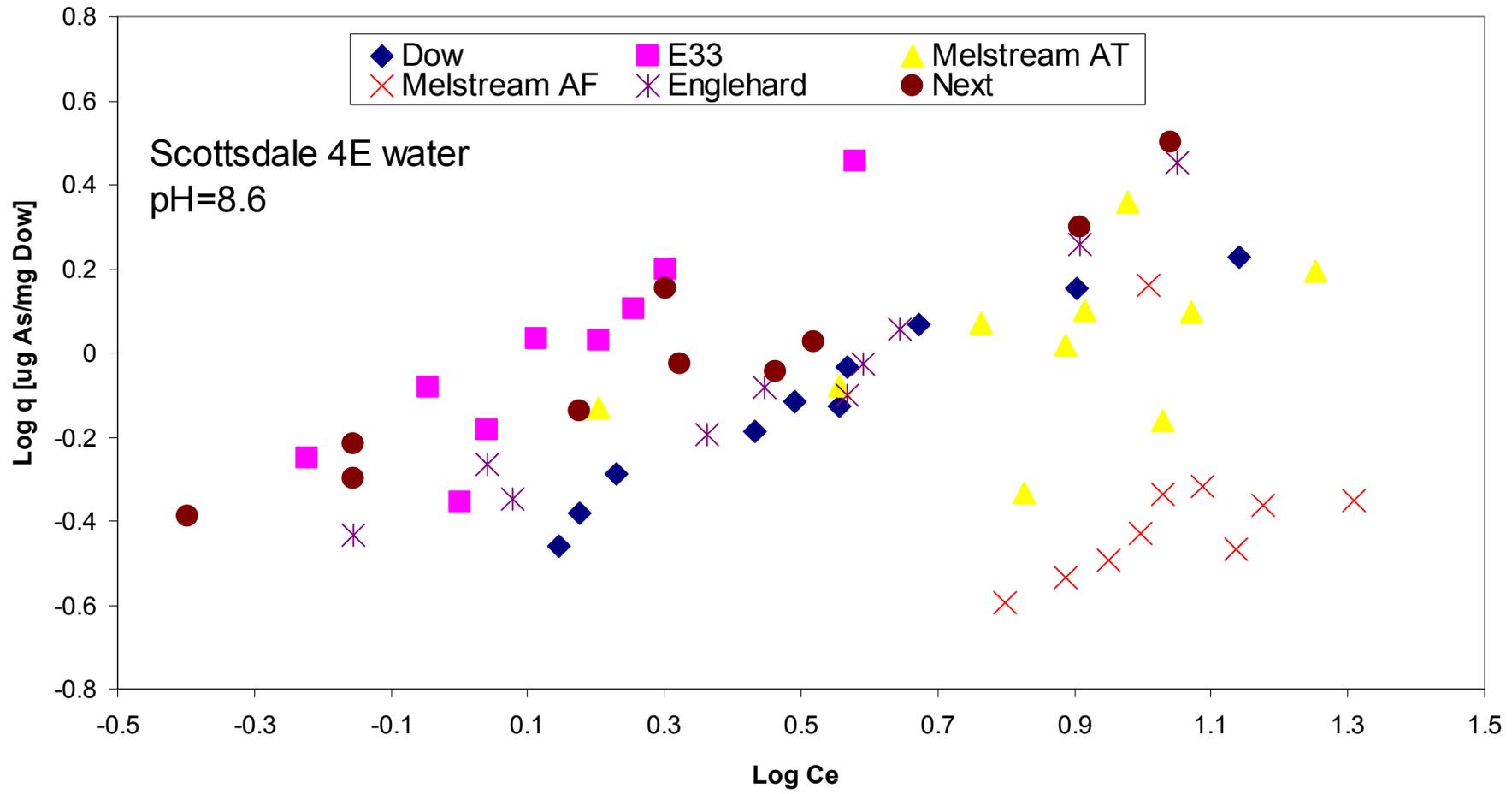
RSSCT Validation – a few of many (pilot- vs RSSCT-scale arsenic breakthrough)



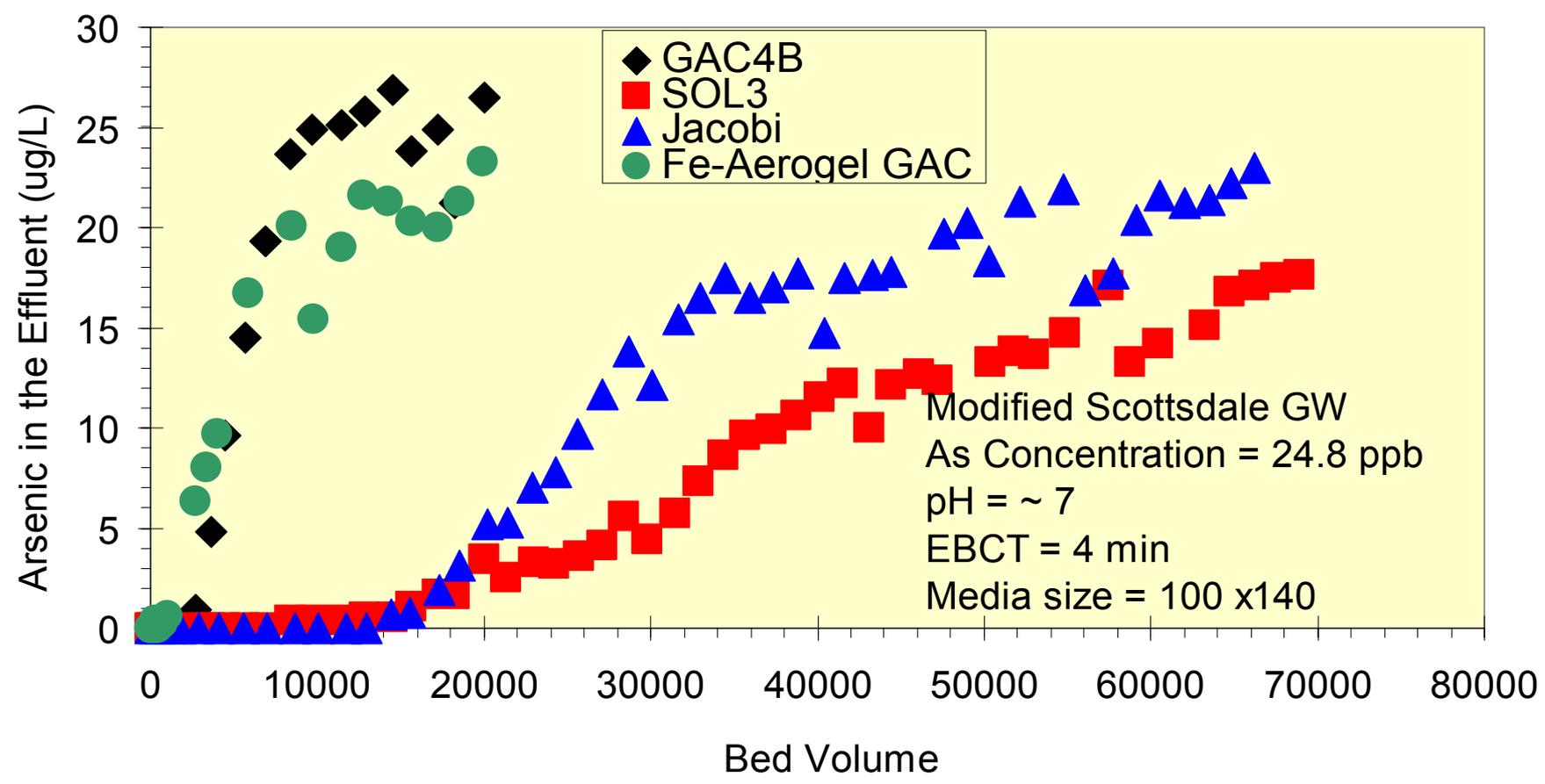
Comparison of New Media



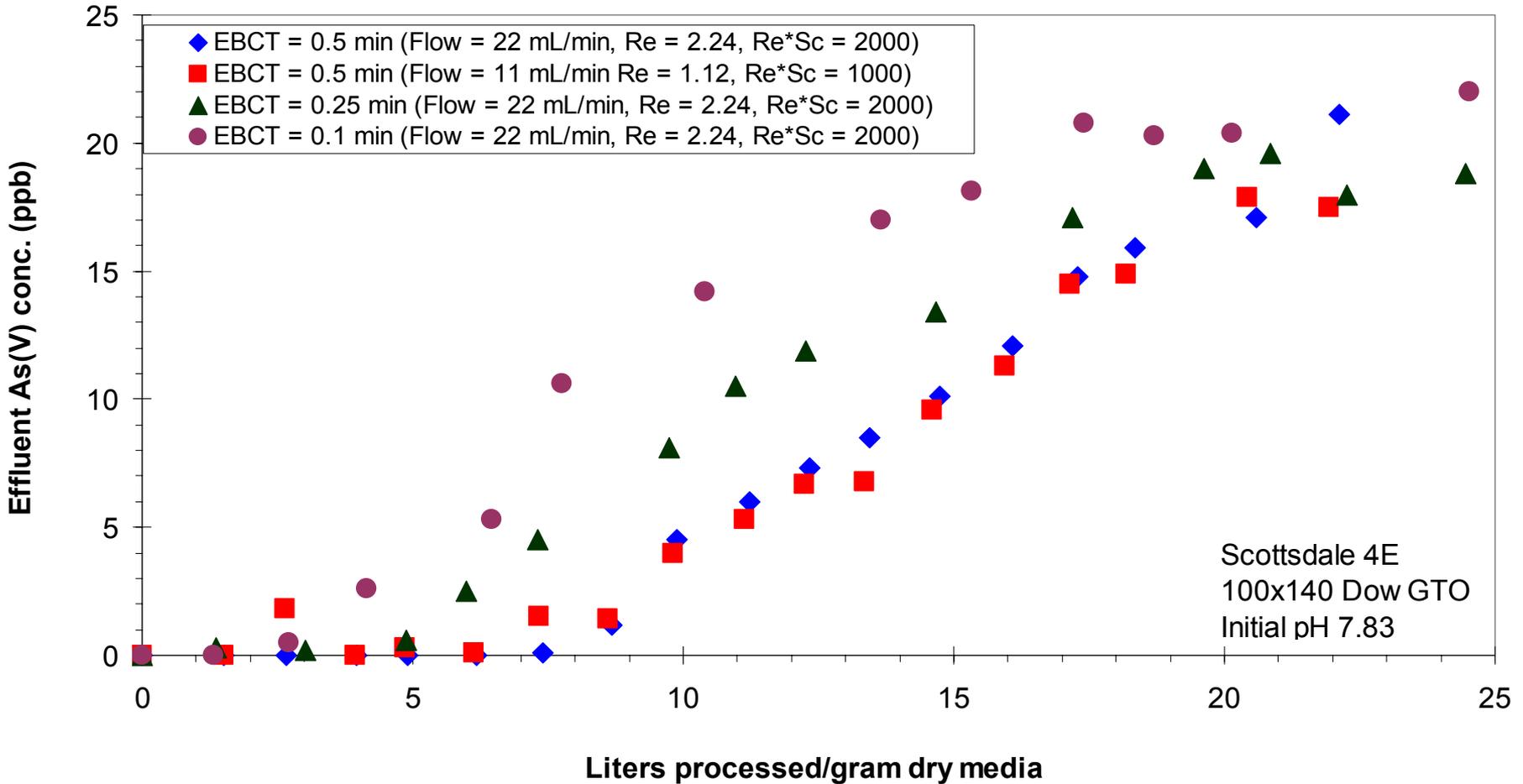
Batch tests with same media



Evaluation of New FeGAC Media (AwwaRF#3079)

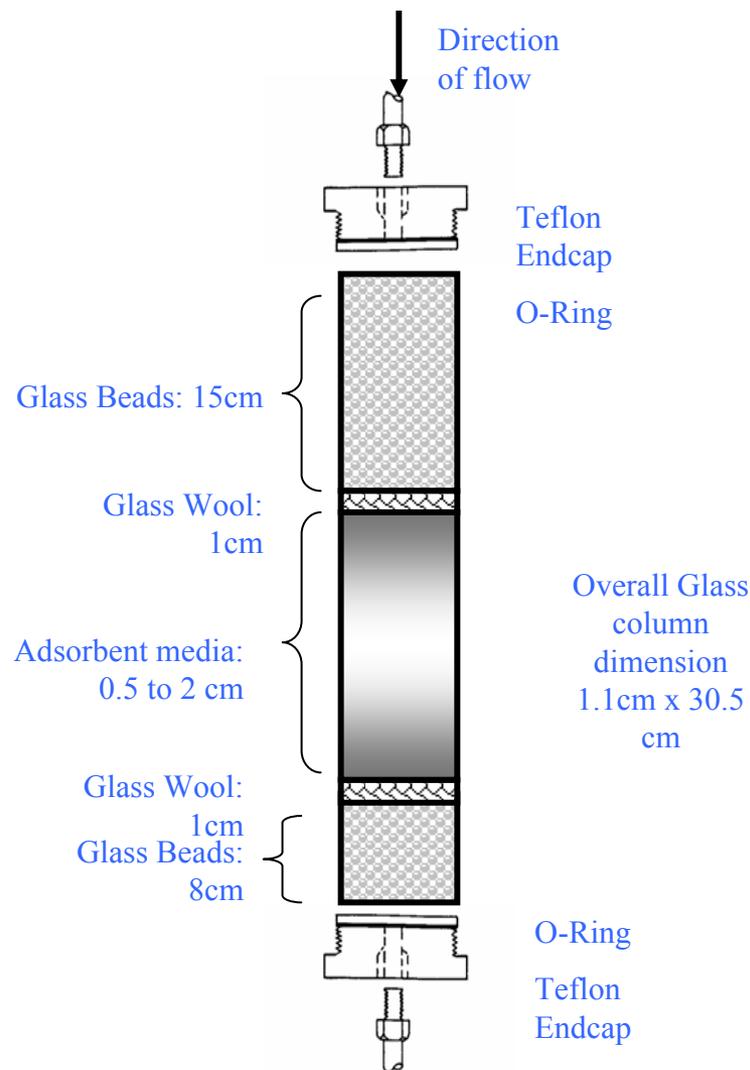


Evaluation of Agglomerated Nanoparticle Based Titanium Media (Effect of very short EBCTs) AwwaRF#3077

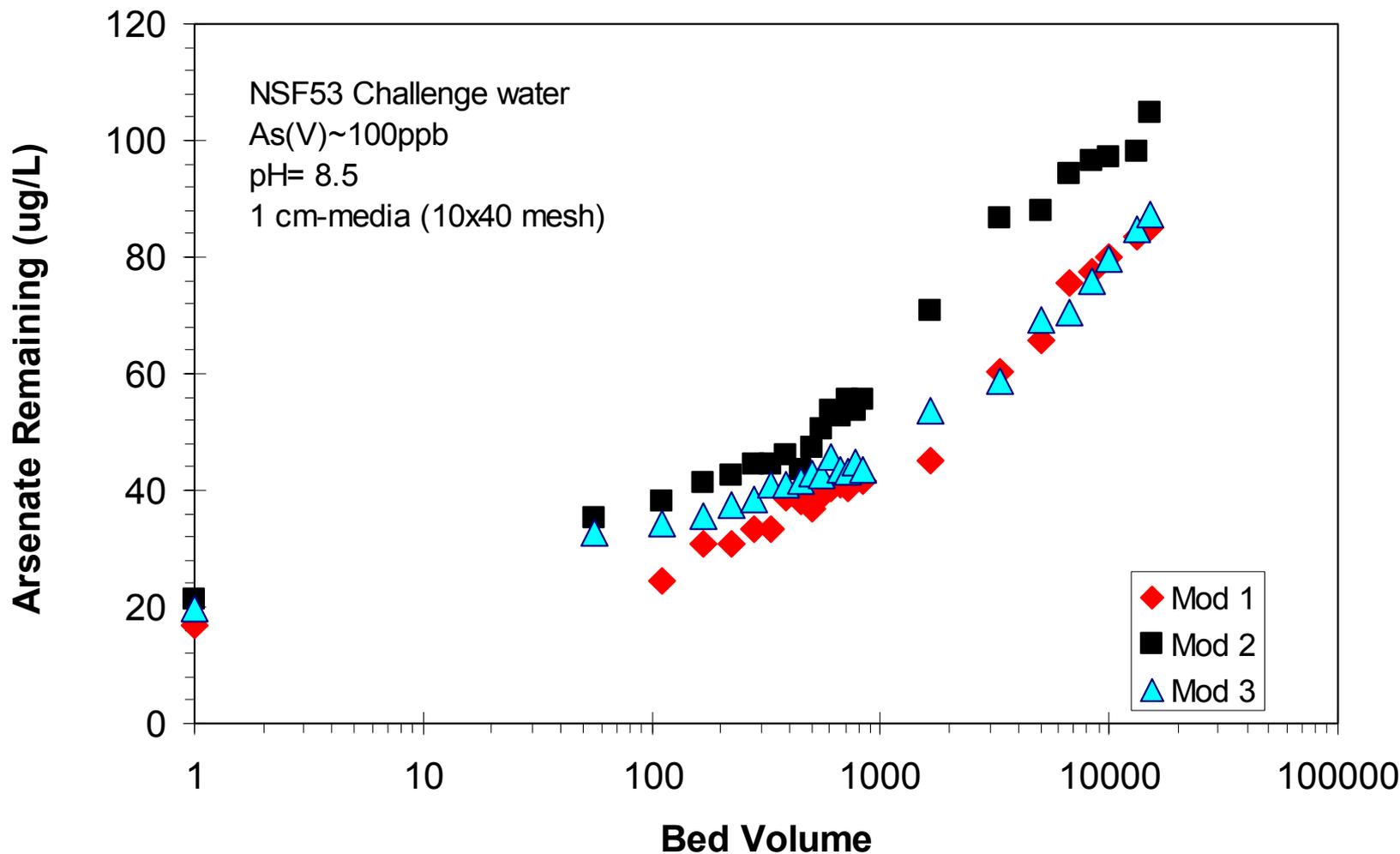


Incipient breakthrough column tests

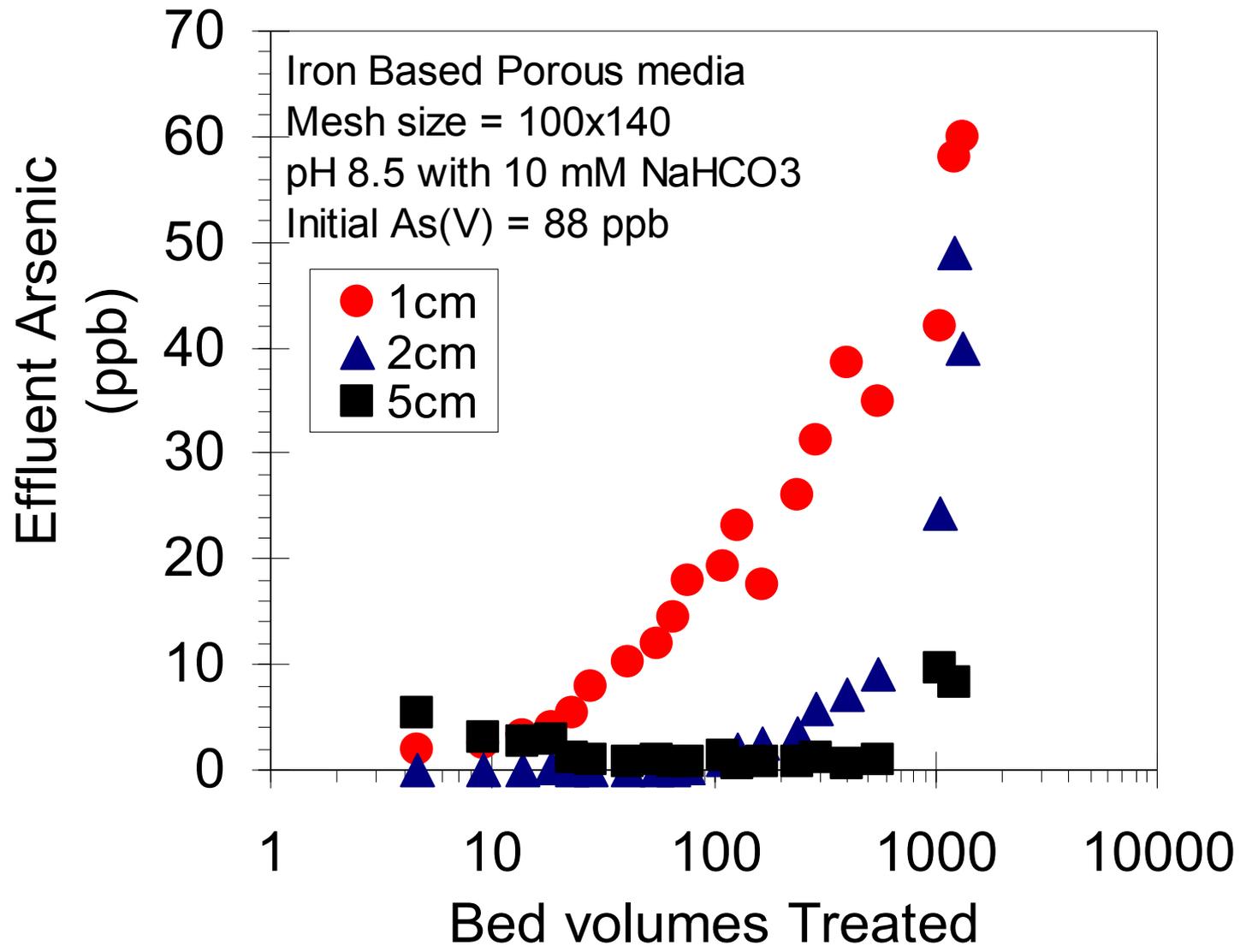
- Use very short columns
- Can use full-size or crushed media
- Short duration tests (< 1 day)
- Initial breakthrough is related to external mass transfer (not diffusion within the media)
- Provide kinetic information for modeling
- Facilitates studies of kinetic limitations of media
- Provide rapid assessment of media formulations or possibly evaluate remaining adsorption capacity of used media



Example Data with Three Full-size Iron Adsorbents



Incipient Breakthrough Data with 100x140 mesh media (AwwaRF #3098)



Dynamic modeling of column tests

A New AwwaRF project (#3098)



○ **Goals:**

- **Surface complexation modeling is the appropriate technique for characterizing single and multi-solute adsorption equilibrium in these systems.**
- **While a crucial first step, adsorption equilibrium relationships alone are inadequate for predicting the performance and bed life of a continuous-flow packed bed, and verification of surface complexation models must include field-scale validation.**
- **Thus, a surface complexation model must be integrated into a dynamic mass transport model.**

○ **Project Tasks**

- 1. Compile Existing Literature**
- 2. Single Solute Arsenate Adsorption Isotherms (E33, GFH, GTO)**
- 3. Multi-Solute Adsorption Isotherms**
- 4. Surface Complexation Model Parameters**
- 5. Packed-Bed Dynamic Mass Transport Model**
- 6. Model Validation**

Link Equilibrium Surface Complexation Models

<i>No.</i>	<i>Reaction</i>	<i>Type</i>	<i>Log K</i>
1.	$\equiv FeOH_{(s)} + H_3AsO_{4(aq)} \leftrightarrow \equiv FeH_2AsO_{4(s)} + H_2O$	Inner-sphere	4.52
2.	$\equiv FeOH_{(s)} + H_3AsO_{4(aq)} \leftrightarrow \equiv FeHASO_{4(s)}^- + H_{(aq)}^+ + H_2O$	Inner-sphere	2.6
3.	$\equiv FeOH_{(s)} + H_3AsO_{4(aq)} \leftrightarrow \equiv FeAsO_{4(s)}^{2-} + 2H_{(aq)}^+ + H_2O$	Inner-sphere	-2.47
4.	$\equiv FeOH_{(s)} + H_3AsO_{3(aq)} \leftrightarrow \equiv FeH_2AsO_{3(s)} + H_2O$	Inner-sphere	4.52
5.	$\equiv FeOH_{(s)} + H_3AsO_{3(aq)} \leftrightarrow \equiv FeHASO_{3(s)}^- + H_{(aq)}^+ + H_2O$	Inner-sphere	-2.70

with Dynamic Mass Transport Models

$$\frac{\partial q(r, t)}{\partial t} = D_s \left(\frac{\partial^2 q(r, t)}{\partial r^2} + \frac{2}{r} \frac{\partial q(r, t)}{\partial r} \right)$$

Arsenic sensing needs for column tests

- Column testing could be facilitated by semi-continuous, autonomous arsenic detection
- Commercialized systems are being developed (TraceDetect)
- ASU is developing its own micro-fiber ASV system

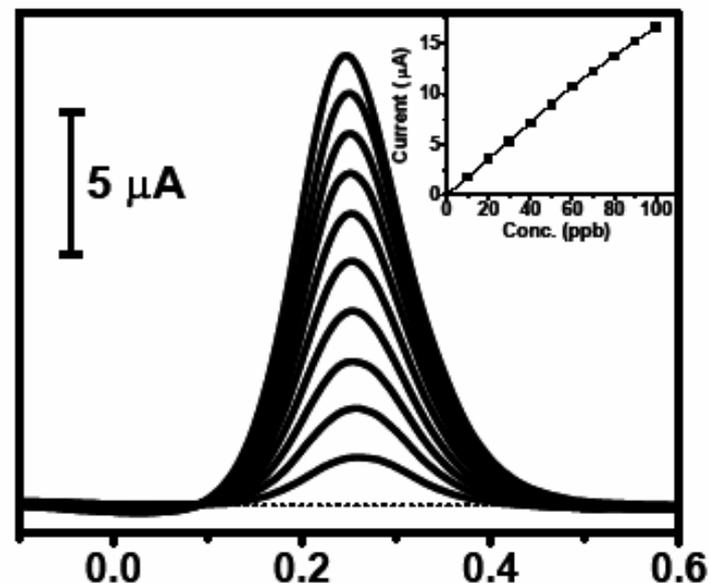
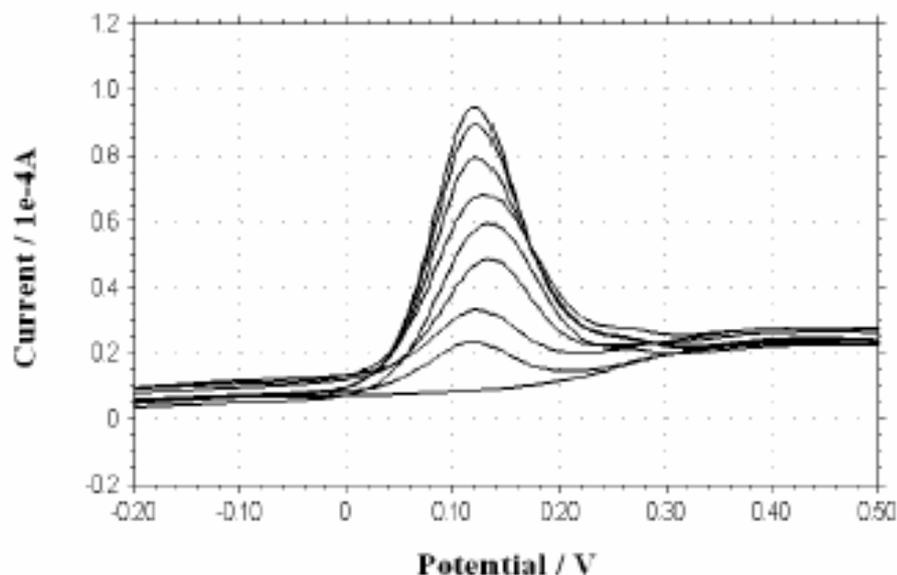


Fig. 4 Linear sweep anodic stripping voltammograms (background subtract) for increasing levels of arsenic in 10 µg/L steps (curves a-j) in the 1M HNO₃ along with the background response (dotted line). Accumulation potential and time, -0.3 V and 90 sec, respectively. Other conditions, as in Fig. 1.

Preliminary Data in Arizona Groundwater

3.1) Detection of Spiking Arsenic in Ground Water



Conditions : electrolyte, ground water in 1 M nitric acid (9:1 vol. ratio)
sample, 0, 20, 40, 60, 80, 100, 120, 140 and 160 ppb As

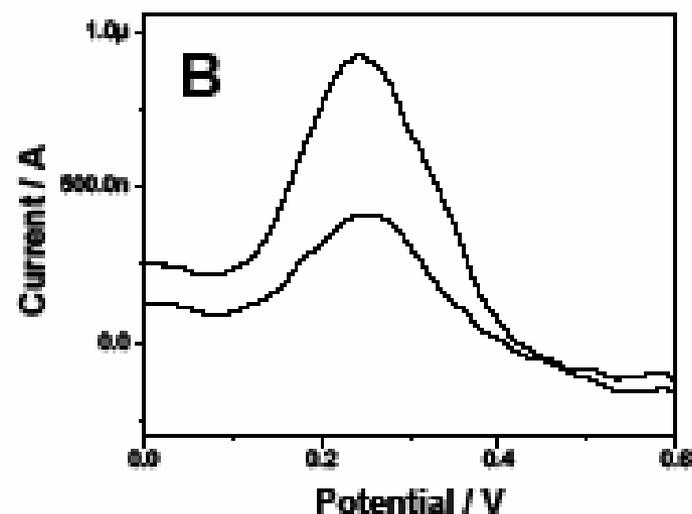


Fig. 4 Linear sweep anodic stripping voltammograms (background subtract B) for a arsenic in 1 µg/L steps in the 1M HNO₃ along with the background response (dotted line). Accumulation potential and time, -0.3 V and 210 sec,

Summary

- **Batch and column tests have their place and should be used to address specific questions**
- **Rapid small scale column tests (RSSCTs) are relatively easy to conduct in parallel and are useful in evaluating different media, variable water quality, or simply screening effects of competing ions in a given water**
- **Incipient column tests are very rapid, but do not necessarily simulate a full-scale application**
- **Linking equilibrium models with dynamic packed bed transport models will likely shed new light on adsorption competition effects and effects of changes in surface chemistry on arsenic adsorption**
- **On-line arsenic sensors are necessary to automate lab column testing and field system monitoring**

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