VANDERBILT UNIVERSITY

LEACHING ASSESSMENT AND DECISIONS FOR USE AND DISPOSAL OF COAL COMBUSTION RESIDUES

David S. Kosson, Ph.D.
Professor and Chairman of Civil and Environmental Engineering
Cornelius Vanderbilt Professor of Engineering
Vanderbilt University
Nashville, Tennessee

November 3, 2011

Disclaimer

These are the results of research by the Vanderbilt research group and my opinions and this should not be construed to represent USEPA or any other organization.

No group - USEPA, industry or environmental advocacy organizations - have sought to influence or constrain my briefing today. However, I am in regular discussions with all of these groups.

Key Messages
Leaching Assessment and TCLP

Leaching assessment is an important tool for evaluating the potential for impact to water resources.

- Leaching is the release of constituents from a solid material into contacting water
- Leaching does not correlate with total content
- Leaching provides the source term for environmental assessment

TCLP was developed to evaluate co-disposal with municipal solid waste.

- Conditions for many disposal scenarios, including CCR disposal, are very different than MSW disposal
- Most currently used leaching tests evaluate only a single condition and do not provide information on the range of environmental conditions known to affect leaching

Key Messages
Leaching Assessment and LEAF

The Leaching Environmental Assessment Framework (LEAF)

- Evaluates leaching over a range of conditions for disposal and use scenarios
- Applicable to a wide spectrum of materials
- Allows distinction between management options
- Includes set of leaching test methods, data evaluation methods, and data management and analysis tools
- Considers range of pH, leaching mechanisms
- Major improvement on current practices, but development also required pragmatic choices to focus on the most important factors to provide tailored answers
- Parallel, coordinated development in EU and other countries

Key Messages
Testing Coal Combustion Residues

A large set of coal combustion residues (CCRs, including fly ash, gypsum and scrubber residues) have been evaluated using the LEAF methods.

LEAF Testing Results Indicate:

- Key Constituents of Potential Concern: arsenic, antimony, barium, boron, cadmium, chromium, mercury, molybdenum, selenium, thallium and vanadium
- There is a very wide range in leaching from fly ash samples from different sources (spans greater than 1000x)
- Different use and disposal options provide a wide range of attenuation factors (this also spans greater than 1000x); estimated attenuation includes consideration of design and location

Key Messages
Testing Coal Combustion Residues

Potential approaches to using LEAF in environmental protection decisions

- Screening, binning (yes/no/maybe) and site/scenario specific evaluations
- Evaluating individual CCRs for specific options
- Evaluating classes of materials or types for use at local, regional or national scales
- Guiding design criteria for engineered systems (e.g., roadways, structural fills, concrete, etc.)

Preliminary cost estimates for using LEAF as assessment & quality control tool

- $0.38 per ton produced
- $100,000 per annum per station

Key Messages
LEAF Status

Under development for more than 15 years for application to wide range of wastes and construction materials

Responsive to EPA SAB concerns regarding TCLP-based leaching assessment practices

Standard Methods planned for completion (Spring 2012)

- Interlaboratory validation (round robin testing) in progress
- Multiple EPA consultations and reviews completed; final reviews and NODA planned

Software tools available (beta versions) for aiding laboratory testing, data management and decision making

Implementation guidance is needed

LEAF Supporting Documentation

A.C. Garrabrants, D.S. Kosson, H.A. van der Sloot, F. Sanchez, and O. Hjelmar (2010) Background Information for the Leaching Environmental Assessment Framework Test Methods, EPA/600/R-10/170, December 2010; http://www.epa.gov/nrmrl/pubs/600r10170/600r10170.pdf.

S.A. Thorneloe, D.S. Kosson, F. Sanchez, A.C. Garrabrants, and G. Helms (2010) “Evaluating the Fate of Metals in Air Pollution Control Residues from Coal-Fired Power Plants,” *Environmental Science & Technology*, 44(19), 73517356, http://pubs.acs.org/doi/pdfplus/10.1021/es1016558.

D. Kosson, F. Sanchez, P. Kariher, L. Turner, D. Delapp, P. Seignette and S. Thorneloe (2009) *Characterization of Coal Combustion Residues from Electric Utilities - Leaching and Characterization Data,* EPA-600/R-09/151, December 2009; http://www.epa.gov/nrmrl/pubs/600r09151/600r09151.html.

F. Sanchez, D. Kosson, R. Keeney, R. DeLapp, L. Turner, P. Kariher, and S. Thorneloe (2008) *Characterization of Coal Combustion Residues from Electric Utilities Using Wet Scrubbers for Multi-Pollutant Control,* EPA-600/R-08/077, July 2008; www.epa.gov/nrmrl/pubs/600r08077/600r08077.pdf.

F. Sanchez, R. Keeney, D. Kosson, R. Delapp and S. Thorneloe (2006) *Characterization of Mercury-Enriched Coal Combustion Residues from Electric Utilities Using Enhanced Sorbents for Mercury Control*, EPA-600/R-06/008, February 2006; http://www.epa.gov/ORD/NRMRL/pubs/600r06008/600r06008.pdf.

F. Sanchez, C.H. Mattus, M.I. Morris, and D.S. Kosson (2002) “Use of a new framework for evaluating alternative treatment processes for mercury contaminated soils,” Environmental Engineering Science, 19(4), 251-269.

D.S. Kosson, H.A. van der Sloot, F. Sanchez, and A.C. Garrabrants (2002) “An integrated framework for evaluating leaching in waste management and utilization of secondary materials,” *Environmental Engineering Science*, 19(3), 159-204.

LEAF Reports in Preparation

Interlaboratory Validation of LEAF Method 1313 and Method 1316
- Fall 2011 release

Relationship Between LEAF Testing Results and Field Leaching
- Spring 2012 release

Interlaboratory Validation of LEAF Method 1315
- Spring 2012 release

Interlaboratory Validation of LEAF Method 1314
- Spring 2012 release

Application of LEAF Test Methods for Evaluating Use and Disposal of Coal Combustion Residues (CCRs)
- Summer 2012 release

Acknowledgements

Vanderbilt University
- A.C. Garrabrants, F. Sanchez, R. DeLapp, S. Sarkar, D. DeLapp

Energy Research Centre of the Netherlands (Petten, NL)
- H.A. van der Sloot*, P. Seignette

DHI (Hørsholm, Denmark)
- O. Hjelmar

ARCADIS-U.S., Inc.
- P. Kariher

U.S. EPA (collaboration & financial support)
- S. Thorneloe - Office of Research and Development (RTP, NC)
- G. Helms, R. Benware, M. Baldwin - Office of Solid Waste & Emergency Response

U.S. Department of Energy, Office of Environmental Management (financial support)

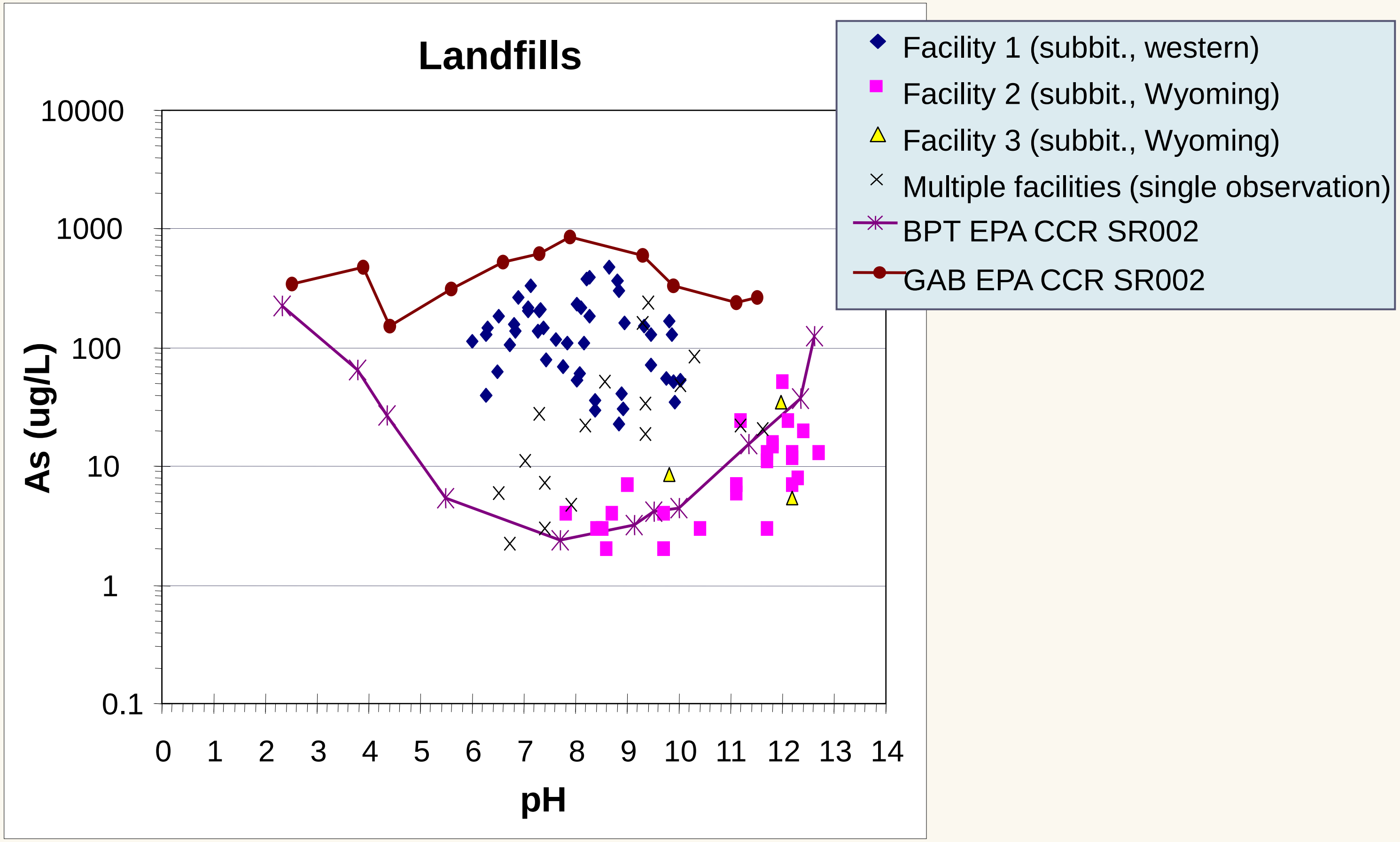
*currently Hans van der Sloot Consultancy, Langedijk, NL

SUPPORTING INFORMATION

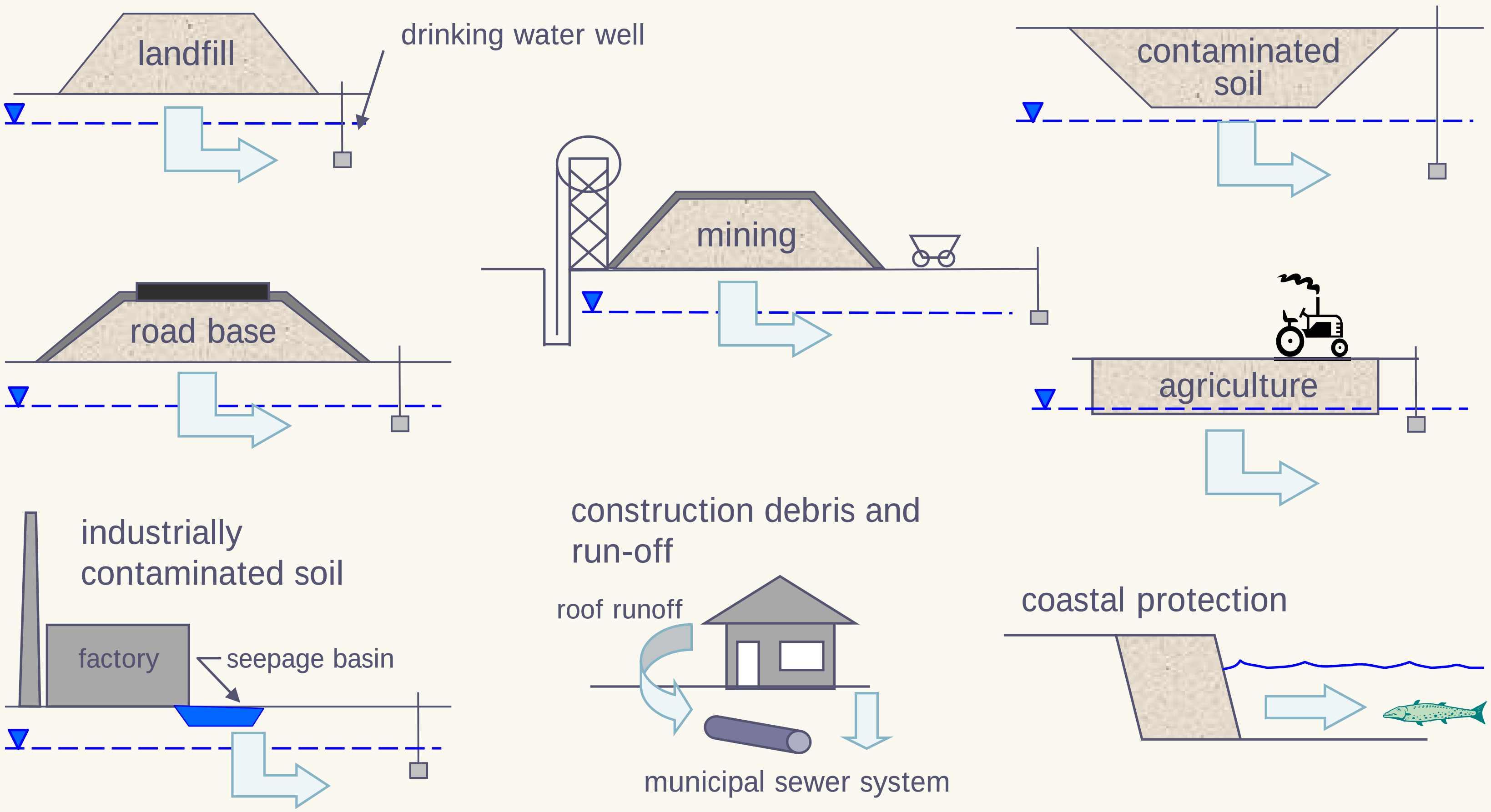
Potential Use of LEAF in
CCR Management Decisions
(LEAF provides source term information)

Field Leaching Data for Landfills (Arsenic)

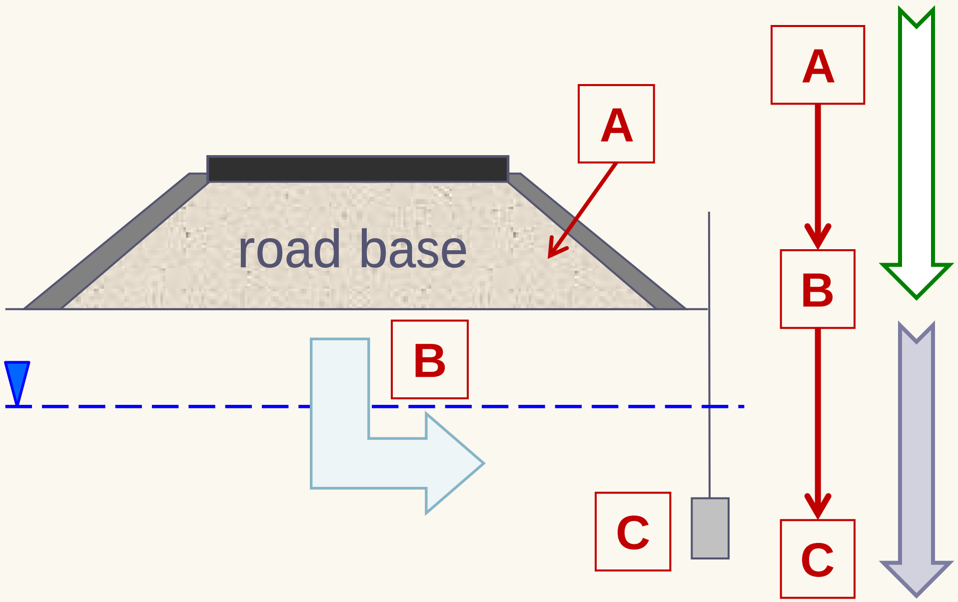
EPRI data in comparison with EPA Lab data



Many Leaching Scenarios …



Common Assessment Approach



Material Leaching in Context of Application *(tests mimic scenario)*

Use as Source Term

Constituent Release from Application Scenario

DAF or Scenario Model

Constituent Concentration at Point of Compliance

Enhanced Assessment Approach

Material Leaching Tests

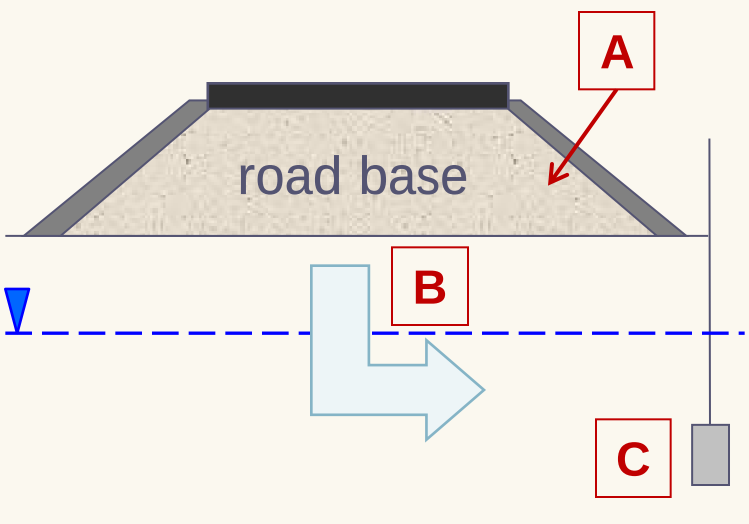
Broad-based characterization of intrinsic leaching behavior

A*

A

B

C



Material Characterization *(tests measure range of intrinsic behavior-LEAF)*

Threshold Definition

Material Leaching in Context of Application (EAF)

Use as Source Term

Constituent Release from Application Scenario

DAF or Scenario Model

Constituent Concentration at Point of Compliance

Cost Estimate

Assuming:

- Quarterly Sampling
- Triplicate Method 1313 - $15,000 + administrative costs
- Analysis for 15 Constituents

American Coal Ash Association (ACAA)

- 72,500,000 tons of fly ash produced in 2008
- 274 coal-fired electric utility generating stations
- $20 to $45 per ton for cement quality fly ash in 2003

Costs of LEAF Testing

- Using ACAA data - 265,000 tons per station on average
- $100,000 (est'd) per annum per station
- $0.38 per ton produced

SUPPORTING INFORMATION

The Leaching Environmental Assessment Framework (LEAF)

Leaching Environmental Assessment Framework

LEAF is a collection of ...

- Four leaching methods
- Data management tools
- Leaching assessment approaches

... designed to identify characteristic leaching behaviors in a wide range of materials.

LEAF facilitates integration of leaching methods which provides a material-specific "source term" release for support of material management decisions.

More information at http://www.vanderbilt.edu/leaching

Leaching Method Development Approach

Characterization of Leaching Behavior (Kosson et al, 2002)

- Parallel and coordinated methods development in the EU
- Applied to anticipated release conditions – source term for release
- Goal to reduce uncertainties of environmental decision making

Address Concerns of EPA Science Advisory Board

- Form of the material (e.g., monolithic, granular)
- Parameters that affect release (e.g., pH, liquid-solid ratio, release rate)

Intended for situations where TCLP is <u>not</u> required or best suited

- Assessment of materials for beneficial reuse
- Evaluating treatment effectiveness (determination of equivalent treatment)
- Characterizing potential release from high-volume materials
- Corrective action (remediation decisions)

Leaching Evaluation Assessment Framework

Measure intrinsic leaching characteristics of material

Evaluate release in the context of field scenario

- External influencing factors such as carbonation, oxidation
- Hydrology
- Mineralogical changes

Geochemical speciation and mass transfer models to estimate release for alternative scenarios

- Model complexity to match information needs
- Many scenarios can be evaluated from single data set

Tiered approach to effective use prior data and reduce testing needs

Do NOT mimic field scenarios with specific tests!
Too many tests with limited data comparability!

Kosson, van der Sloot *et al.*, 2002, Environ. Engr. Sci., 19, 159-203.

LEAF Leaching Methods

Method 1313 – Liquid-Solid Partitioning as a Function of Eluate pH using a Parallel Batch Procedure

Method 1314 – Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio (L/S) using an Up-flow Percolation Column Procedure

Method 1315 – Mass Transfer Rates in Monolithic and Compacted Granular Materials using a Semi-dynamic Tank Leaching Procedure

Method 1316 – Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio using a Parallel Batch Procedure

Note: Incorporation into SW-846 is ongoing; titles and method identification numbers are subject to change

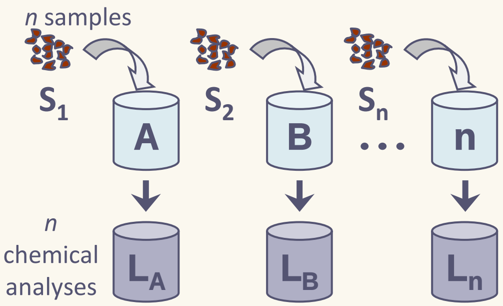
Method 1313 Overview

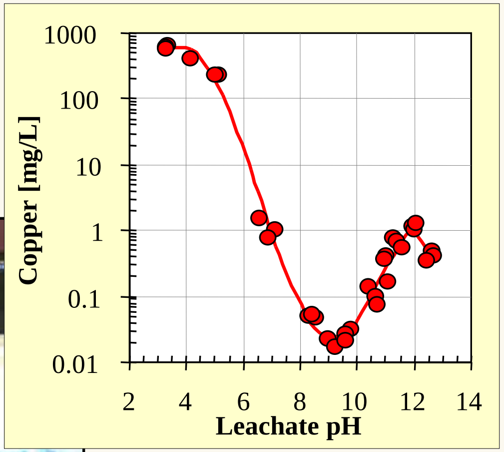
Equilibrium Leaching Test

- Parallel batch as function of pH

Test Specifications

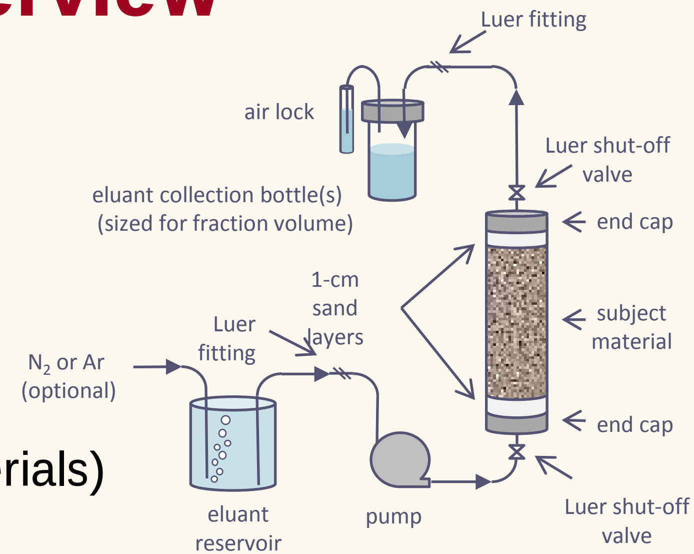
- 9 specified target pH values plus natural conditions
- Size-reduced material
- L/S = 10 mL/g-dry
- Dilute HNO_3 or NaOH
- Contact time based on particle size
  - 18-72 hours
- Reported Data
  - Equivalents of acid/base added
  - Eluate pH and conductivity
  - Eluate constituent concentrations





Titration Curve and Liquid-solid Partitioning (LSP) Curve as Function of Eluate pH

Method 1314 Overview



Equilibrium Leaching Test

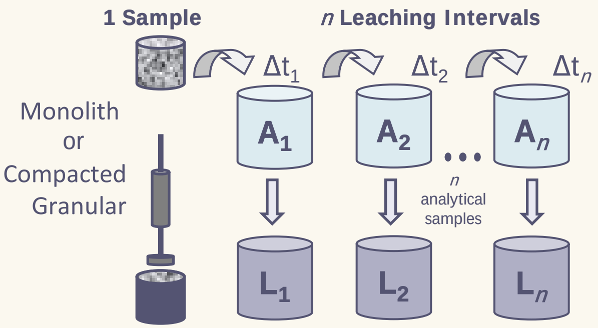
- Percolation through loosely-packed material

Test Specifications

- 5-cm diameter x 30-cm high glass column
- Size-reduced material
- DI water or 1 mM $CaCl_2$ (clays, organic materials)
- Upward flow to minimize channeling
- Collect leachate at cumulative L/S
  - 0.2, 0.5, 1, 1.5, 2, 4.5, 5, 9.5, 10 mL/g-dry
- Reported Data
  - Eluate volume collected
  - Eluate pH and conductivity
  - Eluate constituent concentrations

Liquid-solid Partitioning (LSP) Curve as Function of L/S; Estimate of Pore Water Concentration

Method 1315 Overview



Monolithic

Granular

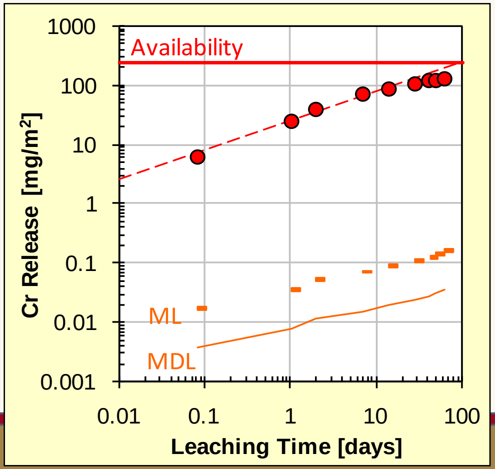
Mass-Transfer Test

- Semi-dynamic tank leach test

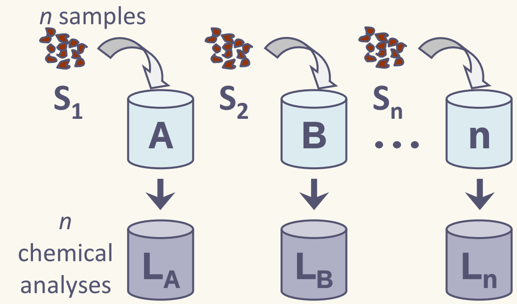
Test Specifications

- Material forms
  - monolithic (all faces exposed)
  - compacted granular (1 circular face exposed)
- DI water so that waste dictates pH
- Liquid-surface area ratio (L/A) of 9±1 mL/cm^2
- Refresh leaching solution at cumulative times
  - 2, 25, 48 hrs, 7, 14, 28, 42, 49, 63 days
- Reported Data
  - Refresh time
  - Eluate pH and conductivity
  - Eluate constituent concentrations

Flux and Cumulative Release as a Function of Leaching Time



Method 1316 Overview

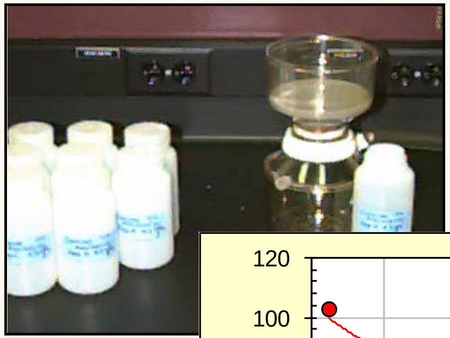


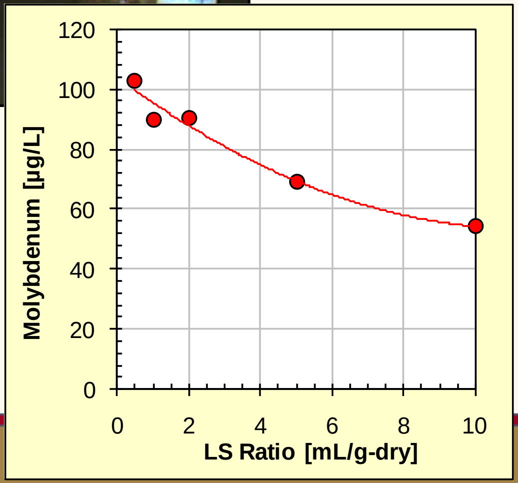
Equilibrium Leaching Test

- Parallel batch as function of L/S

Test Specifications

- Five specified L/S values (±0.2 mL/g-dry)
  - 10.0, 5.0, 2.0, 1.0, 0.5 mL/g-dry
- Size-reduced material
- DI water (material dictates pH)
- Contact time based on particle size
  - 18-72 hours
- Reported Data
  - Eluate L/S
  - Eluate pH and conductivity
  - Eluate constituent concentrations





Liquid-solid Partitioning (LSP) Curve as a Function of L/S; Estimate of Pore Water Concentration

Data Management Tools

Data Templates

- Excel Spreadsheets for Each Method
  - Perform basic, required calculations (e.g, moisture content)
  - Record laboratory data
  - Archive analytical data with laboratory information
- Form the upload file to materials database

LeachXS (Leaching eXpert System) Lite

- Data management, visualization and processing program
- Compare Leaching Test Data
  - Between materials (e.g., As in two different CCRs)
  - Between constituents (e.g., Ba and SO_4 in a cement material)
  - To default or user-defined “indicator lines” (e.g., QA limits, threshold values)
- Export leaching data to Excel spreadsheets
- Freely available at http://www.vanderbilt.edu/leaching

Data Templates

DRAFT METHOD 1313 (Liquid-Solid Partitioning as a Function of pH) LAB DATA

1) Enter particle size and solids content

	Code	Description *(optional)*
Project	ABC	Example project
Material	XYZ	Exaple material
Replicate	A	

Test conducted by:

	Date	Time
Test Start	1/2/xx	2:00 PM
Test End	1/3/xx	1:45 PM
Required Contact Time *	23-25	[hr]

Solids Information

Maximum Particle Size	0.3	[mm]
Minimum Dry Equivalent Mass *	20.00	[g-dry]
Solids Content (default = 1)	0.901	[g-dry/g]
Mass of "As Tested" Material / Extraction	22.20	[g]

* Data based on Draft Method 1313 Table 1.

Extraction Information

LS Ratio	10	[mL/g-dry]
Liquid Volume / Extraction	200	[mL]
Recommended Bottle Size *	250	[mL]

2) Enter acid/base type & normality

Nominal Reagent Information

Acid Type	HNO3	
Acid Normality	2.0	[meq/mL]
Base Type	NaOH	
Base Normality	1.0	[meq/mL]

4) Follow "set-up" recipe

Schedule of Acid and Base Addition

Test Position	T01	T02	T03	T04	T05	T06	T07	T08	T09	B01	B02	B03	totals
"As Tested" Solid [g] (±0.05g)	22.20	22.20	22.20	22.20	22.20	22.20	22.20	22.20	22.20	no solid	no solid	no solid	199.8
Reagent Water [mL] (±5%)	147.80	167.80	185.80	197.80	195.80	193.80	189.80	185.80	178.80	200.00	181.00	150.00	2174.2
Acid Volume [mL] (±1%)	-	-	-	-	2.00	4.00	8.00	12.00	19.00	-	19.00	-	64.0
Base Volume [mL] (±1%)	50.00	30.00	12.00	-	-	-	-	-	-	-	-	50.00	142.0
Acid Normality [meq/mL]	-	-	-	-	2.0	2.0	2.0	2.0	2.0	-	2.0	-	
Base Normality [meq/mL]	1.0	1.0	1.0	-	-	-	-	-	-	-	[illegible]	[illegible]	

3) Enter target equivalents from titration curve

5) Record pH, conductivity, Eh (optional)

6) Verify that final pH is in acceptable range

Target pH	13.0±0.5	12.0±0.5	10.5±0.5	natural	8.0±0.5	7.0±0.5	5.5±0.5	4.0±0.5	2.0±0.5			
Acid Addition [meq/g]	-2.5	-1.5	-0.6	0	0.2	0.4	0.8	1.2	1.9	Water	Acid	Base
Eluate pH	12.80	12.20	10.80	9.20	7.80	5.98	4.79	3.60	2.30			
Eluate EC [mS/cm]												
Eluate Eh [mV]												
? (enter "a" or "r")	✓	✓	✓	✓	✓	✗	✗	✓	✓			
Notes						pH out of range	pH out of range					

LeachXS Lite

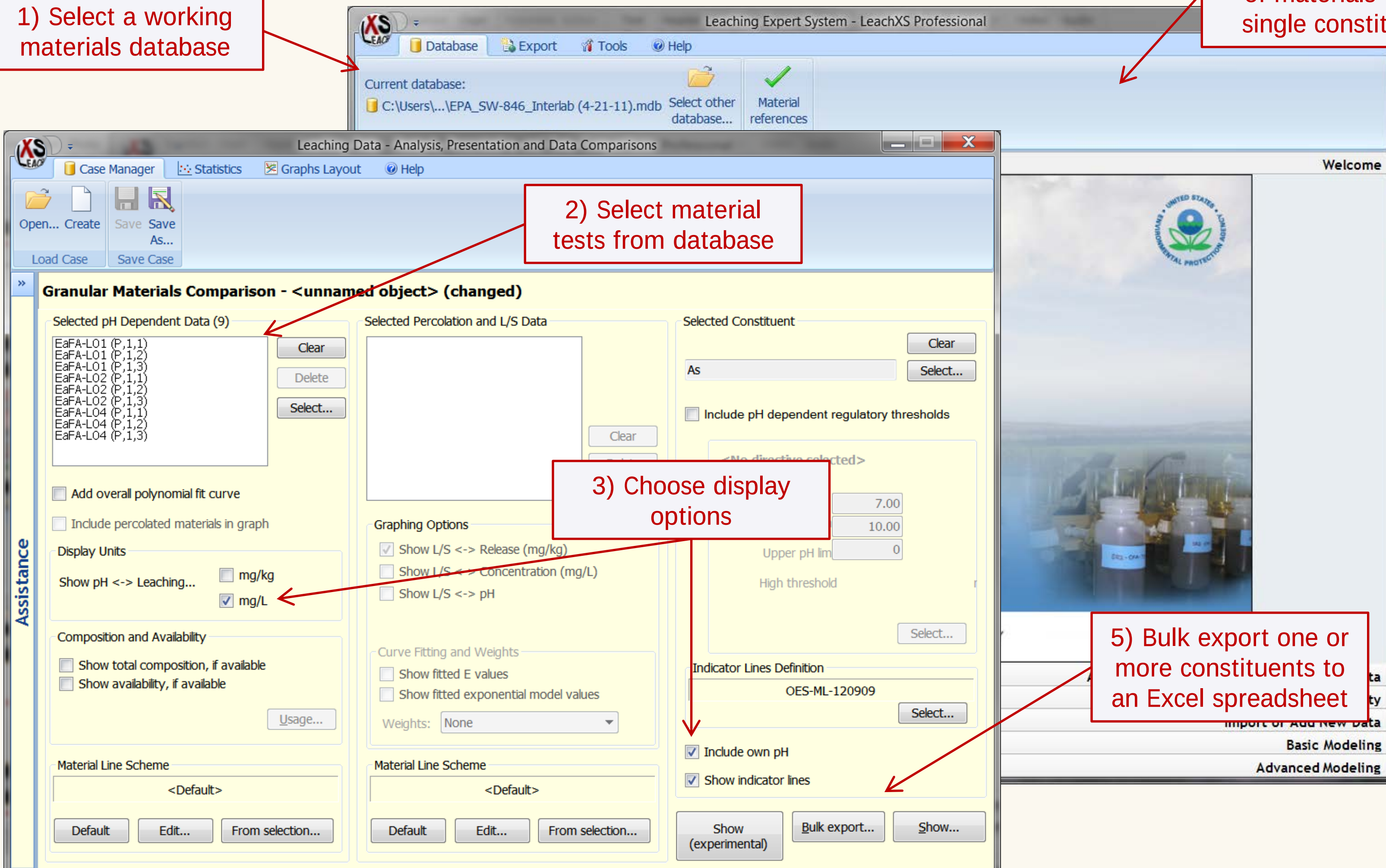
1) Select a working materials database

4) Check comparison of materials for a single constituent

2) Select material tests from database

3) Choose display options

5) Bulk export one or more constituents to an Excel spreadsheet



Use of LEAF to Compare Performance of Coal Combustion Products

EPA Studies on CCR Leaching

Coal Combustion Products ~30 Facilities

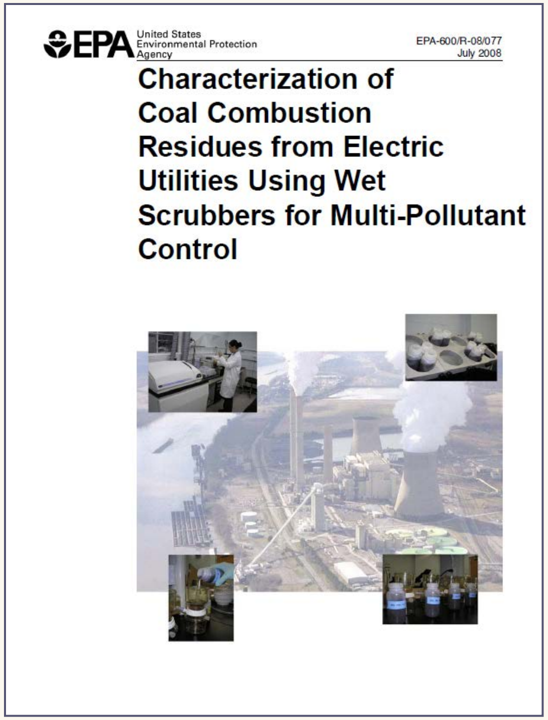
- Fly Ash – 71
- FGD Gypsum – 33
- Scrubber Sludge – 14
- Fixated Stabilized Sludge ~20

Leaching Tests

- Method 1313 – pH Dependence
- Method 1316 – Batch L/S Dependence

Look for Commonalities in Performance ...

- Coal sources
- APC practices
- Other factors



EPA United States Environmental Protection Agency

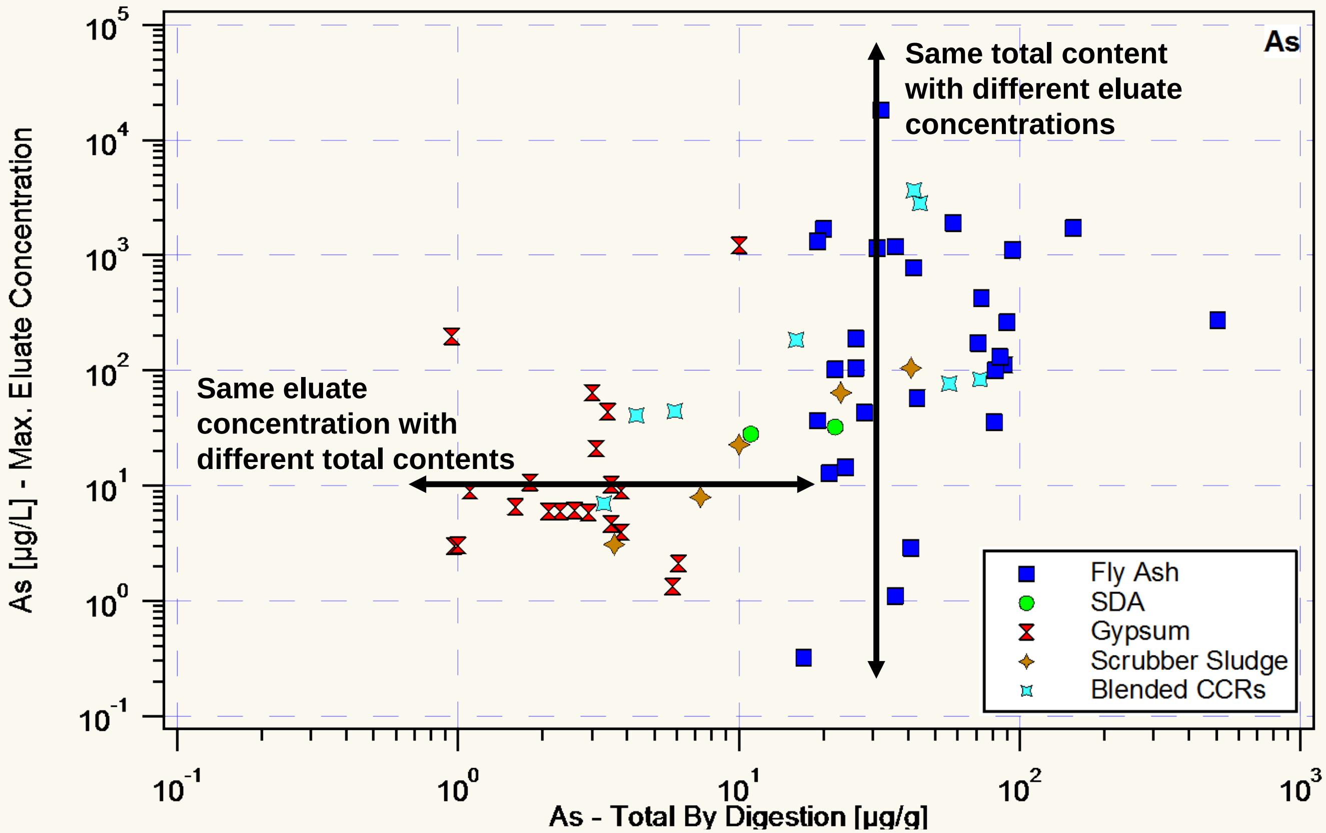
EPA-600/R-08/077
July 2008

Characterization of Coal Combustion Residues from Electric Utilities Using Wet Scrubbers for Multi-Pollutant Control

EPA Reports

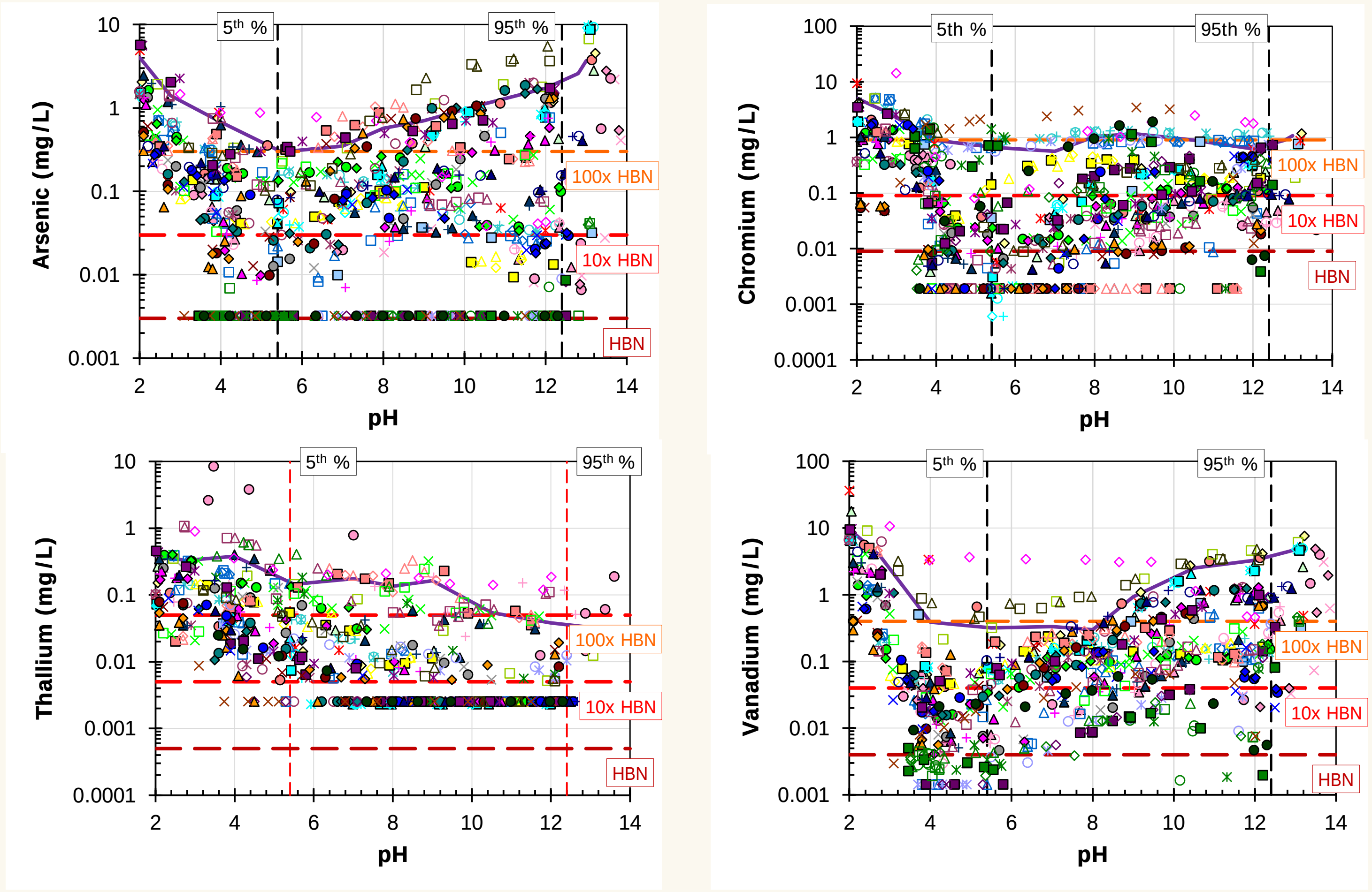
- EPA-600/R09/151
- EPA-600/R-08/077
- EPA-600/R-06/008

Total Content Does Not Correlate to Leaching

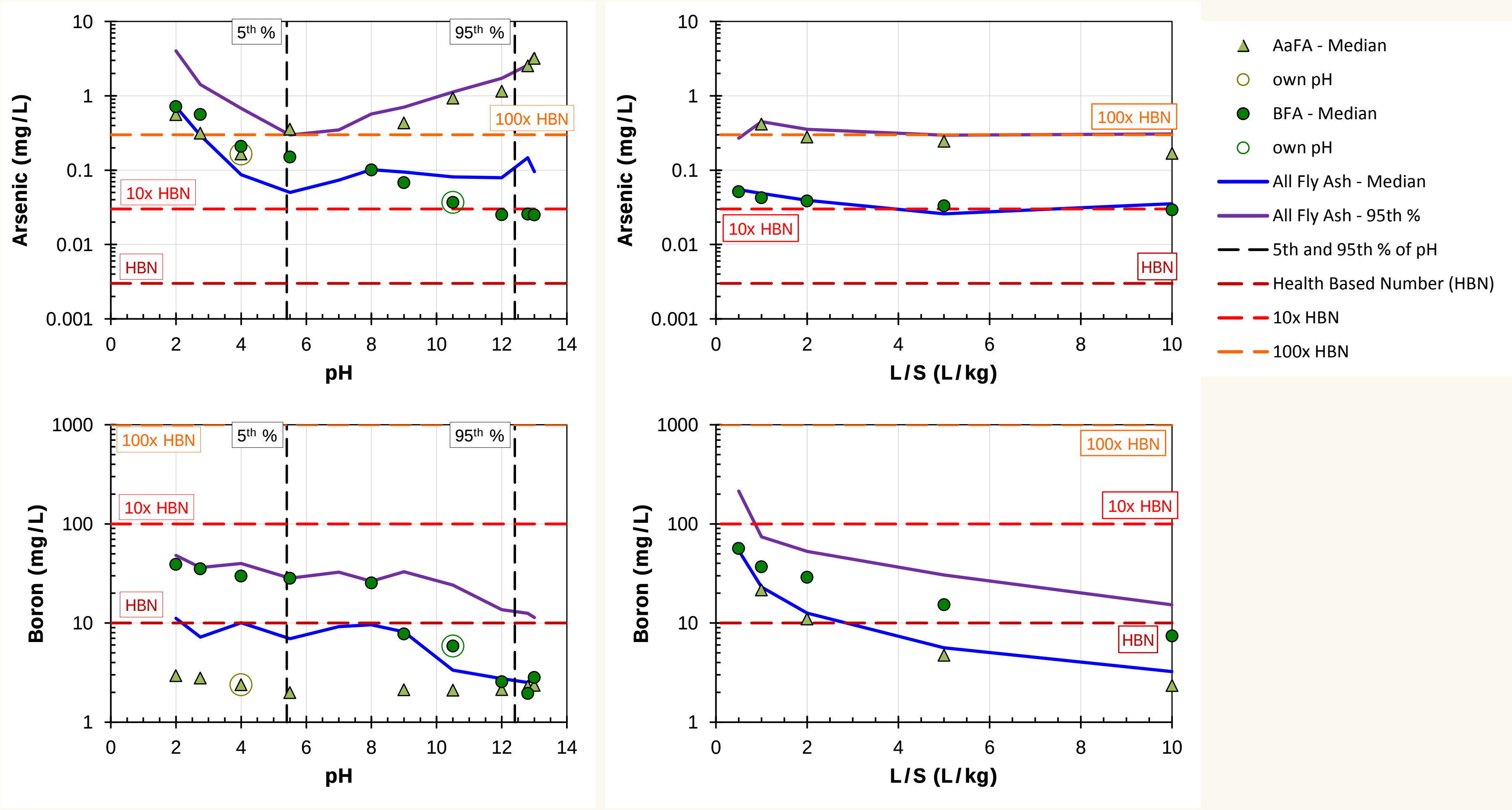


Graphic taken from: Thorneloe, S.; D.S. Kosson; F. Sanchez; A.C. Garrabrants and G. Helms (2010) "Evaluating the fate of metal in air pollution control residues from coal-fired power plants" ES&T, 44, 7351-7356.

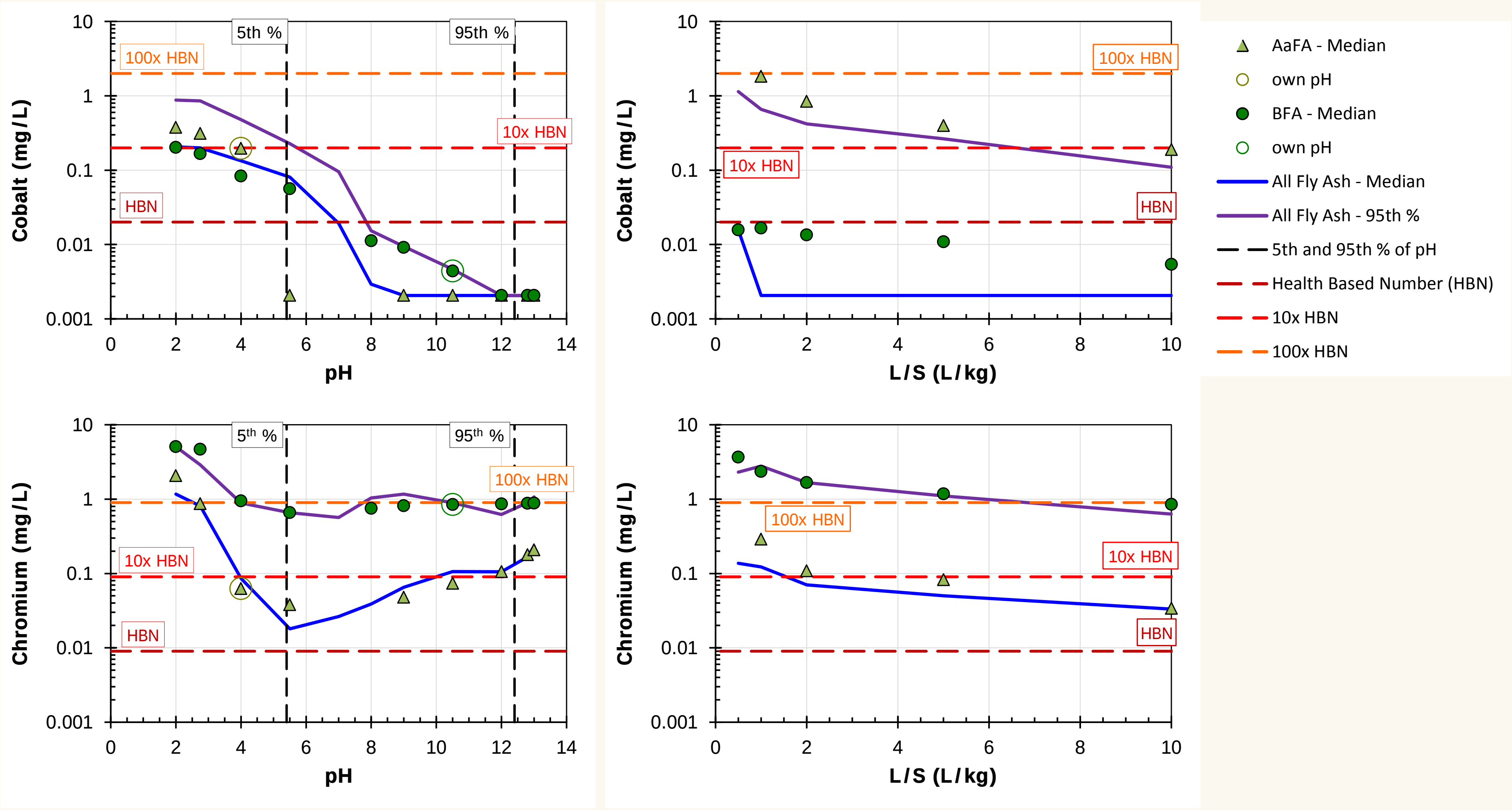
Why is this LEAF approach needed?



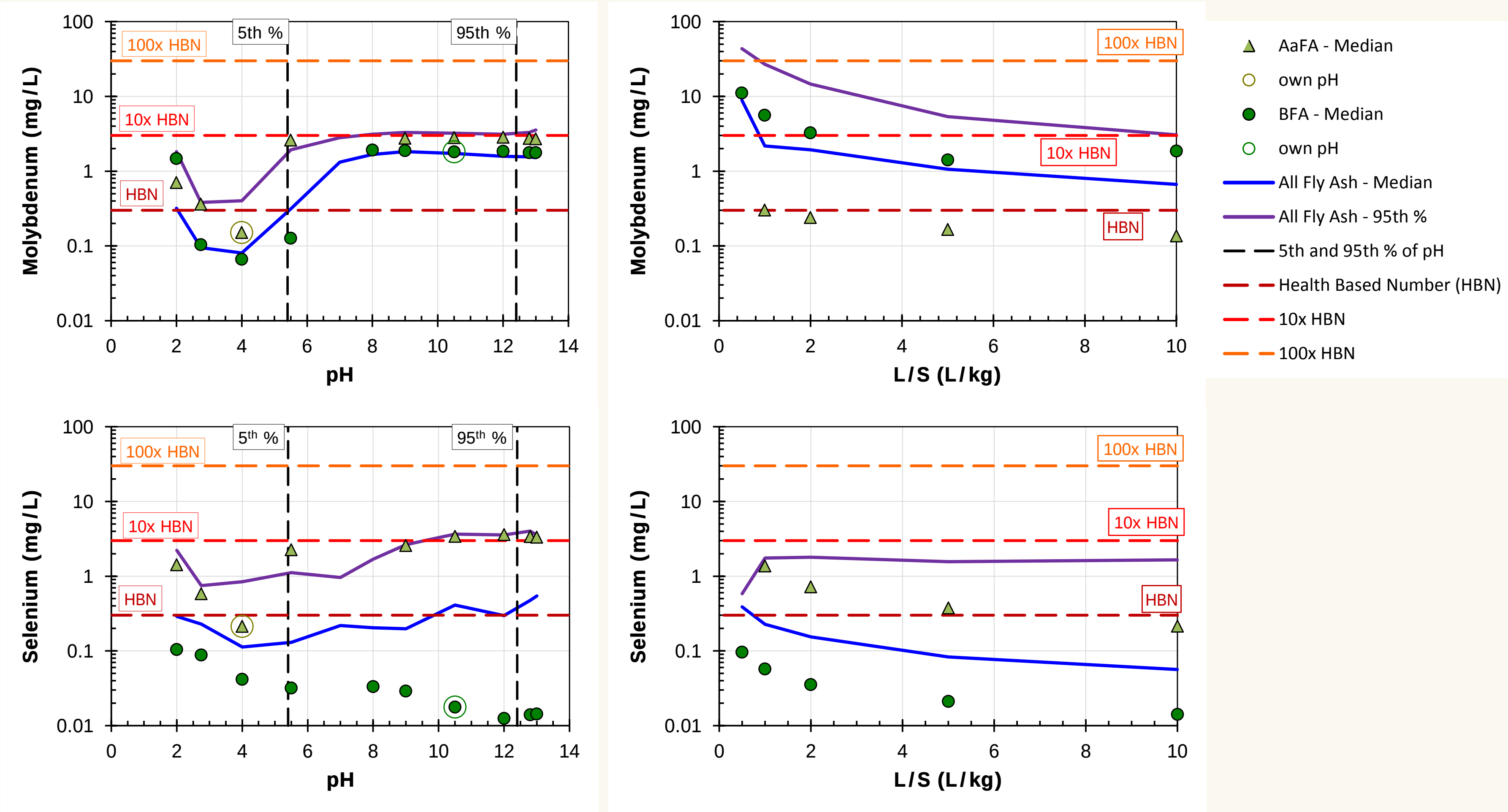
Fly Ash Results



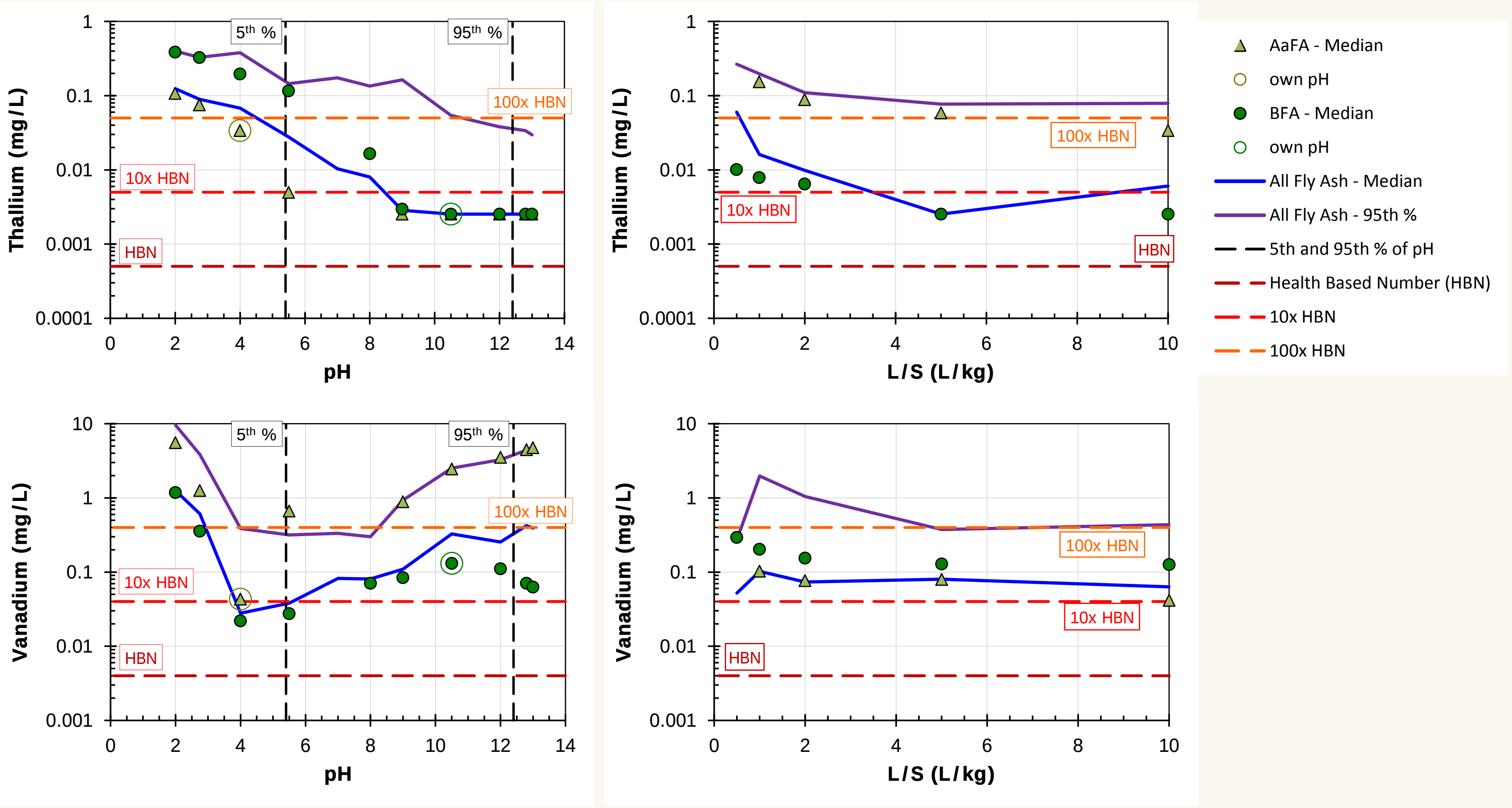
Fly Ash Results



Fly Ash Results

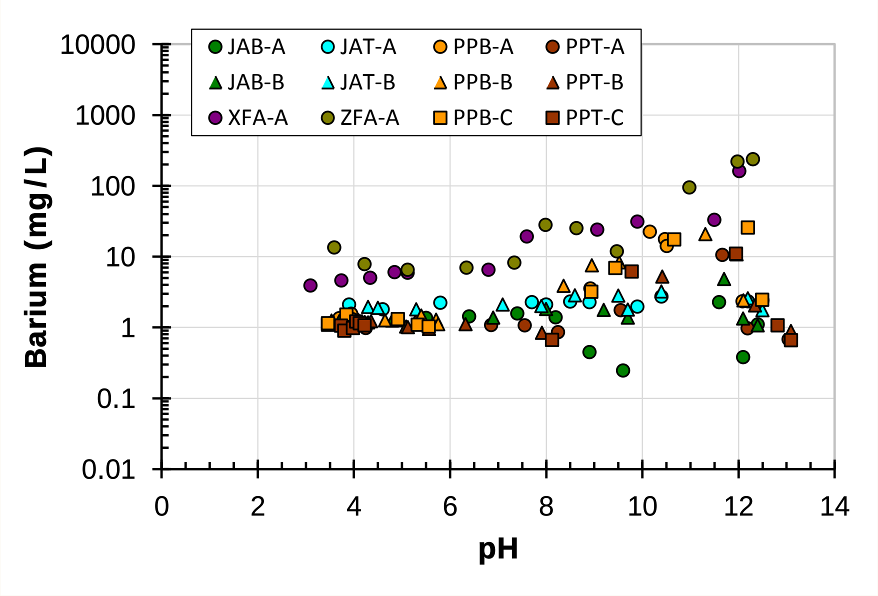


Fly Ash Results

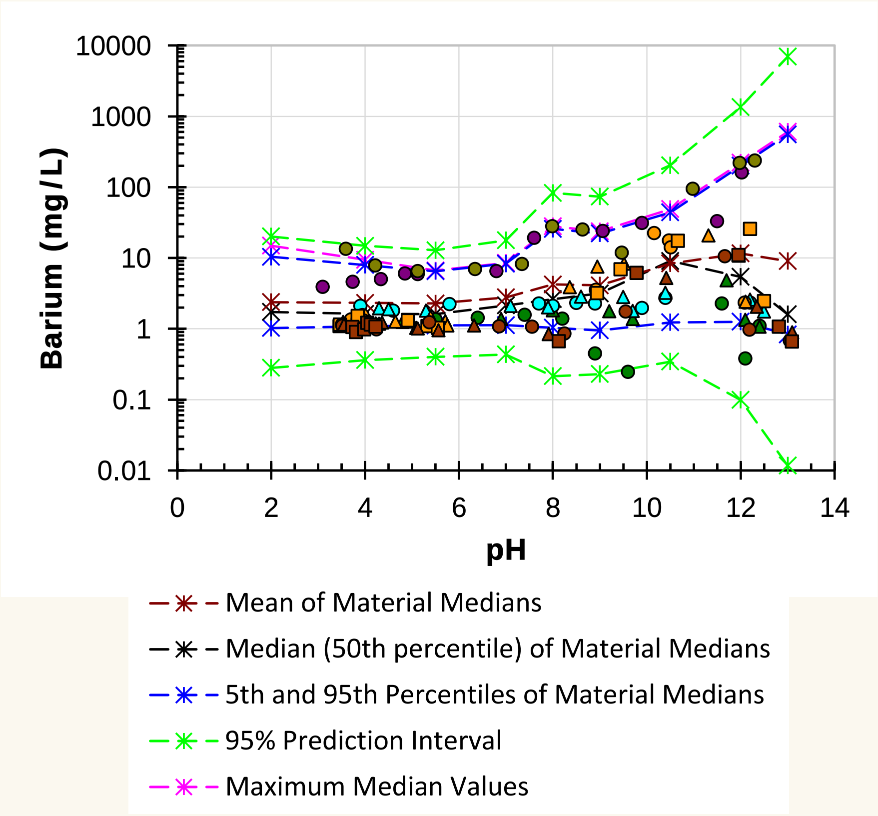


Statistical Representation

Fly Ash (Sub-bituminous Coal)

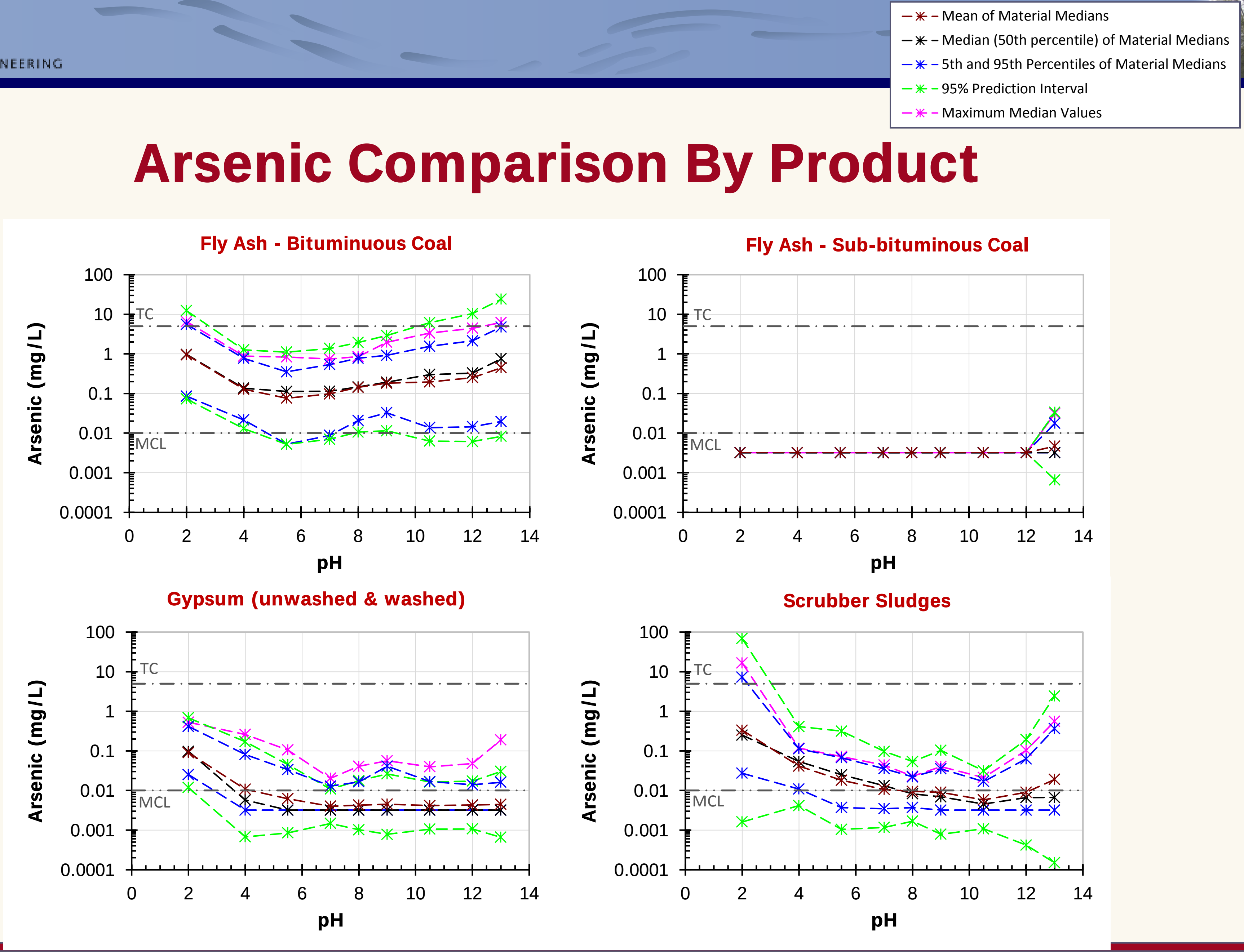


Statistical Overlay

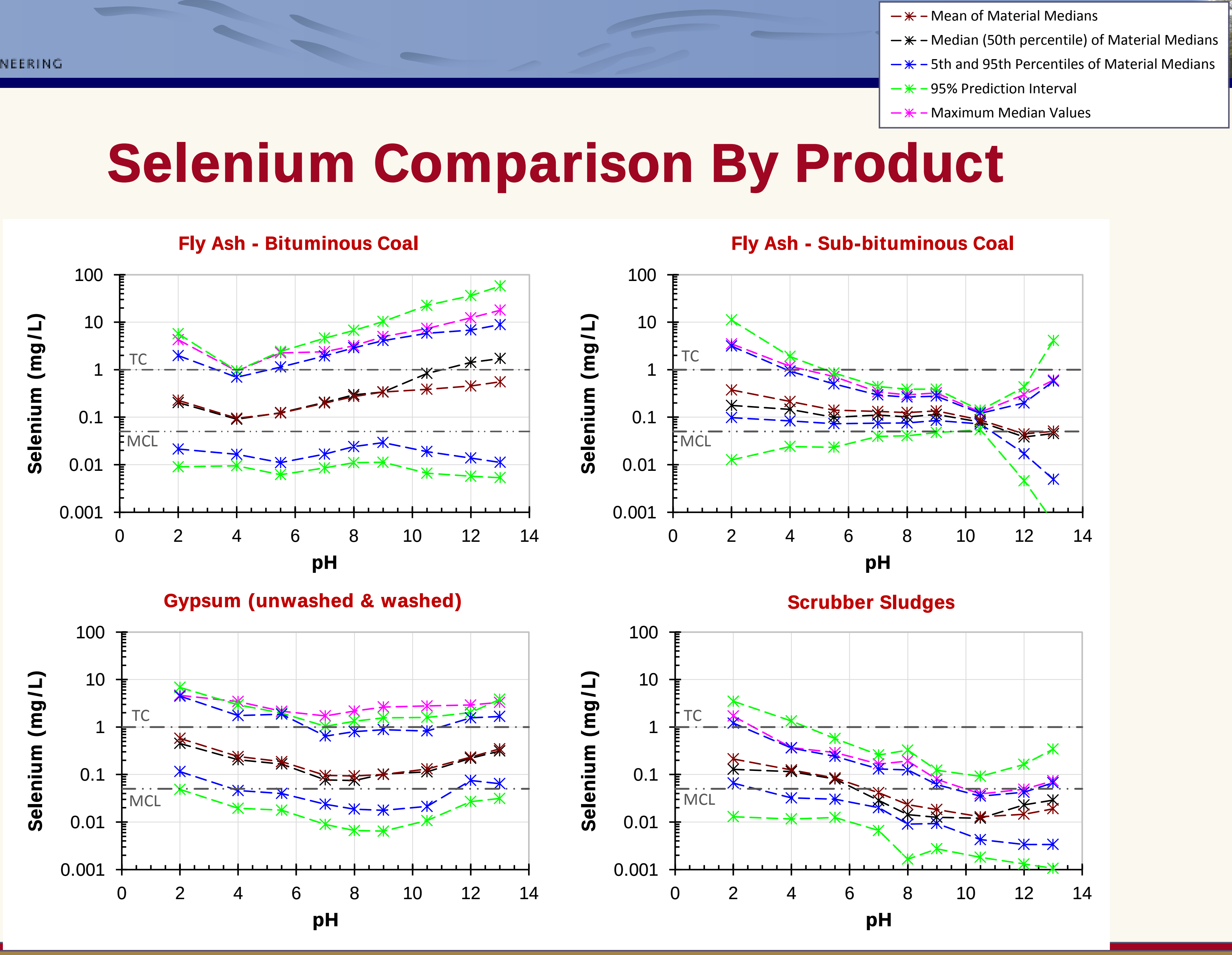


SCHOOL OF ENGINEERING

Arsenic Comparison By Product



Selenium Comparison By Product



Conclusions

LEAF

- Evaluates leaching behavior using a tiered approach that considers the effect of pH, liquid-to-solid ratio, and material form on release
- Supporting software (LeachXS-Lite) available for data entry, analysis, visualization, and reporting
- Prepared for inclusion into SW846, EPA's compendium of test methods for waste and material characterization

Comparison of Coal Combustion Products

- Statistical representations using LEAF data provides insights into conditions most-significantly affecting environmental performance
- Supports decision-making regarding optimization of processes and end use (e.g., disposal or reuse)