



# Application of New Leaching Protocols for Assessing Beneficial Use of Solid Wastes in Florida

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**University of Florida**

**October 14, 2014 TAG Meeting**

# Presentation Objectives

- Review the objectives and methodology of the project
- Provide TAG with an overview of LEAF methods and questions that have been raised in our work
- Give examples of recent research
- Gather feedback from the TAG
- Michael Hoffmeister
  - Project objectives and tasks
- Justin Roessler, Dr. Ma
  - Examples of recent applications of LEAF as part of Florida beneficial use assessments
- B Intrakamhaeng, Weizhi Cheng
  - Observations from some recent work comparing LEAF with other leaching procedures

# Uses of Leaching Tests

- Hazardous waste determination
  - TCLP is used to determine whether a solid waste is a toxicity characteristic hazardous waste (**40CFR261**)
- Waste treatment
  - TCLP is used to determine whether hazardous waste is sufficiently treated prior to land disposal (**40CFR268**)
- Beneficial use
  - SPLP is commonly used by regulatory agencies to assess leaching risk from beneficially used waste materials
- Other

# Hinkley Center Evaluations of Beneficial Use



Milled Asphalt



Street Sweepings



RSM from C&D Debris

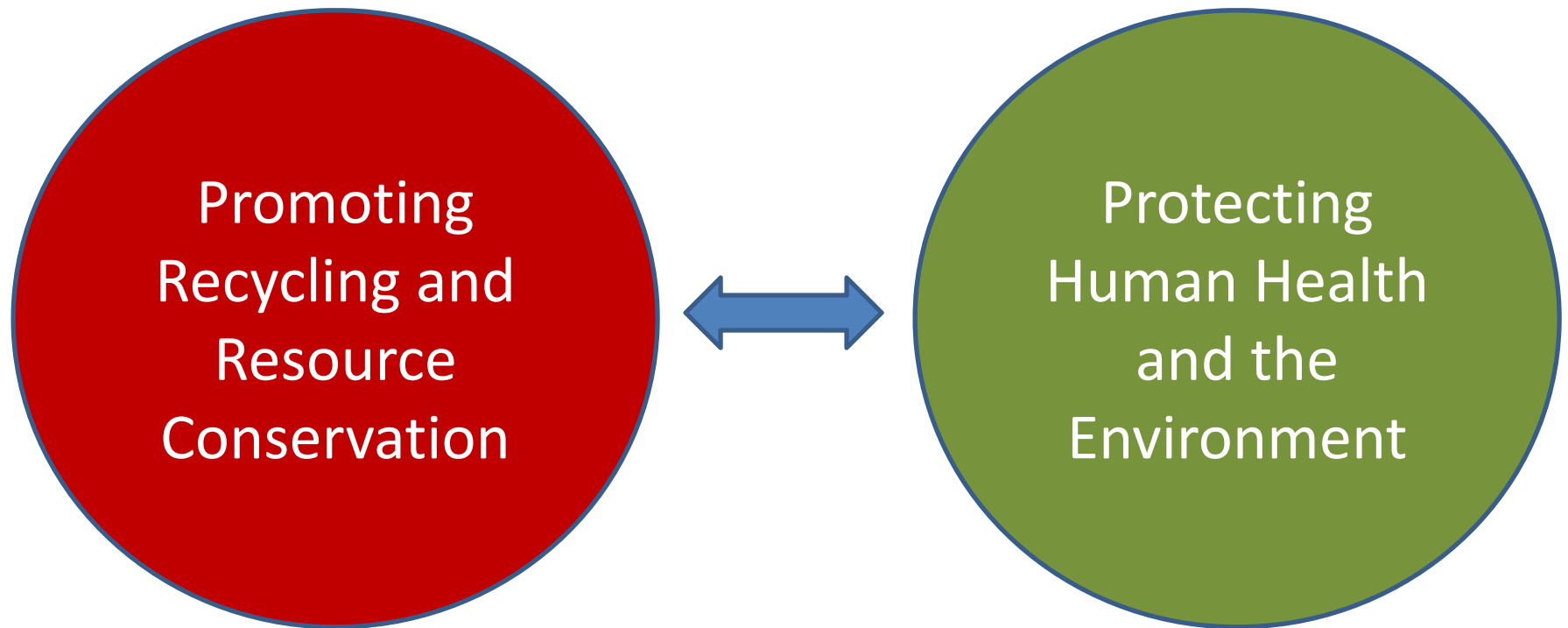


Drinking Water Sludge

# Hinkley Center Evaluations of Beneficial Use



# Challenge



# Leaching Tests for Beneficial Use

- The TCLP may not be a good predictor since it is designed to simulate a landfill environment
- The SPLP is similar to the TCLP but it uses a simulated rainwater as the leaching solution.
- New EPA leaching tests in SW-846:
  - Leaching Environmental Assessment Framework (LEAF)
  - Provides a framework to characterize the waste under a larger scope of release conditions

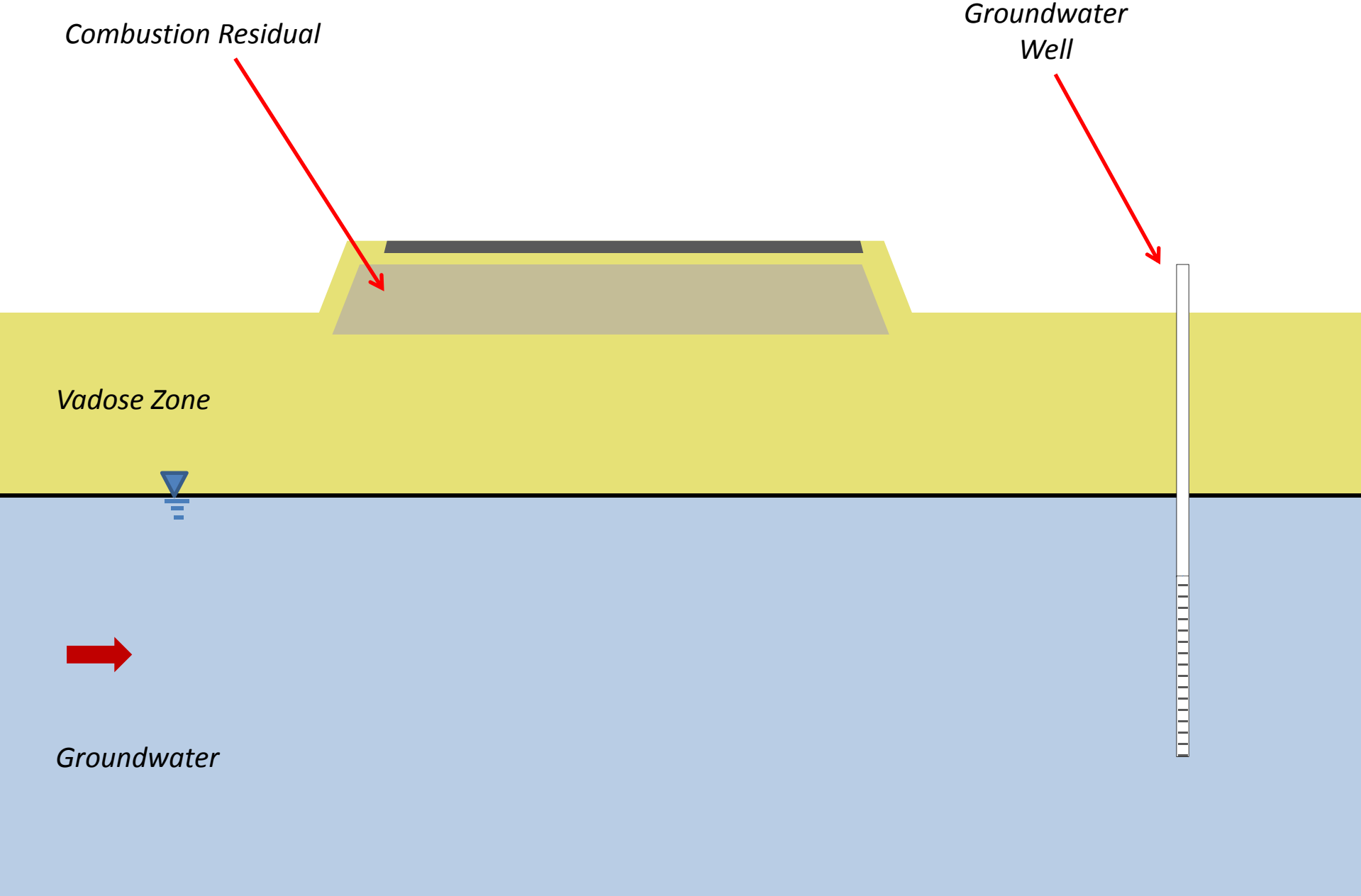


*Example FL GCTLs*

Element	GCTL (mg/L)
Aluminum (Al)	0.2
Arsenic (As)	0.01
Barium (Ba)	2
Cadmium (Cd)	0.005
Chromium (total)	0.1
Cobalt (Co)	140
Copper (Cu)	1
Iron (Fe)	0.3
Lead (Pb)	0.015
Manganese (Mn)	50
Mercury (Hg)	0.002
Selenium (Se)	0.05
Silver (Ag)	0.1
Vanadium (V)	49

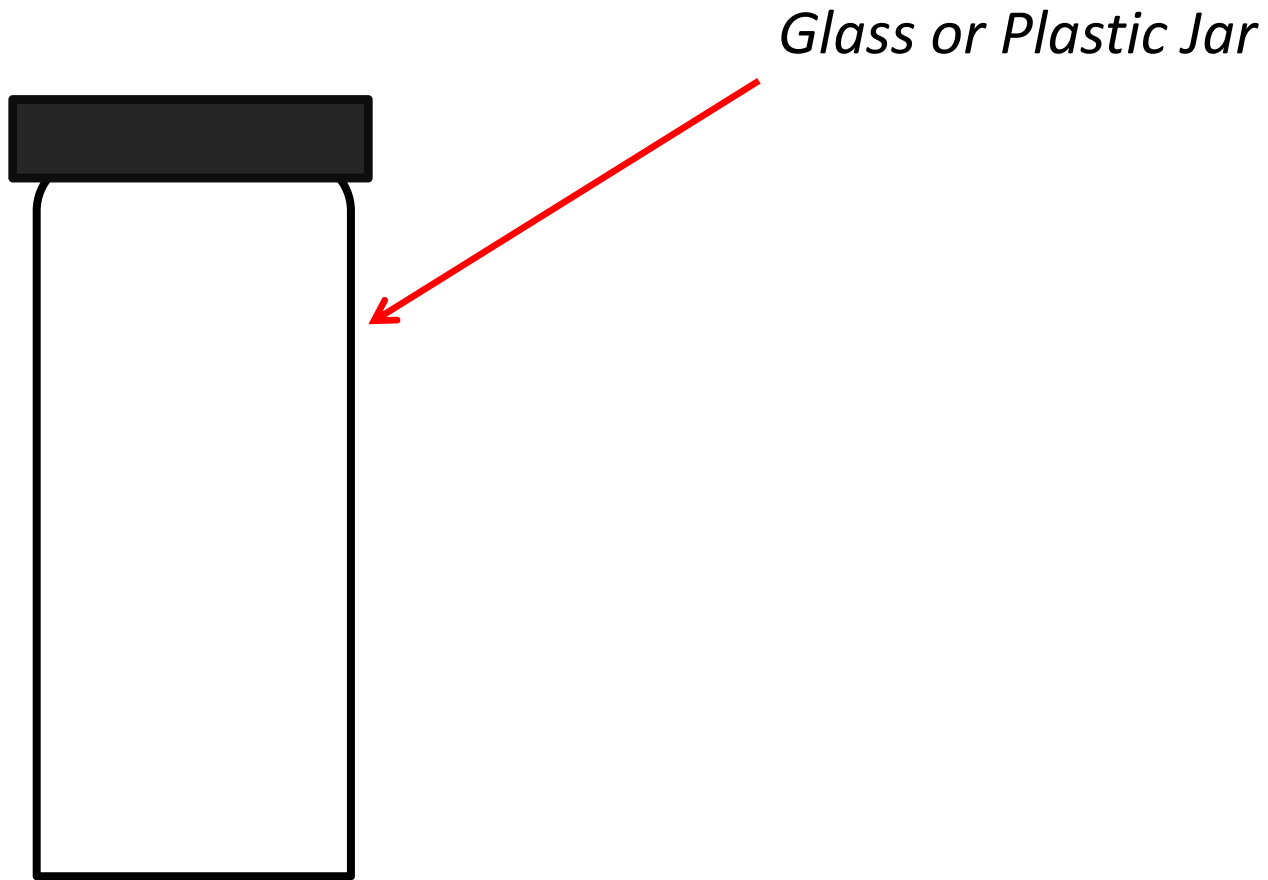
*Typical practice is to compare leaching test results to GCTL or similar threshold*

# What we are trying to assess?

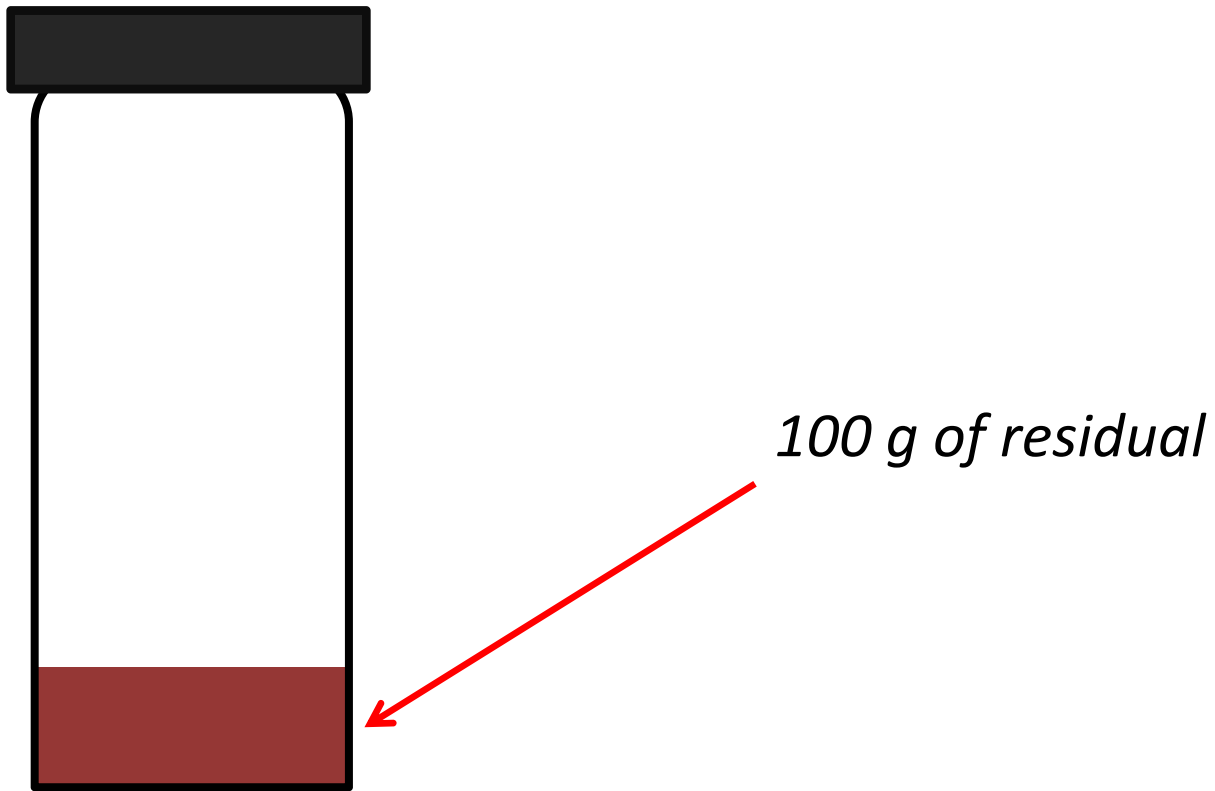




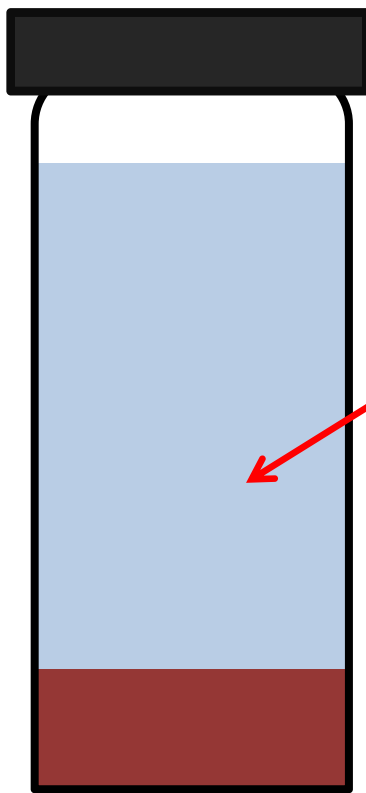
# Consider a Typical Leaching Test



# Consider a Typical Leaching Test



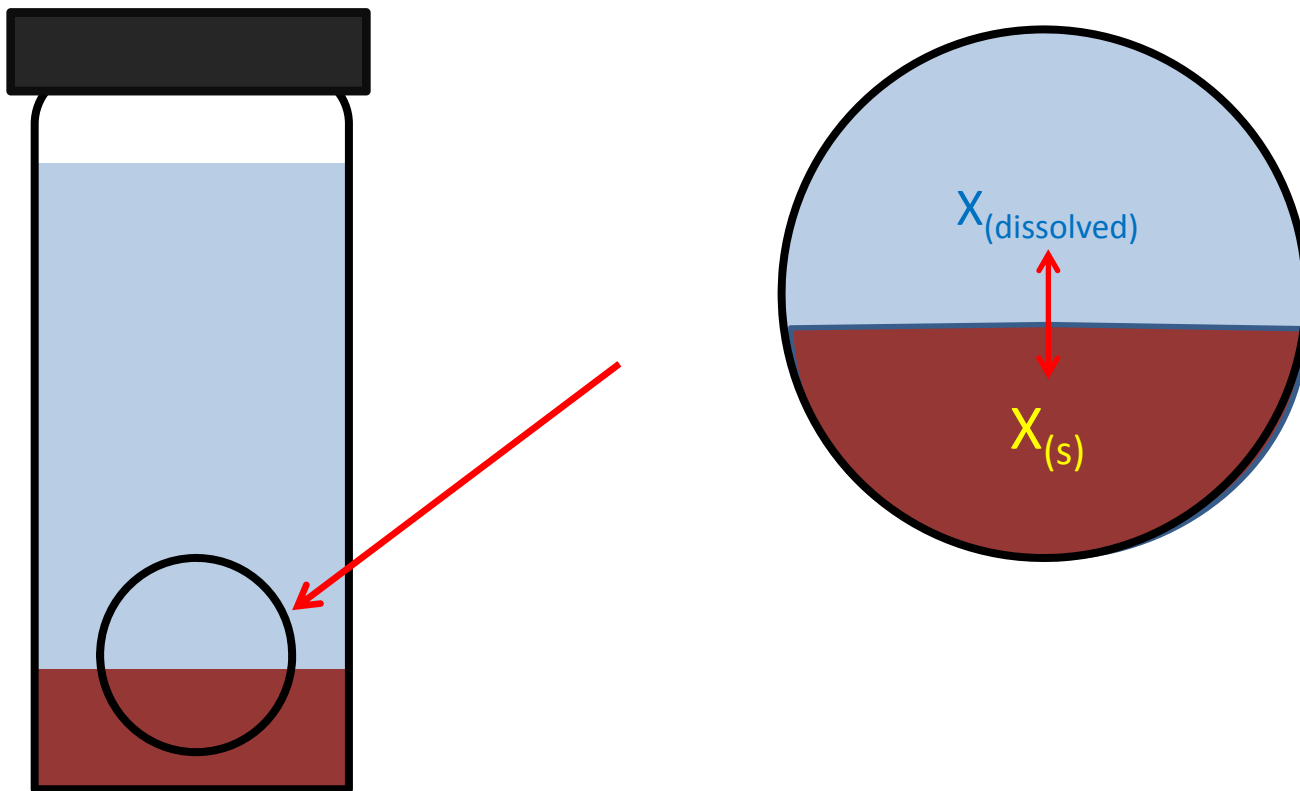
# Consider a Typical Leaching Test



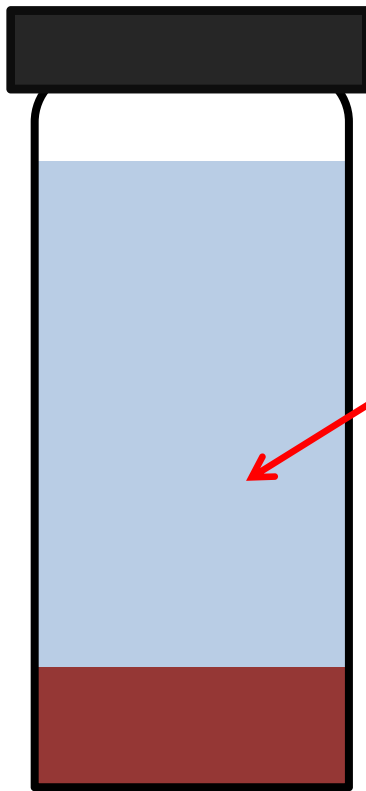
*2 L of leaching solution*

This is a batch test.  
Other types of leaching tests  
include dynamic batch tests  
and flow-through column  
tests.

# Consider a Typical Leaching Test



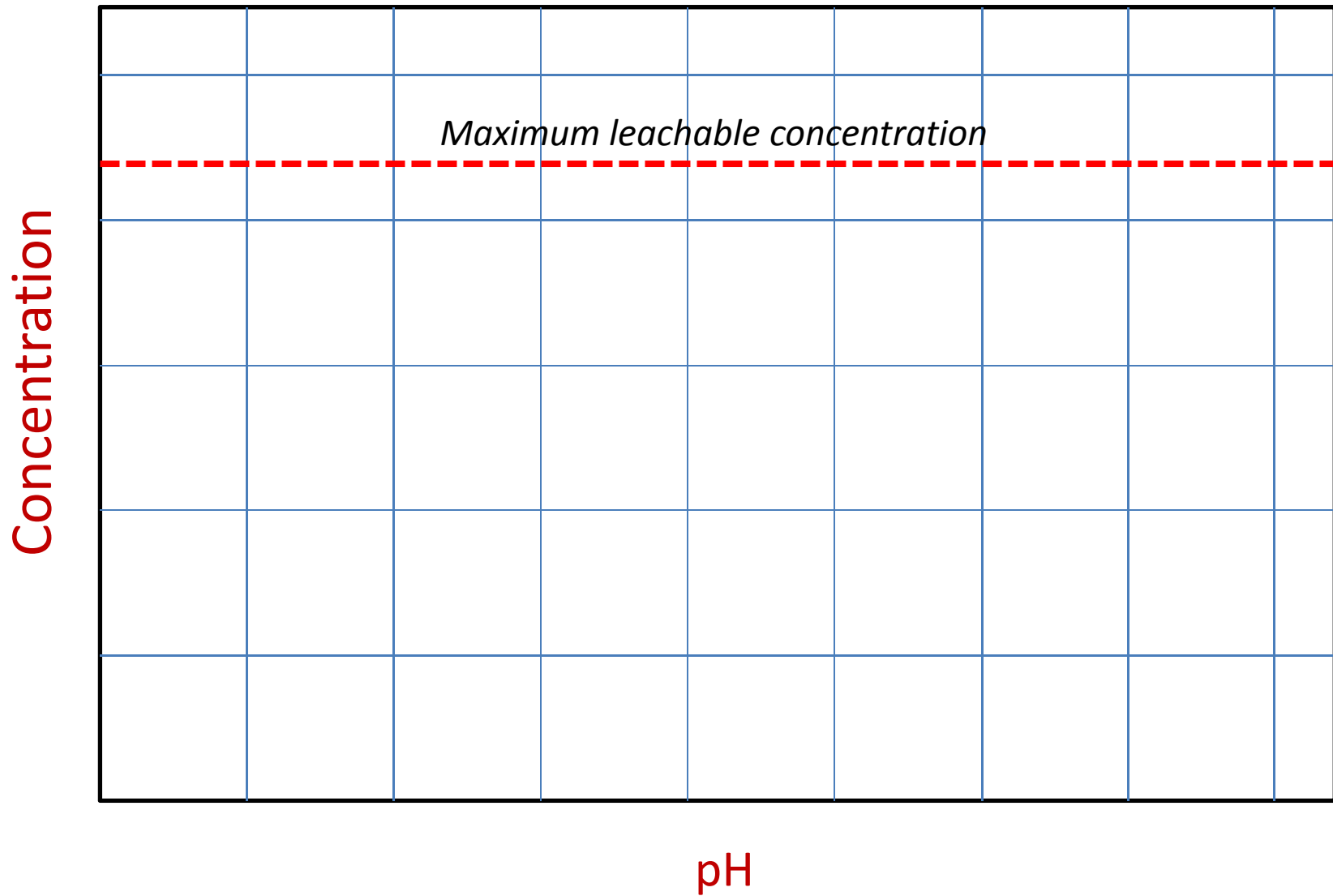
# What Impacts Leaching?



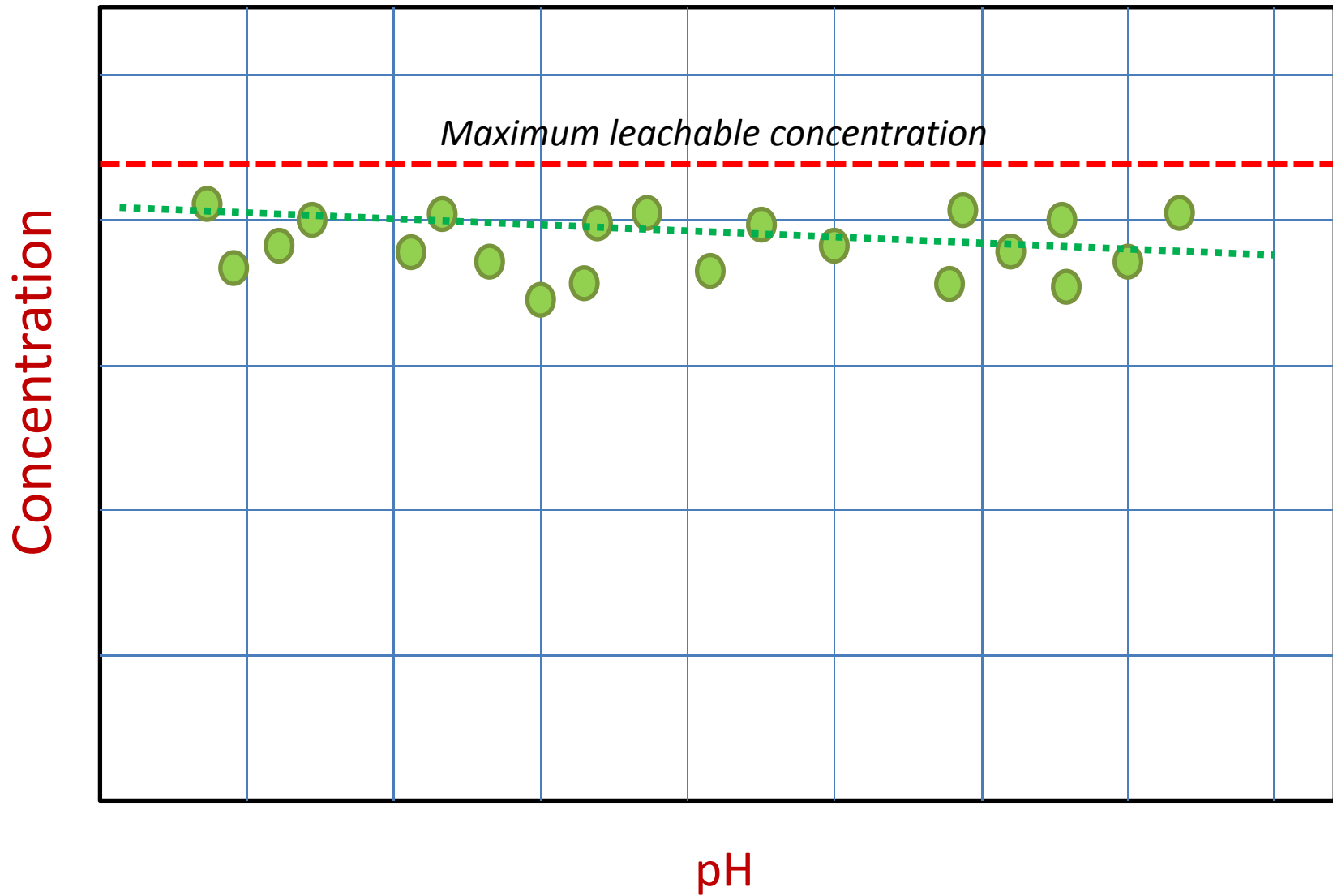
## Leaching Solution Chemistry

- TCLP: Buffered acetic acid solution with pH = 4.8 or 2.3
- SPLP: Unbuffered solution of nitric and sulfuric acid with pH = 4.2 or

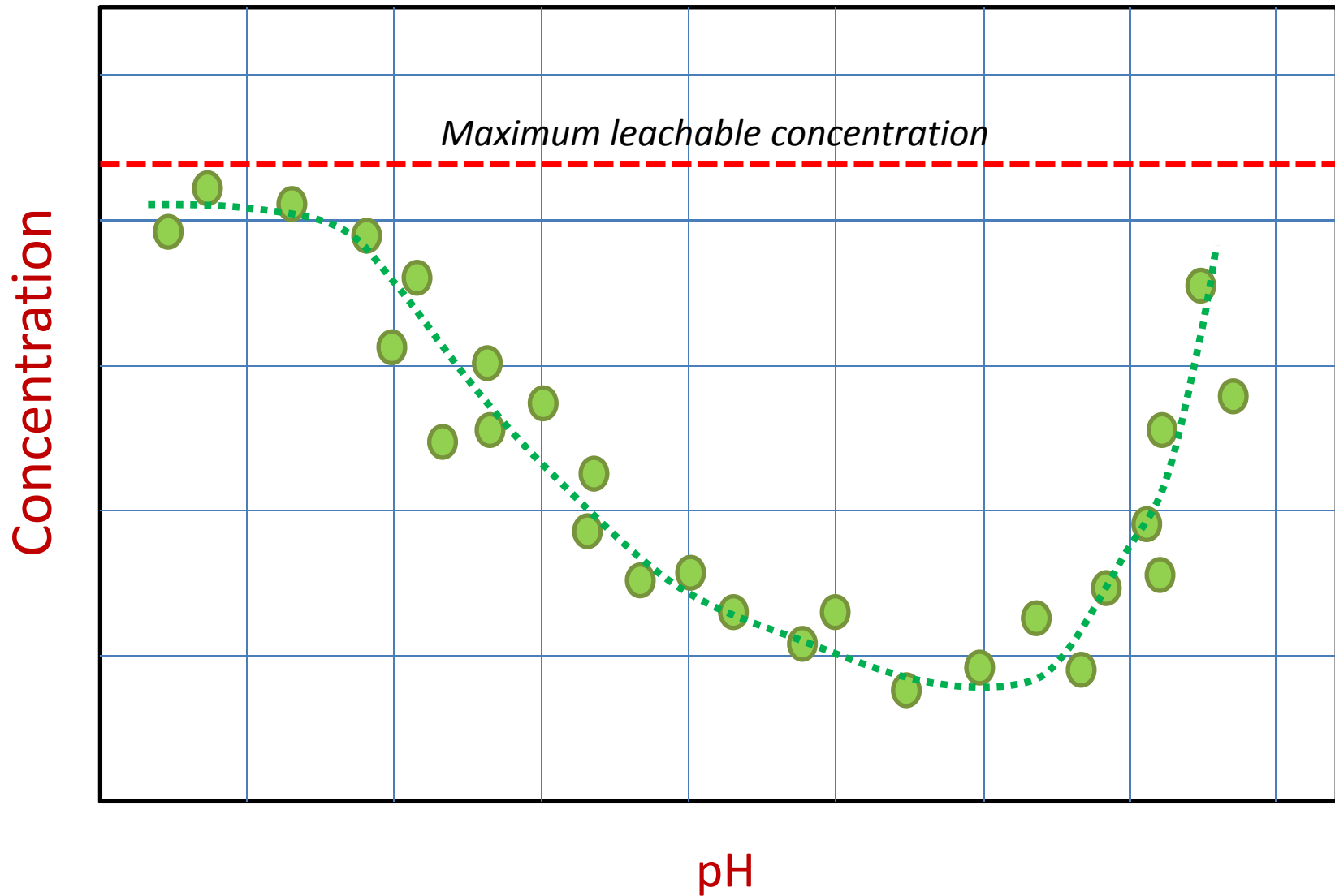
# Impact of pH



# Impact of pH: Soluble Salt

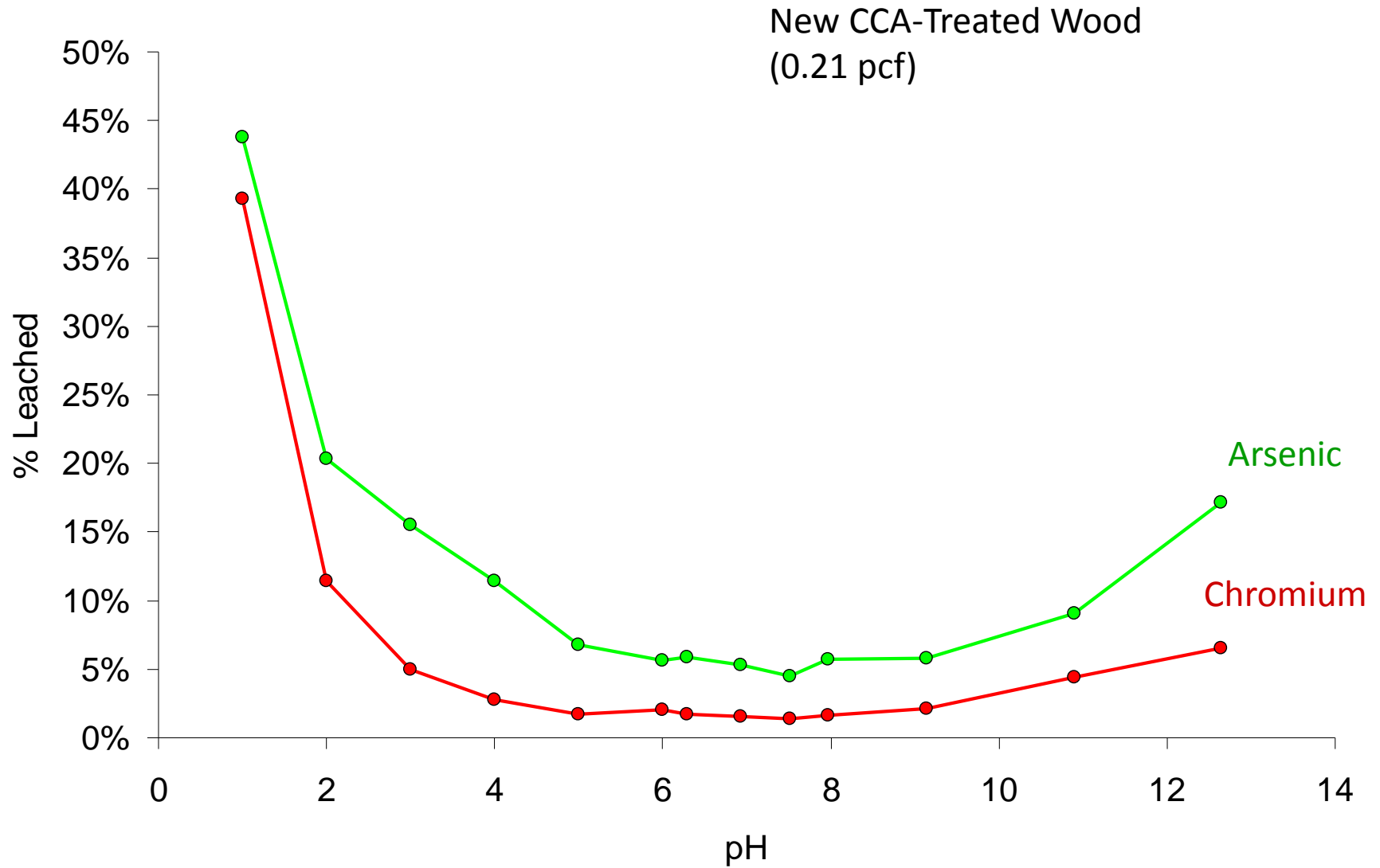


# Impact of pH: Amphoteric

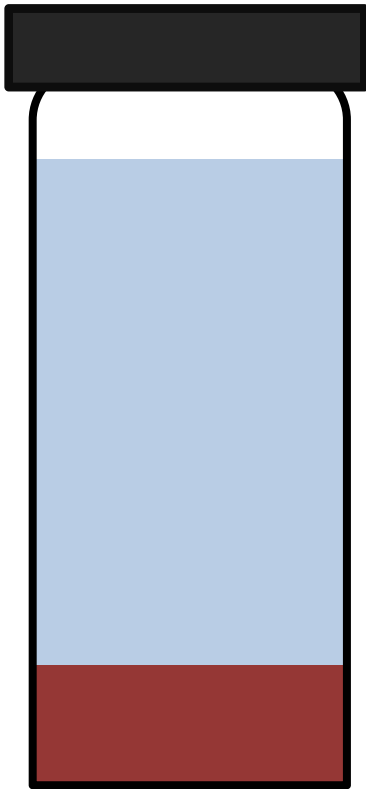




# Impact of pH



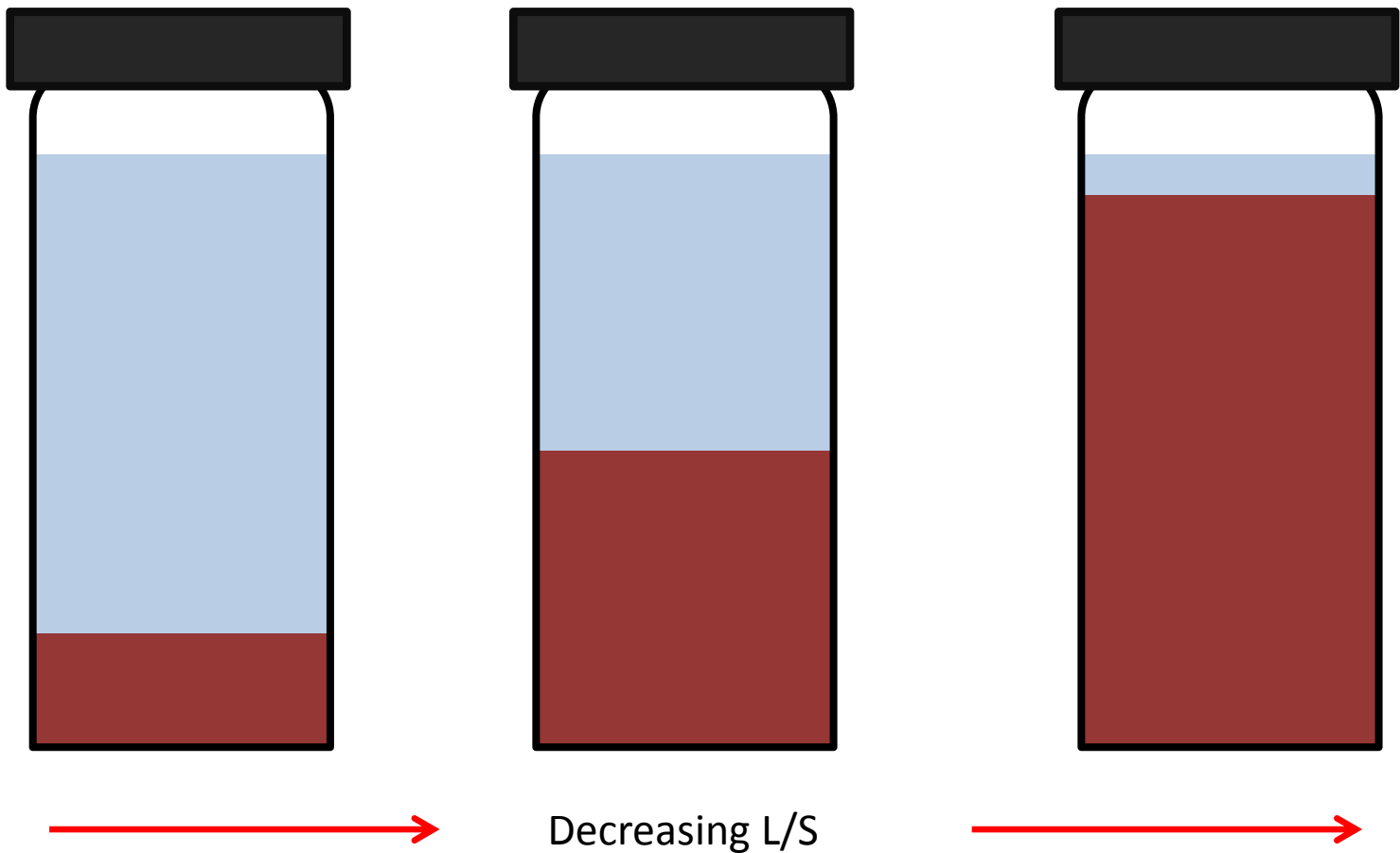
# What Impacts Leaching?



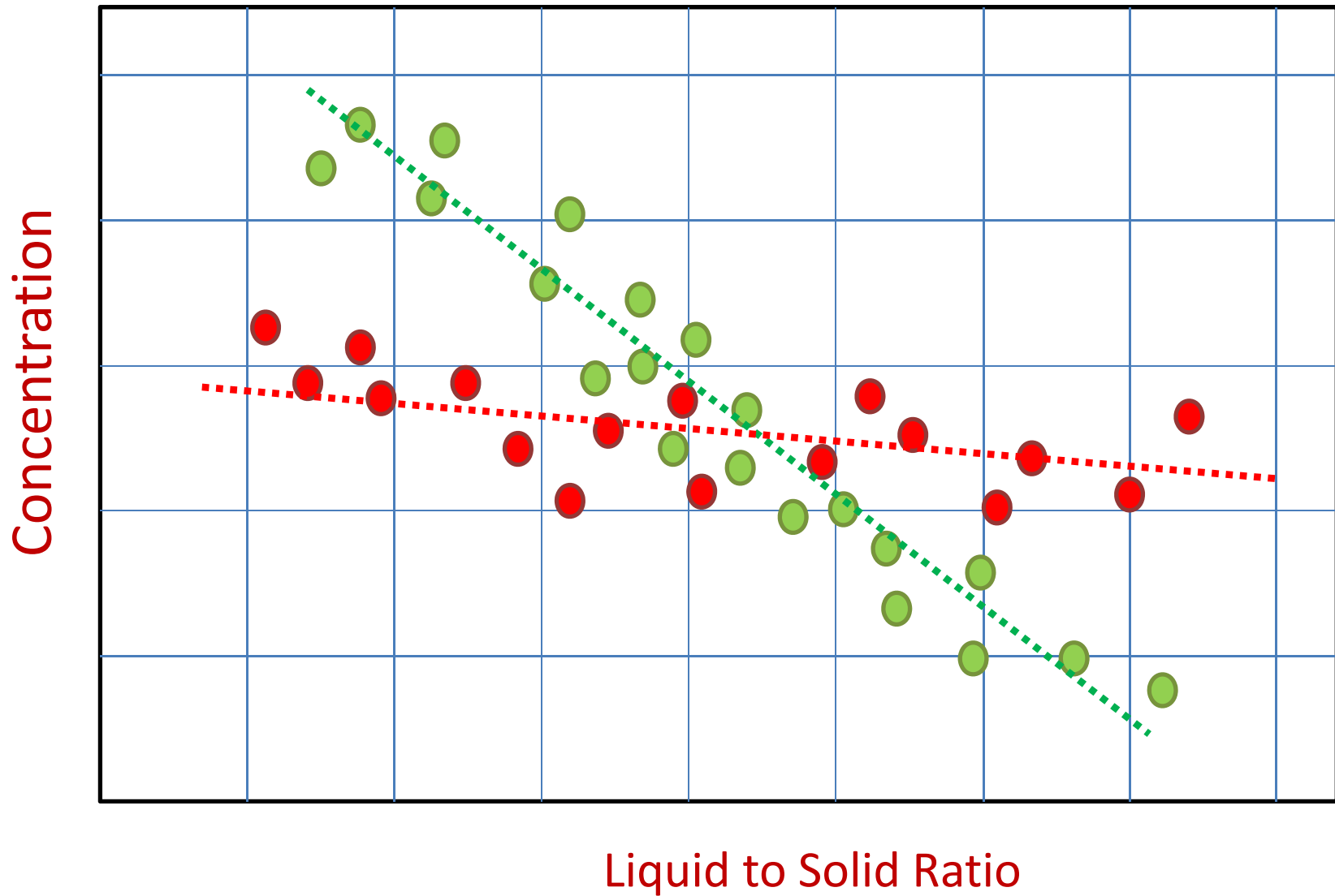
Liquid to Solid Ratio

→ TCLP and SPLP: 20 to 1

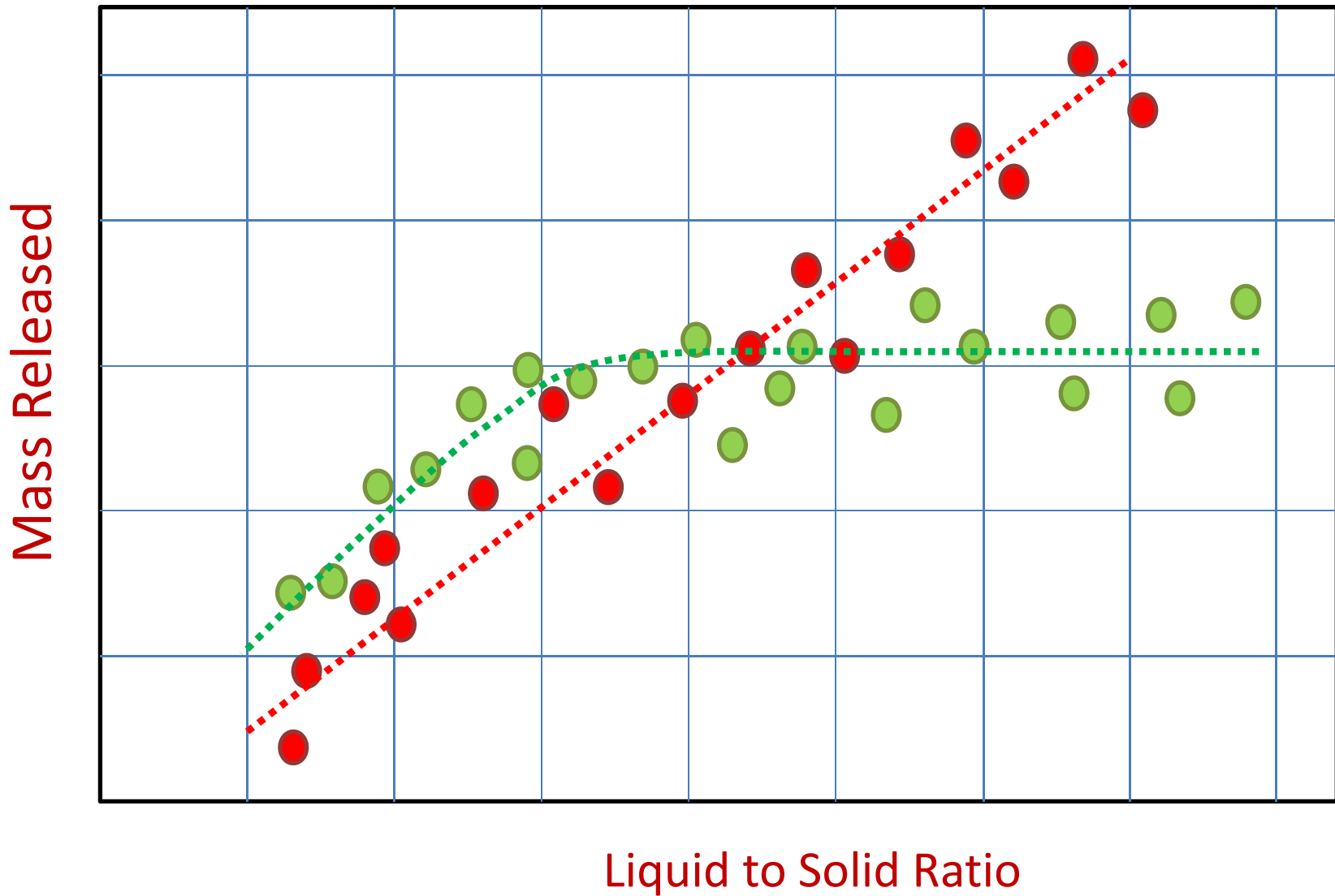
# What Impacts Leaching?



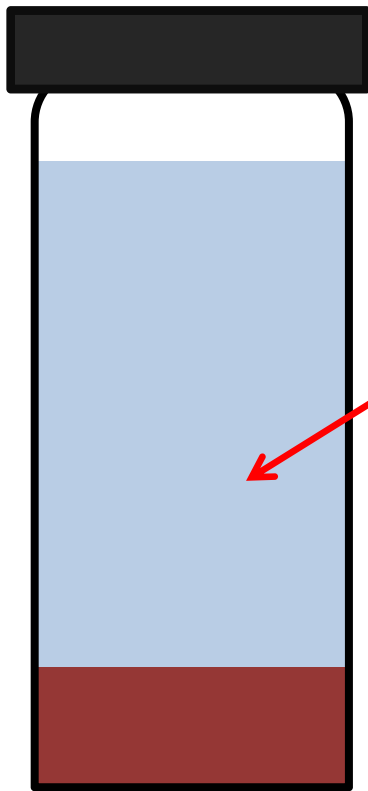
# Impact of Liquid to Solid Ratio



# Impact of Liquid to Solid Ratio



# What Impacts Leaching?

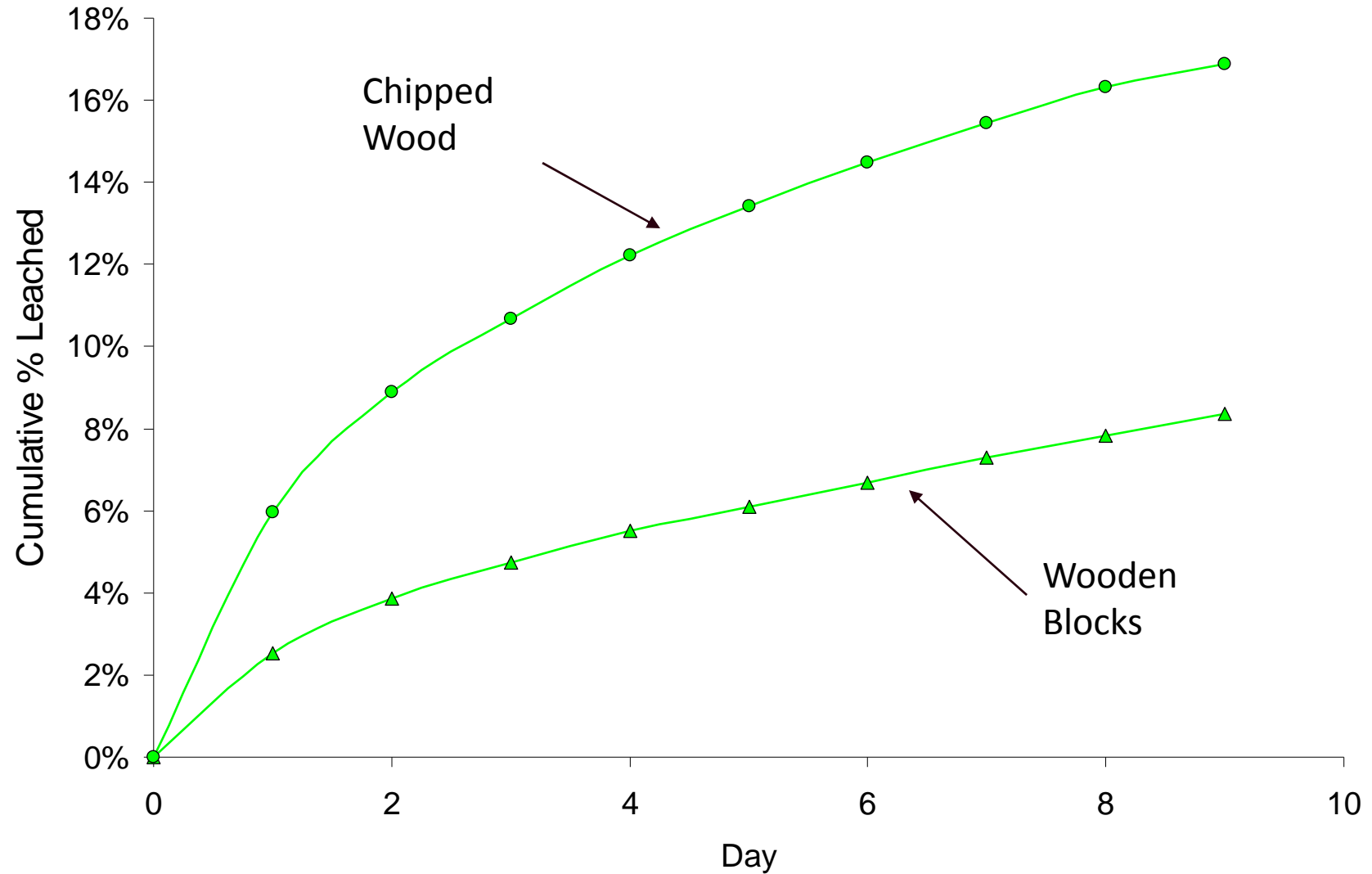


Leaching Time

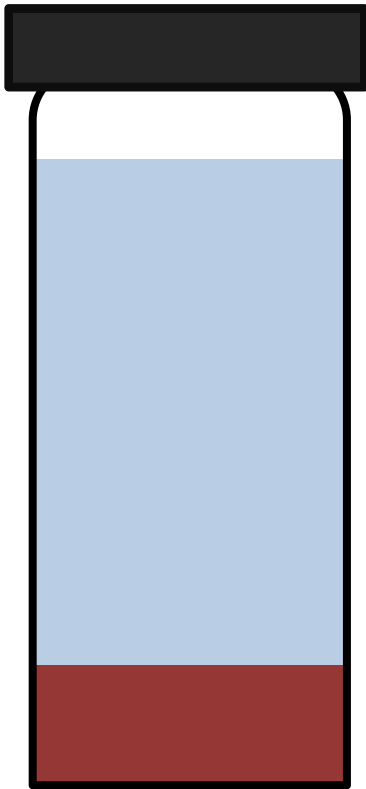
→ TCLP and SPLP: 18 +/- 2 hours

# Impact of Time

## Multiple Extraction Procedure (Arsenic)



# What Impacts Leaching?



Redox Potential?

Oxidizing or reducing  
environment



# EPA Leaching Tests

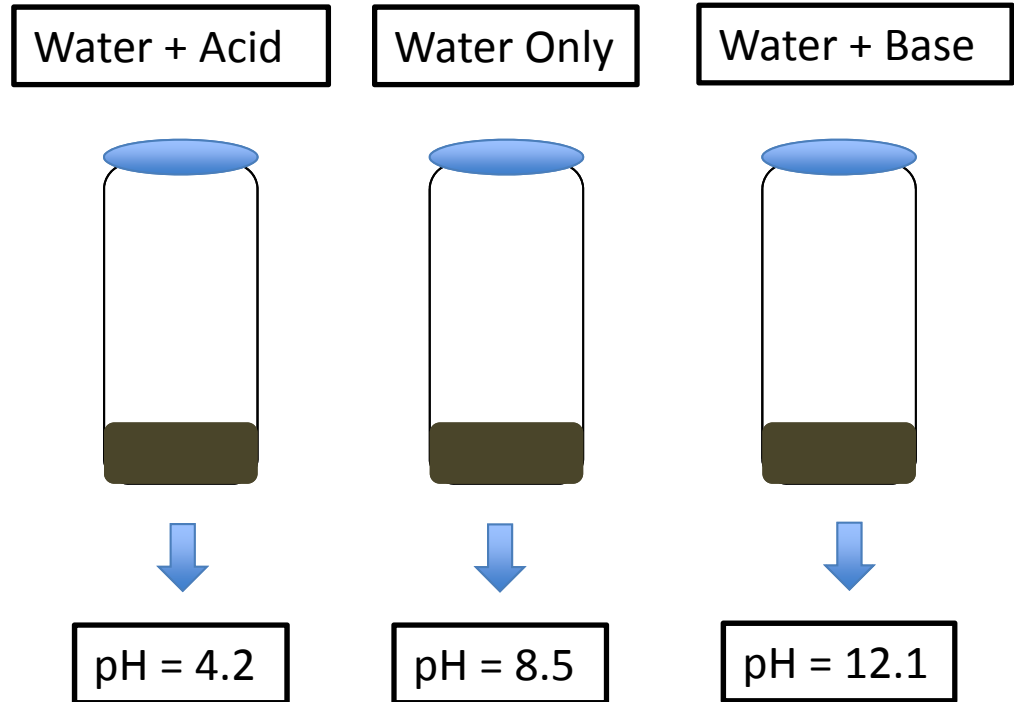
- *Method 1311* “Toxicity Characteristic Leaching Procedure”
- *Method 1312* “Synthetic Precipitation Leaching Procedure”
- *Method 1313* “Liquid-Solid Partitioning as a Function of Extract pH for Constituents in Solid Materials using a Parallel Batch Extraction Procedure”
- *Method 1314* “Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio for Constituents in Solid Materials using an Up-flow Percolation Column Procedure”
- *Method 1315* “Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials using a Semi-dynamic Tank Leaching Procedure”
- *Method 1316* “Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio for Constituents in Solid Materials using a Parallel Batch Extraction Procedure”

# Method 1313

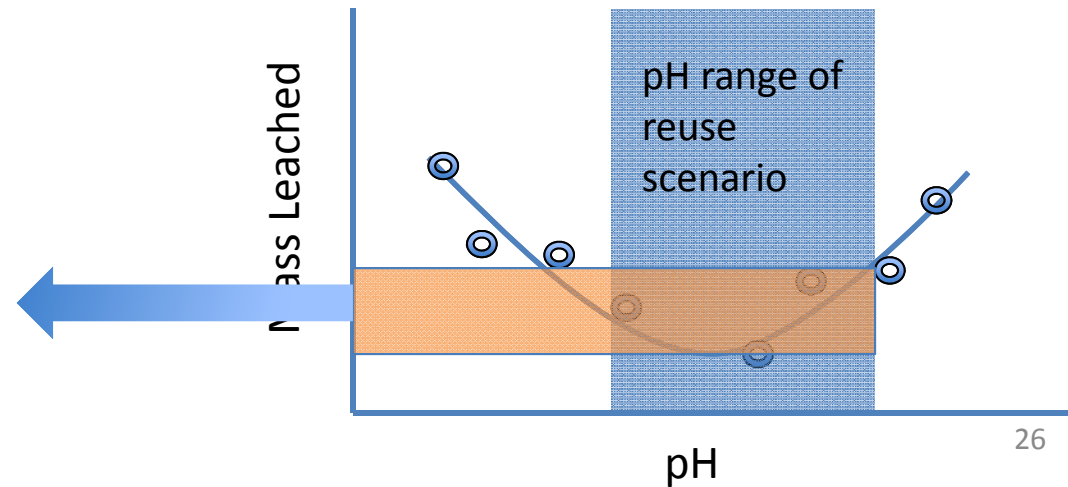
Parallel batch extraction done at a 10:1 liquid to solid ratio (10ml/g-dry) at up to 9 final pH values

Samples rotated for 24-72 hours

Goal: determine the leachability of the material for a range of pH values



Expected leaching within pH range

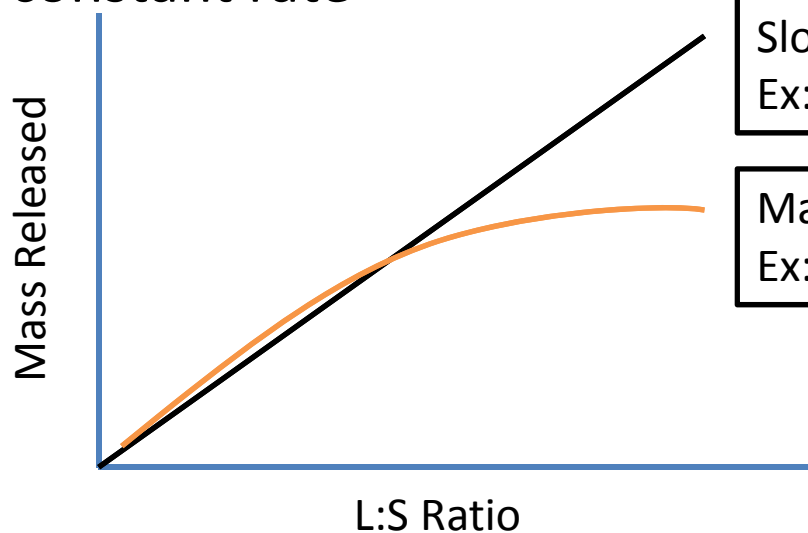
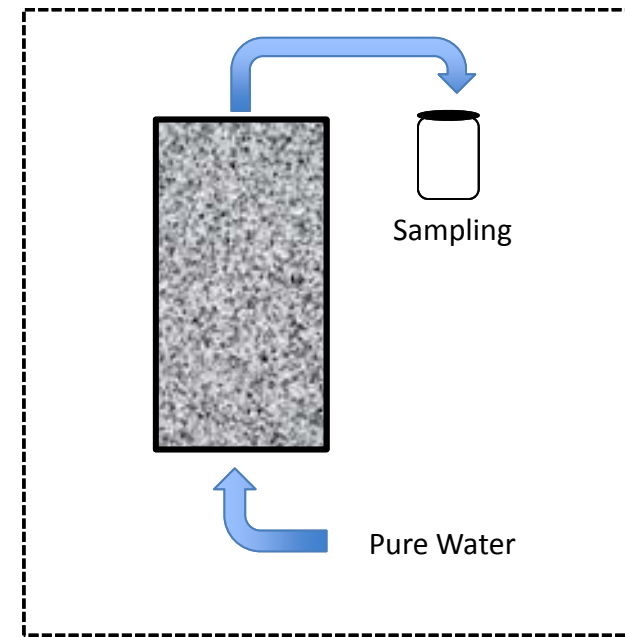


# Method 1314

Column leaching test with constant upward flow of pure water.

Samples are taken at prescribed days to achieve specific L/S ratios

Goal: Determine which constituents wash out quickly and which dissolve into the water at a constant rate



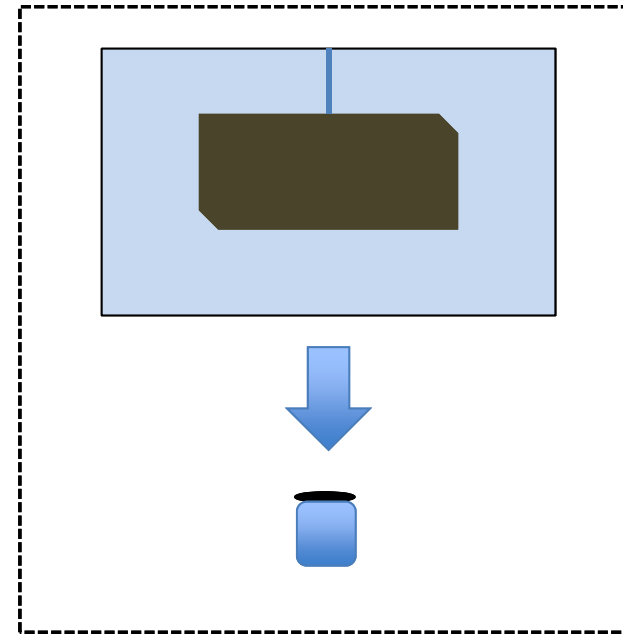
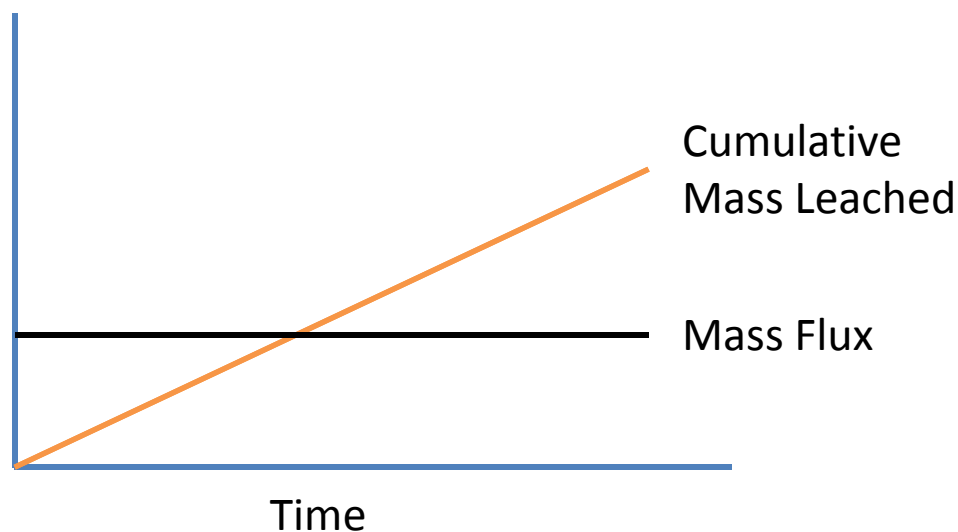
Slope  $\sim 1$ : Mass release controlled by dissolution  
Ex: As, Fe (mineral bound)

Mass release controlled by surface availability  
Ex: K, Na, Cl (very soluble elements)

# Method 1315

Monolithic material sample (e.g. a brick) or a compacted granular material is submerged in a tank of water and allowed to soak for prescribed times. Water is periodically sampled and analyzed for constituents of concern. New water replaces the old.

Goal: Determine time-dependent release rates under monolithic conditions



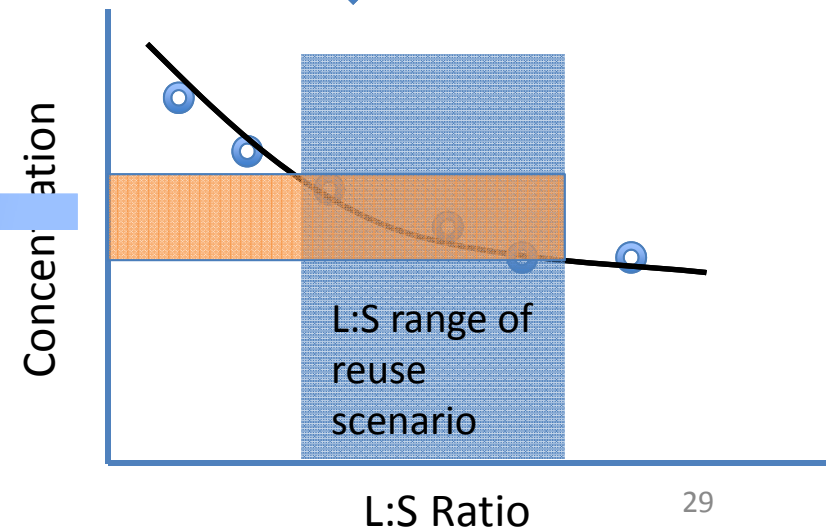
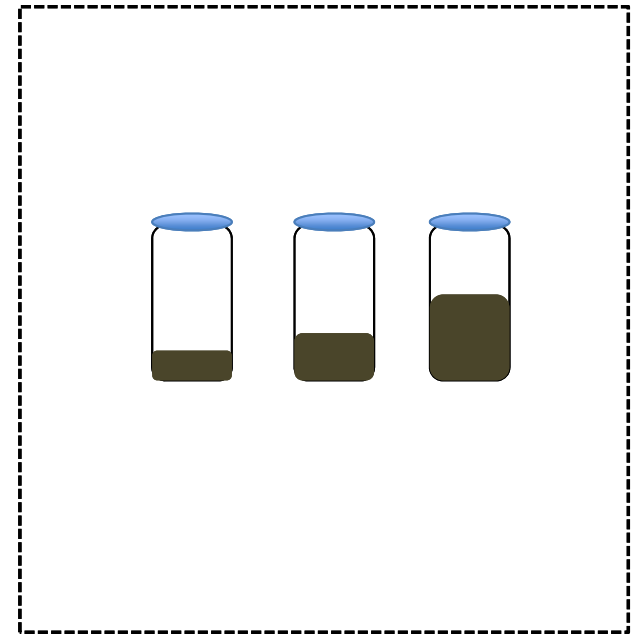
This information can help in predicting mass release in the long run

# Method 1316

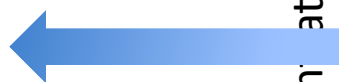
## Interpreting Results

Parallel batch performed at five different liquid to solid ratios.

Similar to 1313 but more rapid.



Expected leaching within L:S range



# Example Questions

## Analytical

- How do new tests compare to SPLP?
- What particle size is appropriate to use?
- How do the different filters impact the results?

## Application

- Which pH regime should be the target regime?
- How do you evaluate leachate concentrations that change over time?
- For different reuse scenarios, what is the most appropriate test to use and how?

# Project Objectives

- Document LEAF Methods
  - Testing procedures

LEAF  
Leaching Environmental Assessment Framework



- Guidance for practitioners
  - Intent
  - Differences
  - Application

# Literature Review

- Application of leaching protocols
  - Refereed literature
  - Industry and government
  - International experience
- Identify candidate waste streams

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 **Journal of Environmental Management**  
journal homepage: [www.elsevier.com/locate/jenvman](http://www.elsevier.com/locate/jenvman)



**Effect of water treatment additives on lime softening residual trace chemical composition – Implications for disposal and reuse**

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**ABSTRACT**

Drinking water treatment residues (WTR) offer potential benefits when recycled through land application. The current guidance in Florida, US allows for unrestricted land application of lime softening WTR; alum and ferric WTR require additional evaluation of total and leachable concentrations of select trace metals prior to land application. In some cases a mixed WTR is produced when lime softening is accompanied by the addition of a coagulant or other treatment chemical; applicability of the current guidance is unclear. The objective of this research was to characterize the total and leachable chemical content of WTR from Florida facilities that utilize multiple treatment chemicals. Lime and mixed lime WTR samples were collected from 18 water treatment facilities in Florida. Total and leachable concentrations of the WTR were measured. To assess the potential for disposal of mixed WTR as clean fill below the water table, leaching tests were conducted at multiple liquid to solid ratios and under reducing conditions. The results were compared to risk-based soil and groundwater contamination thresholds. Total metal concentrations of WTR were found to be below Florida soil contaminant thresholds with Fe found in the highest abundance at a concentration of 3600 mg/kg-dry. Aluminum was the only element that exceeded the Florida groundwater contaminant thresholds using SPLP (95% UCL = 0.23 mg/L; risk threshold = 0.2 mg/L). Tests under reducing conditions showed elevated concentrations of Fe and Mn, ranging from 1 to 3 orders of magnitude higher than SPLP leachates. Mixed lime WTR concentrations (total and leachable) were lower than the ferric and alum WTR concentrations, supporting that mixed WTR are appropriately represented as lime WTR. Testing of WTR under reducing conditions demonstrated the potential for release of certain trace metals (Fe, Al, Mn) above applicable regulatory thresholds; additional evaluation is needed to assess management options where reducing conditions may develop.

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# Project Objectives

- Examine previous beneficial use assessments in Florida



# Florida Beneficial Use Leaching Assessment

- Street sweepings
- Catch basin/SW sediments
- Waste-to-energy ash
- Milled asphalt pavement
- Coal combustion residuals
- Recovered waste-amended concrete

How may have LEAF impacted decision?

# Project Objectives

- Perform leaching tests on three specific waste streams
- Selected from:
  - Previous assessments in FL
  - Feedback from project TAG



# LEAF Testing

- LEAF tests
- SPLP and total concentration
- Answer questions from previous tasks:
  - How LEAF methods are applied
  - Added insight



# Guidance Document

- Final Report
  - Utility of LEAF methods for beneficial use decisions
- Tutorial on LEAF methods
  - Differences from existing procedures
  - How they may be applied
- Potential ideas for guidance document



# How have we used LEAF?

- Several examples where LEAF has been used by our research team to help with a beneficial use assessment
  - Sludge from water treatment
  - Waste to energy ash
- We have also evaluated other wastes
  - Coal ash
  - Mining Waste
  - Electronic Waste

# Our Approach

- SPLP testing still conducted
  - Screening tool
  - Needed for a comparison
- LEAF testing conducted to better assess contaminant release under specific reuse conditions
- LEAF testing conducted to examine waste treatment options
  - What can be done to make material leach less



# Drinking Water Sludge

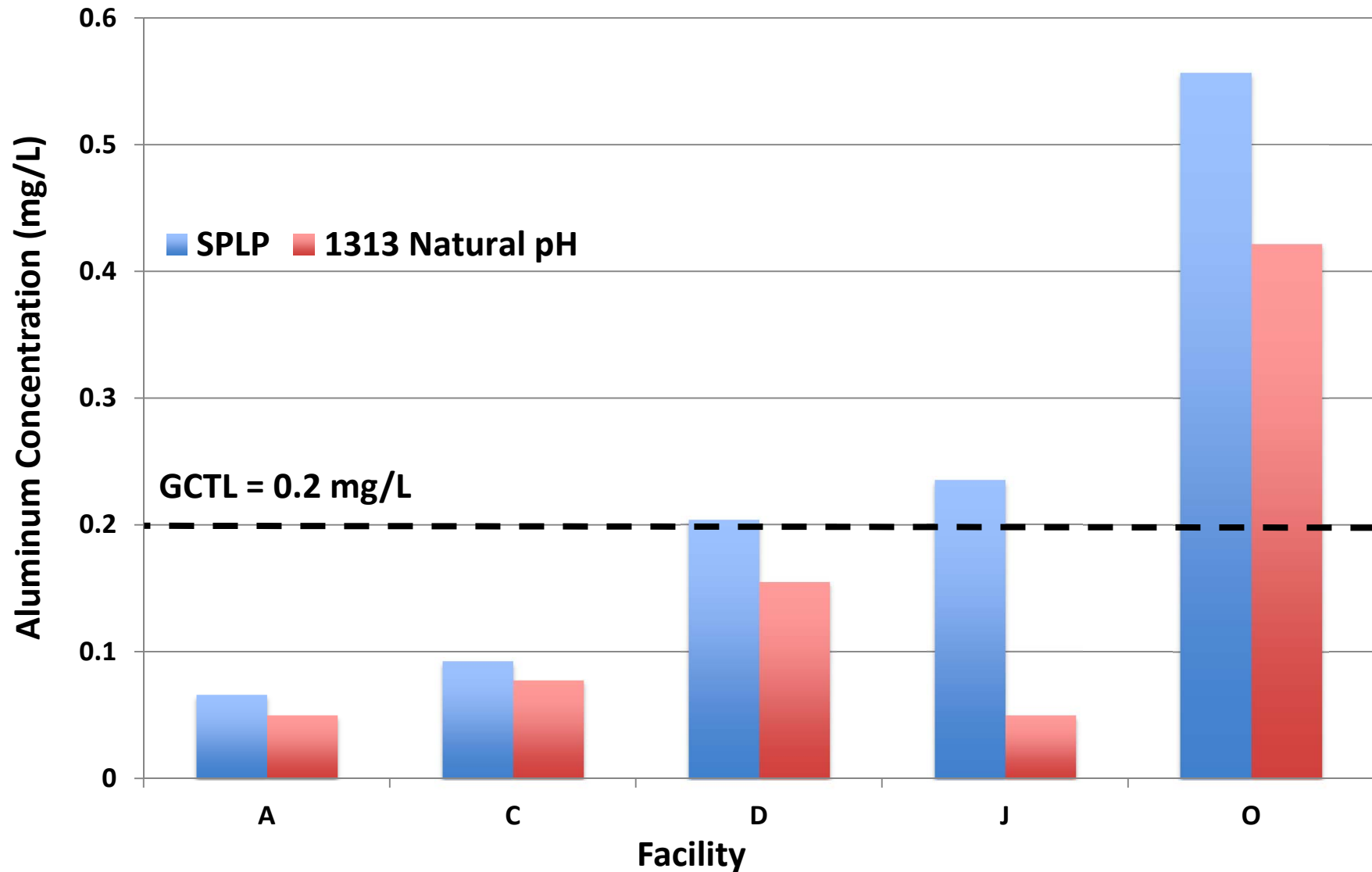


# Drinking Water Sludge

- Assess the effect of additional treatment additives and possibility for use as a “clean fill” in water bodies
- Aluminum a potential concern with respect to leaching
- Consider the scenario where values are compared directly to target levels



# Method Natural pH and SPLP



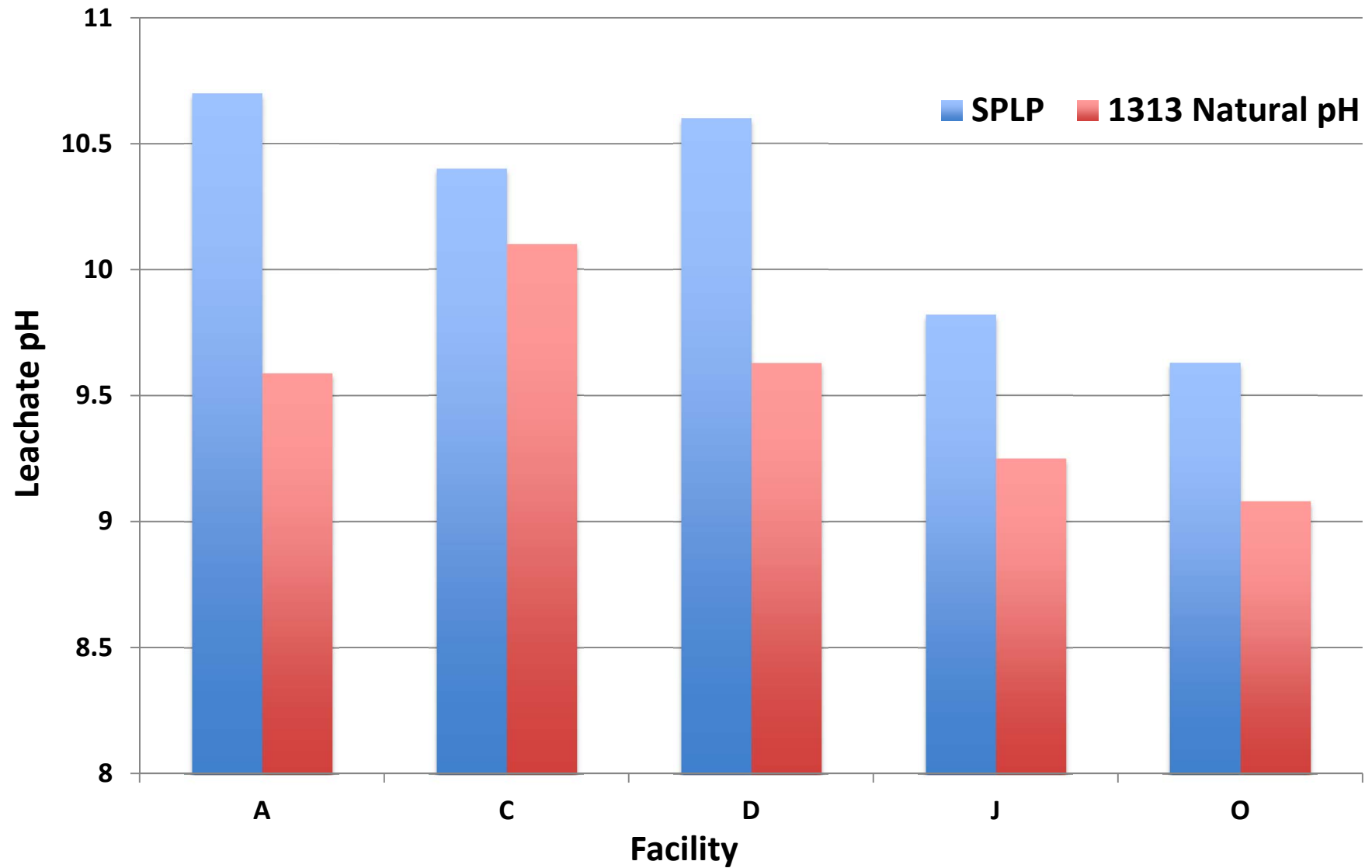
# Leaching Results

Natural pH – pH when immersed in water at a liquid to solid ratio of 10

Method 1313 (Natural pH), Method 1316 (L/S – 10)

- Some would argue this is a more representative batch test than SPLP
- For some of the facilities tested SPLP concentrations were elevated when compared values at the natural pH
- In one instance method 1313 values were on different side of GCTL than SPLP
  - Mean and 95% UCL

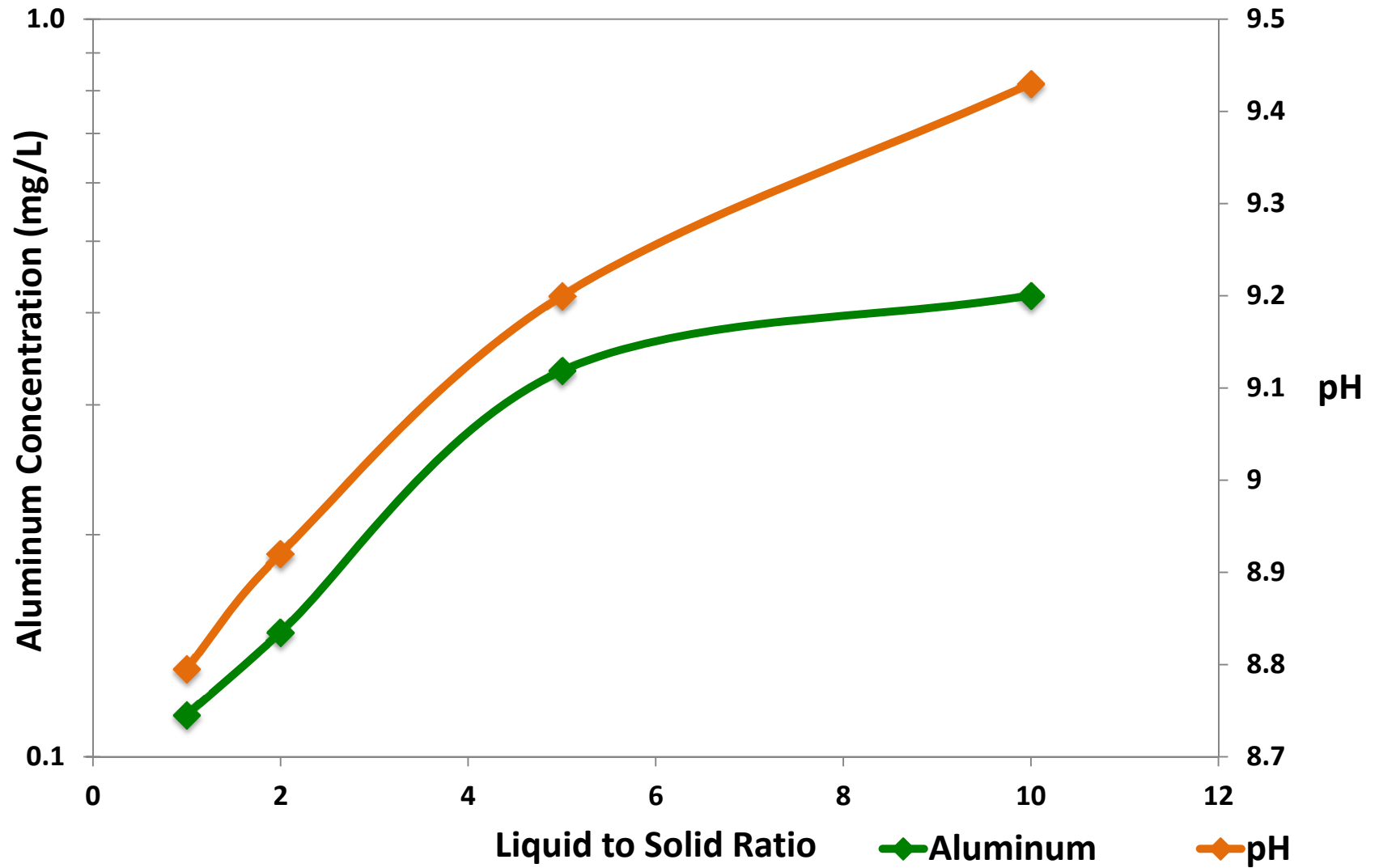
# pH - Method 1313 and SPLP



# Explaining Differences

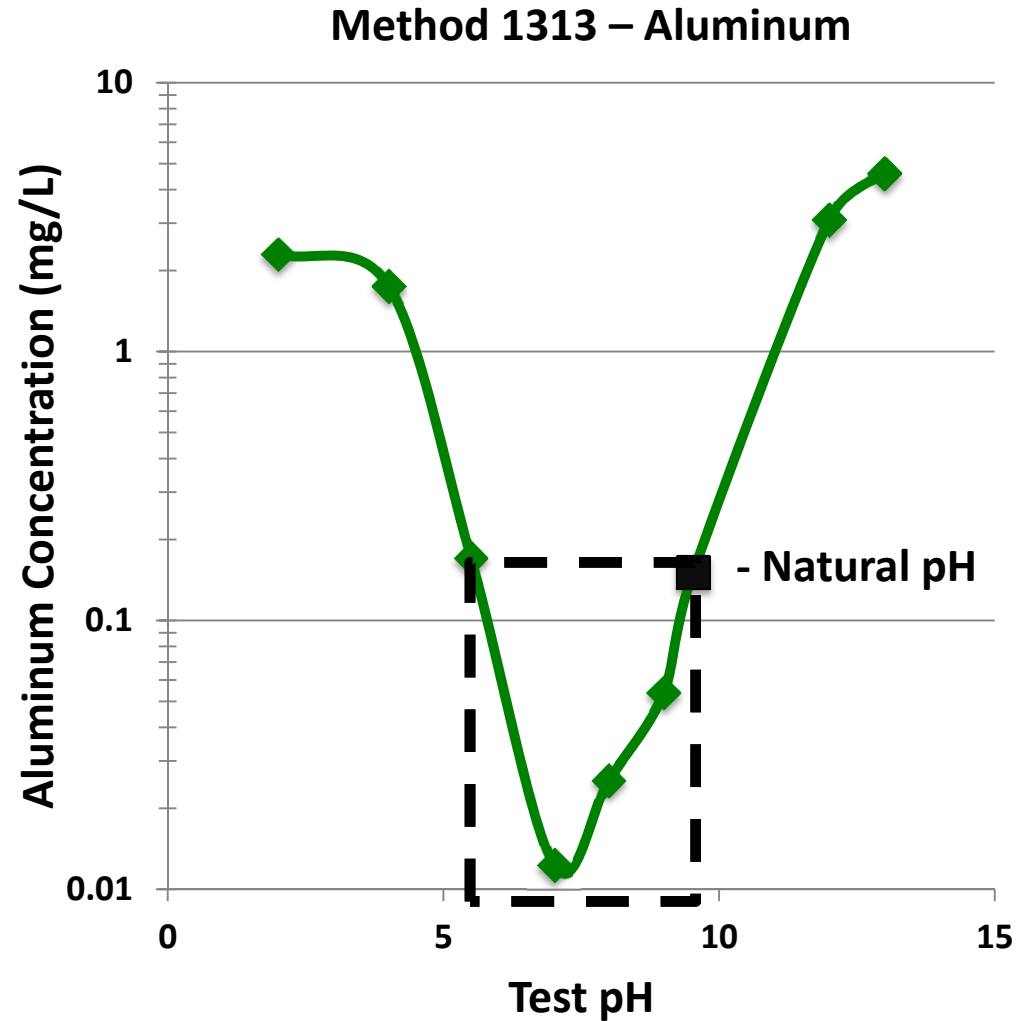
- Differences in leachate pH between SPLP could explain discrepancy in concentrations
- SPLP test is conducted at a higher liquid to solid ratio and you would expect that pH would be lower
- Conduct Method 1316 – Batch Leaching as a function of liquid to solid ratio
  - Large number of facilities
  - Speed of testing, cost

# Method 1316



# Drinking Water Sludge Summary

- SPLP and natural pH leaching can differ significantly
  - Implications for risk assessment
  - Which test is more representative?
- LEAF helps to demonstrate leaching of Al in pH range of water bodies below GCTL





# Beneficial Use Assessment Pasco County – WTE Bottom Ash

- Conduct standard batch test SPLP
- Identify COPCs
  - GCTLs
- Which elements elevated above GCTLs?
  - Lead, Antimony, Molybdenum

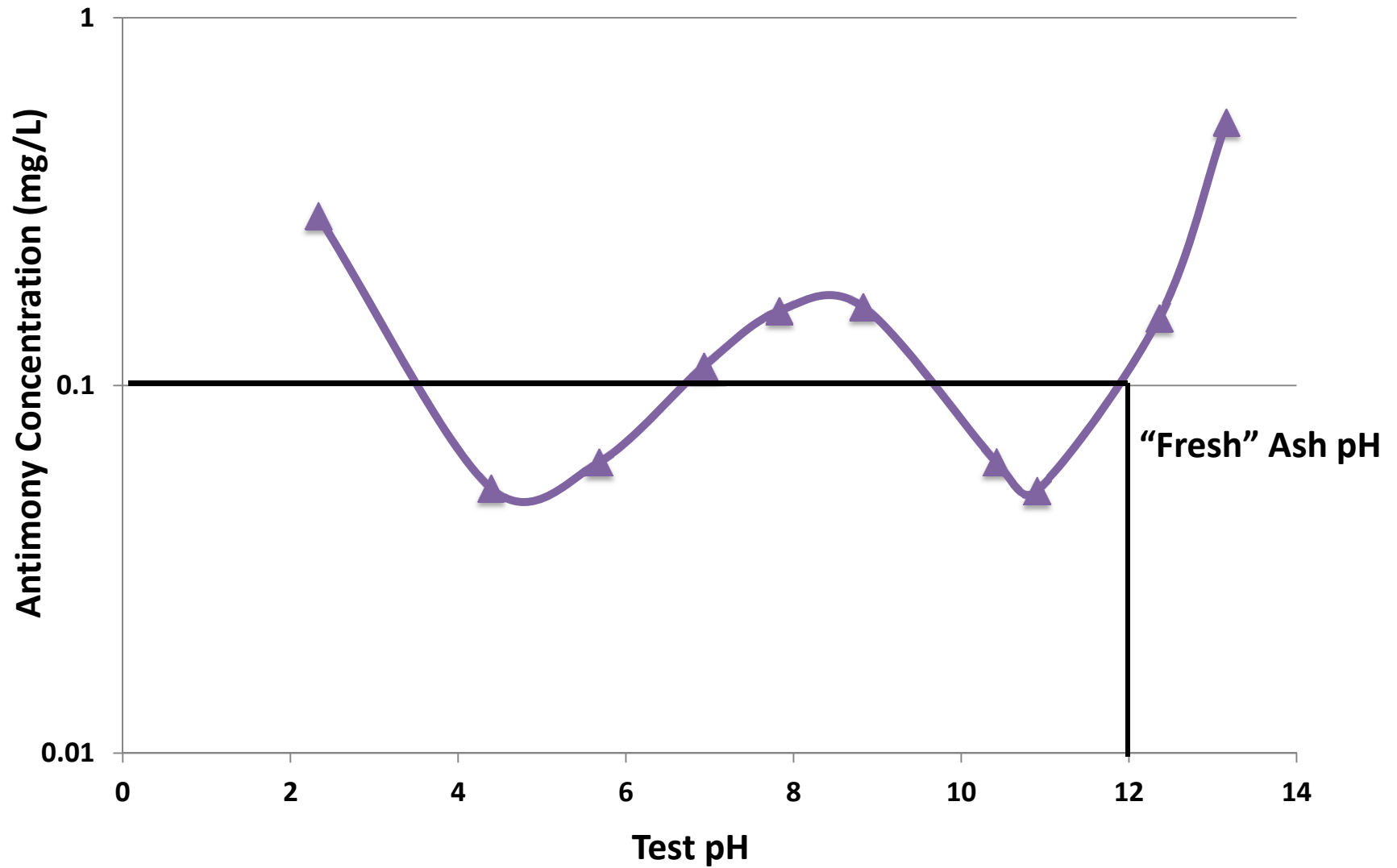


# What Can We Do to Decrease Leaching?

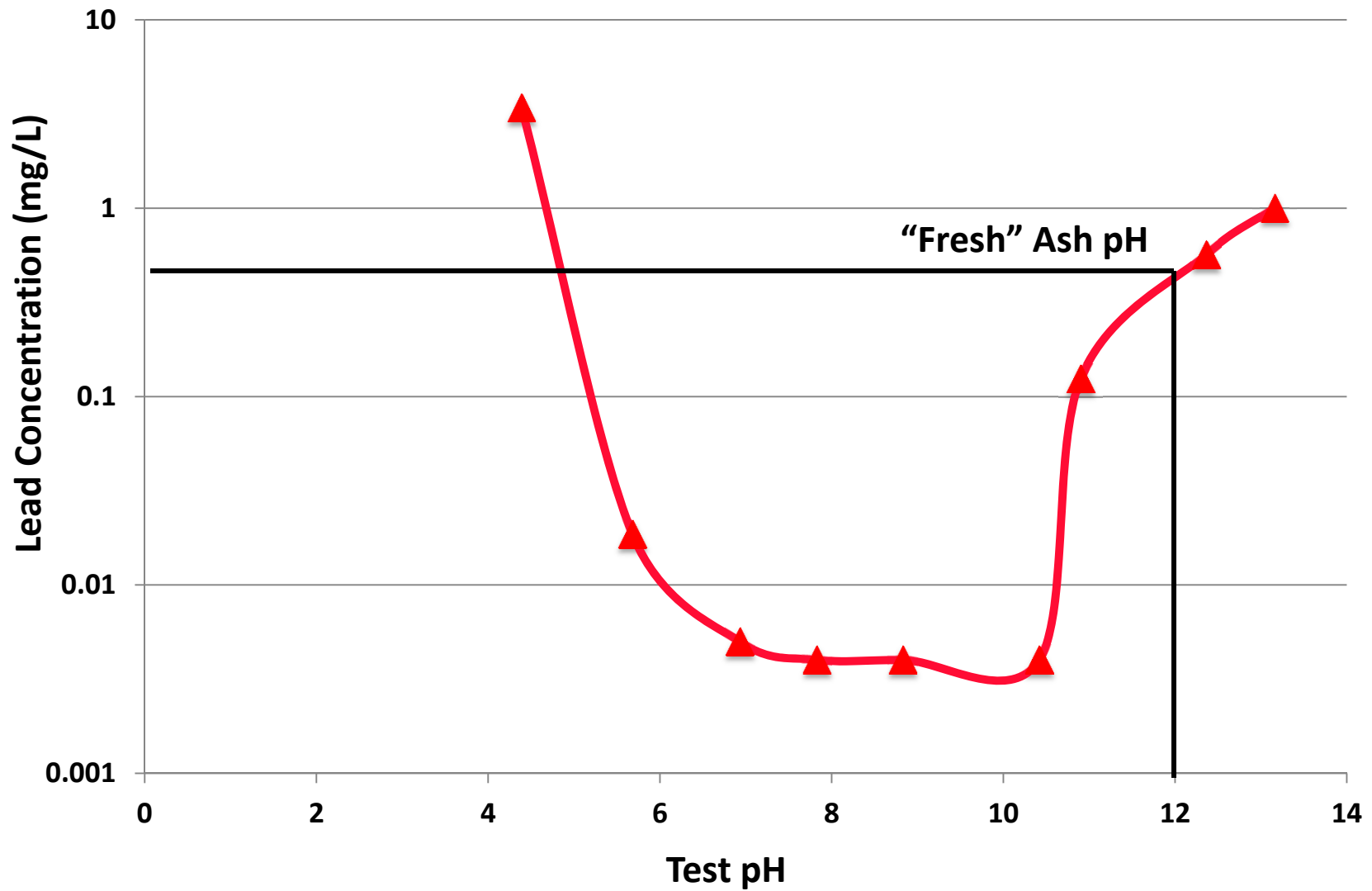
- Aging has been demonstrated to reduce leaching of WTE ash
- Use LEAF to examine leaching of aged material
- pH changes due to carbonation
- Wash-off of elements due to precipitation



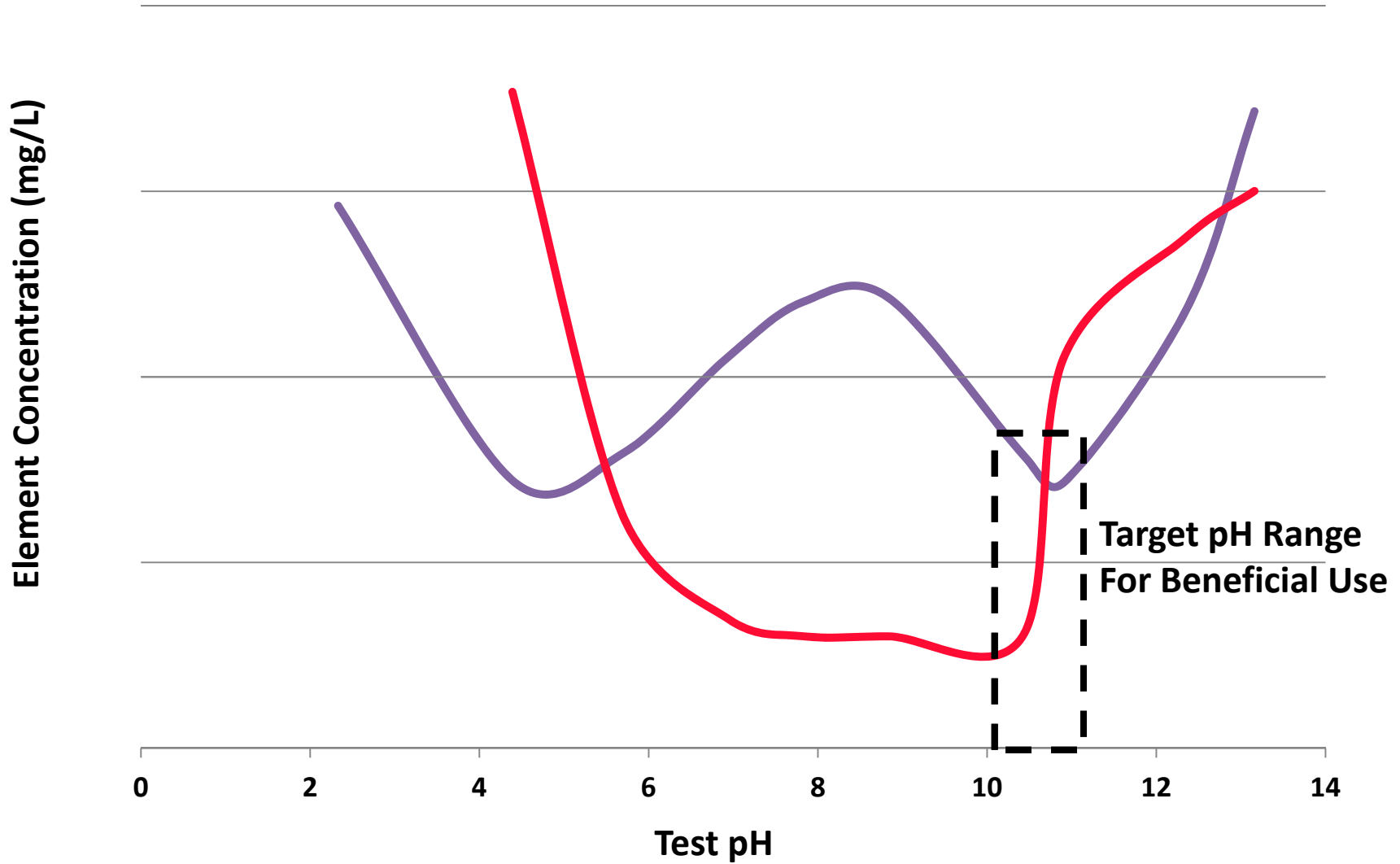
# Method 1313 - Antimony



# Method 1313 - Lead



# Optimum Final pH

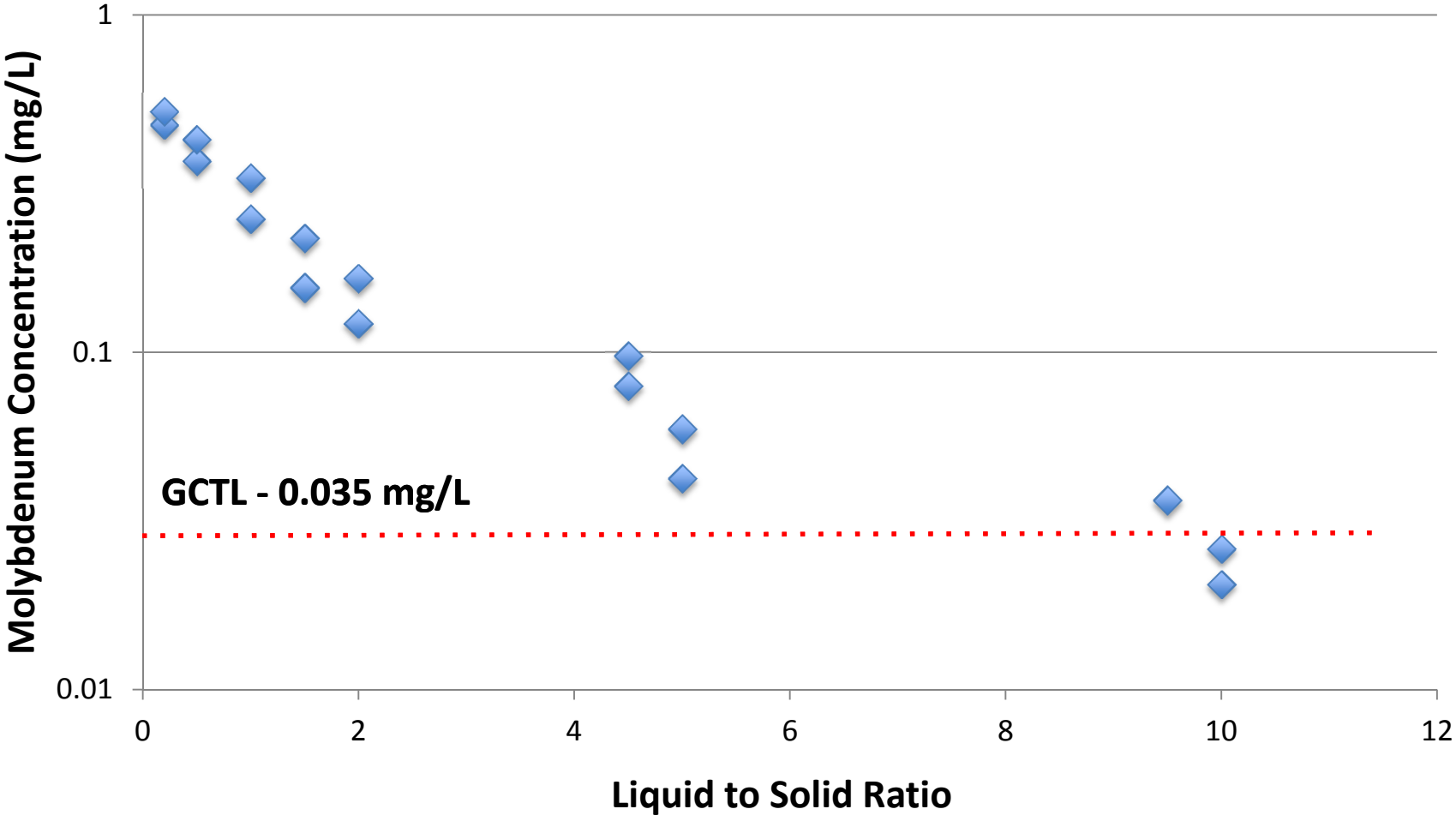


# Molybdenum Concentrations

- Initially elevated with respect to a direct comparison to GCTLs
- Concentration decreased throughout duration of column test
- Based on method 1313 data this is not expected to be related to pH changes
- “Surface Wash-Off” release mechanism



# Method 1314- Molybdenum Leaching



# What Did We Learn?

- LEAF allows us to better understand leaching of WTE ash
- pH changes influencing leaching
  - Lead, Antimony
  - Helped to select optimal pH range, ageing time
- Decrease in Molybdenum concentrations over time
  - Loss of Mo while “Aging”
  - Expected decrease over time

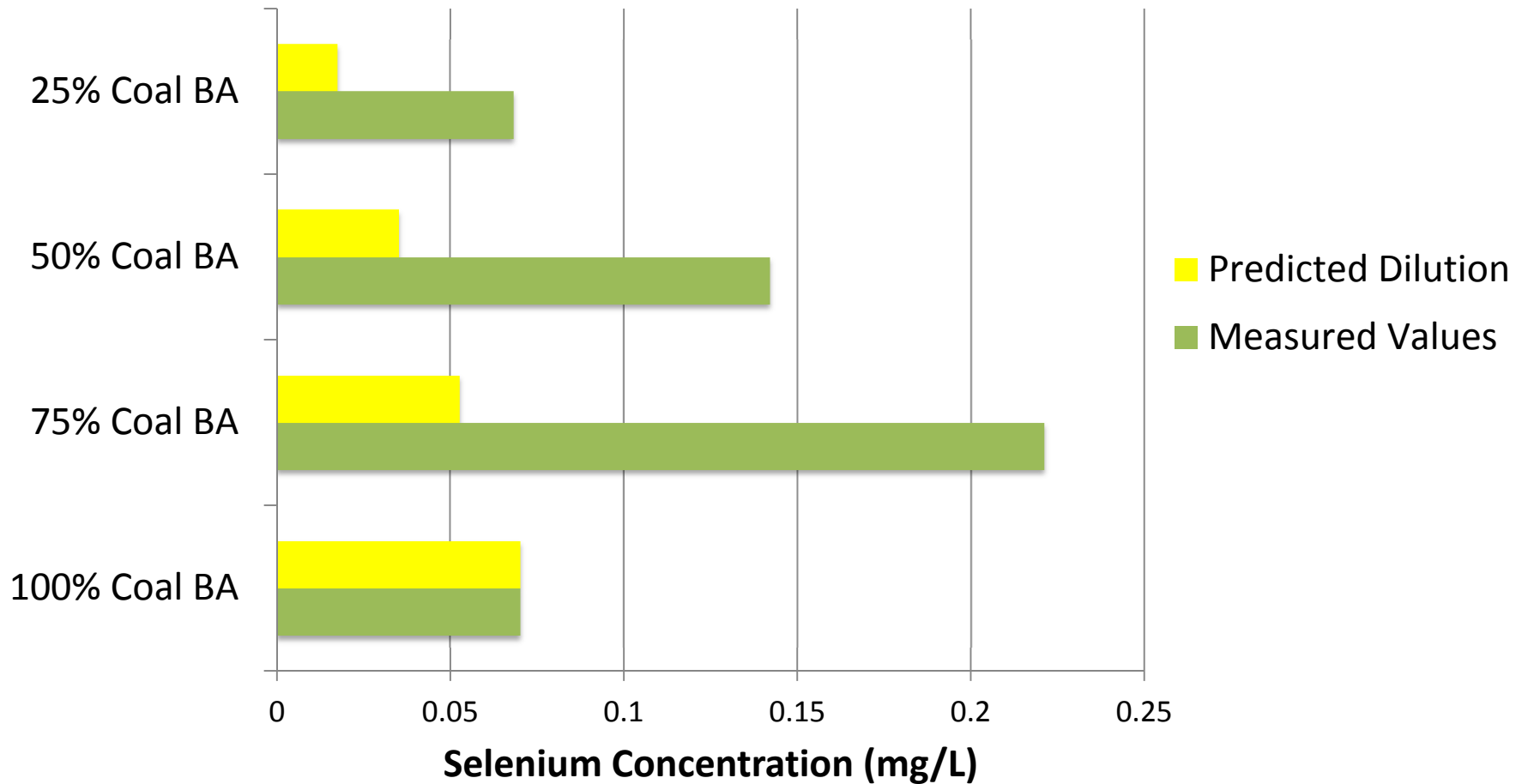


# LEAF Assessment - Blending Coal Bottom Ash

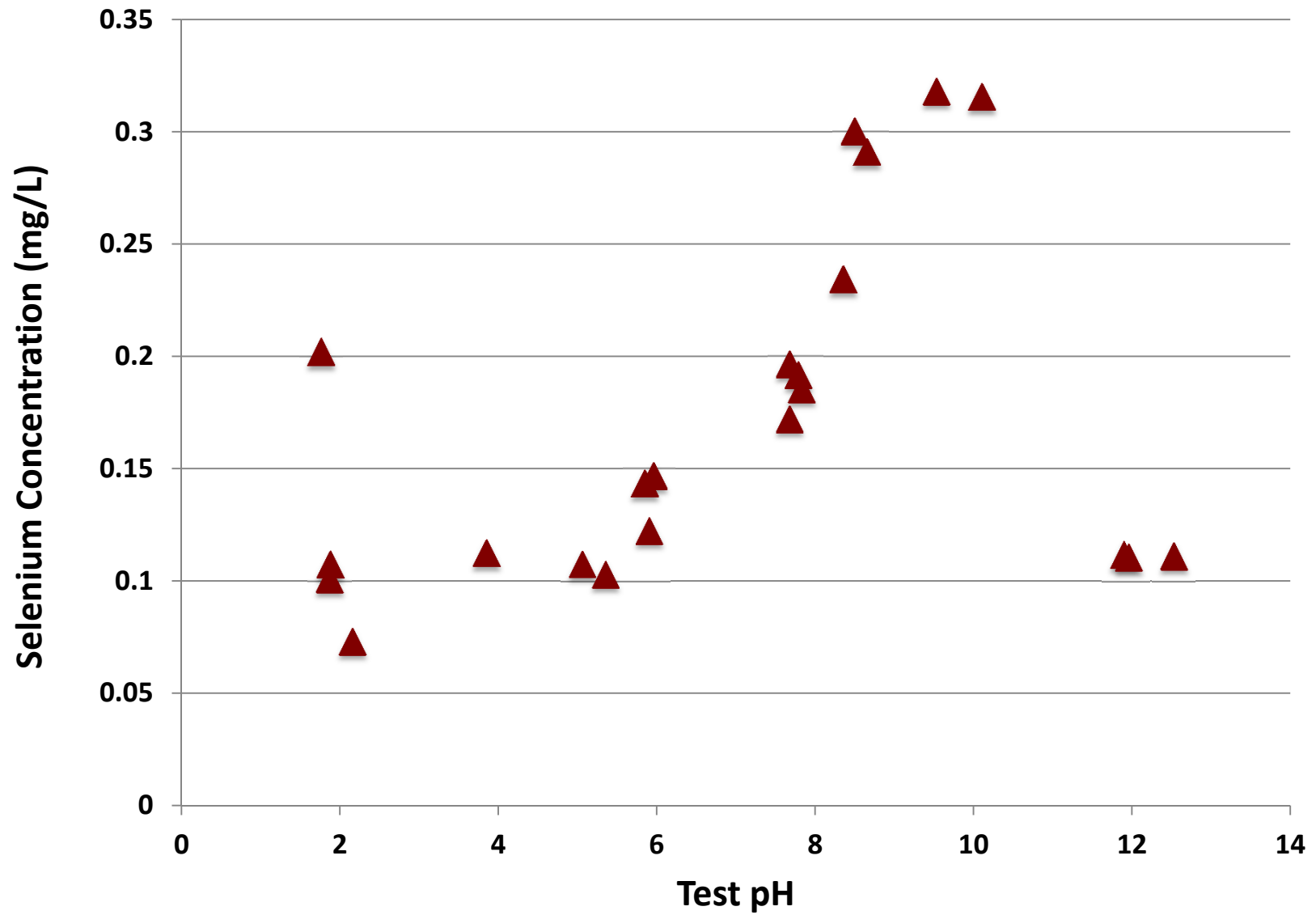
# Coal Bottom Ash

- Relatively inert material
- SPLP test results produced majority of leachate concentrations below GCLTs
  - Exception was Se within 10% of threshold
- Materials testing values (LBR) low
  - Experimented by blending bottom ash with lime rock to increase strength
- 50/50 blend able to achieve x2 strength
  - How would blending effect leaching?

# Coal Bottom Ash-Lime Rock Blends



# Selenium



# Blending

- Trying to improve the structural characteristics of the material had unintended consequences
- Differences between SPLP and natural pH
  - SPLP pH – 5.3 “Natural” pH - 7.7
  - Natural pH selenium leaching:  
0.184 mg/L (3 x SPLP values)
  - 50:50 ash/lime rock blends: pH- 8.0
- By mass you would expect the concentrations of blends to be diluted
  - Better understanding because of LEAF testing and proper interpretation of results

Which Batch Leaching Test Best  
Represents Monofill Disposal  
Conditions?

# Methodology

- Samples



Bottom Ash Greater 3/8"



Bottom Ash Less 3/8"



Mixed Ash



Fly Ash

# Methodology

- Leaching method
  - Batch Tests
    - TCLP (EPA method 1311)
      - TCLP#1; (pH = 4.93±0.05)
      - TCLP#2; (pH = 2.88±0.05)
    - SPLP (EPA method 1312); (pH = 4.2)



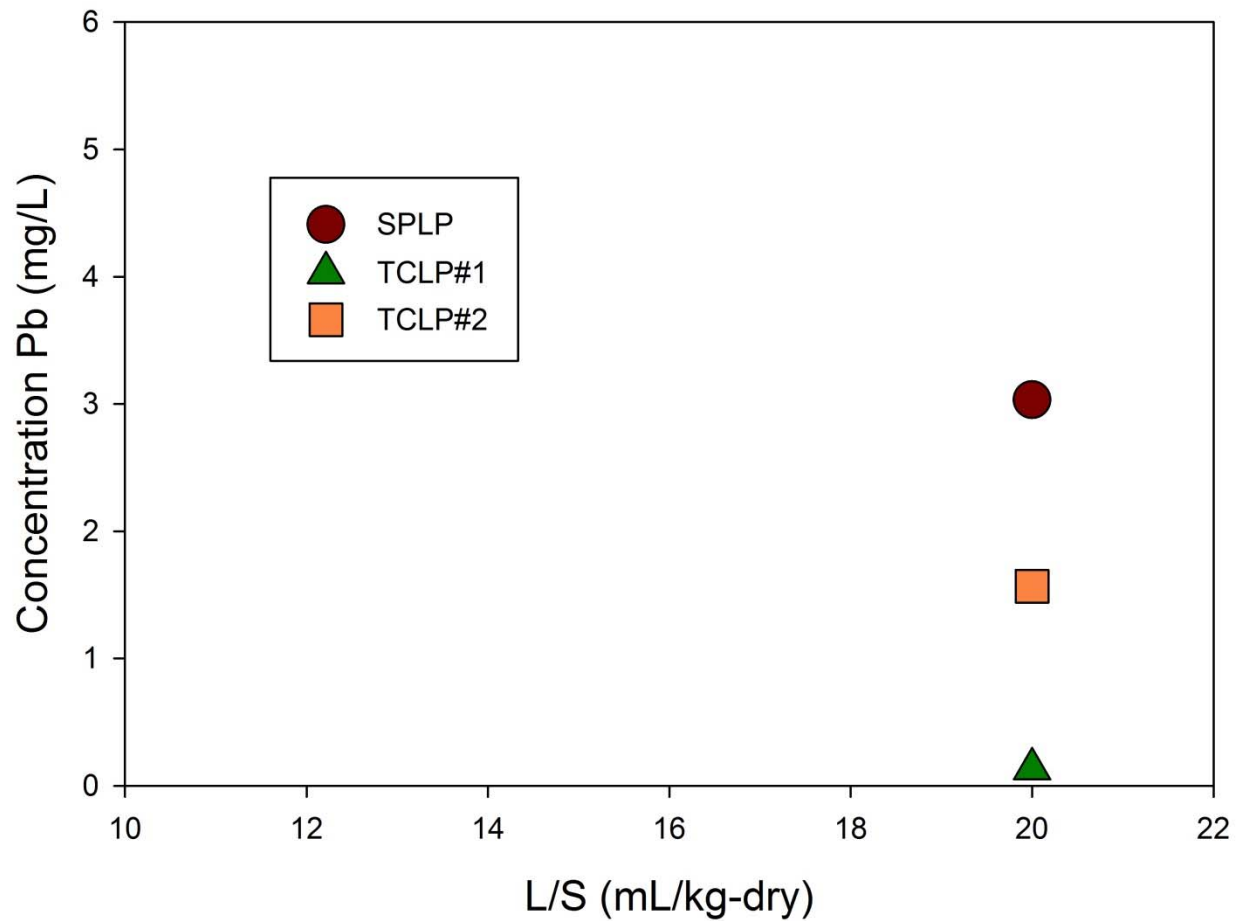


# Methodology

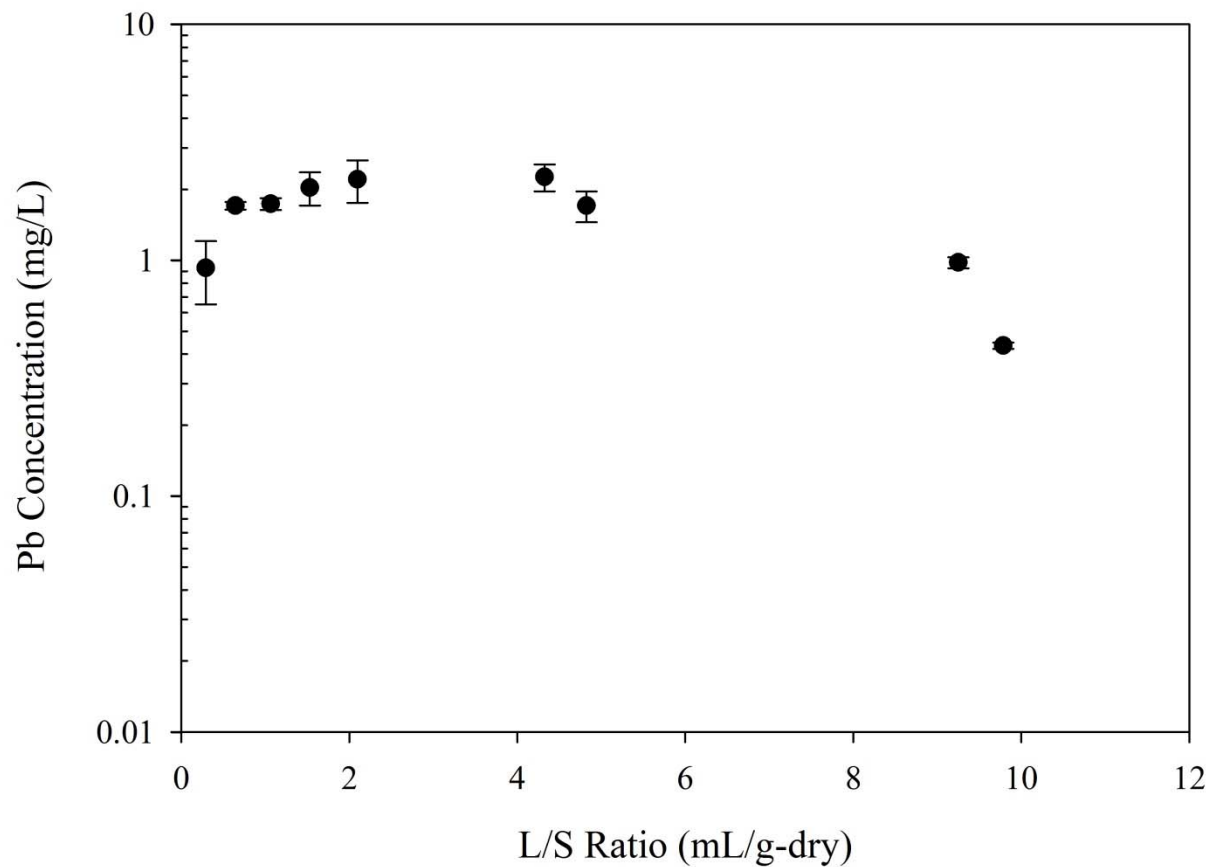
- Column test (EPA Method 1314)



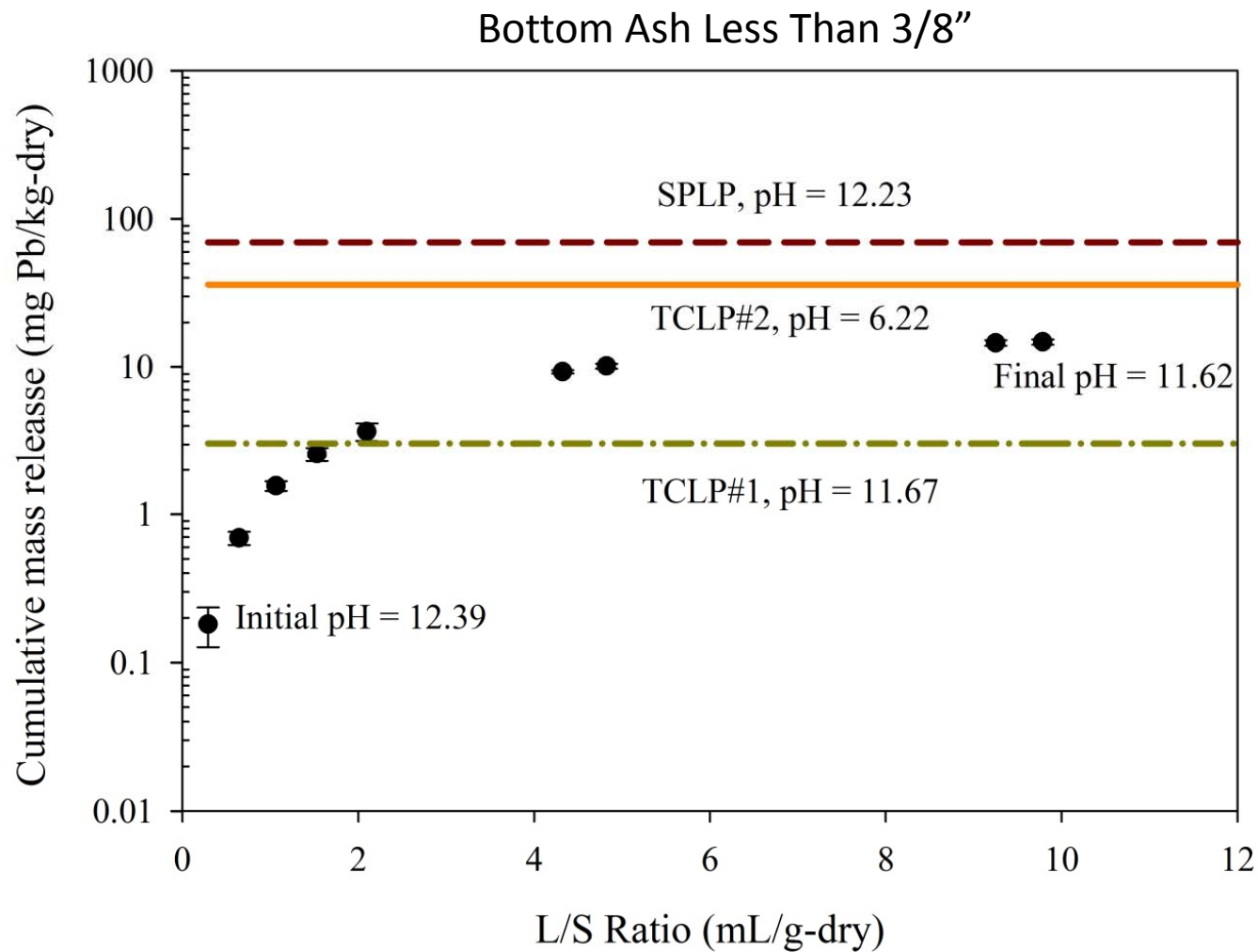
# An Example Result: TCLP/SPLP (Bottom Ash Less than 3/8")



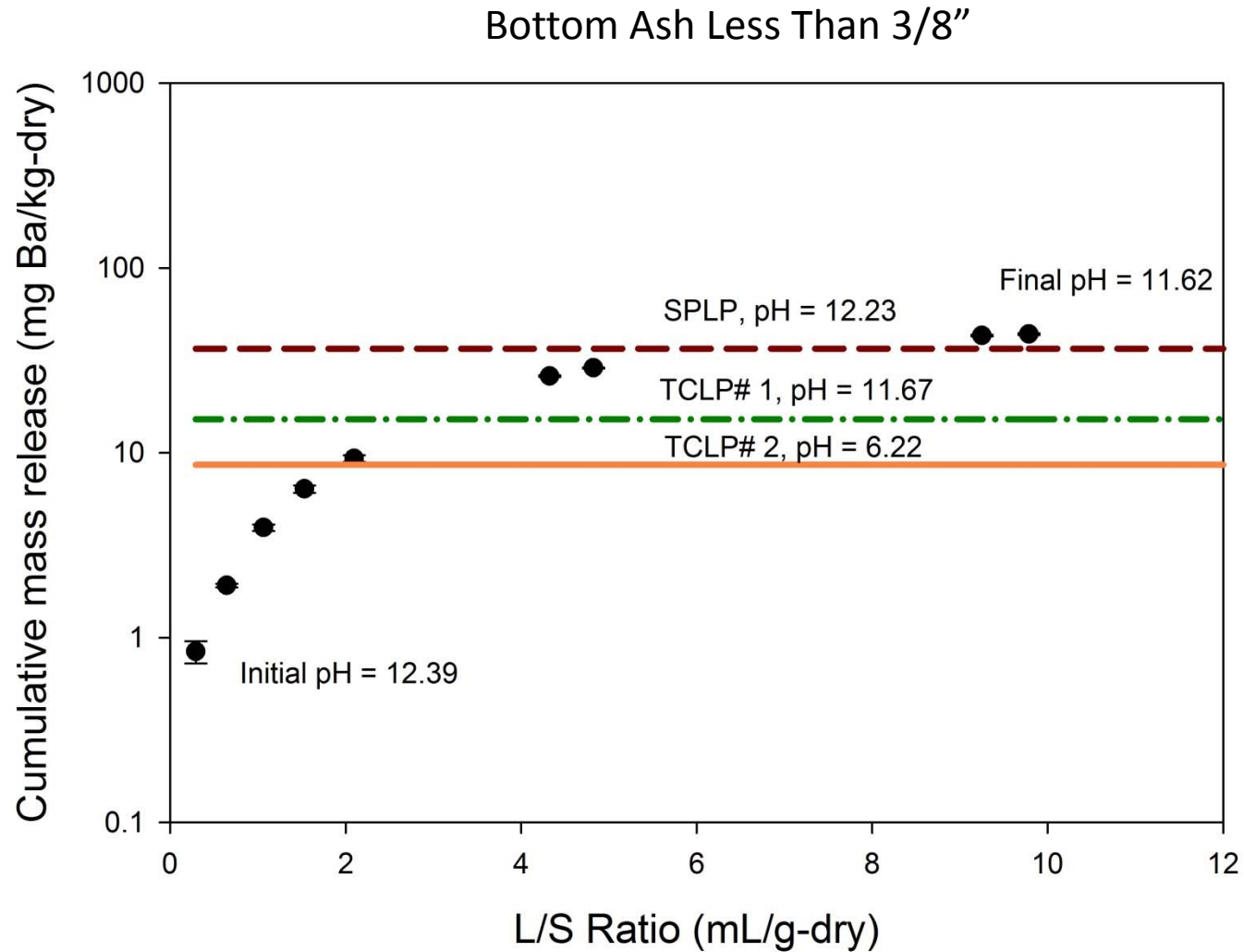
# An Example Result : Column Test (Bottom Ash Less Than 3/8")



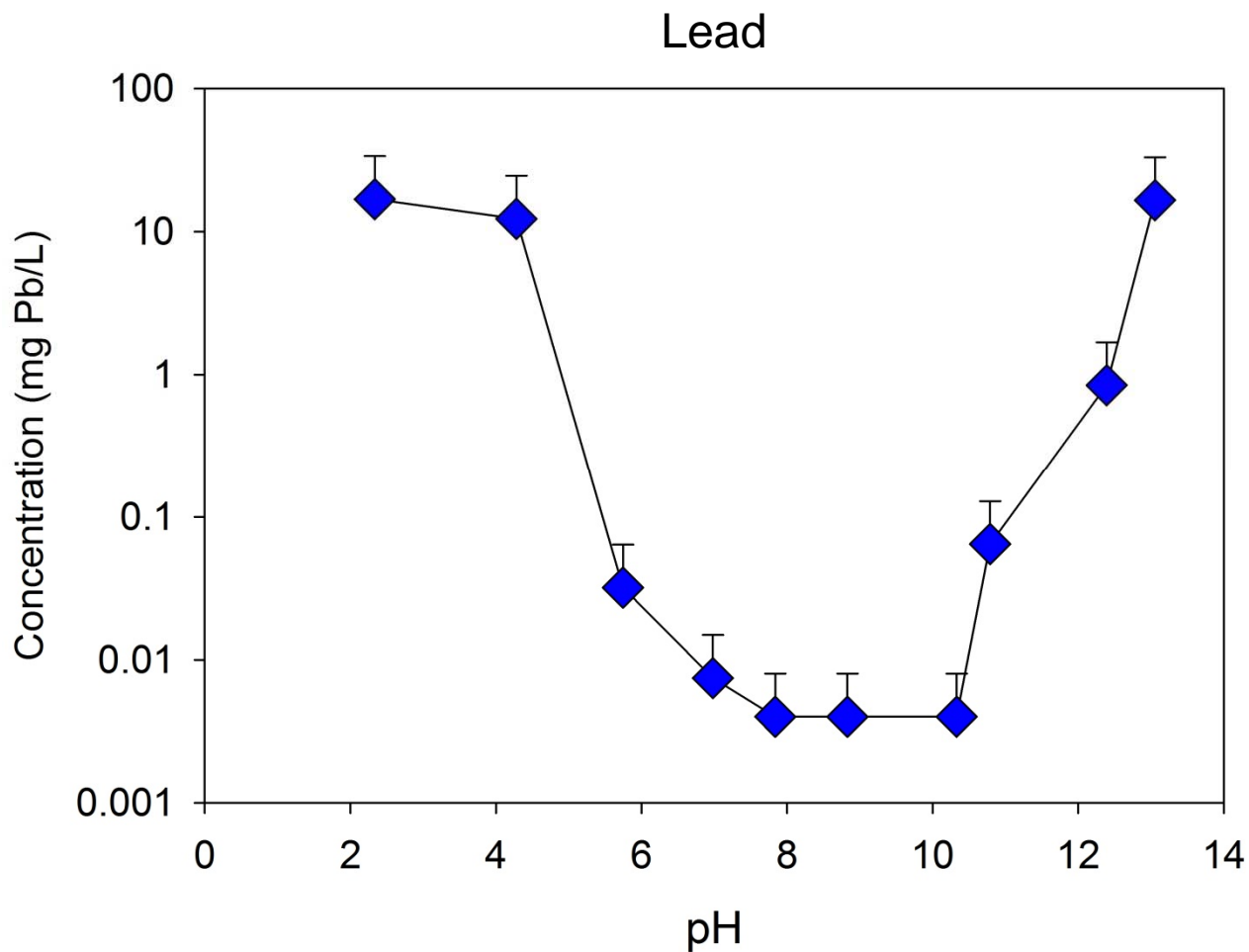
# Concentrations Normalized to mg/kg



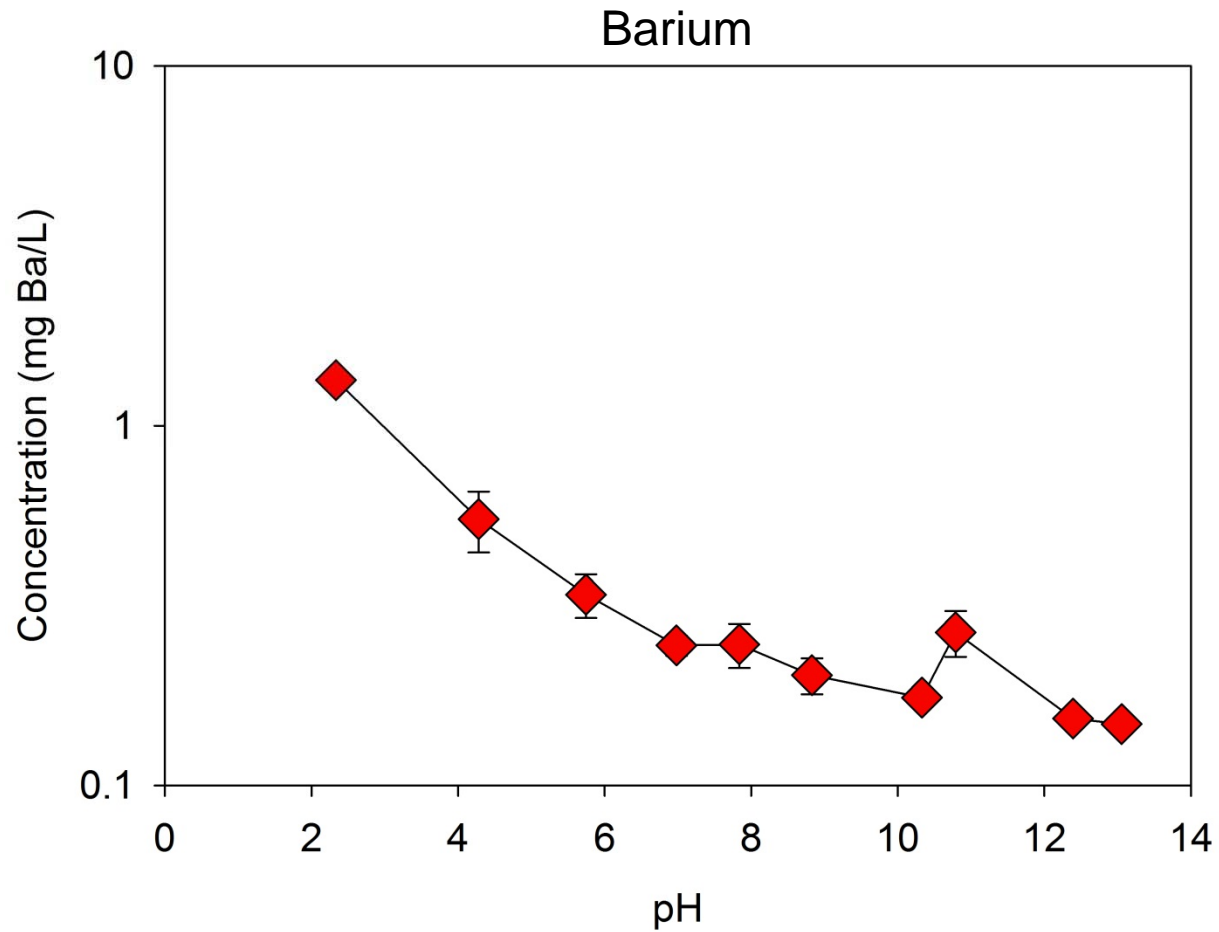
# Comparing Leaching Tests



# EPA Method 1313 Bottom Ash Less Than 3/8"



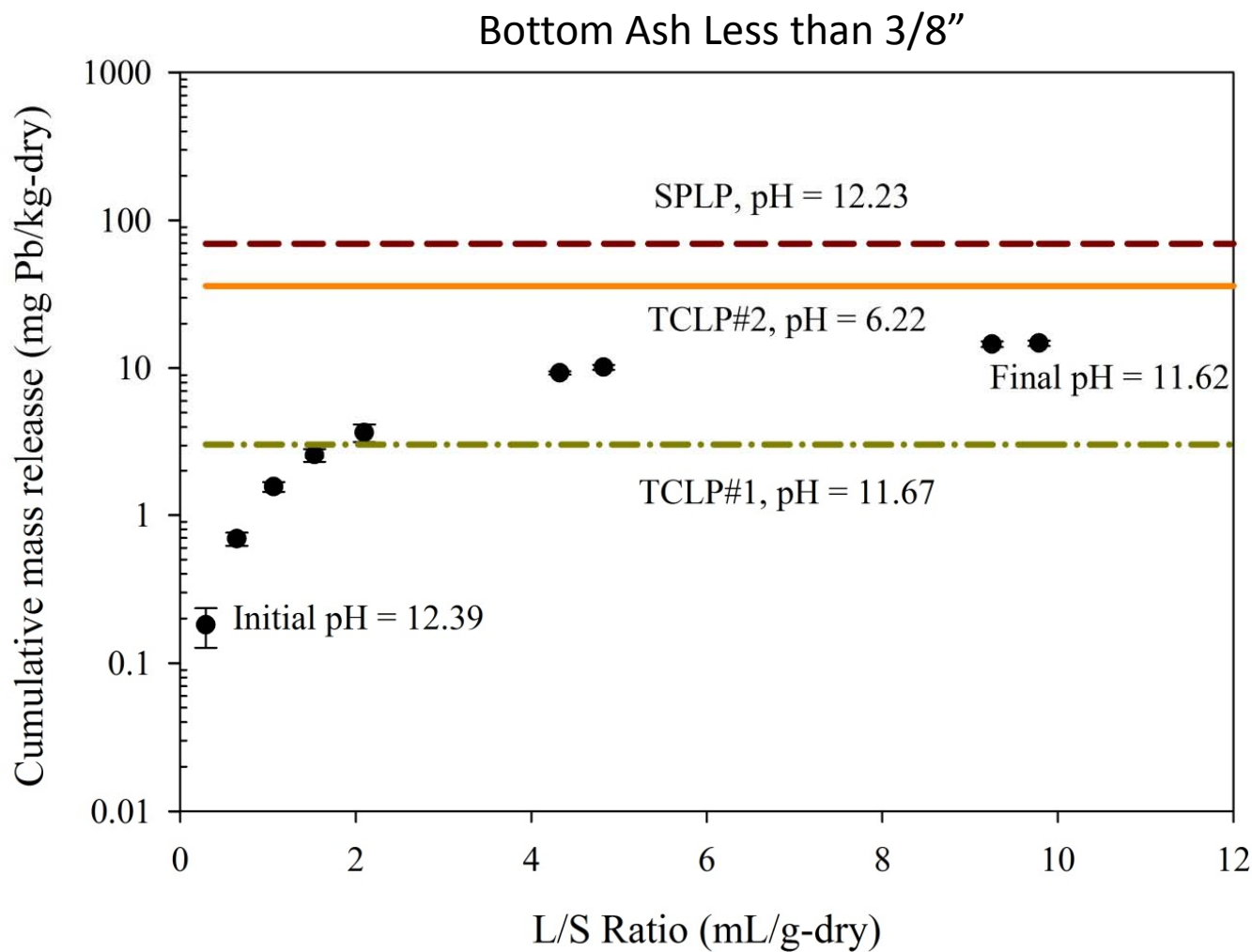
# EPA Method 1313 Bottom Ash Less Than 3/8"



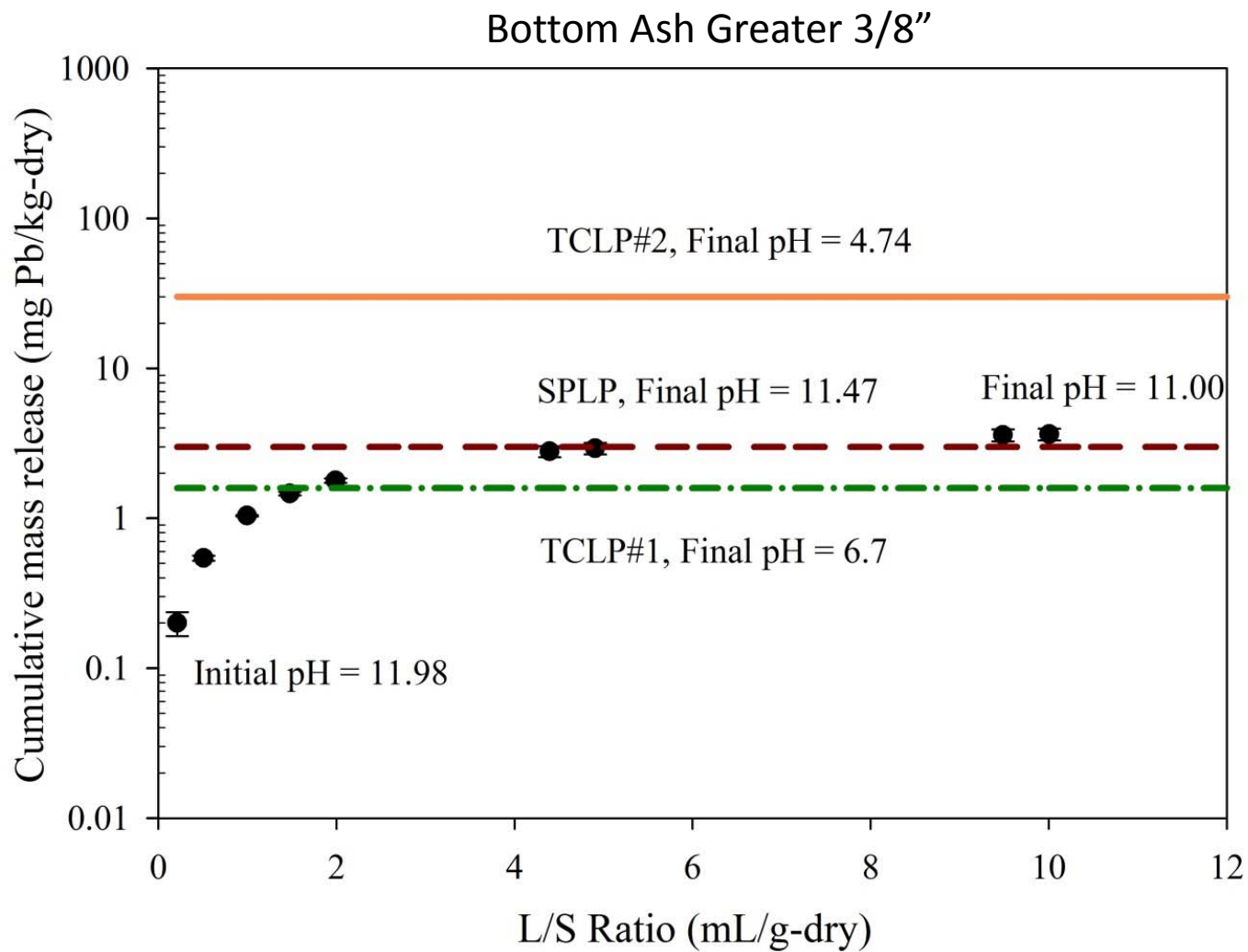
Does the Particle Size Effect Trace  
Metal Leachability?



# Comparing Particle Size



# Comparing Particle Size



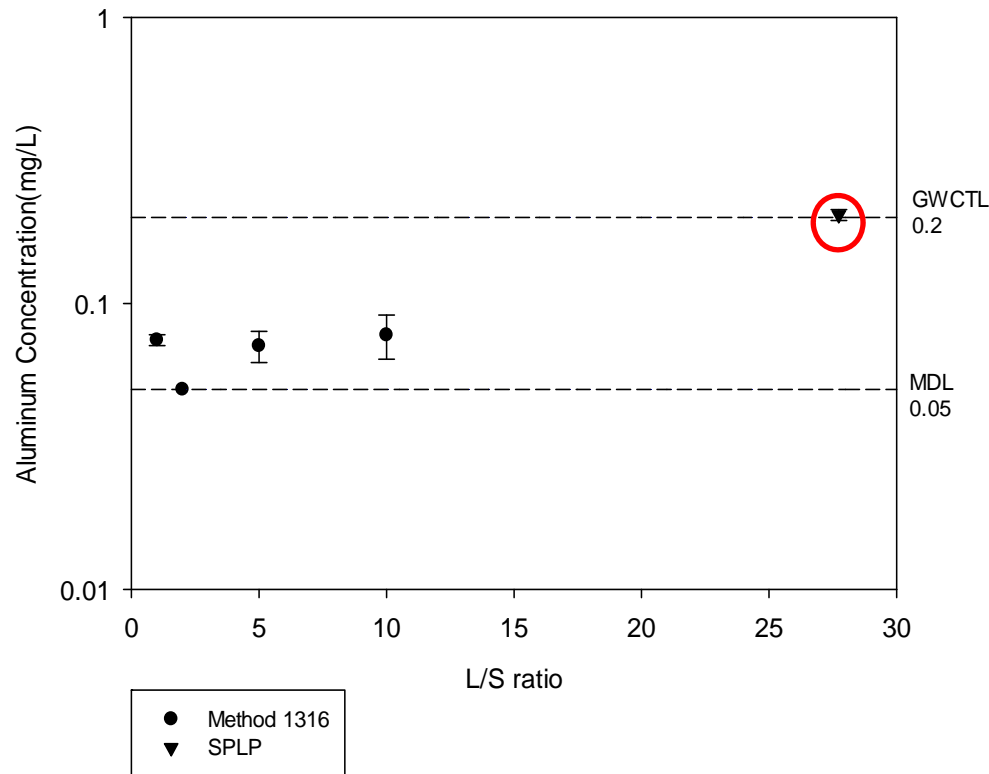
# Particle Size

- Batch test can't account for all variables that affect leaching
- Many factors control leaching:
  - pH is a major factor
  - Specific element solubility
  - Particle size

# Assessing the Differences Between the SPLP and LEAF Batch Leaching Methods

# How Does SPLP Compare to LEAF?

- Correlation between laboratory leaching tests and beneficial use conditions



Aluminum release as a function of L/S  
SPLP result is added for comparison

# Differences Between SPLP and LEAF

Parameters	SPLP	LEAF (1313, 1316)
<b>Solution</b>	SPLP Solution (pH=4.2)	Reagent Water
<b>Time</b>	18 hours	Particle Size Dependent (Up to 72 hours)
<b>L/S</b>	2000 mL-eluent/100 g-wet	10.0 ml-eluent/g-dry material
<b>Particle Size</b>	pass 3/8" sieve	Various
<b>Filter</b>	0.7 $\mu\text{m}$ glass fiber	0.45 $\mu\text{m}$ polypropylene

Particle Size (85% less than) (mm)	US Sieve Size	Minimum Dry Mass (g-dry)	Contact Time (h)	Recommended Vessel size (mL)
0.3	50	20 $\pm$ 0.05	24 $\pm$ 2	250
2.0	10	40 $\pm$ 0.1	48 $\pm$ 2	500
5.0	4	80 $\pm$ 0.1	72 $\pm$ 2	1000

Table 1. Extraction Parameters as Function of Maximum Particle Size (LEAF)

# Synthetic Precipitation Leaching Procedure (SPLP)

- A key leaching test in risk assessment for the beneficial use of solid waste materials
- Historically important in the field of solid waste management
- Simulates waste material exposure to slightly acidic rainfall conditions
- Results often compared to the GWCTL for decision making

# LEAF Methods

- Provides a more robust dataset
- Wider range of pH and site-specific conditions

However....

- Lack of guidance on how to properly interpret the data
- Inappropriate use of the large volume of data is possible
- Increased range of pH may not be representative of actual site conditions
- May contradict SPLP data
- Inconsistency



# Materials

ID	Sample	Particle Size Reduction
1	Coal Fly Ash	N/A
2	WTE Bottom Ash	3/8" and #4 Sieve
3	Electronic Waste	3/8" and #4 Sieve
4	Mine Tailings	N/A



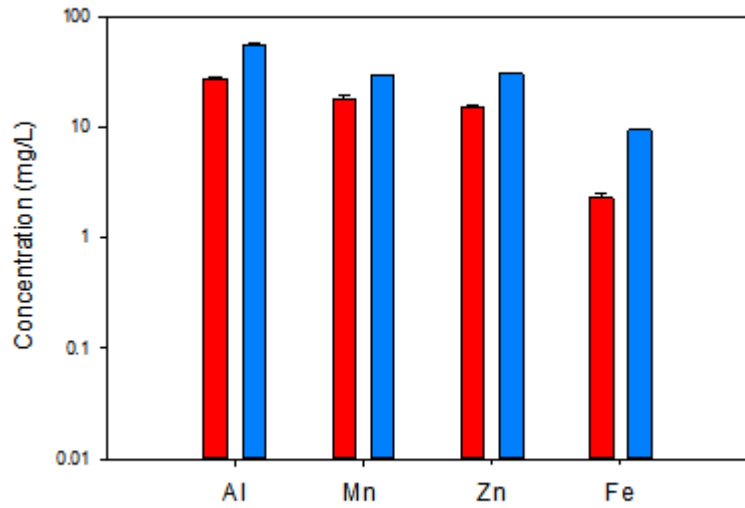
# Methodology

	Evaluation of Each Factor				
Parameter	Solution	Time	L/S	Particle Size	Filter
Solution	S, s	S	S	S	S
Time	T	T, t	T	T	T
L/S	L	L	L, l	L	L
Particle Size	Z	Z	Z	Z, z	Z
Filter	F	F	F	F	F, f

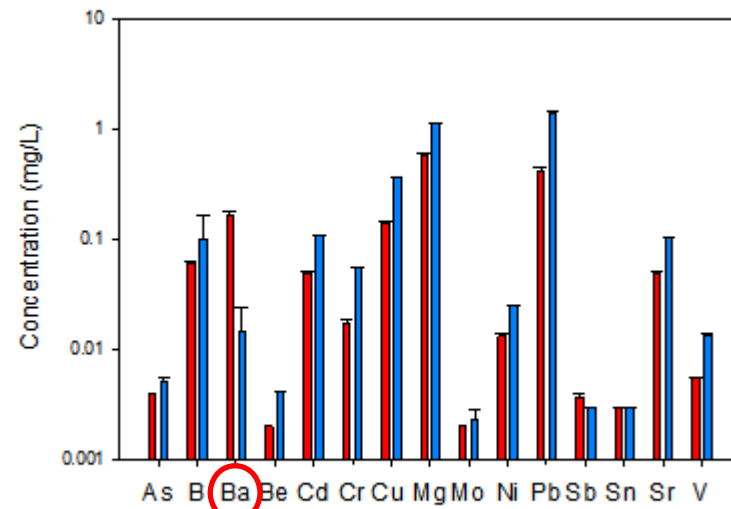
S=Reagent Water    s=SPLP solution    T=72 hrs    t=18hrs    L=10.0 ml-eluent/g-dry material  
 l=2000 mL-eluent/100 g-wet material    Z=#4 sieve    z=3/8" sieve  
 F=0.45  $\mu$ m    f=0.7 $\mu$ m

# LEAF and SPLP Conducted by the Book

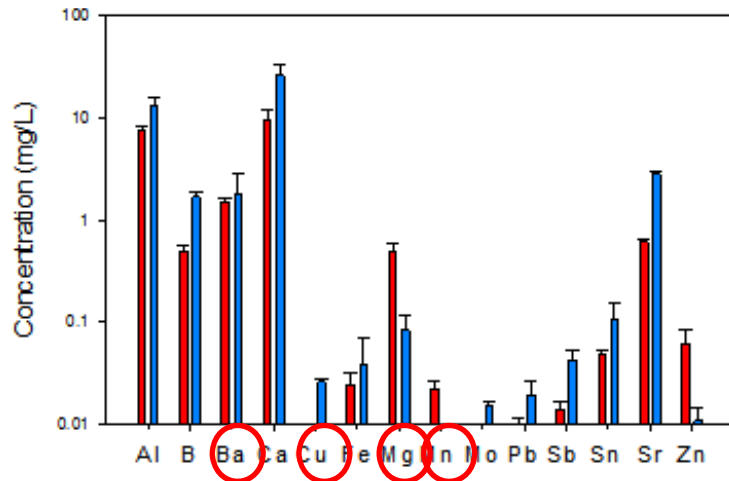
Mine Tailings



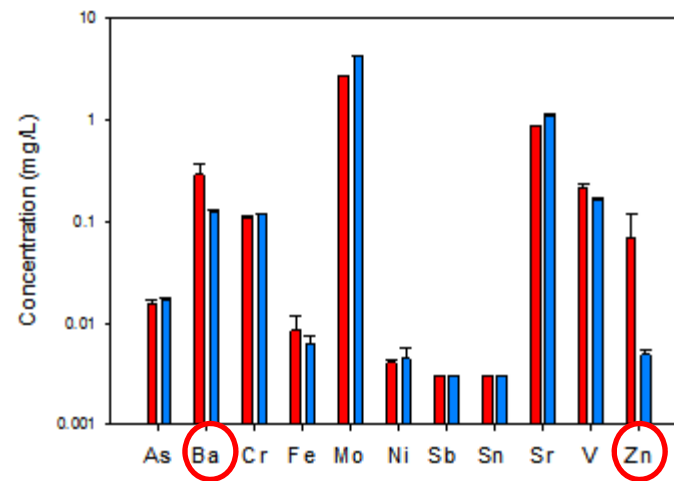
Mine Tailings



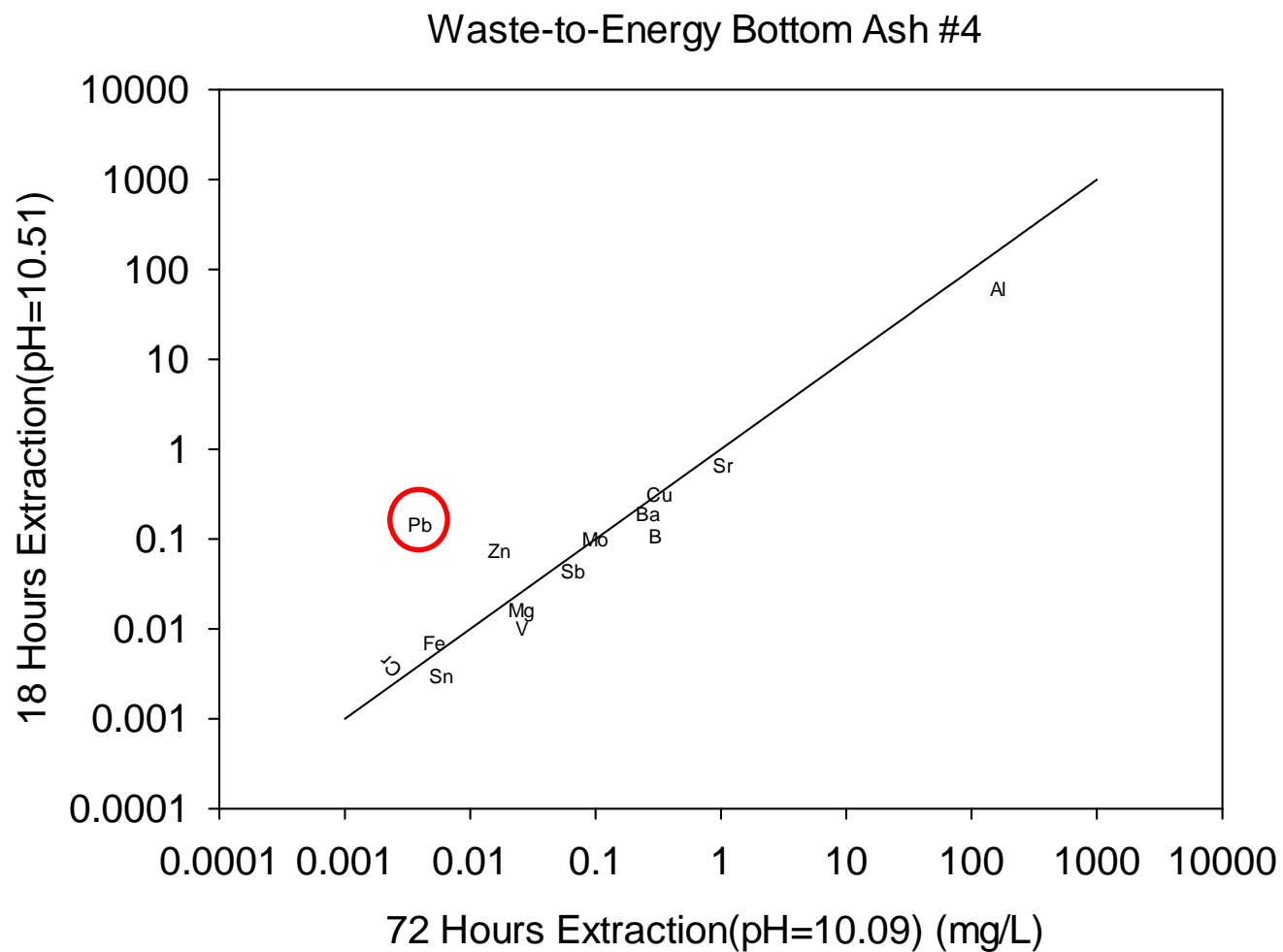
Electronic Wastes #4



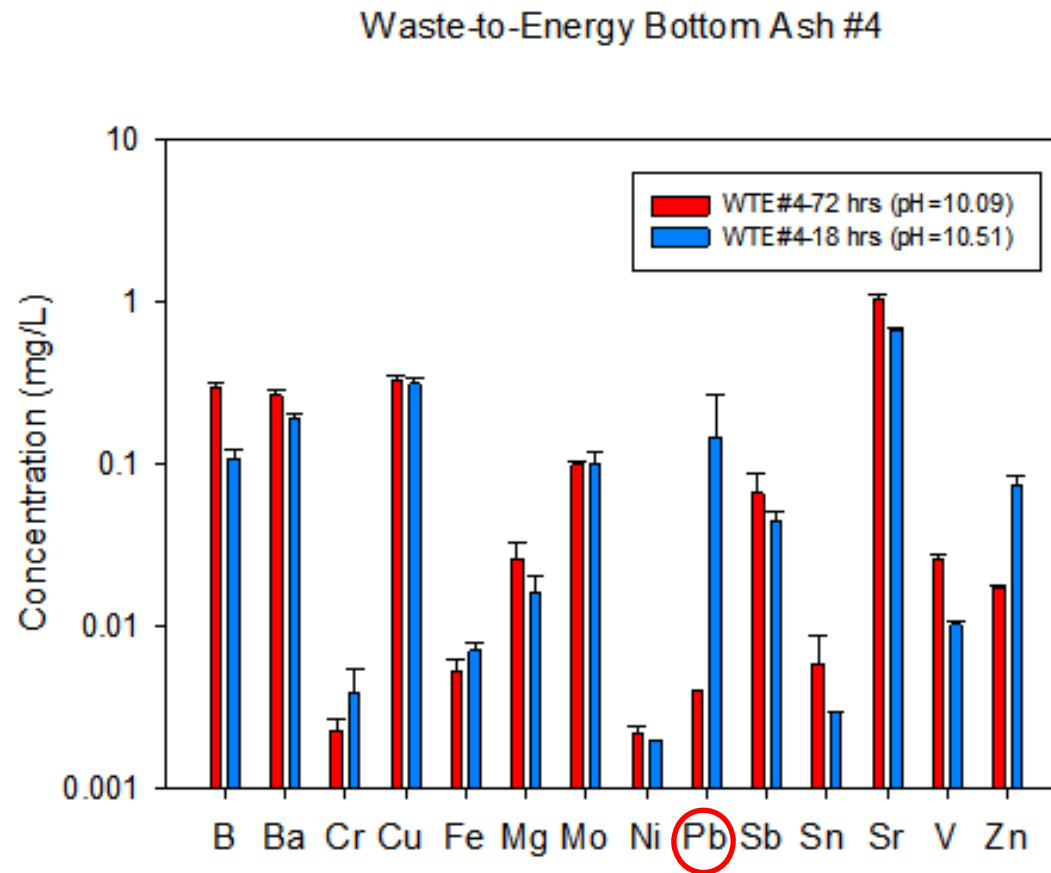
Coal Fly Ash



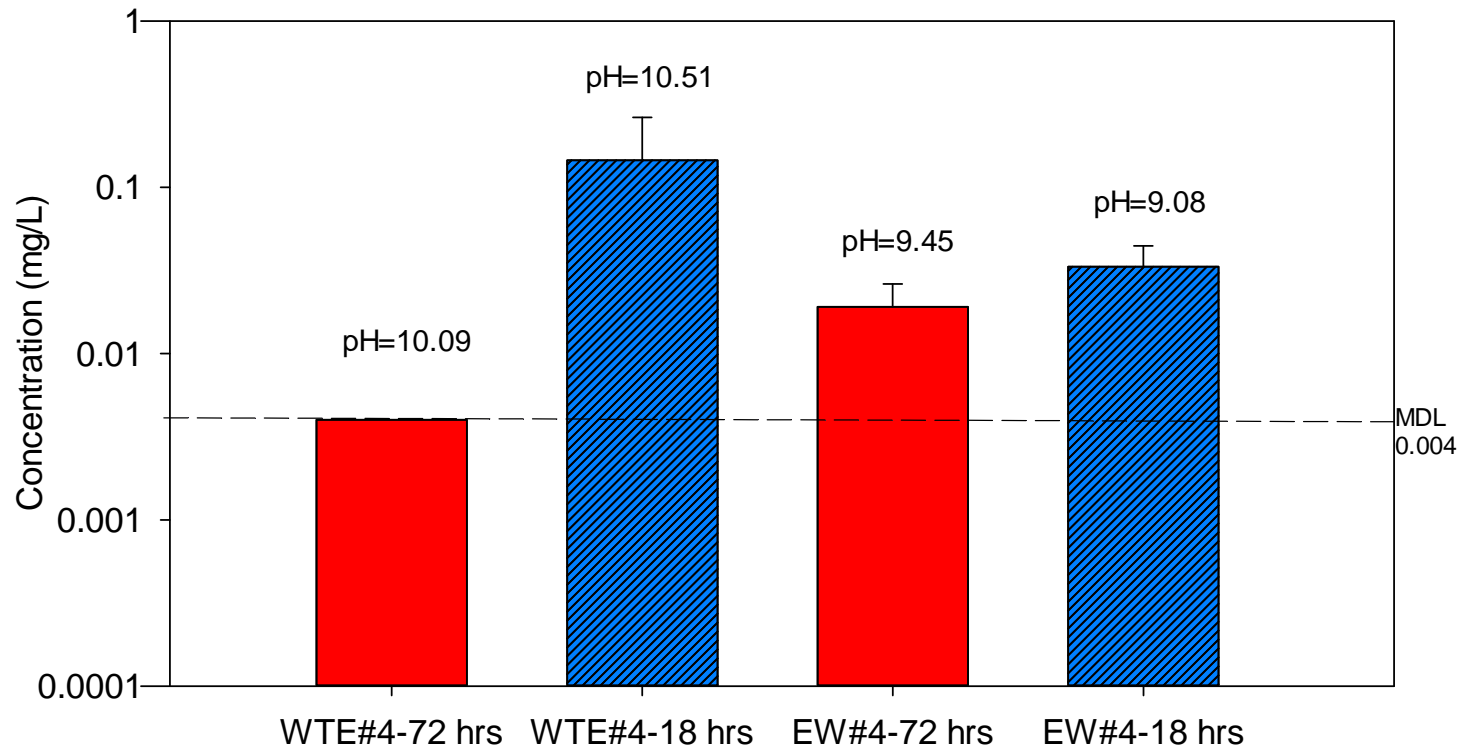
# Influence of Extraction Time



# Influence of Extraction Time

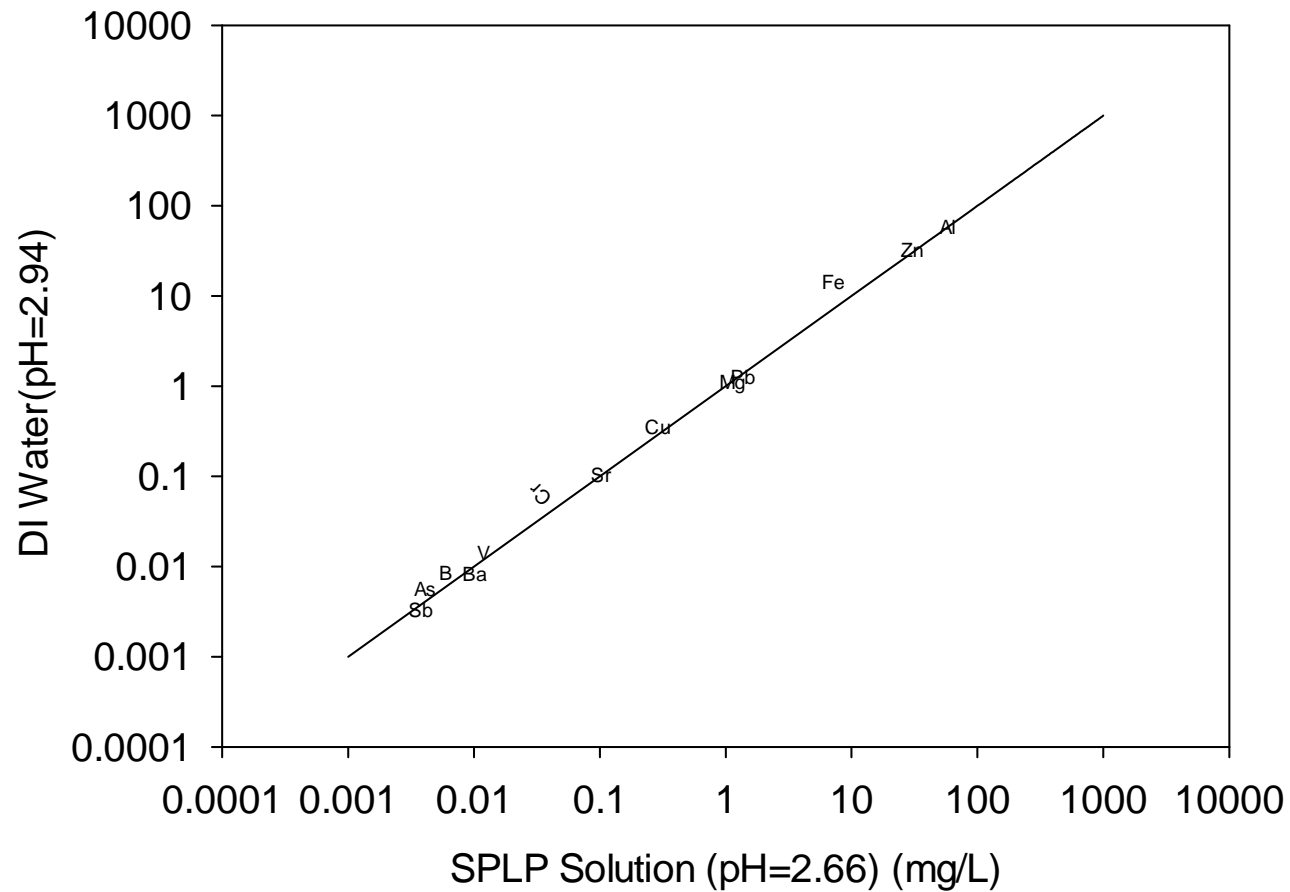


# Extraction Time-Lead



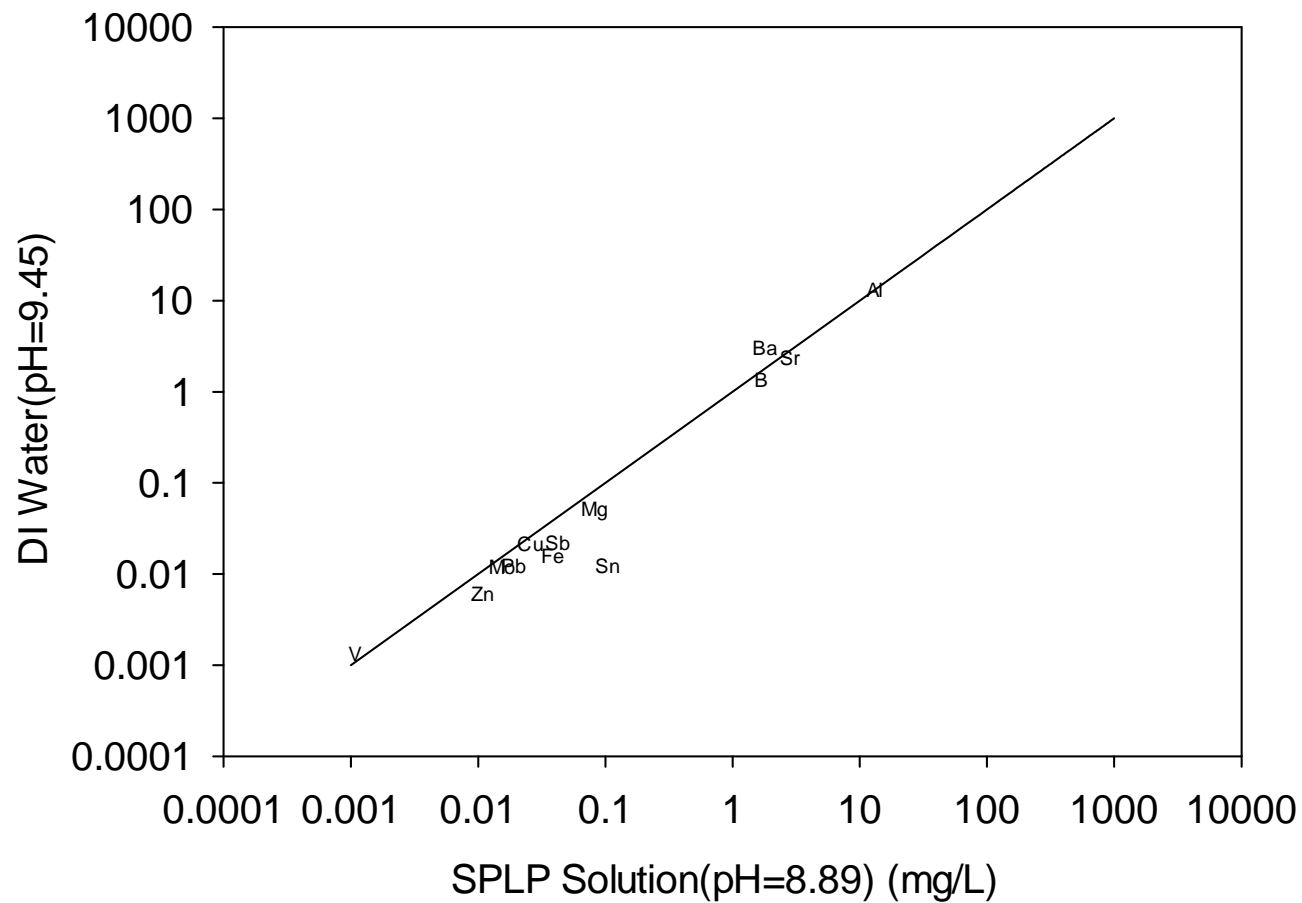
# Influence of Extraction Solution

Mine Tailings



# Influence of Extraction Solution

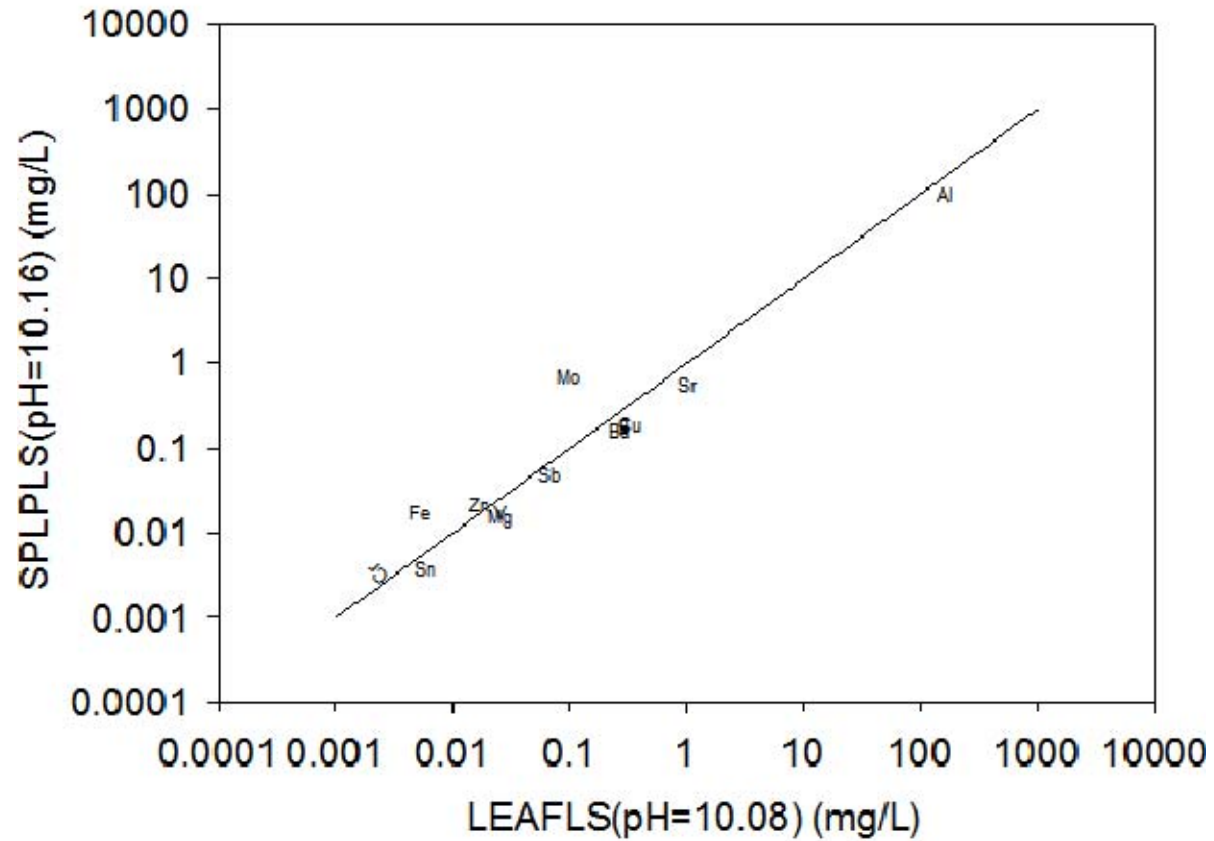
Electronic Wastes #4





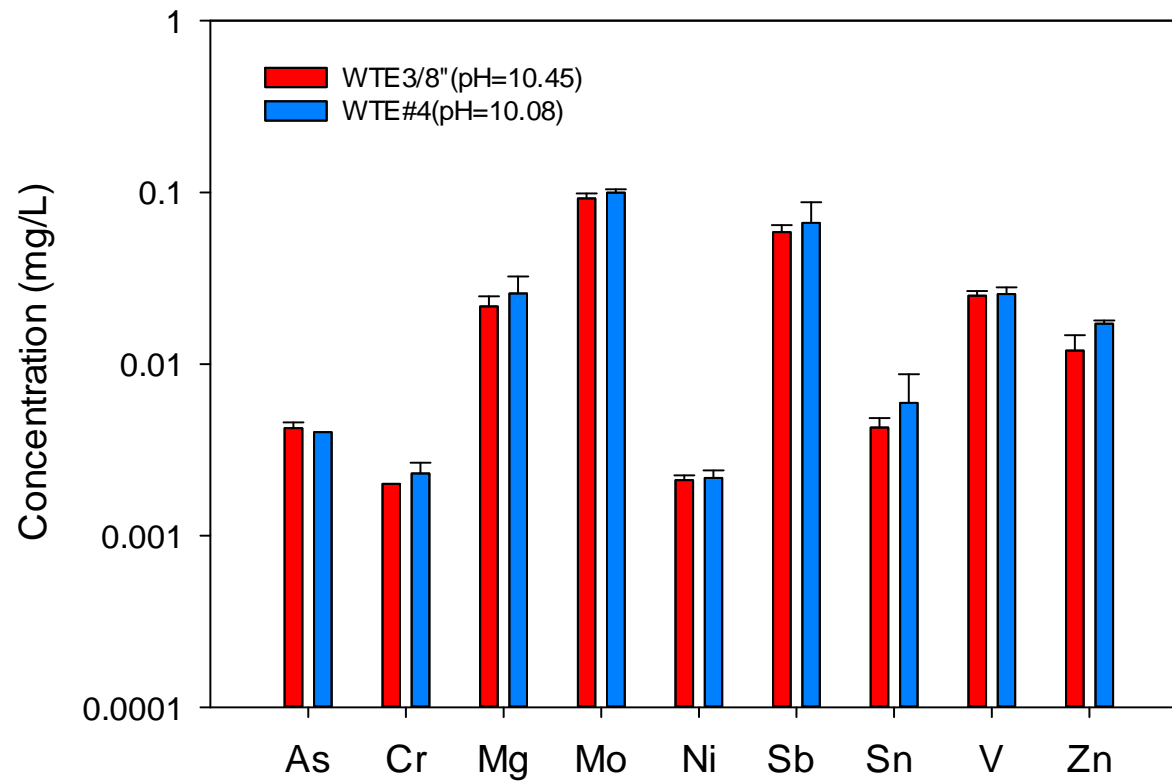
# Influence of Liquid to Solid Ratio

Waste-to-Energy Bottom Ash #4



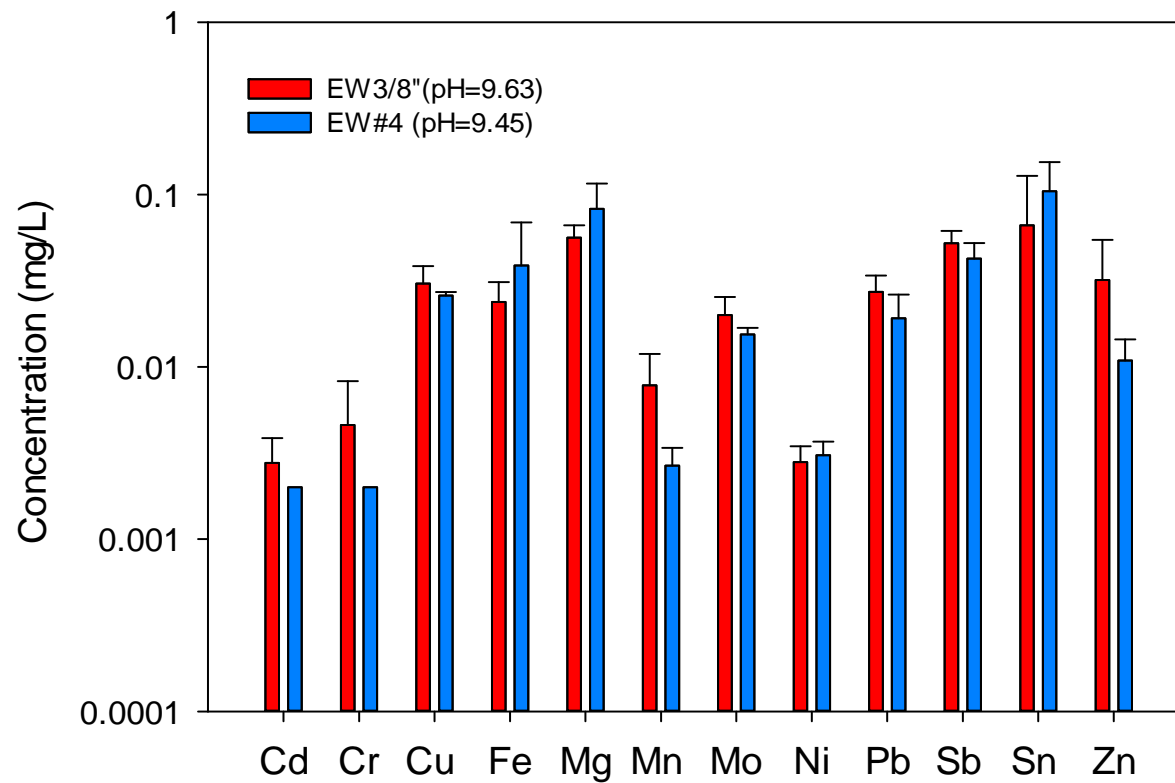
# Influence of Particle Size

Waste-to-Energy Bottom Ash



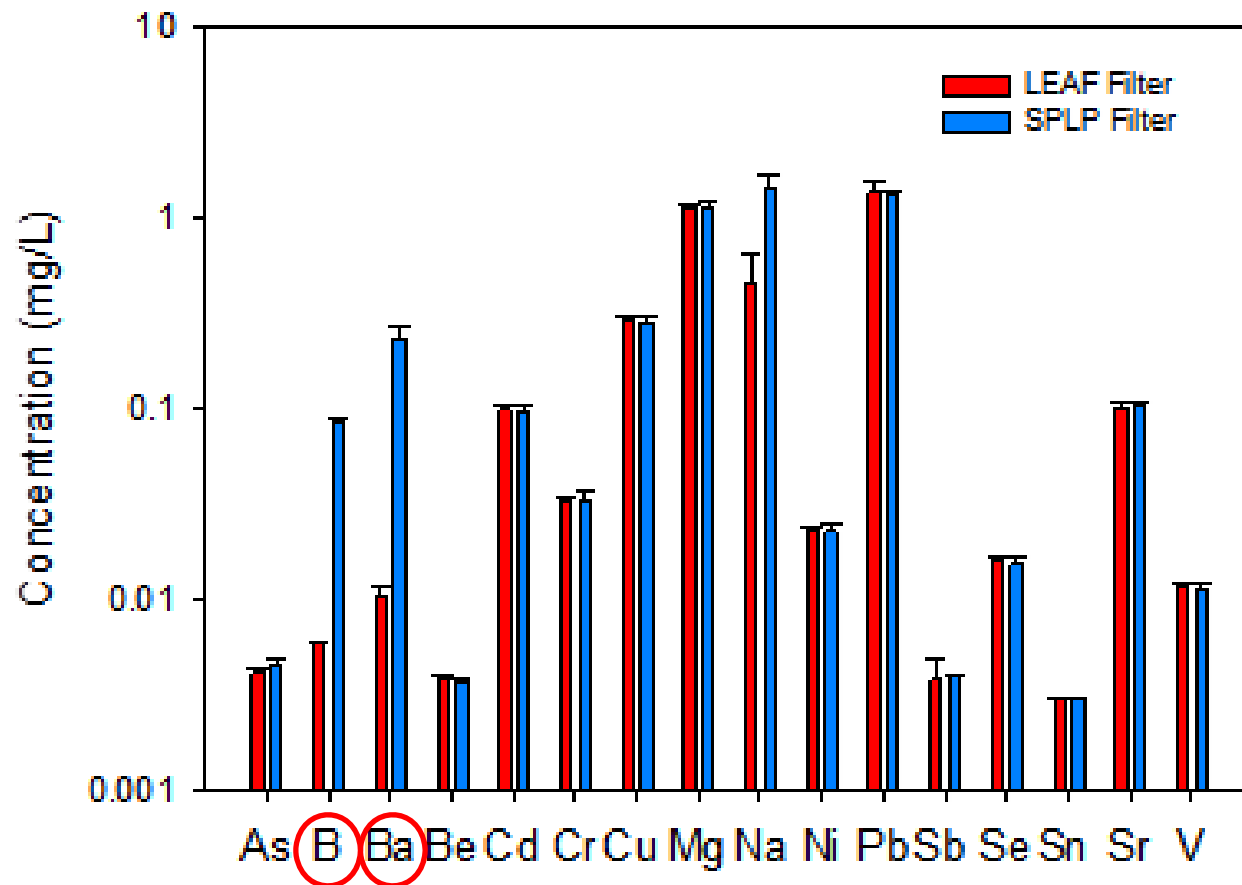
# Influence of Particle Size

Electronic Wastes



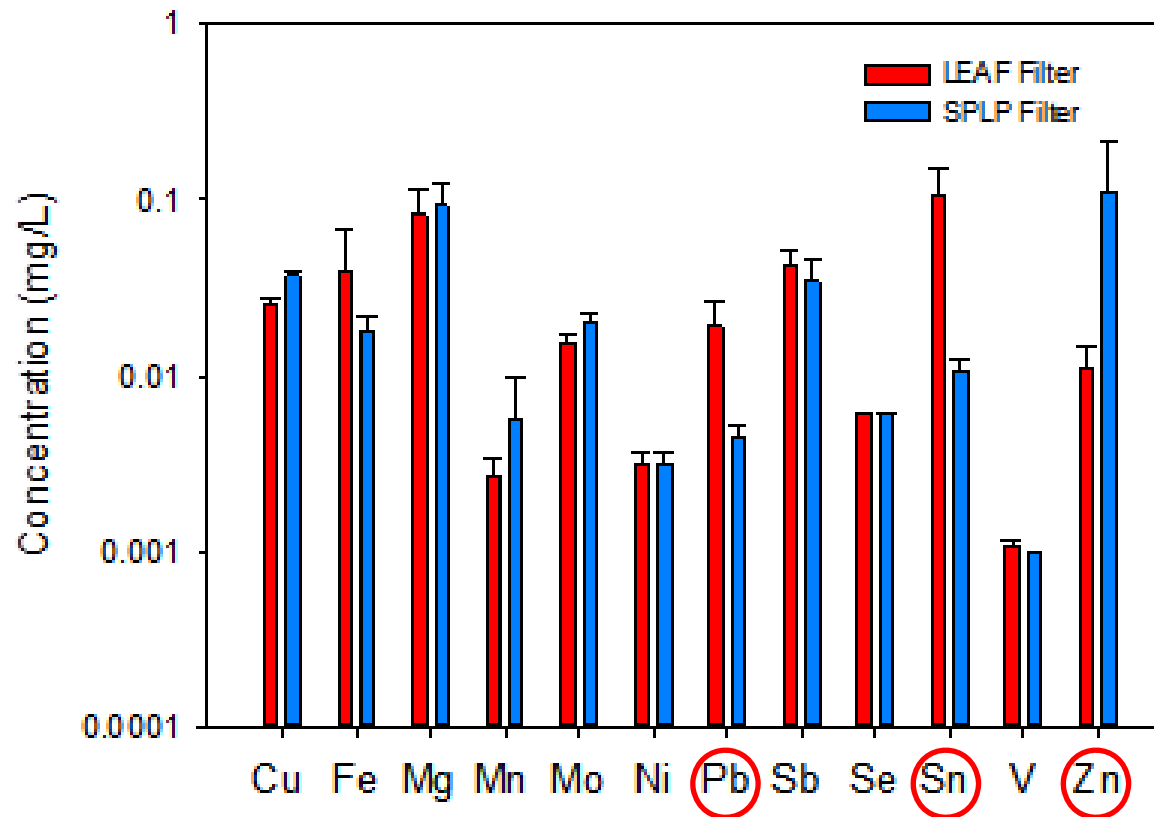
# Influence of Filter

Mine Tailings



# Influence of Filter

Electronic Wastes #4



# Feedback from TAG

- What information would you like to see?
- What is the best way to present the information so that the Florida solid waste community can readily access and utilize?

<http://pages.ees.ufl.edu/townsend/>

<http://pages.ees.ufl.edu/townsend/research/hc14/>