Characterization of Arsenic and Selenium in Coal Fly Ash to Improve Evaluations for Disposal and Reuse Potential

Award #DE-FE0031748

DOE-NETL 2020 FE R&D Virtual Project Review Meeting –
Sensors and Controls

Presenting:

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Project Team

<u>Duke University</u>

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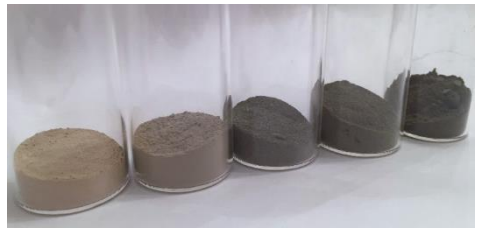
<u>External Advisors</u>:

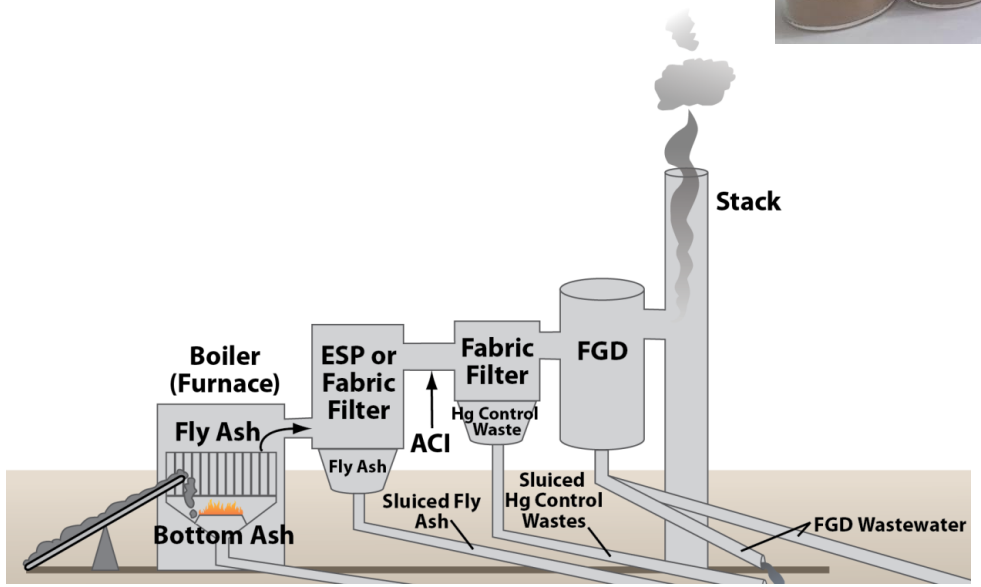
SEFA Group

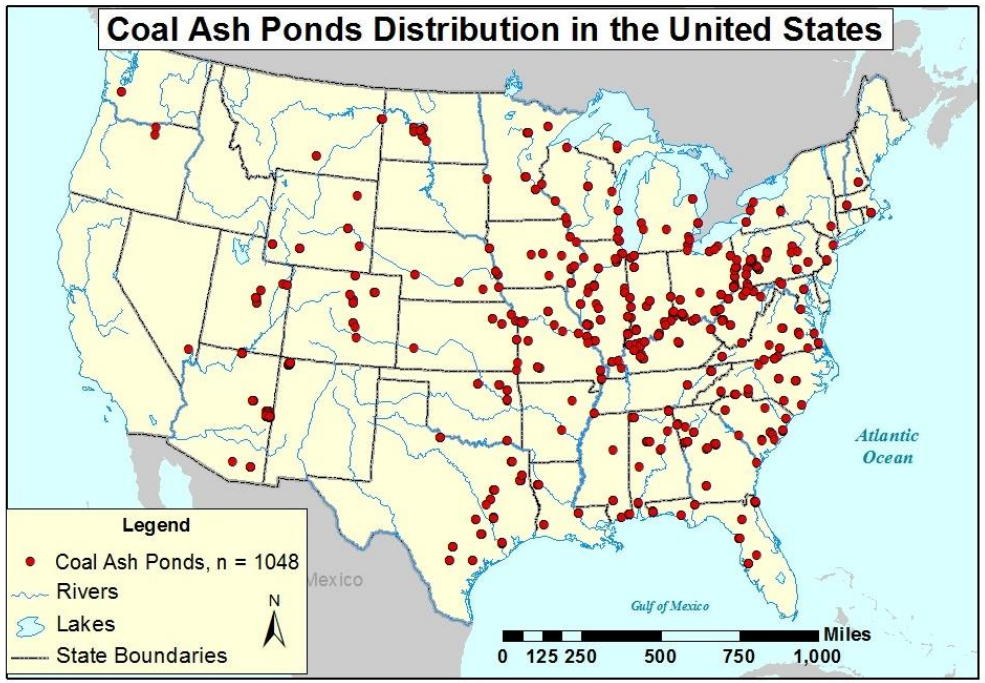
Santee Cooper

Motivation and Significance

Coal Combustion Residues:
~100 million tons yr^{-1} in U.S.







~60% for beneficial use
fly ash - concrete
gypsum - drywall

(American Coal Ash Association)

~40% stored/discarded
as unused solid waste

Motivation and Significance

Coal ash disposal sites

Dan River Steam Station (NC), Feb. 2014

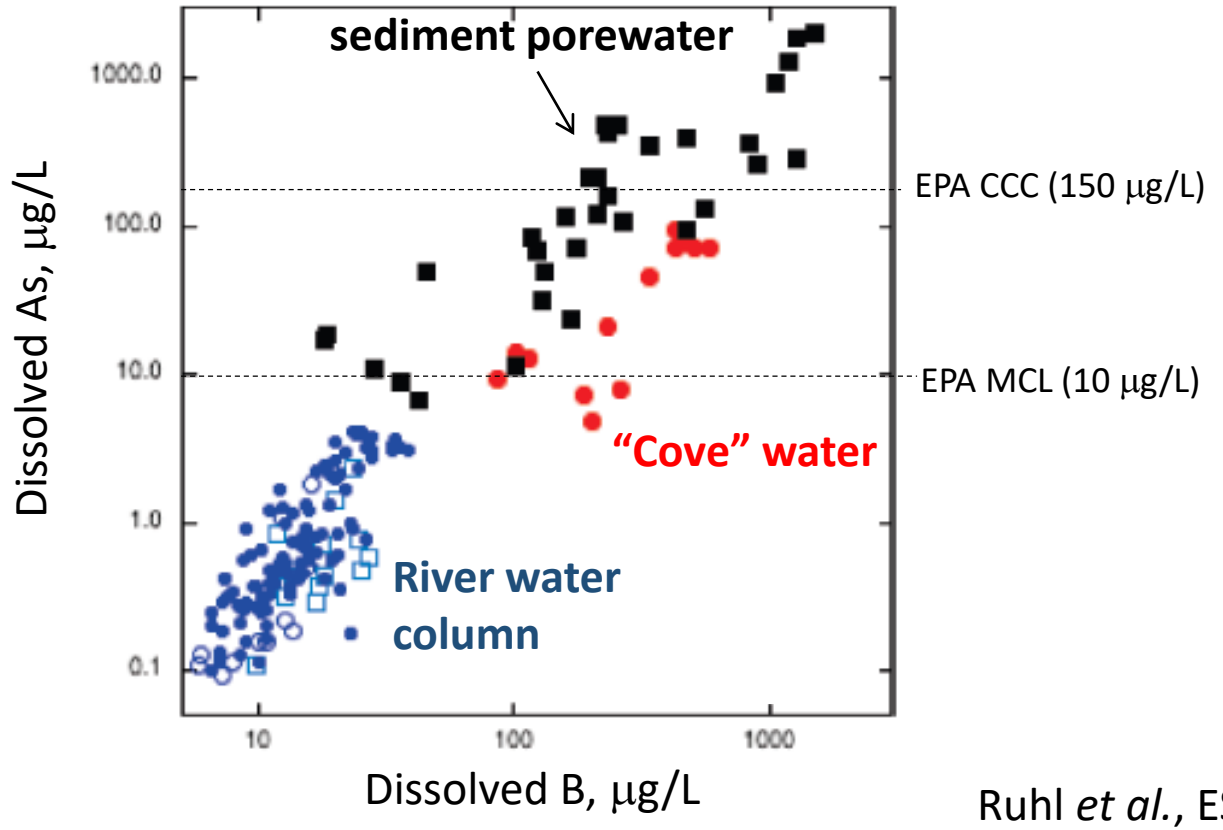
Sutton Plant at Sutton Lake (NC), Sept. 2018

TVA Kingston (TN), Dec. 2008

Motivation and Significance

Arsenic and selenium are coal ash constituents that can pose problems near disposal sites

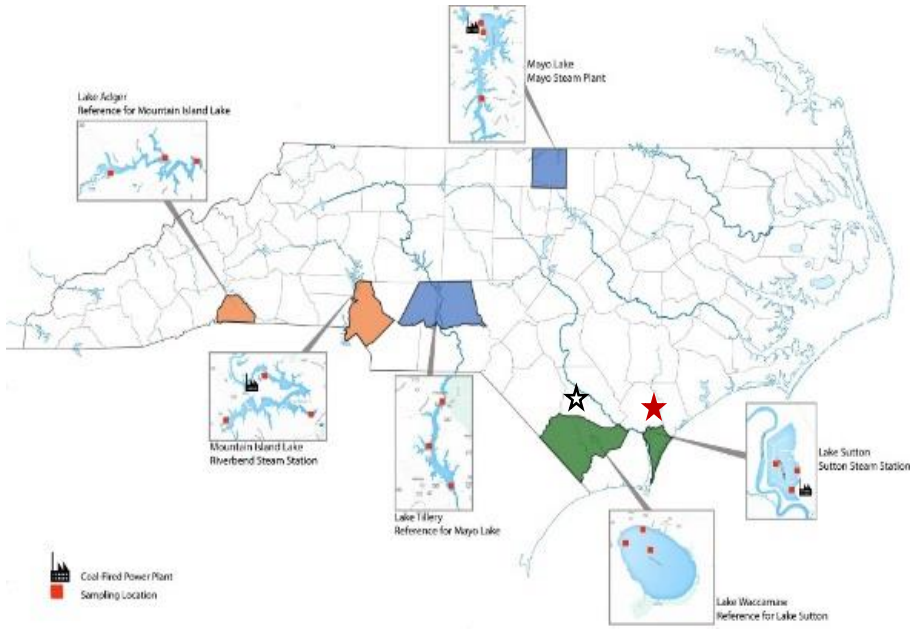
TVA-Kingston coal ash spill disaster:
River water and sediments



Ruhl *et al.*, ES&T 2010

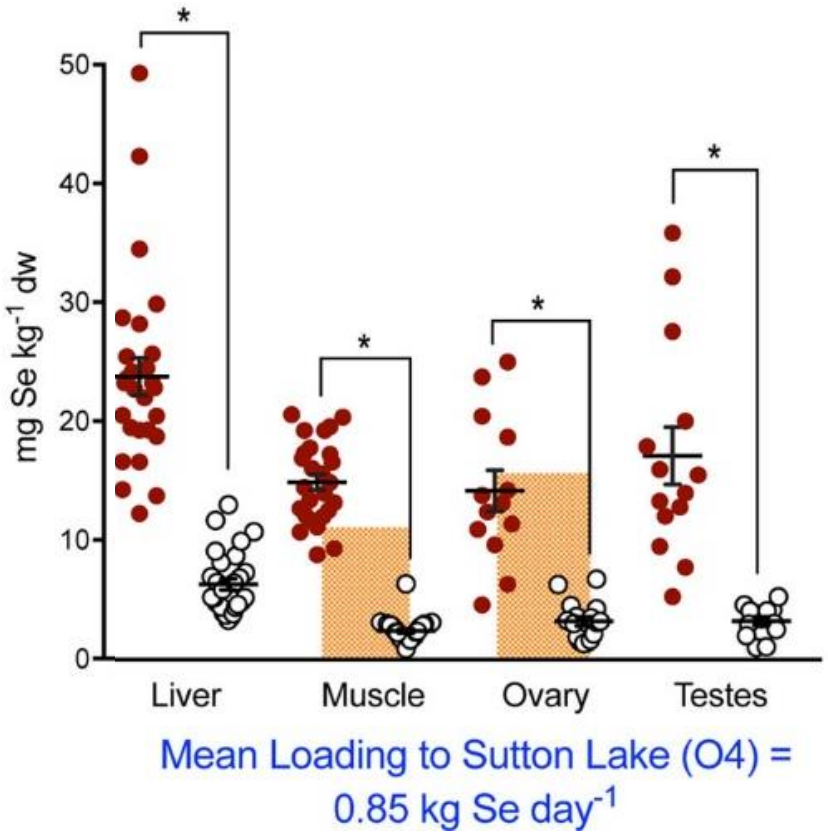
Motivation and Significance

Arsenic and selenium are coal ash constituents that can pose problems near disposal sites



Selenium in fish

Sutton Lake, NC (near coal ash pond) vs. **Lake Waccamaw, NC** (reference site)



Brandt et al, *ES&T*, 2017

Statement of Project Objectives

Project goal:

To improve methods to evaluate arsenic and selenium risk potential in coal fly ash

Coal Fly Ash
- Coal feedstock
- Boiler type
- Air pollution controls (SCR)
- Operations (startup, steady state)

1) Arsenic and Selenium analysis methods

Deterministic
- ICP-MS
- Synchrotron XAS (bulk and microprobe)

Semi-Quantitative
- X-ray fluorescence
- X-ray photoelectron spectr.
- Infrared spectr.
- Speciation of leachable As/Se

As, Se content, valence states, mass distribution

2) Correlate material analyses with As/Se leaching

As, Se mobilization potential
TCLP, LEAF

3) Perform broad survey of fly ashes

Today's presentation

1. Solid State XRF for arsenic and selenium content
2. Microscale speciation of As and Se in fly ash
3. Leaching and transformation potential of As and Se

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Correlate material analyses with As/Se leaching

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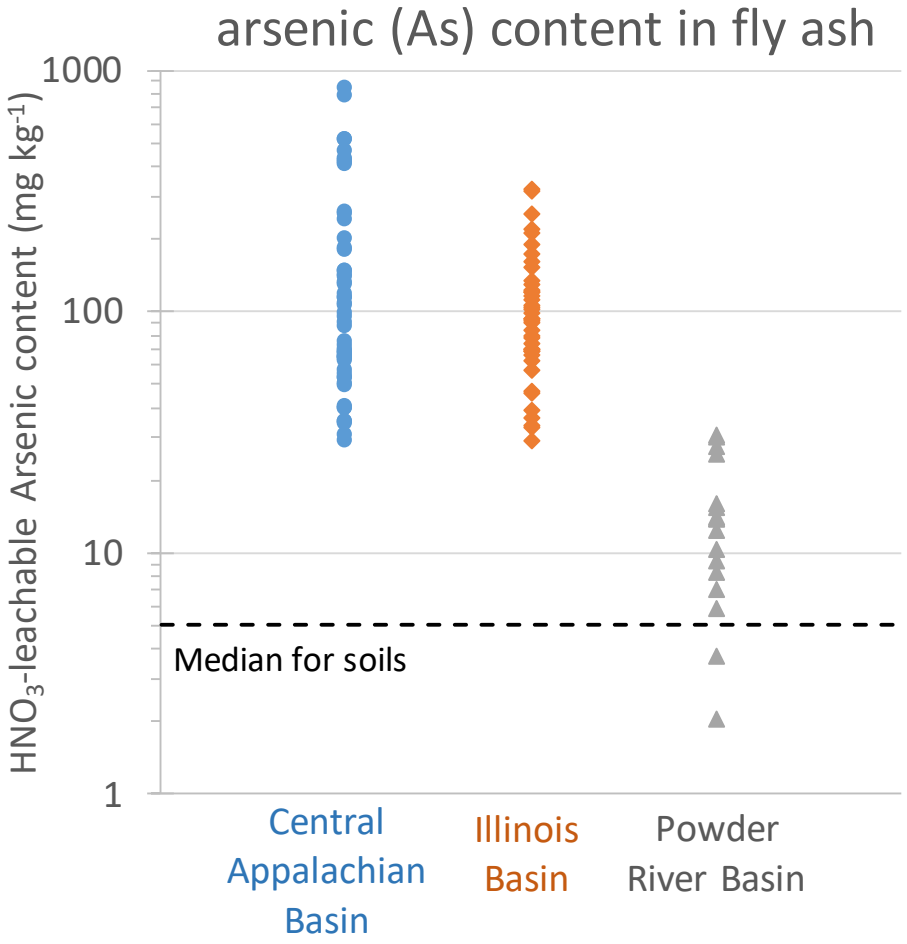
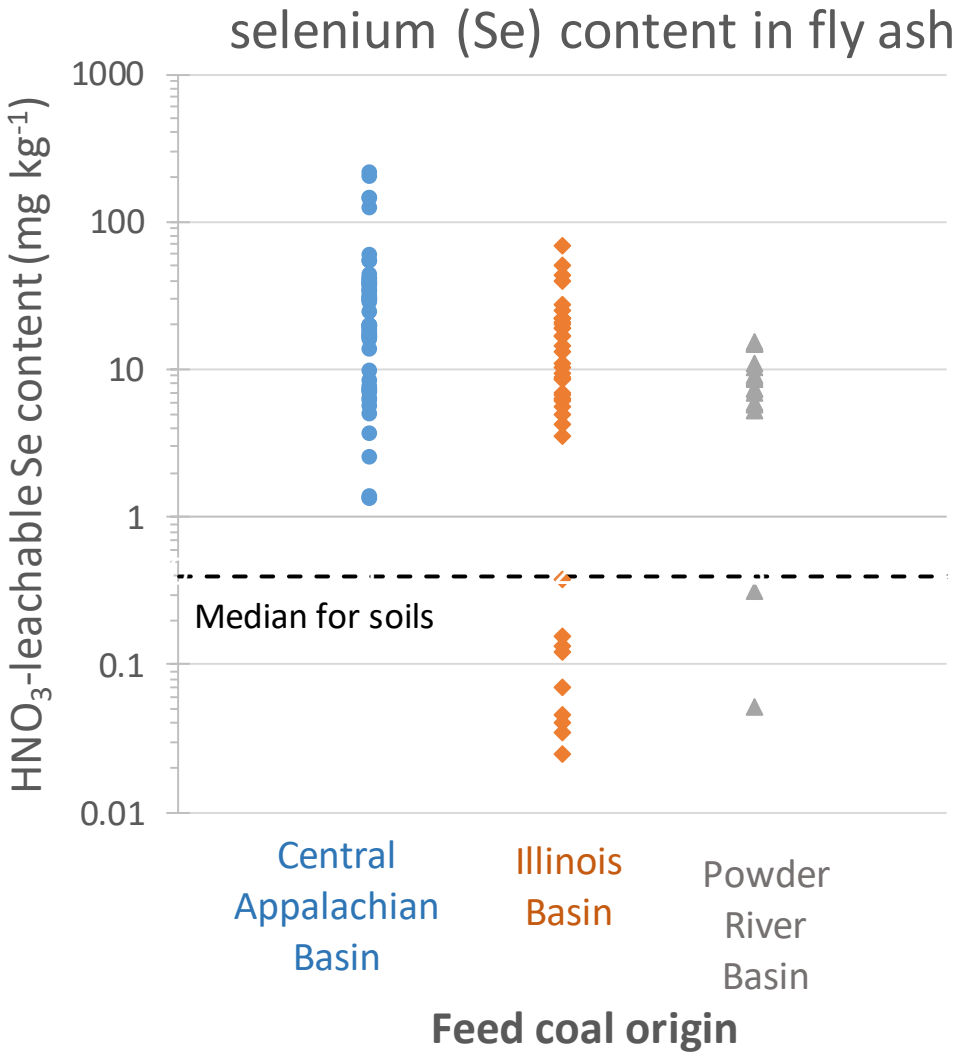
1. Total Arsenic and Selenium Contents in Coal Fly Ash

- Widely variable amounts of As and Se in coal fly ash
- Depends partly on the type of feed coal





Taggart et al. 2016 ES&T

1. Total Arsenic and Selenium Contents in Coal Fly Ash

Fly ash materials representing:

- Feed coals
- Combustor types
- Post-combustion flue gas treatment

Coal fly ash samples for this project

Sample ID (labelled by location)	Feed Coal	Year		Total As (mg/kg)	Total Se (mg/kg)
KY #1	App	2015	storage silo	132	16
KY #3	App	2006		7150	208
KY #3	IL	2012 2013	No lime Lime injection	123 70	6 44
KY #4	IL	2012		135	17
KY #5	App	2018	Startup mode w/ SCR Baseline mode w/ SCR	41.5 26.1	13.4 6.6
TN #1	App	2011		44	19
TX #1	PRB	2015		51	18
GA #1	PRB	2015		24	13
NM #1	San Juan	2013		23	6

1. Total Arsenic and Selenium Contents in Coal Fly Ash

Analysis Parameter

total As/Se content

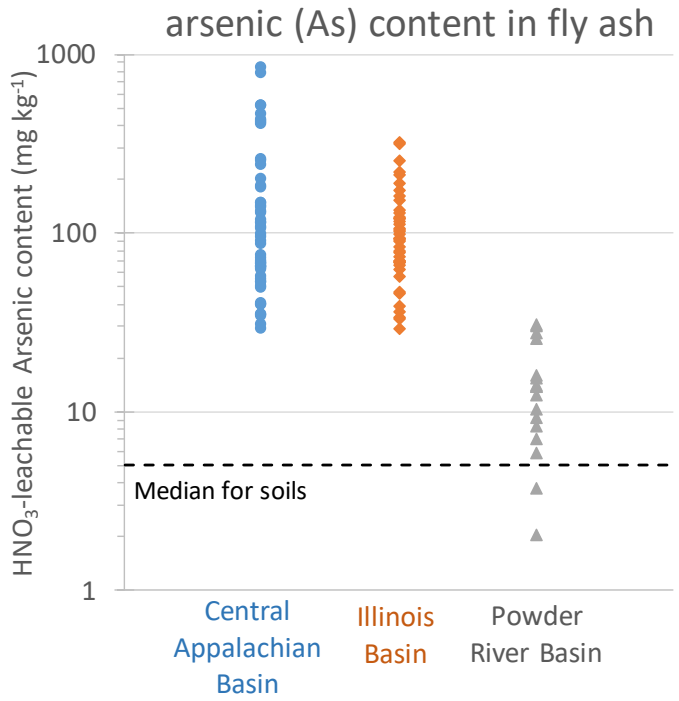
speciation and mass distribution

Analysis Methods

Deterministic

- ICP-MS after acid digestion

- Synchrotron X-ray Absorption Spectroscopy (bulk and microprobe)



Disadvantages :

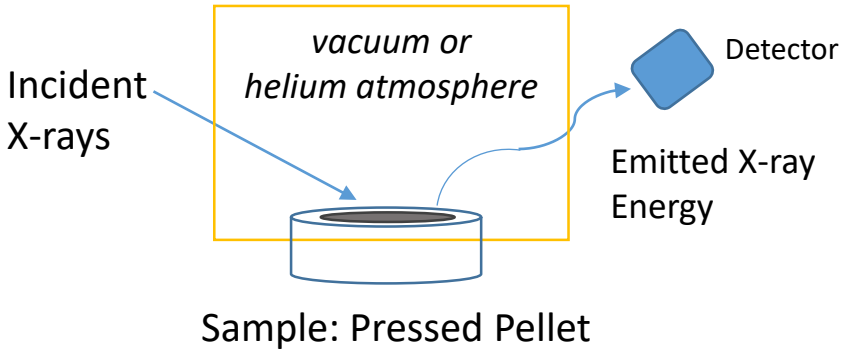
- Involves hazardous chemicals
- Labor intensive
- Requires advanced technical expertise
- Limited access to equipment

1. Total Arsenic and Selenium Contents in Coal Fly Ash

Analysis Parameter	Analysis Methods	
	Deterministic	**Semi-Quantitative**
total As/Se content	•ICP-MS after acid digestion	•X-ray fluorescence •Infrared spectroscopy
speciation and mass distribution	•Synchrotron X-ray Absorption Spectroscopy (bulk and microprobe)	•X-ray photoelectron spectroscopy •Speciation of leachable As/Se via LC-ICPMS

1. Total Arsenic and Selenium Contents in Coal Fly Ash

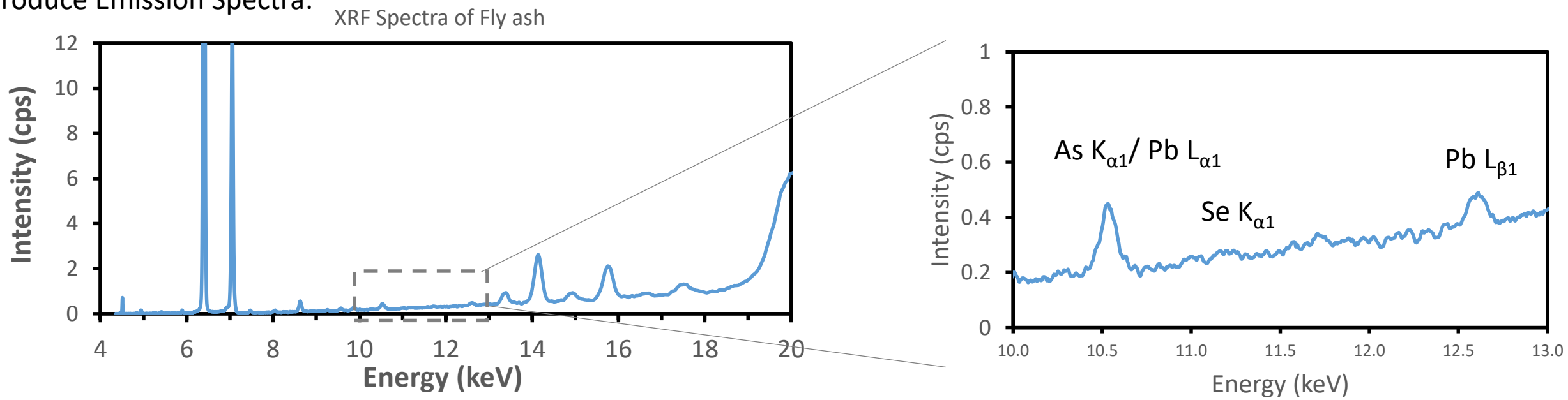
X-ray Fluorescence (XRF for arsenic analysis)



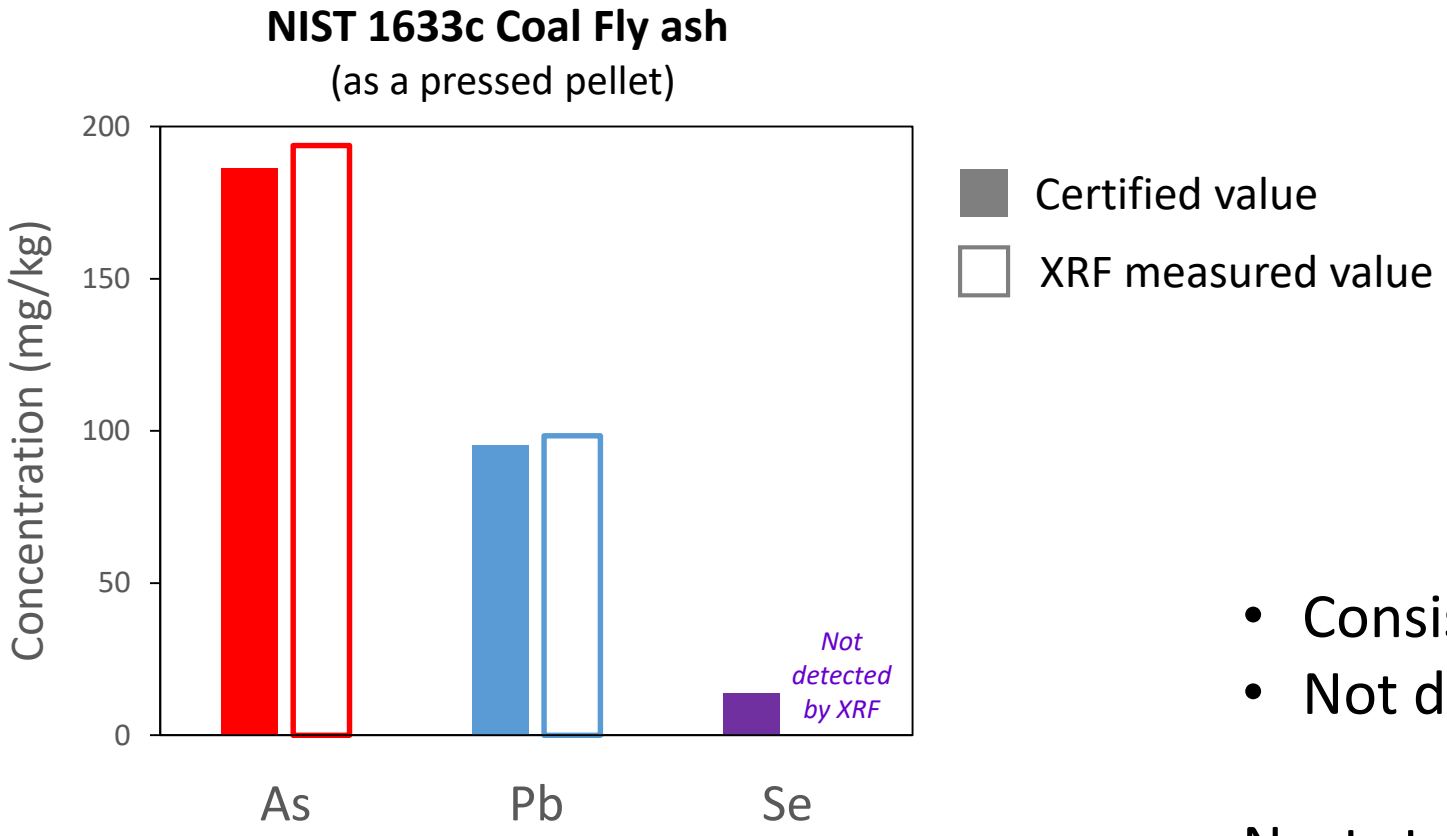
Emission energies: As $K_{\alpha1}$-10.54 keV
Pb $L_{\alpha1}$ -10.55 keV
Pb $L_{\beta1}$ -12.61 keV
Se $K_{\alpha1}$ -11.22 keV

As and Pb have a similar emission energy.
Need to collect Pb $L_{\beta1}$ emission to determine As.

Produce Emission Spectra:



1. Total Arsenic and Selenium Contents in Coal Fly Ash



- Consistent results for Arsenic, Lead
- Not detected for Selenium

Next steps:

Additional samples

Optimization for Se

Today's presentation

1. Solid State XRF for arsenic and selenium content
2. **Microscale speciation of As and Se in fly ash**
3. Leaching and transformation potential of As and Se

Coal Fly Ash
- Coal feedstock
- Boiler type
- Air pollution controls (SCR)
- Operations (startup, steady state)

Perform broad survey of fly ashes

Arsenic and Selenium analysis methods

Deterministic
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- Speciation of leachable As/Se

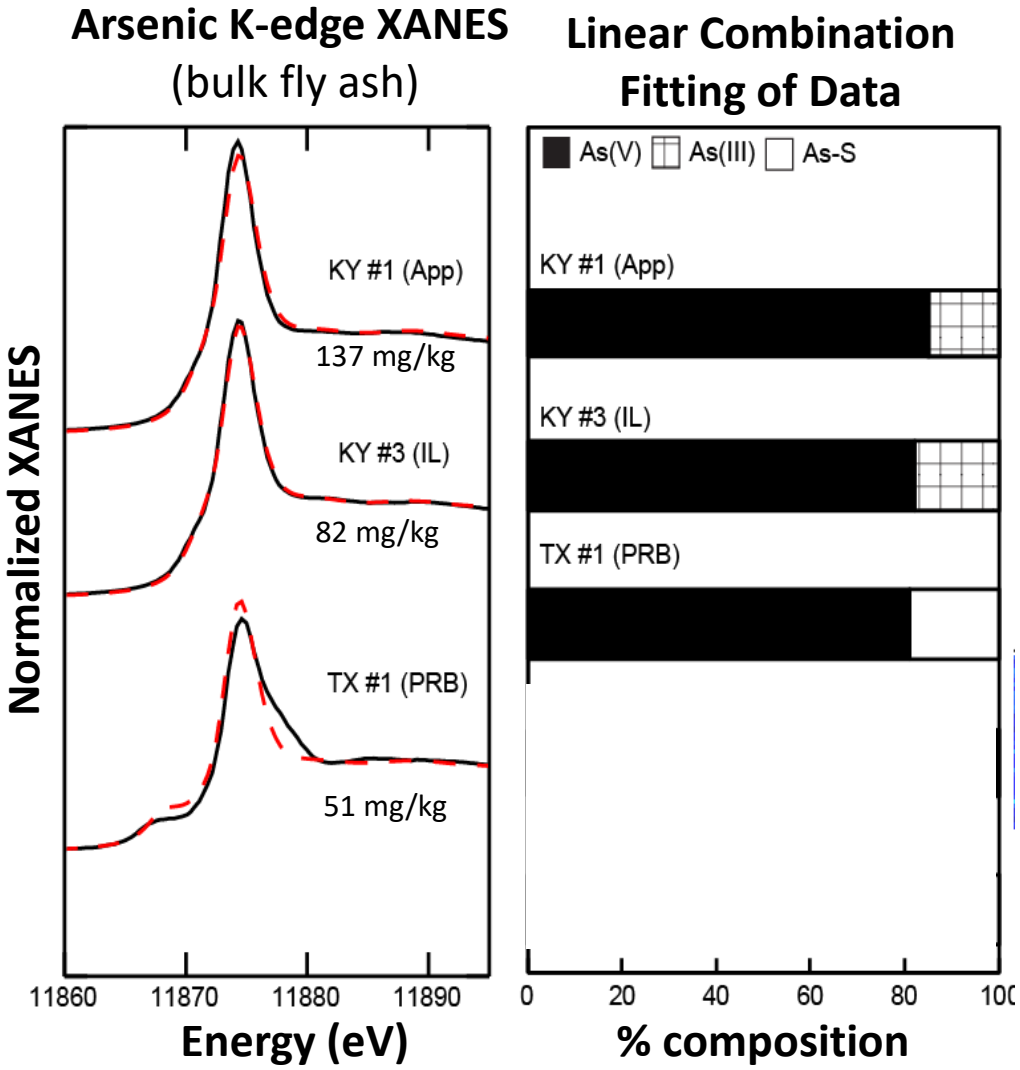
As, Se content, valence states, mass distribution

Correlate material analyses with As/Se leaching

As, Se mobilization potential
TCLP, LEAF

2. Microscale speciation of Arsenic in fly ash

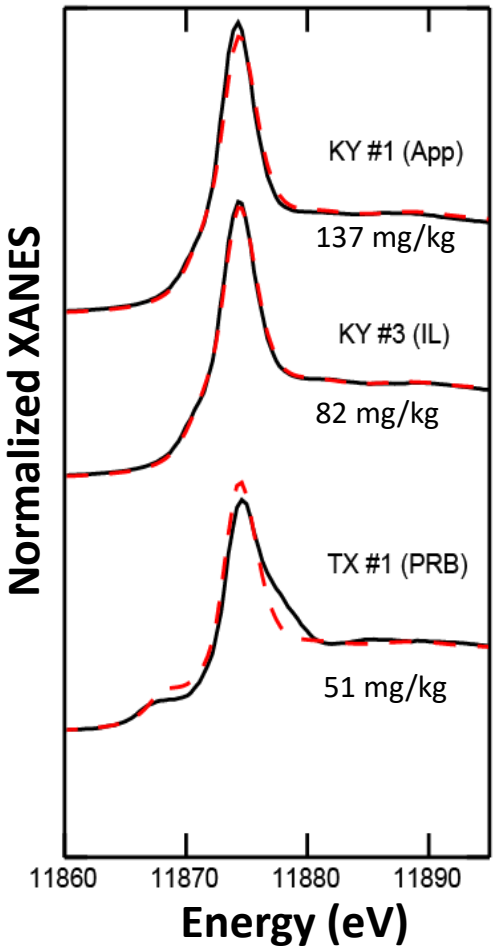
Arsenic is mostly As(V) oxidation state (e.g., AsO_4^{3-} anion)



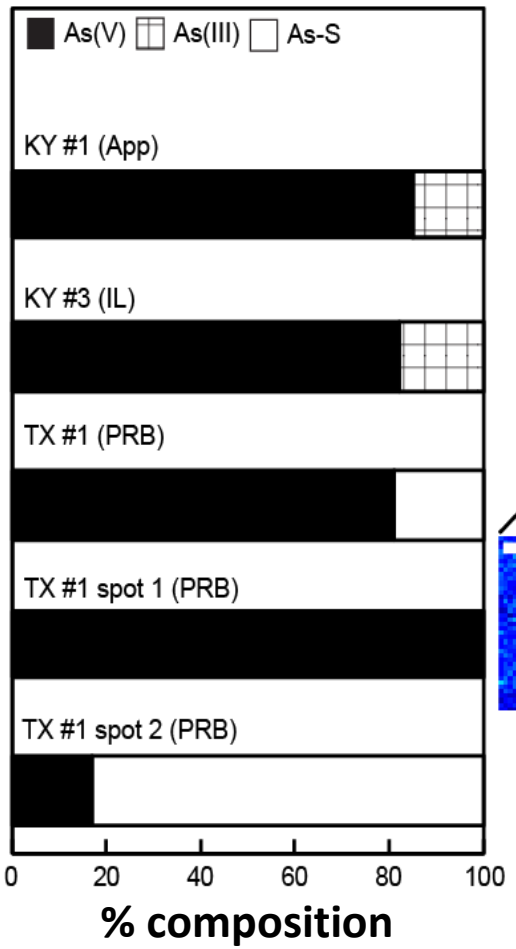
2. Microscale speciation of Arsenic in fly ash

Arsenic is heterogeneously distributed within fly ash grains

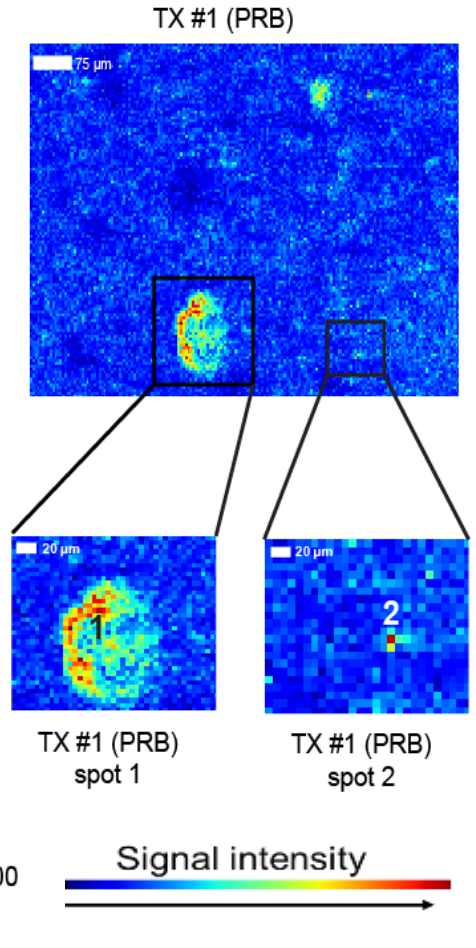
Arsenic K-edge XANES
(bulk fly ash)



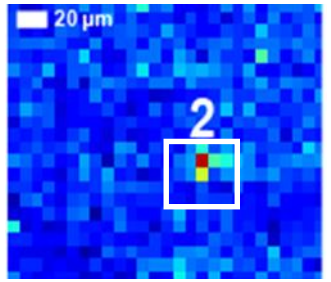
Linear Combination Fitting of Data



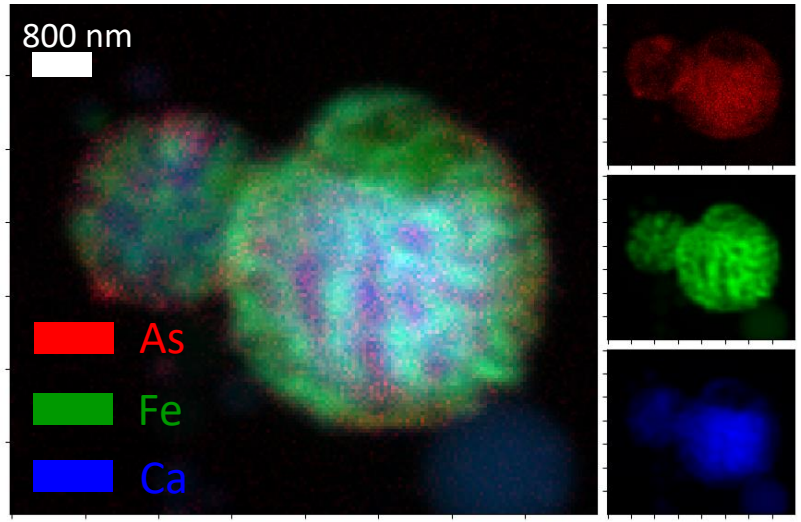
Arsenic spatial distribution (μ-XRF)



TX#1 (PRB)



nano-XRF

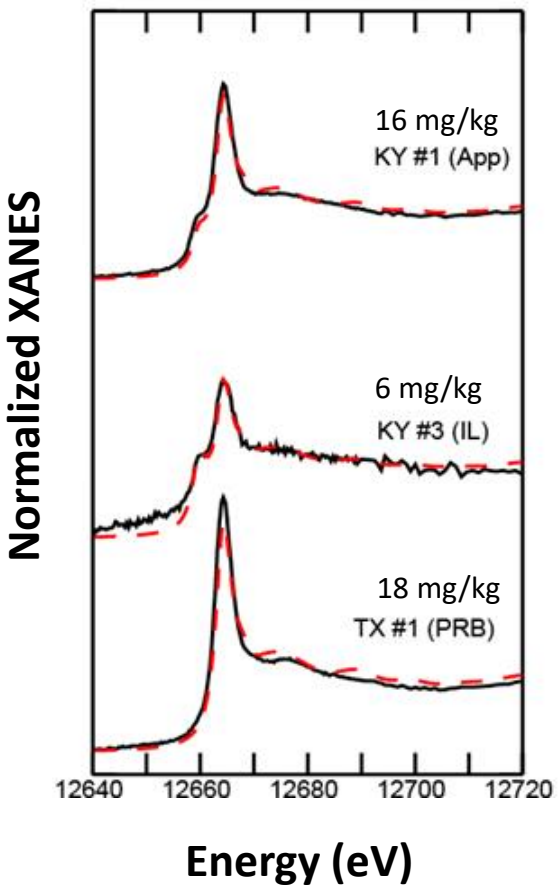


Arsenate As(V) is in one grain and mixed valence As in another grain

2. Microscale speciation of Selenium in fly ash

Selenium is heterogeneously distributed within fly ash grains

Selenium K-edge XANES
(bulk fly ash)



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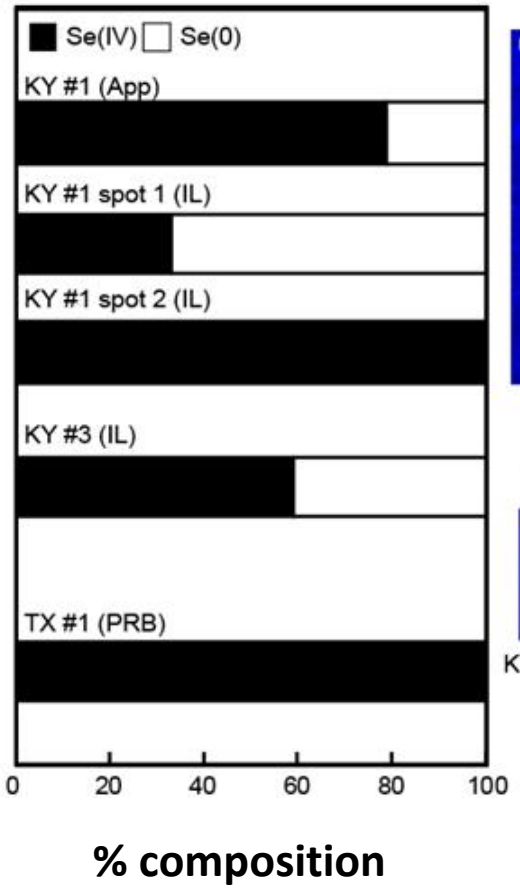
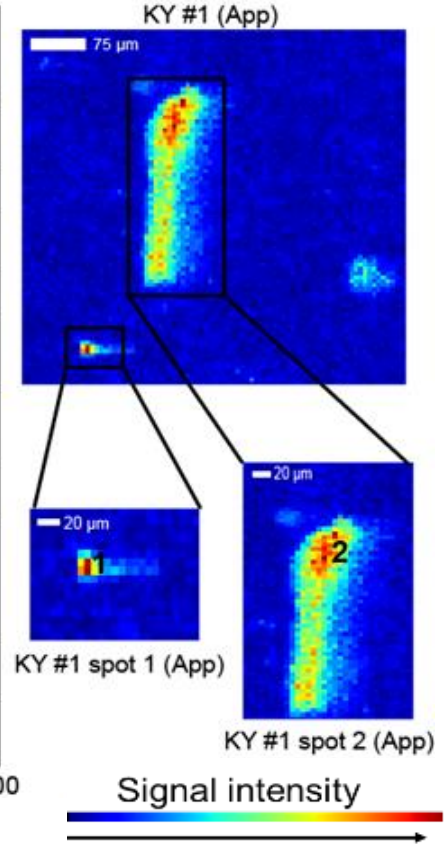
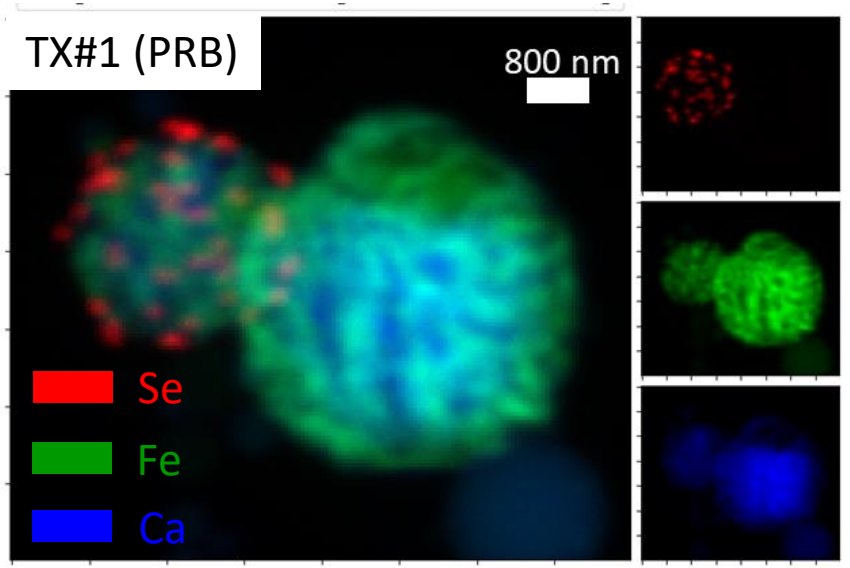


Selenium spatial distribution (μ-XRF)



nano-XRF

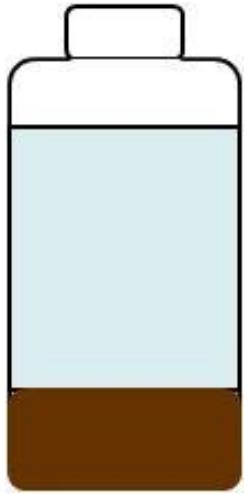


Selenite Se(IV) is in one grain and mixed valence Se in another grain

3. Leaching and transformation potential of As and Se

Toxicity Characteristic Leaching Protocol

50 g ash per liter



Mix for 18 hr

Aqueous concentrations and speciation of As and Se

Compare with properties of fly ash

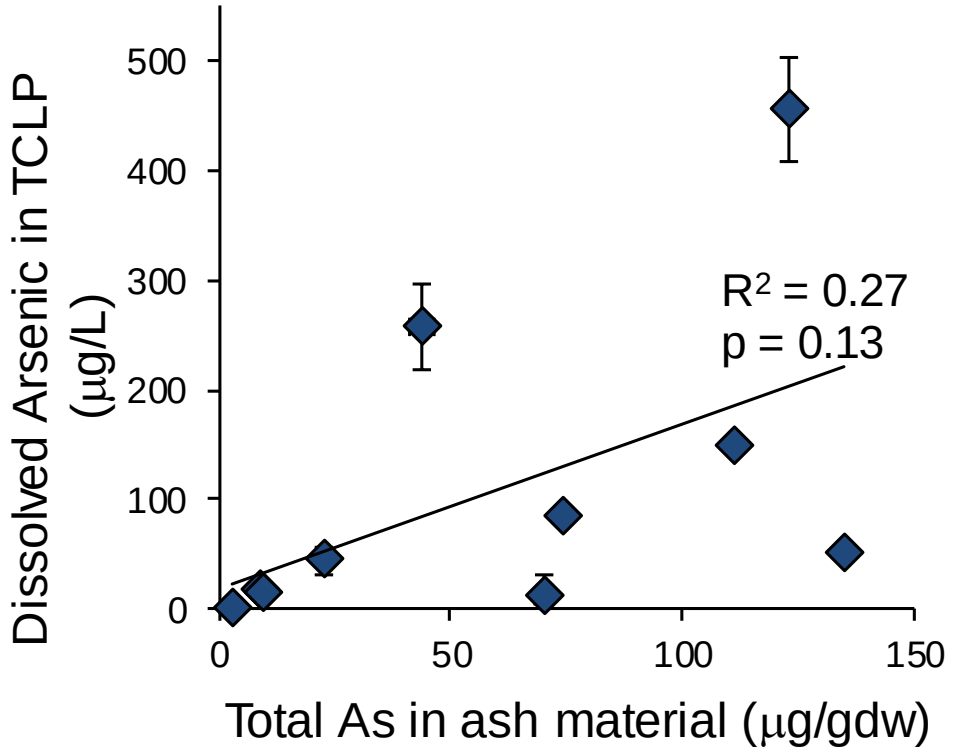
- Chemical composition
- Coal feedstock
- Combustion conditions

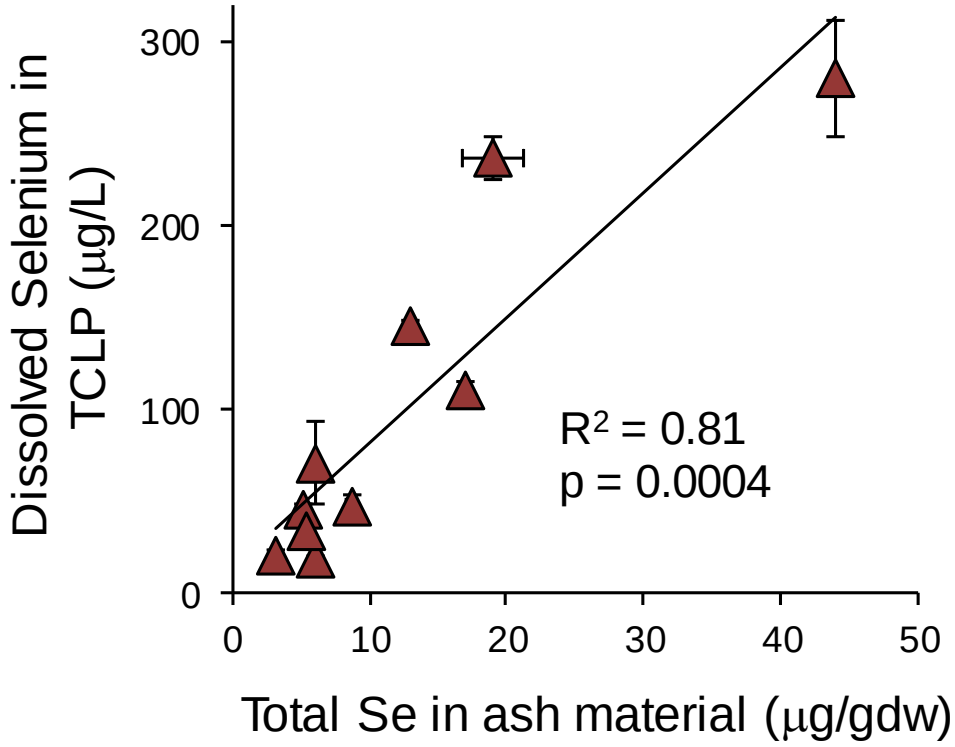
Leachate composition:

- Deionized water
- 0.2 mM acetate/acetic acid (pH 4.9)

3. Leaching and transformation potential of As and Se

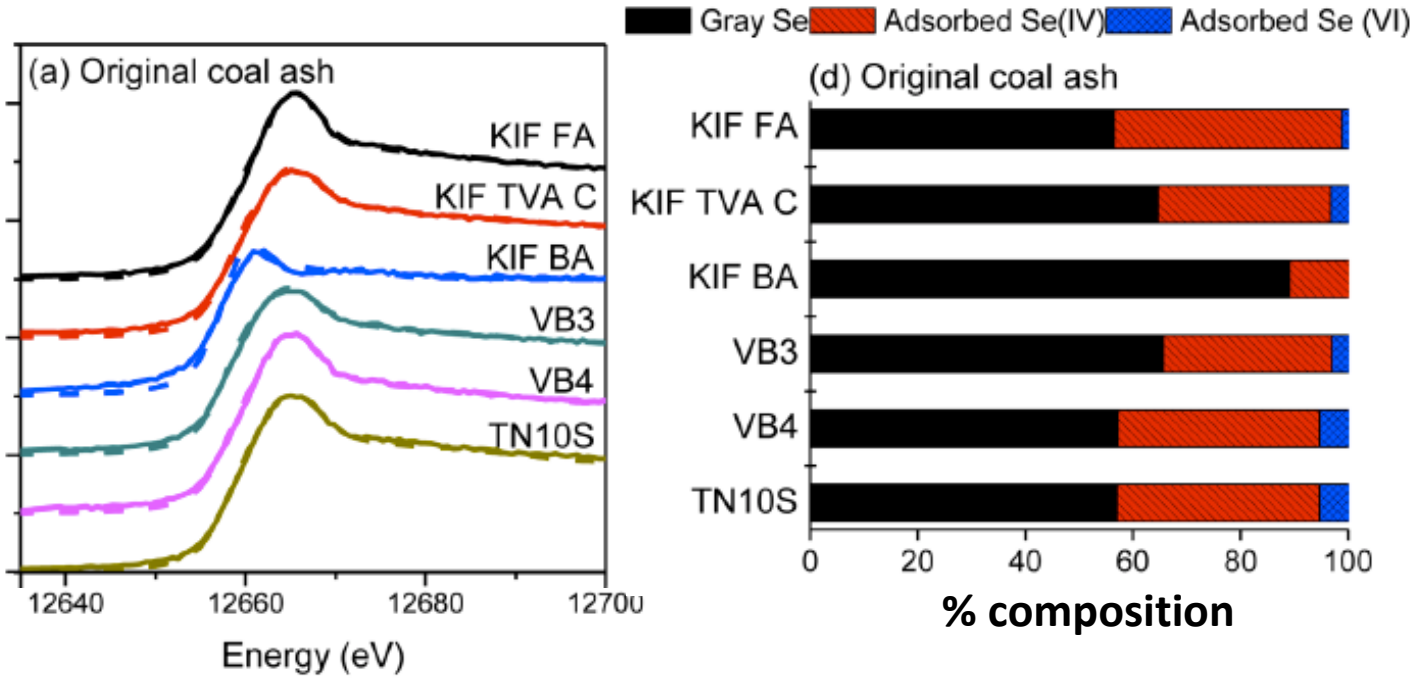
- Total elemental content is not always informative of leachable concentrations.
- Speciation of As and Se may be an important factor.

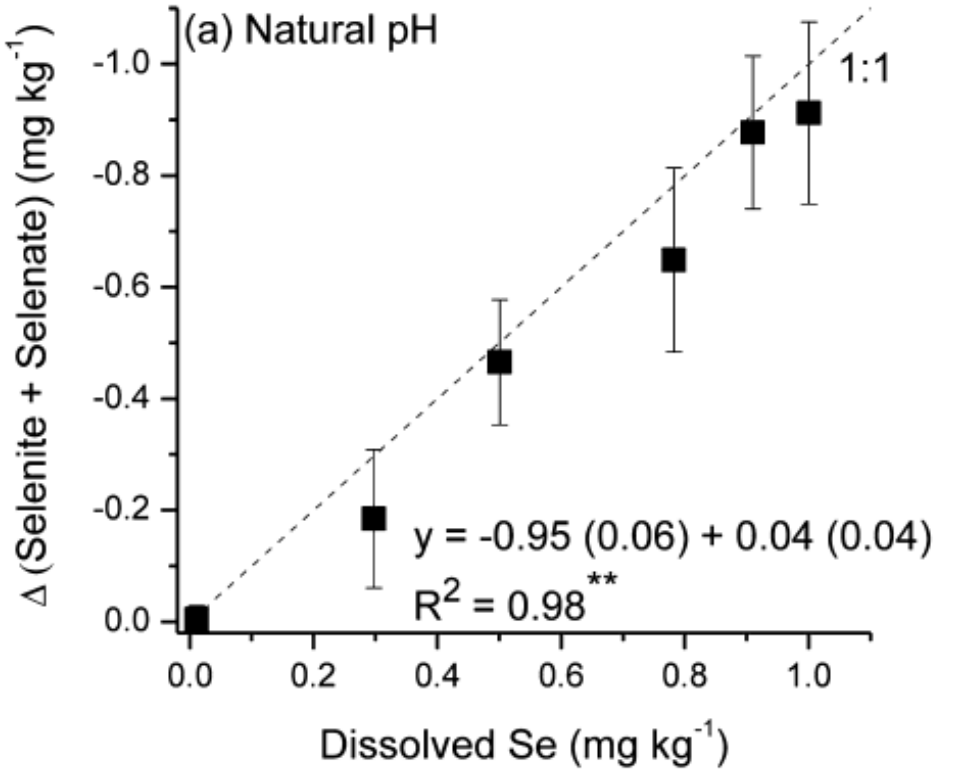




Schwartz et al. 2018 *Environmental Engineering Science*

3. Leaching and transformation potential of As and Se



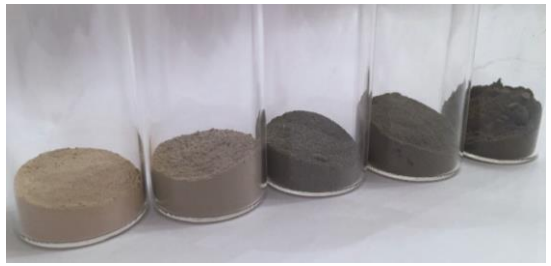


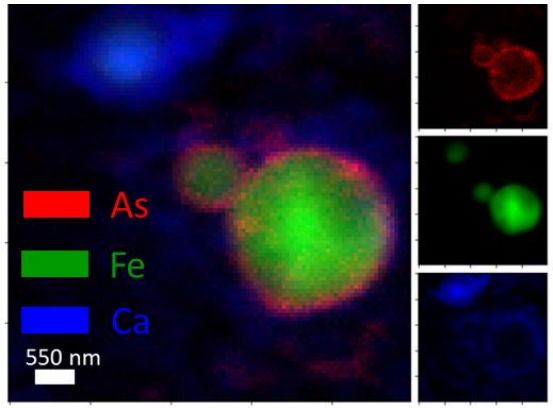
Liu et al. 2013 *ES&T*

Leaching potential of selenium may be related to the amount of oxidized forms: selenite (Se^{IV+}) and selenite (Se^{VI+})

Summary

- Total As and Se contents in fly ash: Modified XRF analysis method
- Arsenic is primarily As(V); Selenium is a mixture Se(0), Se(IV)
- Both elements are heterogeneously distributed, suggesting a distribution of reactivity and leaching potentials
- Total As and Se in fly ash vary with feed coal type and alone does not indicate mobilization potential





Synchrotron facilities: SSRL and NSLS-II

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