Fly Ash Geochemistry: Current Course of Investigations

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Geochemistry Overview

Elemental & isotopic characterization, stratigraphic profiling

Ash stability – dissolution – leaching potential

Fly ash geochemistry

Metal/metalloid speciation and complexation

Mobility - Bioavailability

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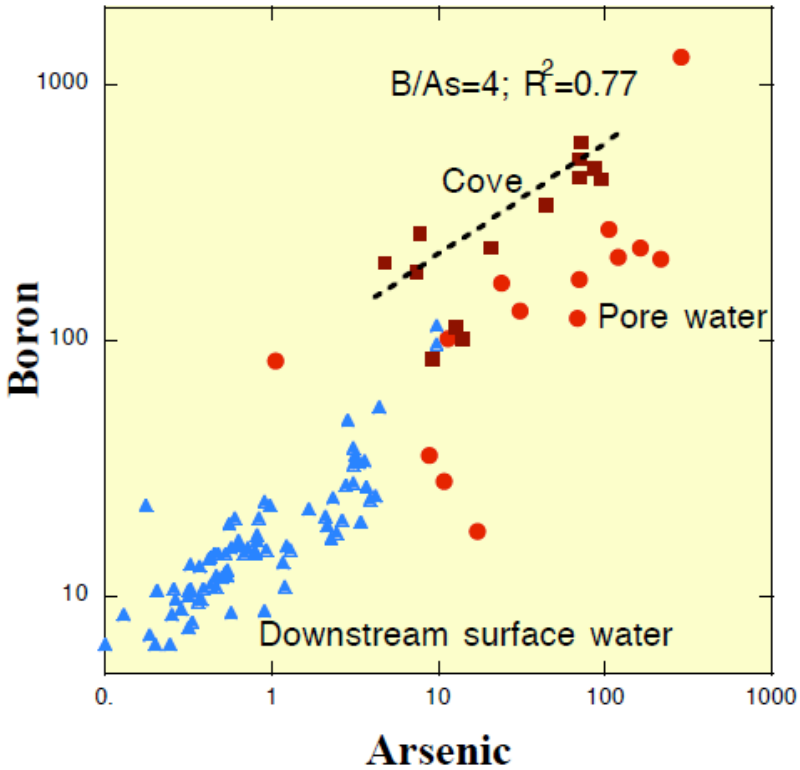
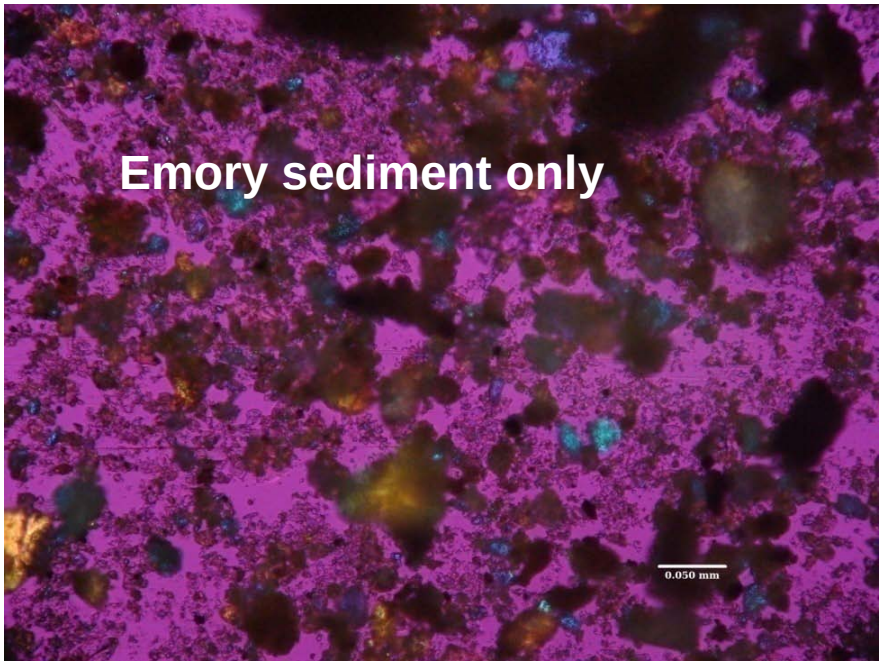
I. Ash Location/Identification

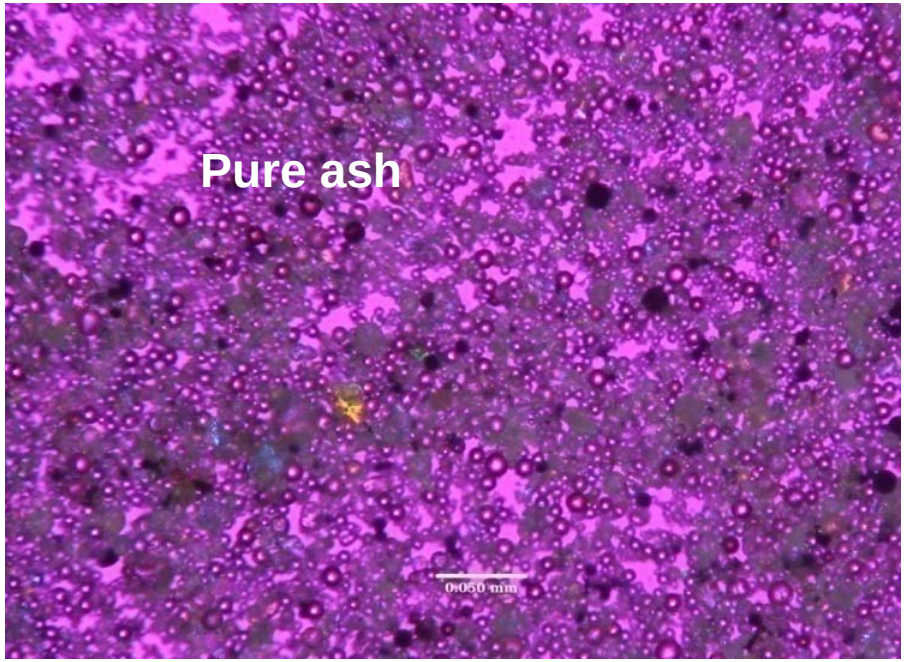
- Focus is on:
  - Boron, strontium, and mercury isotope ratios,



Vengosh et al., Duke University

Geomorphology of ash deposits

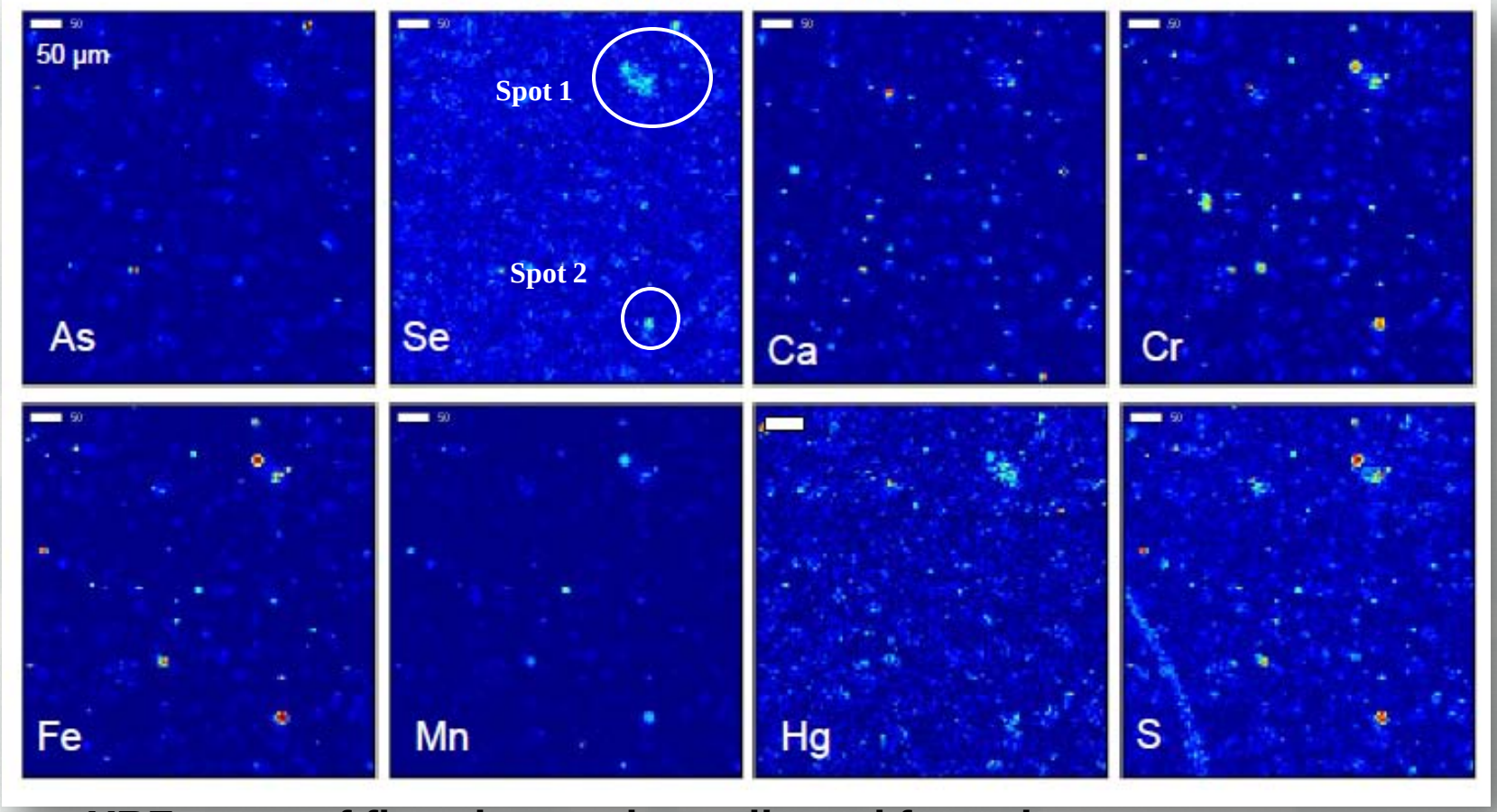




- **Evaluating use of a Sub-Bottom Profiler (SBP) to characterize areas of deposition of ash in the Emory, Clinch, and Tennessee Rivers,**
- **interpreting stratigraphy of cores collected from those areas, and evaluating geochemical speciation of metals in the deposited ash and sediments**

Sidle, Appalachian State University

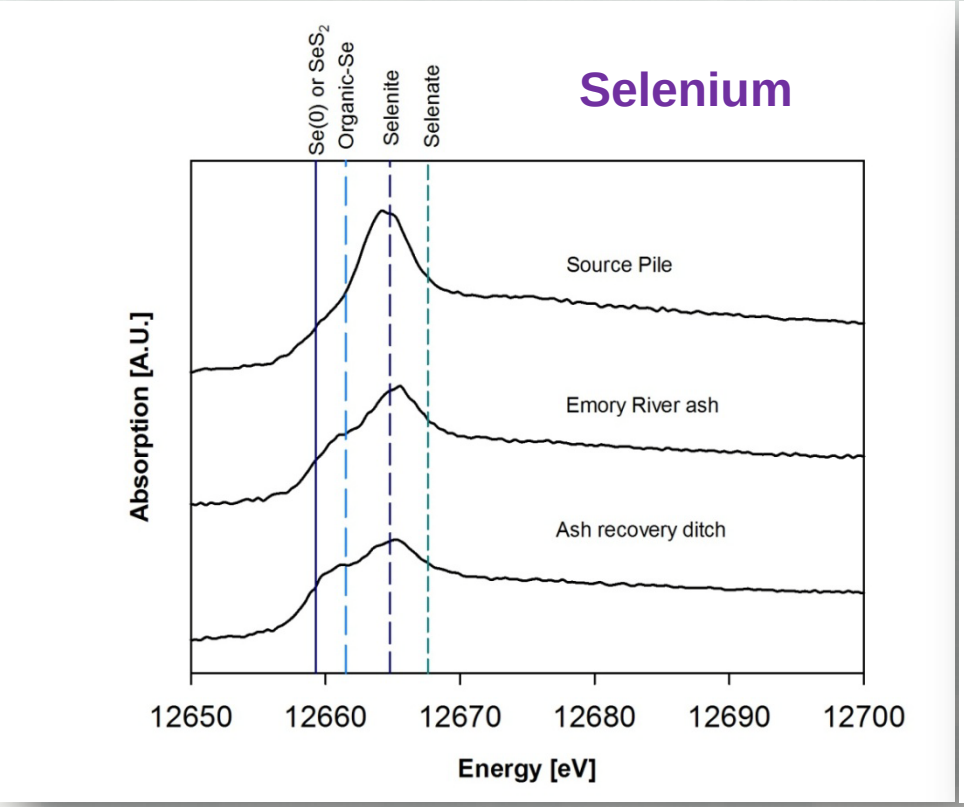
II. Metal speciation & complexation

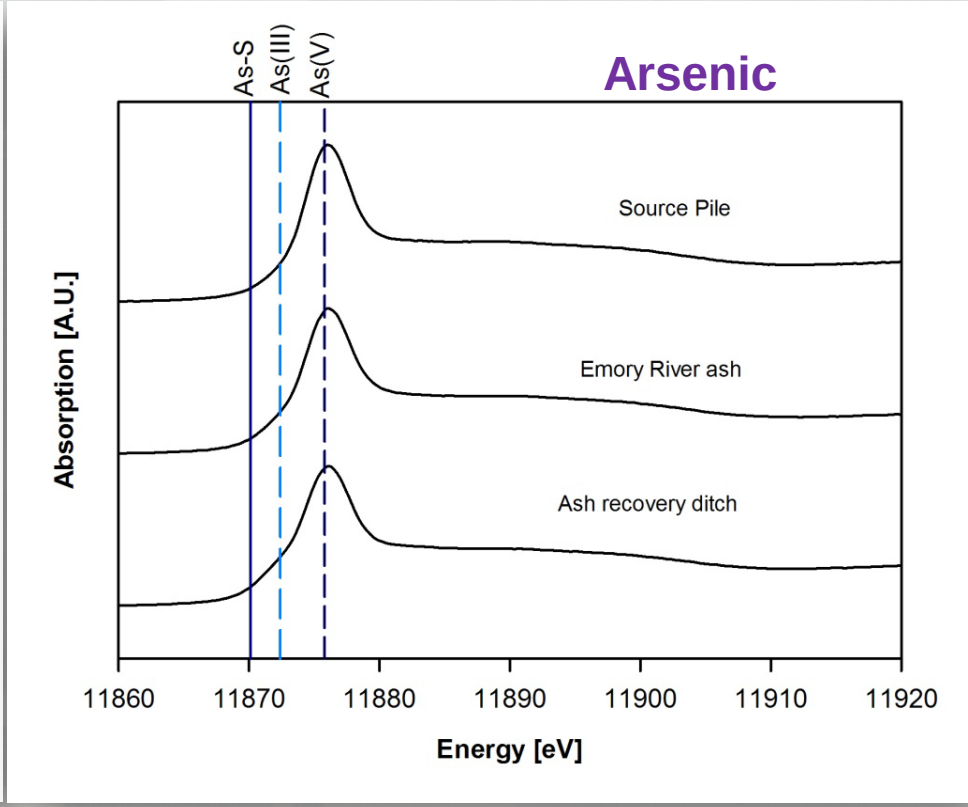


µ-XRF maps of fly ash samples collected from the remaining source pile – ERDC, 2009

Steevens et al., 2009; Chappell et al., In preparation

Bulk XANES of Arsenic & Selenium

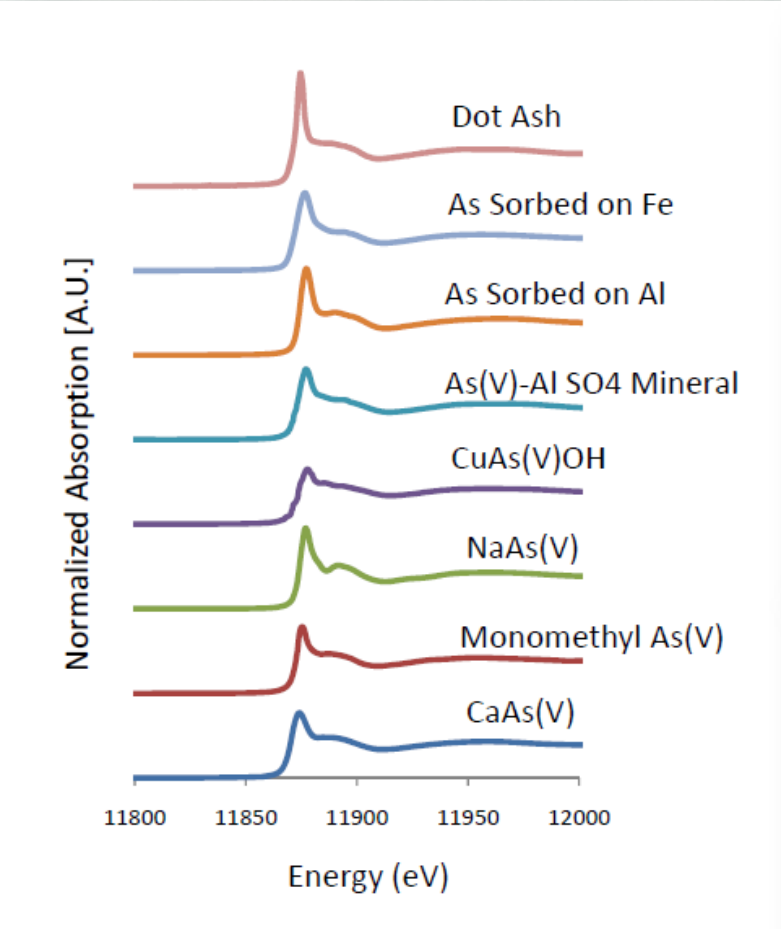


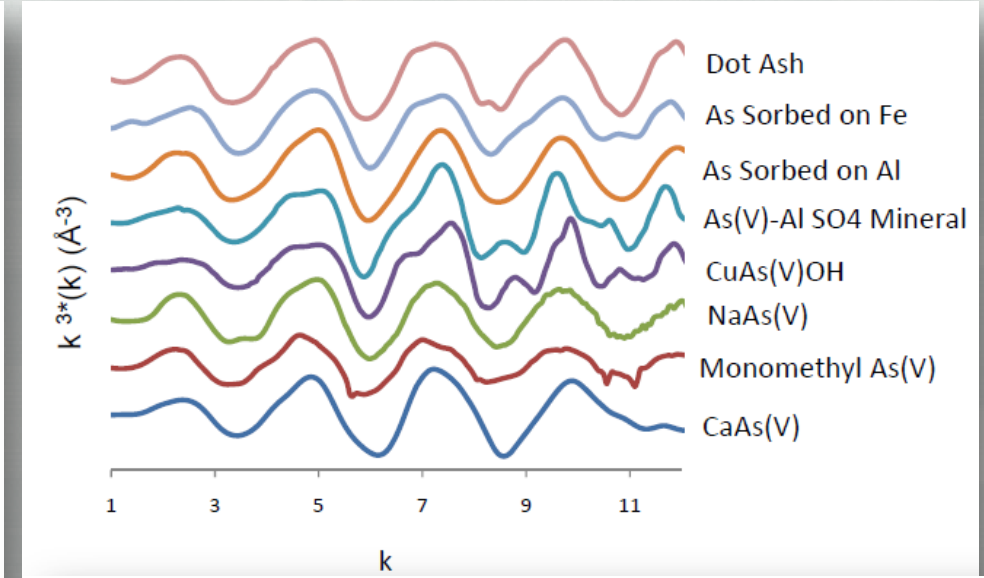


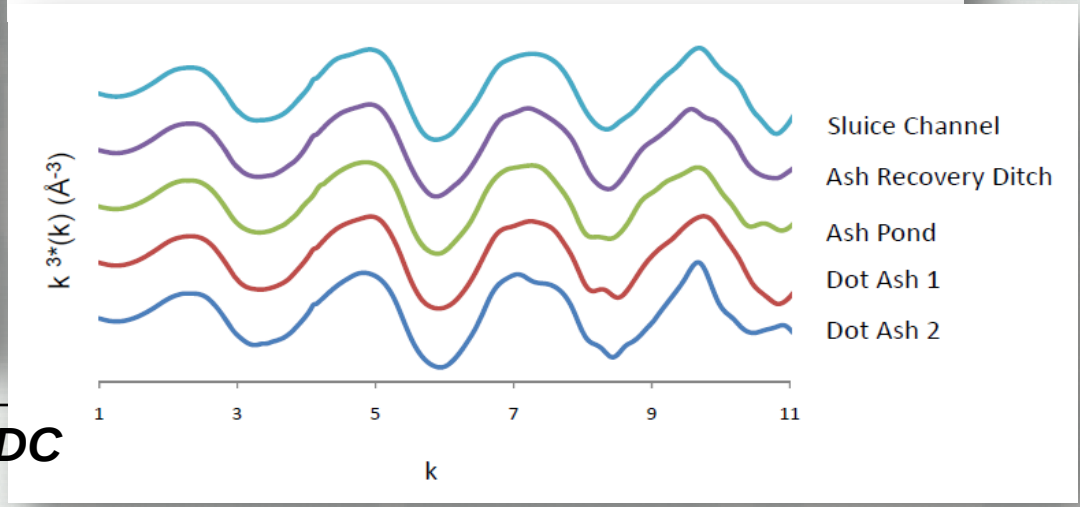
Source Pile: mainly Se (IV)
Emory River & ARD: Mixture of Se(IV), organoselenium (-II), Se(IV)-sulfides

Source Pile: mainly As(V)
Emory River & ARD: mostly As(V) with some As-sulfides

As speciation for DOT classification



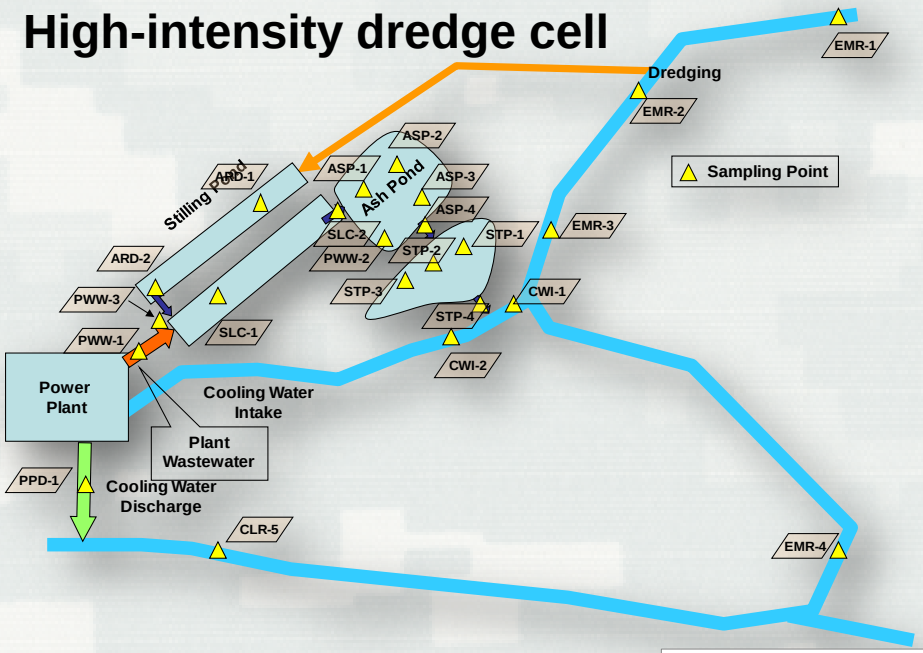


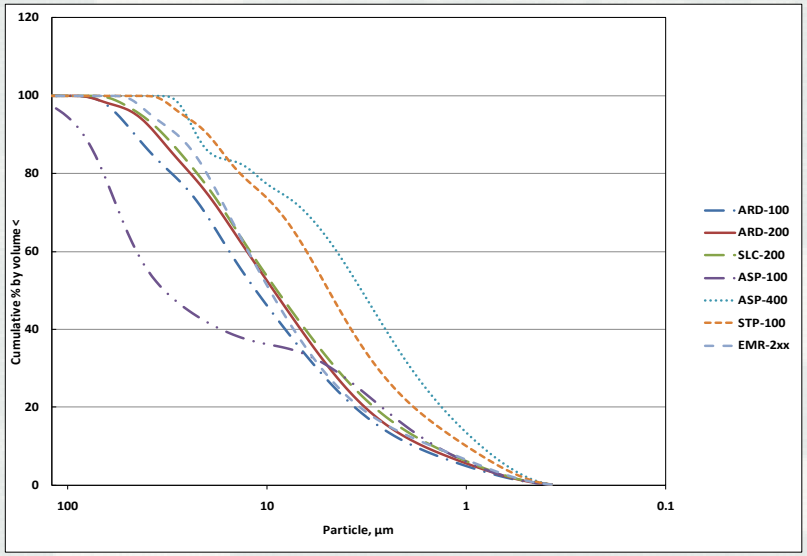


Seiter and Chappell, U.S. Army ERDC

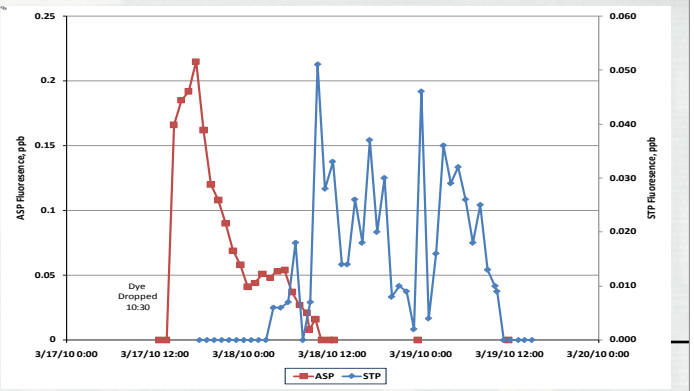
Time-critical studies (ERDC)

High-intensity dredge cell

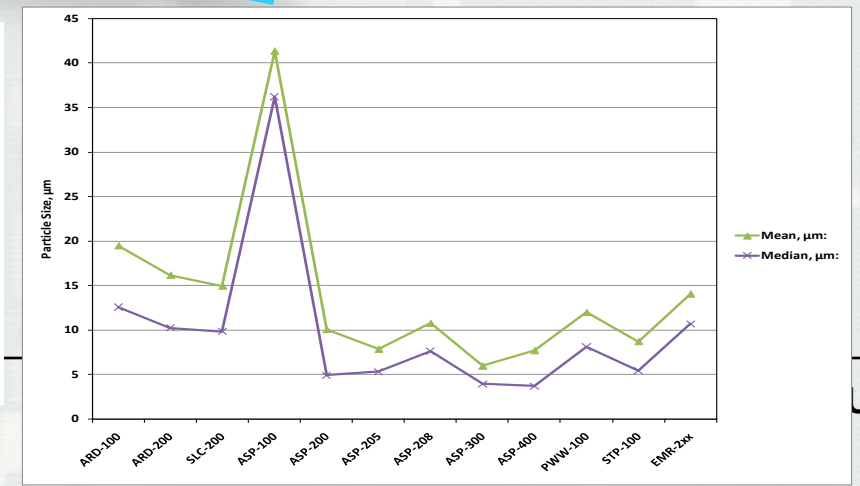




Grain size measurements



Dye tracer studies



Mean & median PSD

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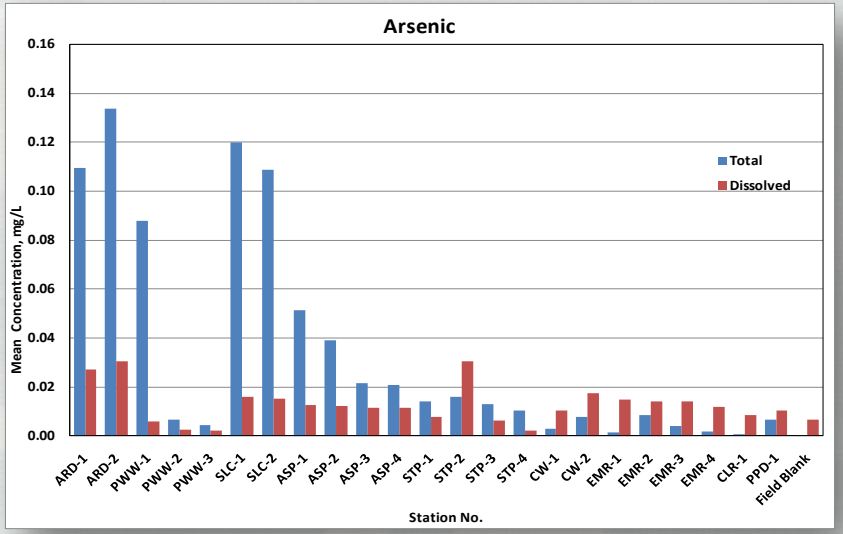
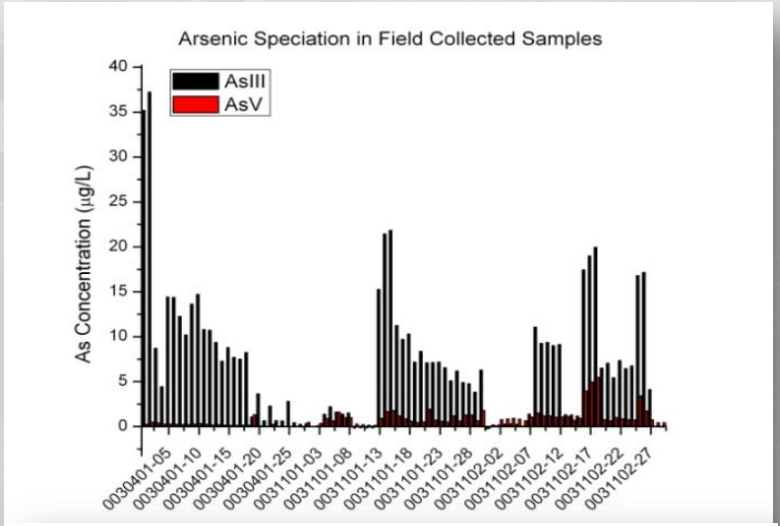
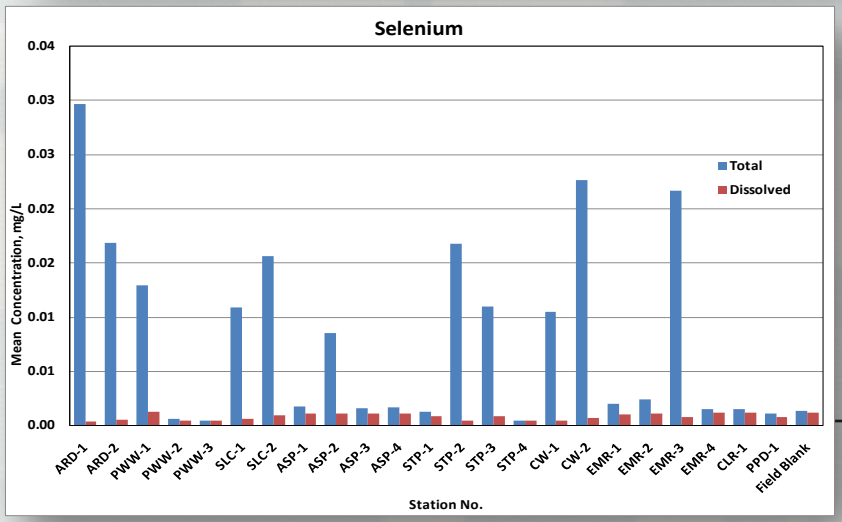
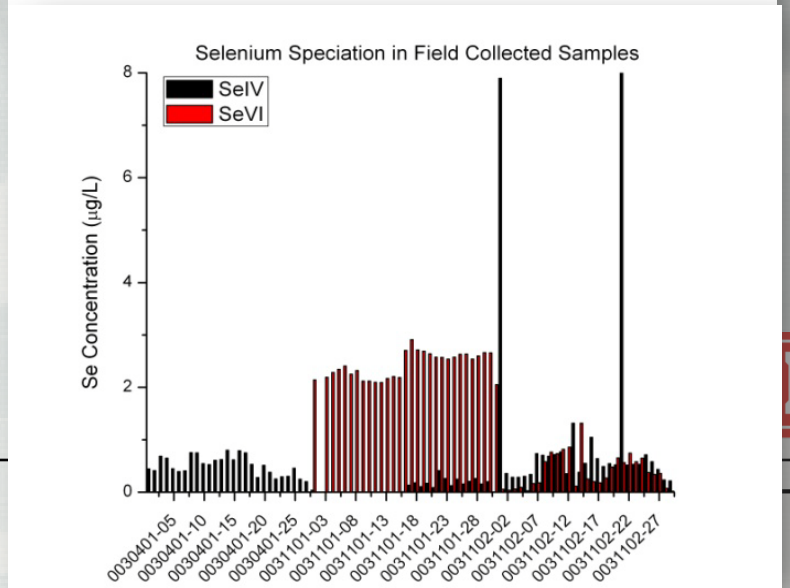
Aqueous As and Se speciation during high-intensity dredge









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Relating Chemical Speciation to Dissolution Kinetics and Bioaccumulation

Dean Hesterberg (PI), Owen Duckworth, and David Buchwalter (North Carolina State University)

Overall Goal: to determine how chemical forms of metals affect their mobilization to the aqueous phase and their bioavailability to algae and toxicity to insect larvae.

The Results may lead to improved predictive models of mobility and toxicity, and thus better risk assessments, based on chemical characteristics of fly ash.

Chemical Speciation

- X-ray absorption spectroscopy
- X-ray diffraction
- Electron and X-ray microscopy

Bioaccumulation

- Uptake of metals from solution by periphyton
- Accumulation of metals by mayfly larvae grazing on periphyton from uptake experiments

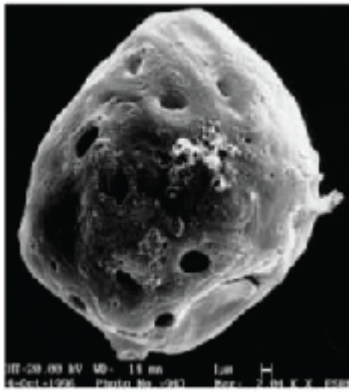
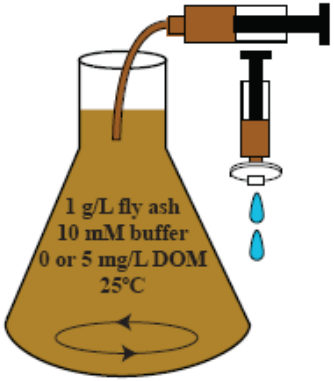


Image: Rindby et al. (2003)

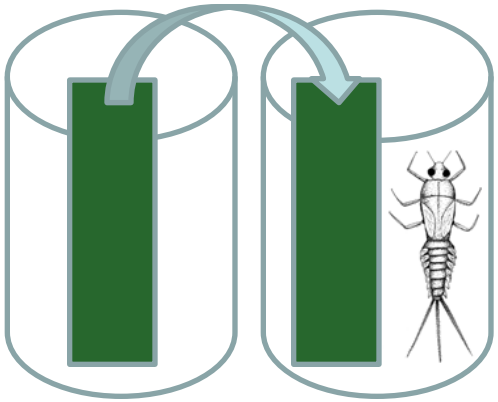
Chemically characterized ash sample

Relates speciation to reactivity



Supernatant from dissolution experiments

Relates reactivity to bioavailability



Dissolution

- Kinetic profiles of metal solubilization
- Batch dissolution approach to simulate oxic and anoxic riverene environments

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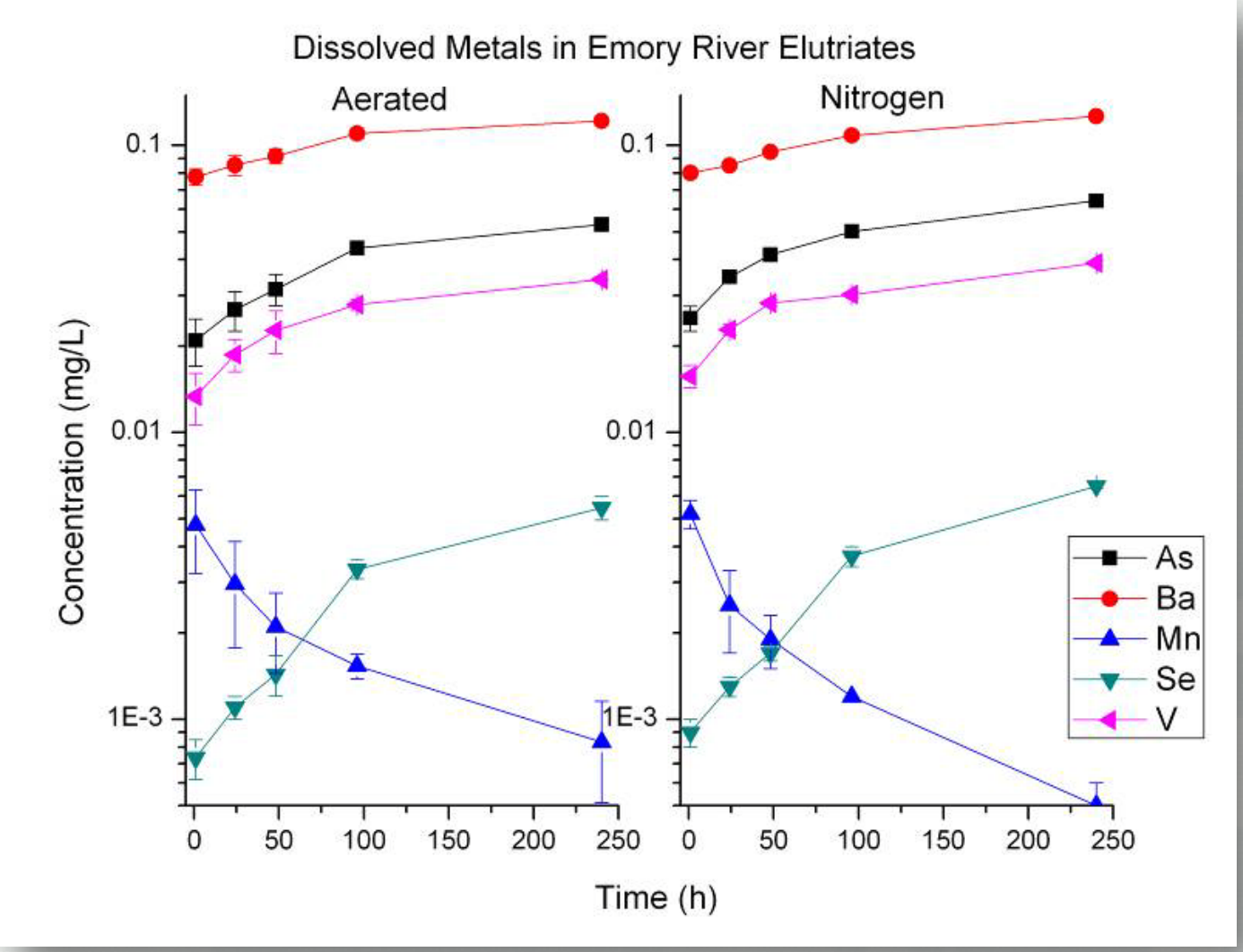
NC STATE UNIVERSITY

III. Ash stability – dissolution potential



Elutriate studies: ERDC

Bednar et al., 2010, Chemosphere

Leaching potential

- Sedwick and Cutter (Old Dominion University)
  - Novel flow-through leaching method
  - Estimates of fractional dissolution and/or uptake
- Ryan (Univ. Colorado) and Aiken (USGS):
  - They plan to conduct batch leaching at
    - different mixing energies (characteristic of rivers),
    - varying pH values, and
    - varying concentrations of dissolved organic matter.
- Vengosh et al. (Duke University):
  - Effects of Ca content of ash and various environmental factors (e.g., pH, redox, humic matter, sulfate-reducing bacteria) on metals/metalloid dissolution, methylation potential of any mercury in the ash, and
  - Chemical equilibrium modeling of the dissolution process using MINEQL

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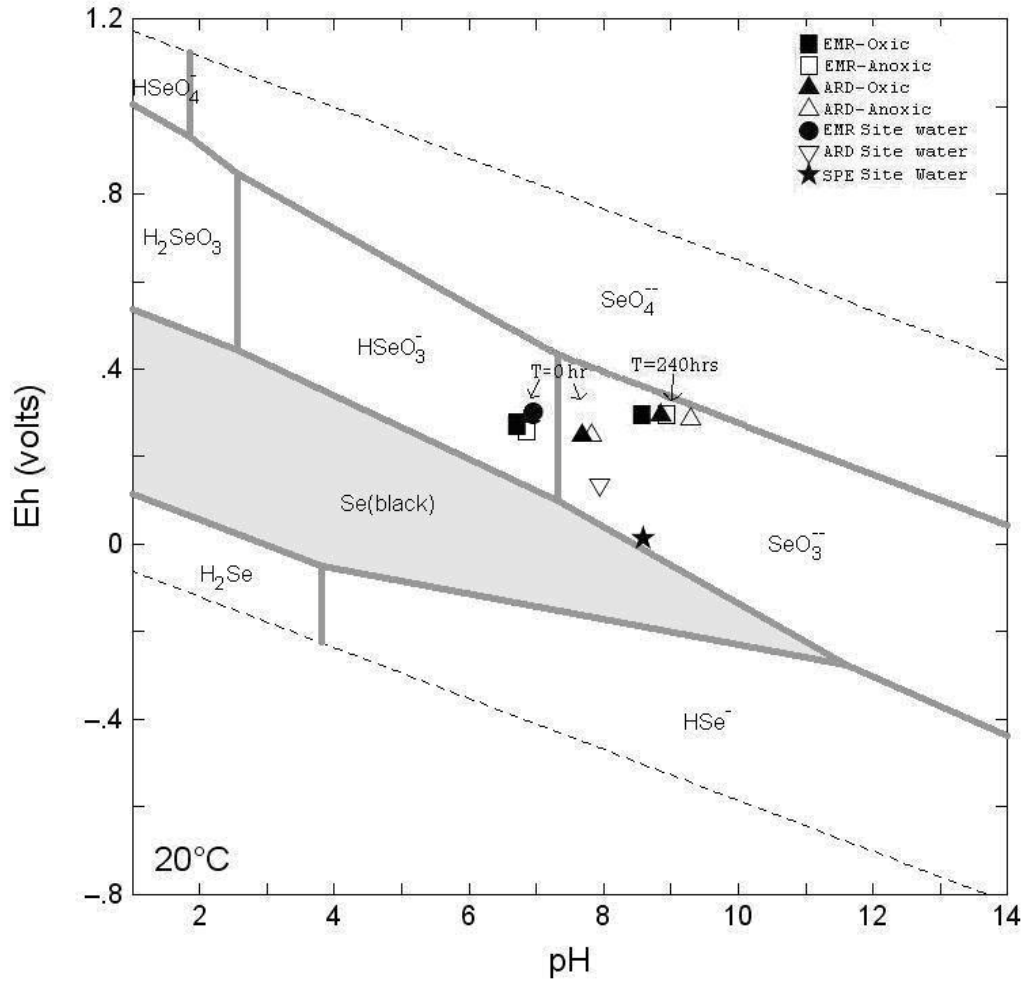
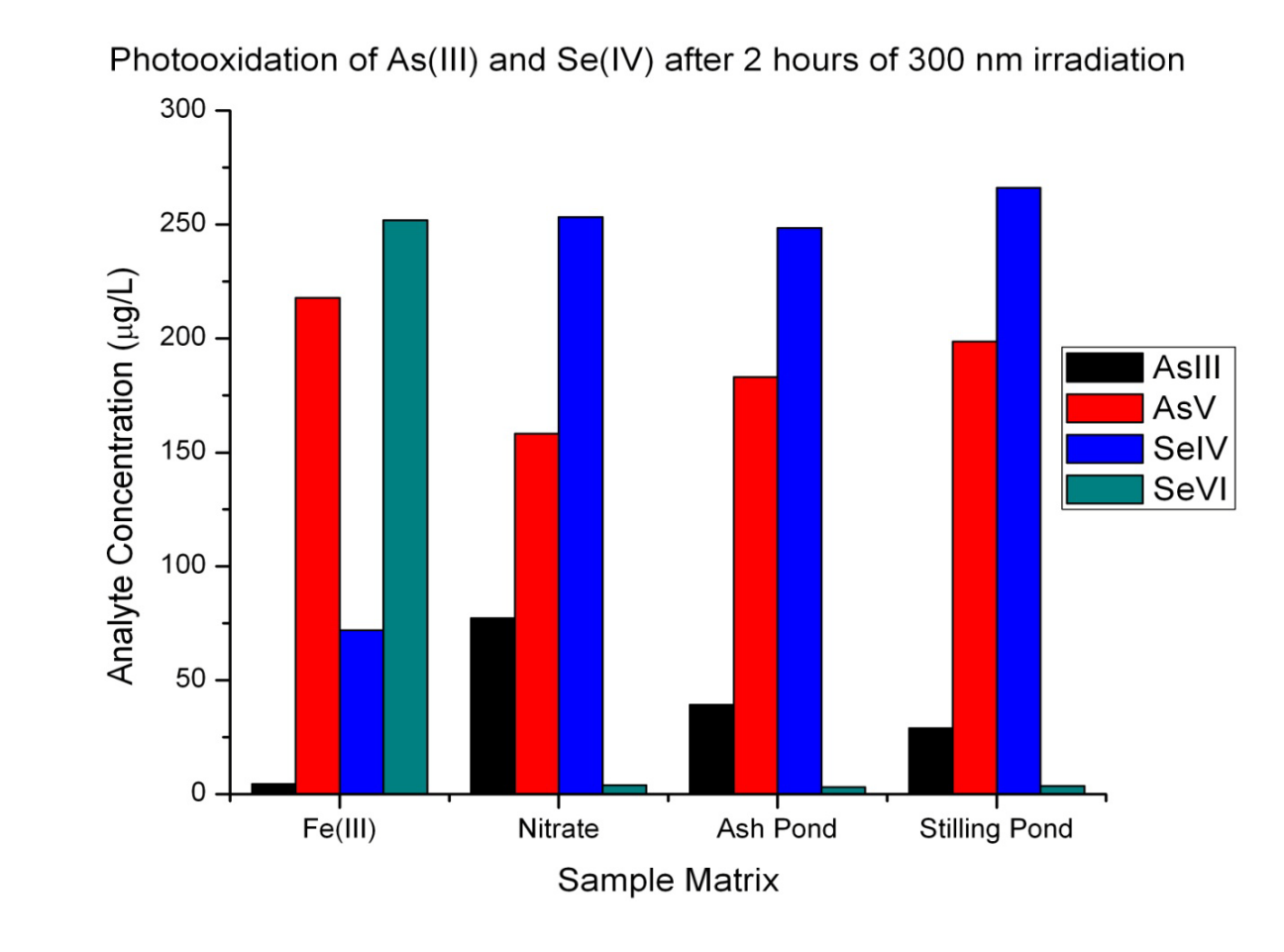
Thermodynamic analysis: Pourbaix diagrams

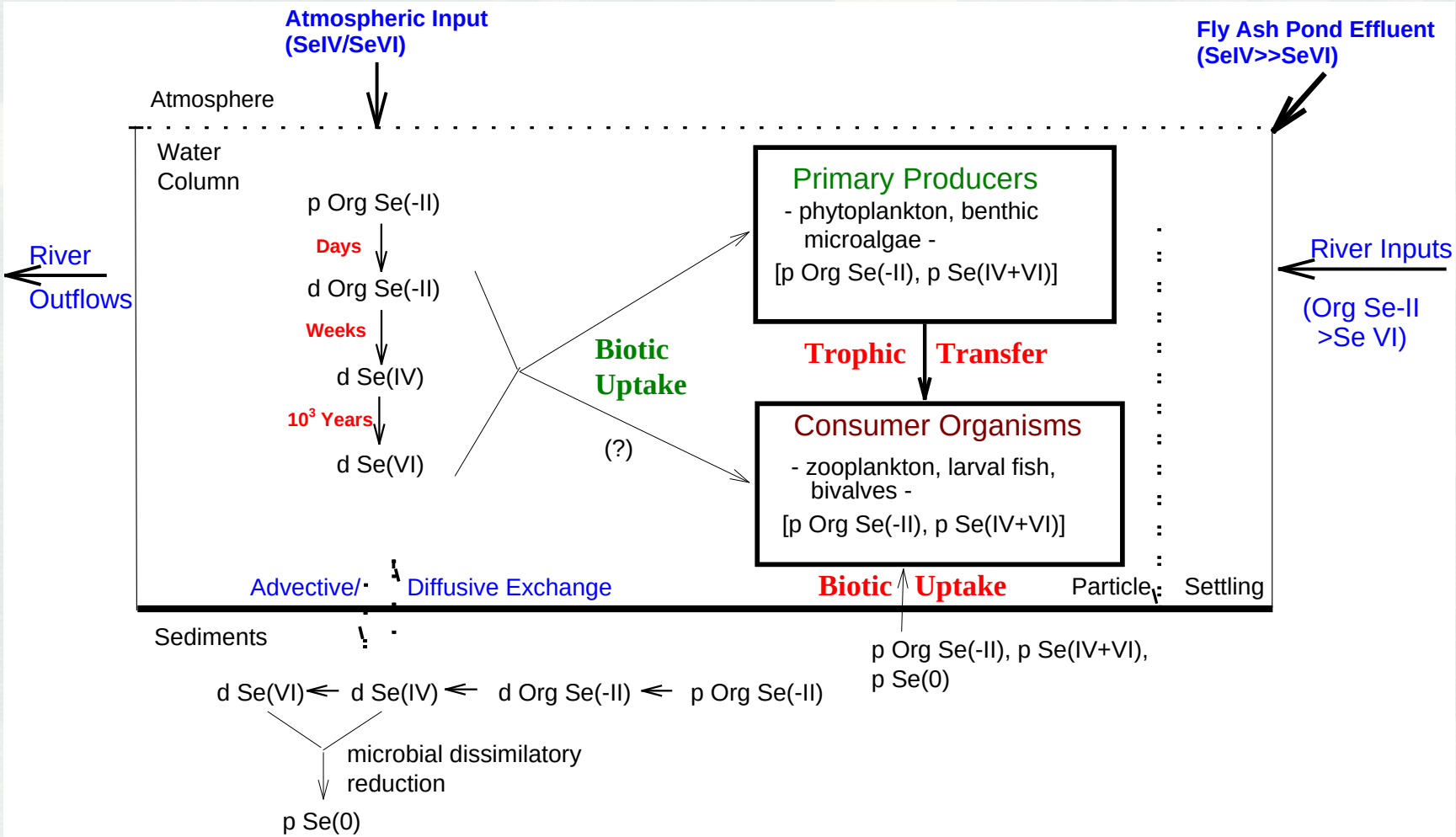


Susceptibility of As (III) and Se(IV) photooxidation in ARD



IV. Mobility & Bioavailability

Selenium biogeocycling in the river system

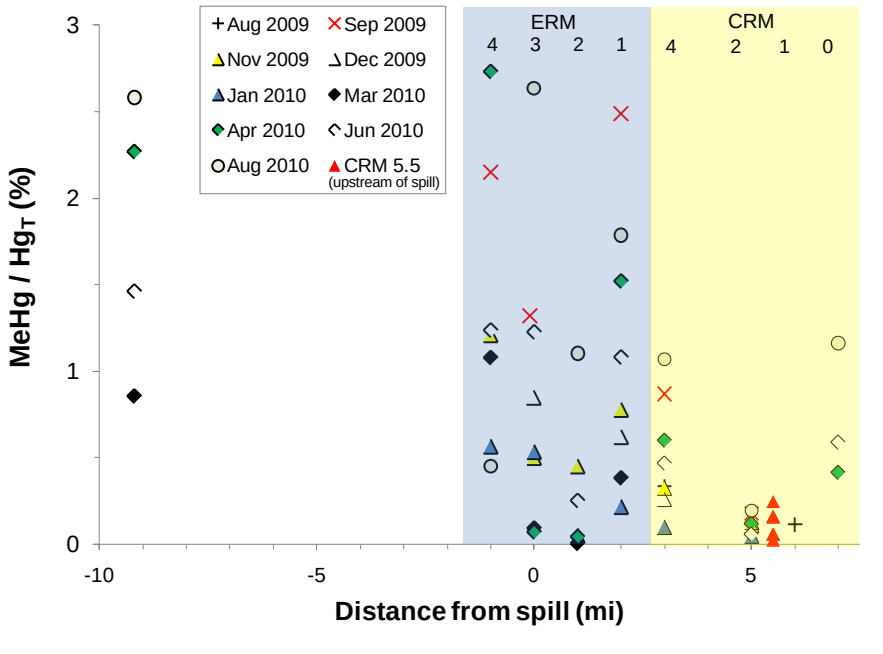


SETAC poster presentation:

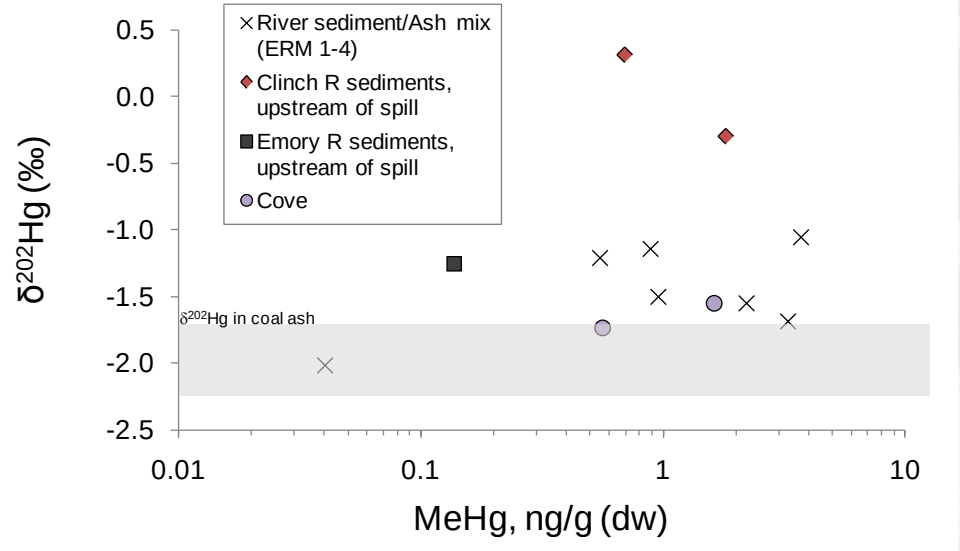
Methylmercury contamination of river sediments near the coal ash spill at the Kingston Fossil Plant, TN

Deonarine A., Hsu-Kim H., Ruhl L., and Vengosh A.
Duke University
Bartov G., Johnson T.
University of Illinois, Urbana-Champaign

Methylmercury in Emory and Clinch Rivers



Hg isotope tracking



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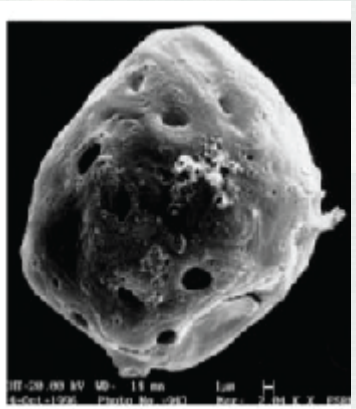

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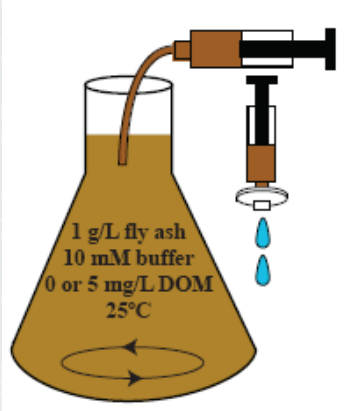

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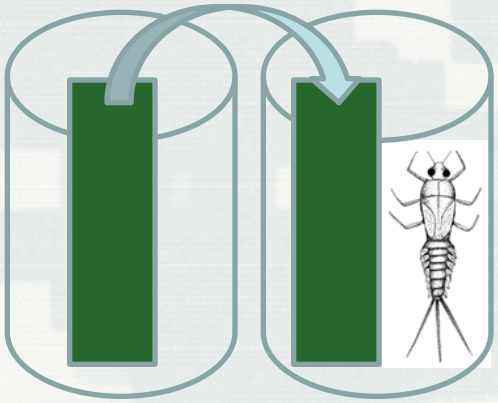

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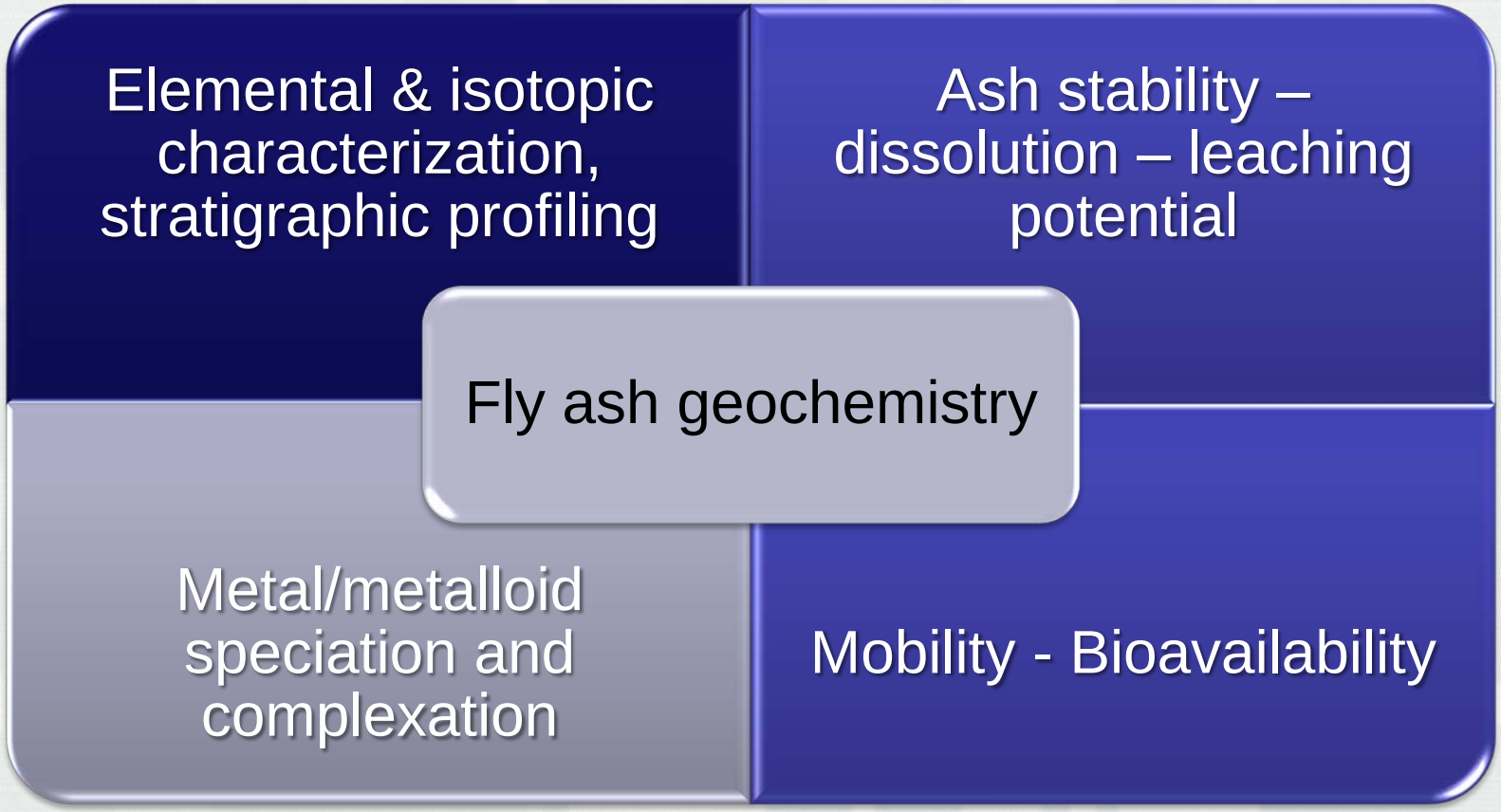
Summary



- **Linking geochemistry with potential bioavailability and toxicity**
- **Extrapolation of findings to the Clinch & Tennessee River systems**

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