

# Mobility of Hg, Ni, As, Se, Cd, Pb from Coal Utilization By-Products

Carl E. Hensman, Ph.D.  
Frontier GeoSciences Inc.  
414 Pontius Avenue North  
Seattle WA 98109  
206-957-1427  
[CarlH@frontiergeosciences.com](mailto:CarlH@frontiergeosciences.com)

Project Manager - Lynn Brickett  
U.S. DOE National Energy Technology Laboratory  
P.O. Box 10940  
626 Cochrans Mill Road  
Pittsburgh PA 15236



# U.S. DOE Focus

- The CUBs being initially tested are generated from mercury control projects awarded in 2003 and 2004 by NETL.
  - ongoing analysis through 2007
- Some of the technologies may deposit additional quantities of mercury onto the CUBs.
- The goal of this effort will be to determine the ultimate fate of mercury in the byproduct streams.
- In doing so, this effort will support NETL's Innovation for Existing Plants Program goals.
  - Maintaining current utilization practices of coal utilization byproducts and increasing utilization to 50% by 2010.
- Also monitoring Ni, As, Se, Cd, Pb.
  - affects some of the experimental design

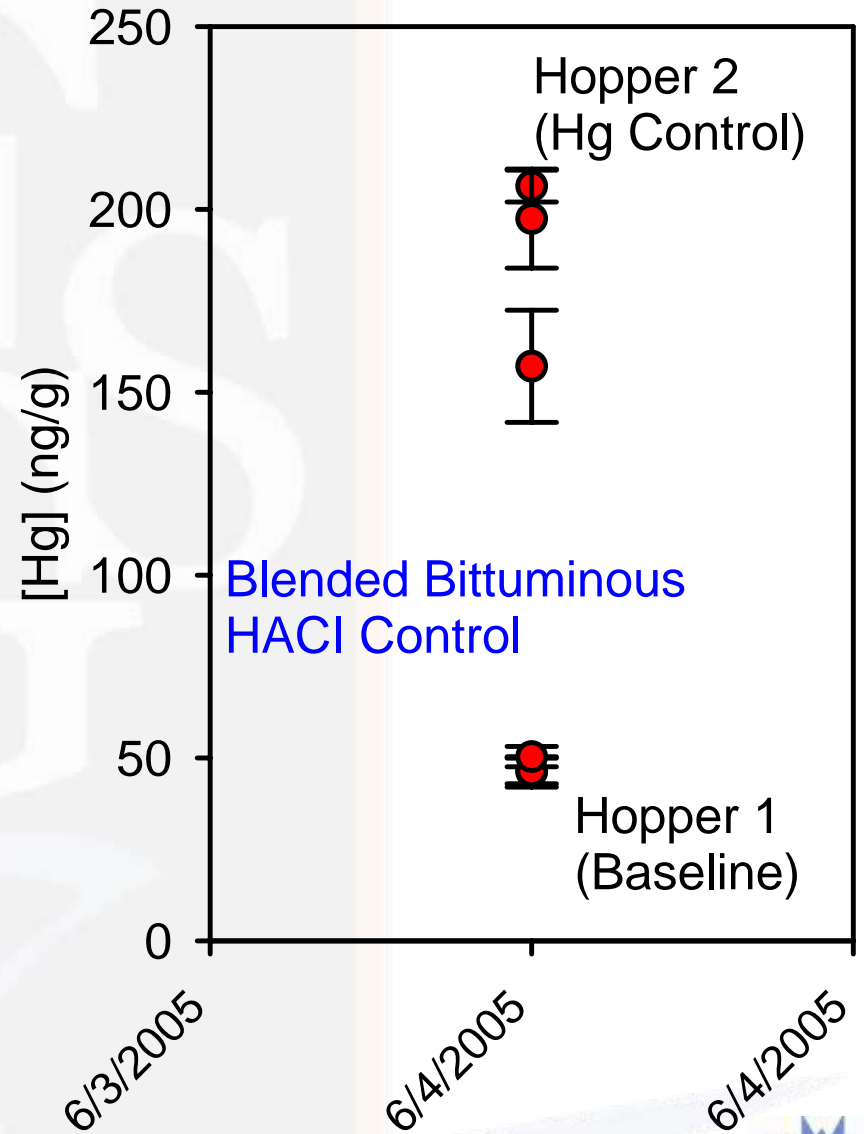
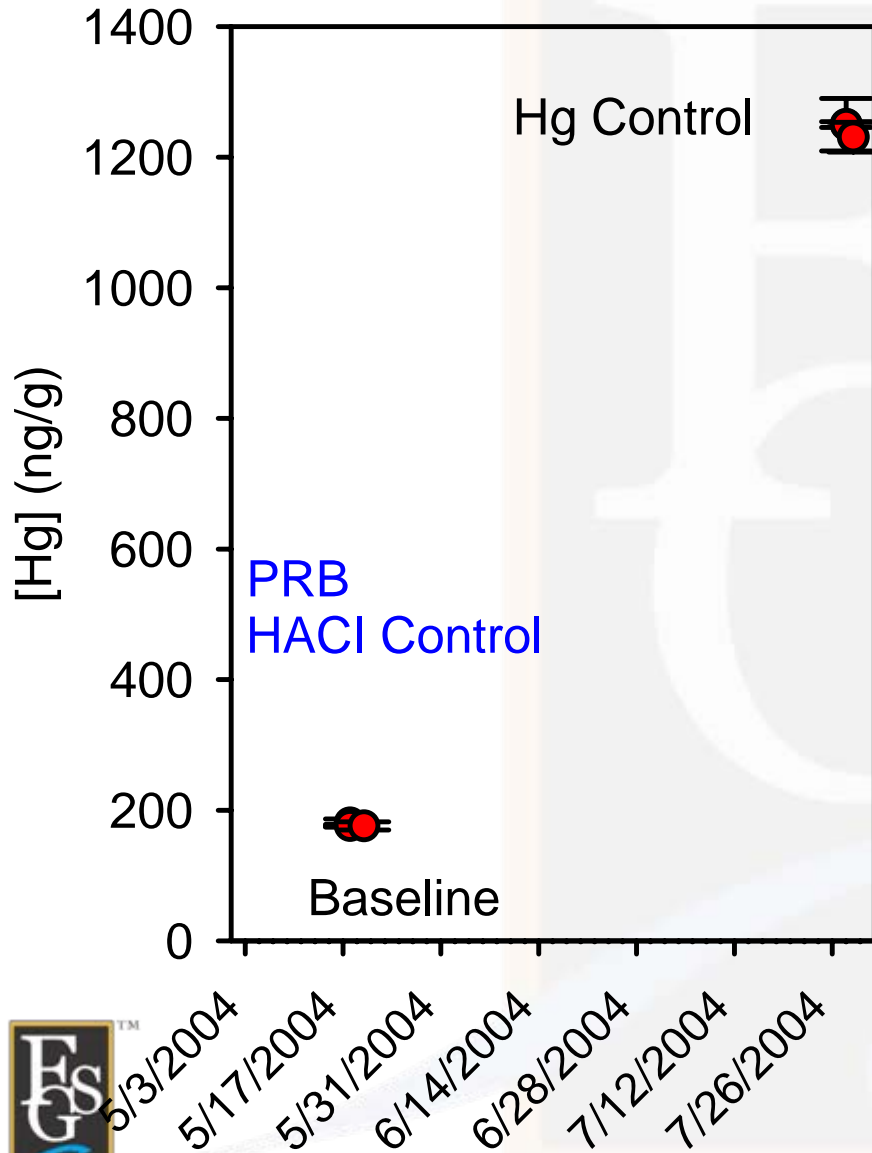


# CUBs Study Areas

- Total Hg, Ni, As, Se, Cd, Pb analysis
- Leaching of Hg, Ni, As, Se, Cd, Pb
- Thermal release of Hg, Ni, As, Se, Cd, Pb
- Microbial mobility of Hg, Ni, As, Se, Cd, Pb
- Halides



# Sampling Schemes (n=3)



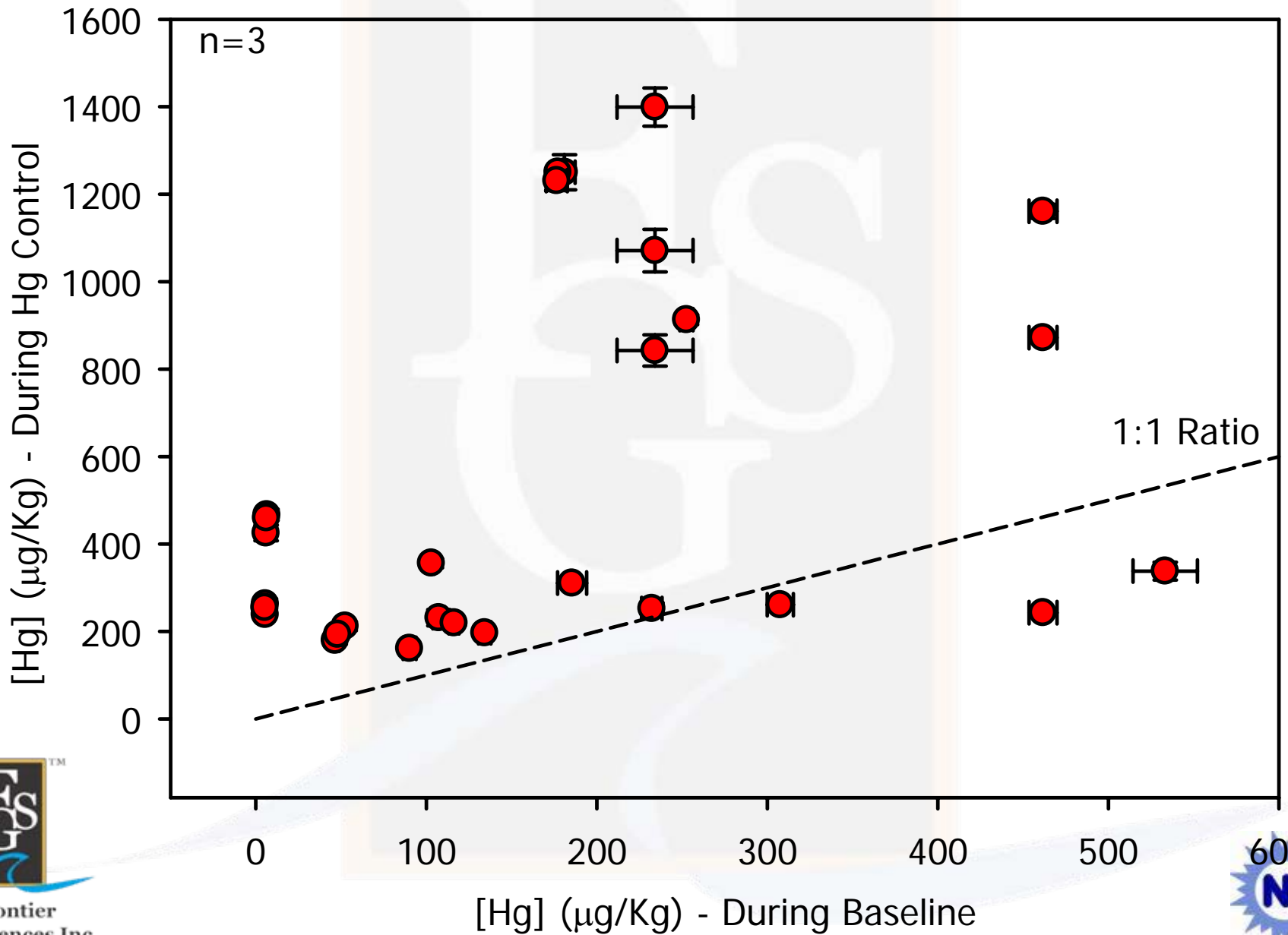
# CUBs – Total Concentrations

(Hg, Ni, As, Se, Cd, Pb)

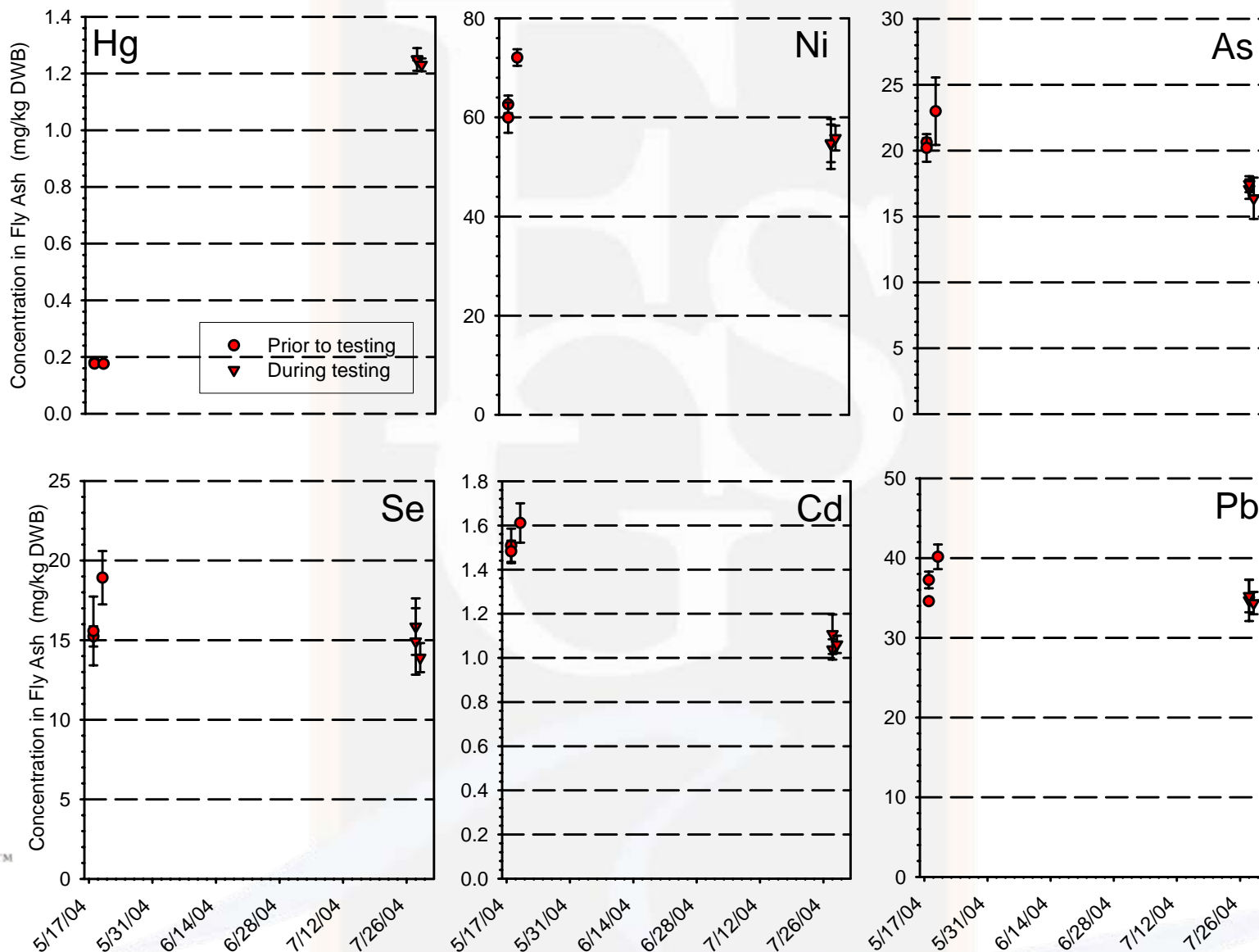
- HNO<sub>3</sub>/HCl/HF bomb digest with evaporative reflux with HNO<sub>3</sub> for removal of insoluble fluorides
- Project QA – CRMs, blind re-analysis
- Analytical QA – Standard Frontier analytical QA
  - 3 Prep blank
  - Matrix spike
  - Analytical spike
  - Matrix and analytical duplicate analysis



# Hg Totals



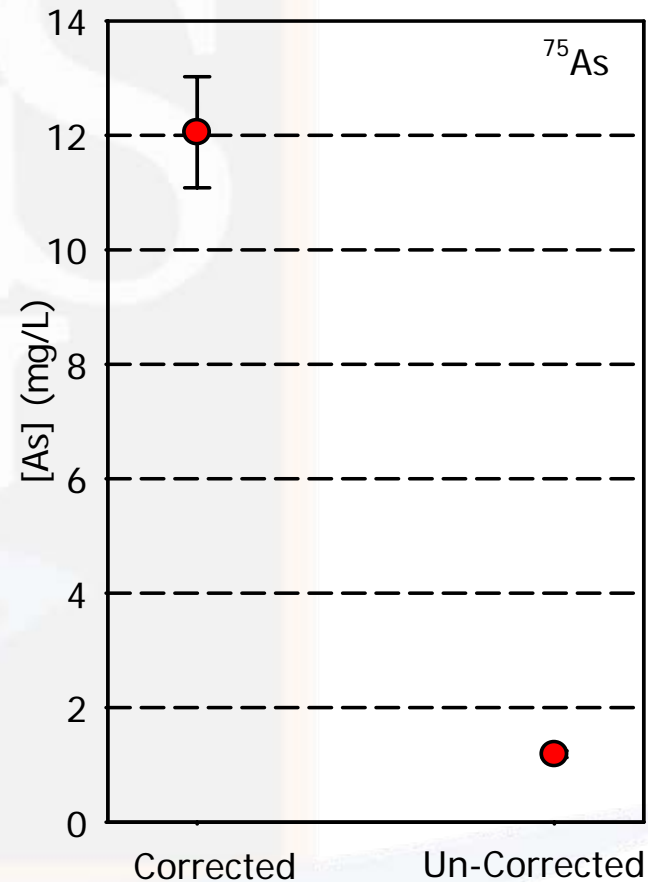
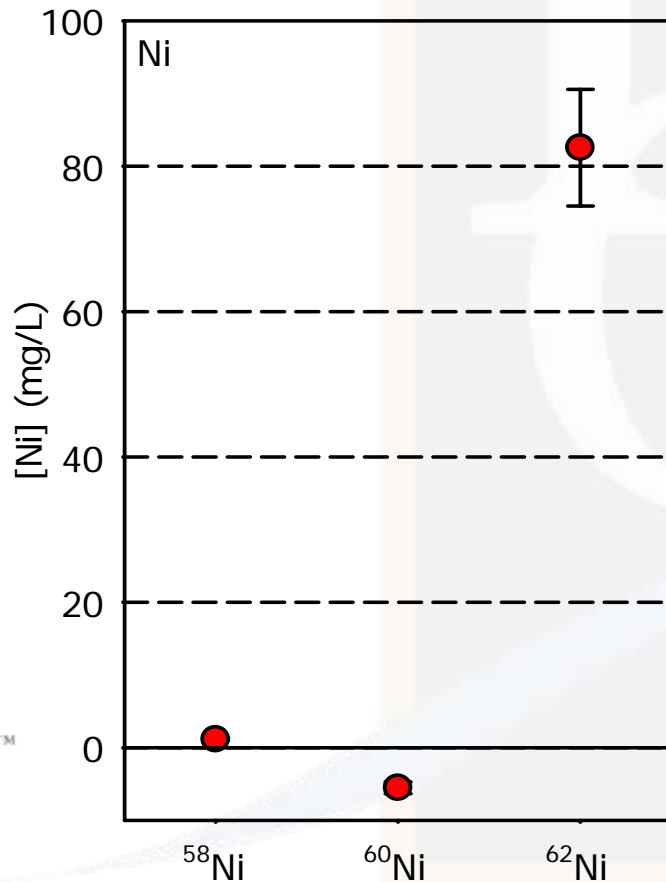
# Totals – 360 MW, HACL + Coal Additive, PRB



# Totals - Analytical Issues

- $^{60}\text{Ni}$  and  $^{62}\text{Ni}$  isotopes have molecular interferences
- $^{58}\text{Ni}_r = ^{58}\text{Ni}_m - (0.003052 * ^{56}\text{Fe}_m)$
- $^{56}\text{Fe}_m$  requires DRC-ICP/MS

- $^{75}\text{As}_r = ^{75}\text{As} - 3.127 * (^{77}\text{Se} - (0.873 * ^{82}\text{Se}))$
- $^{82}\text{Se}$  has interference from  $^{81}\text{Br}^1\text{H}$





# CUBs – SPLP Leaching Protocol

- Synthetic Precipitation Leaching Procedure (SPLP)
  - promulgated EPA method 1312
  - definable results since 1986
- Method is modified to sub-sampling at T=18 hours, T=14 days and T=28 days
  - accounts for secondary mineral formation of ettringite (known to immobilize arsenic and selenium)
- Solid at 28 days is sub-sampled for mass balance



# SPLP Operational Considerations



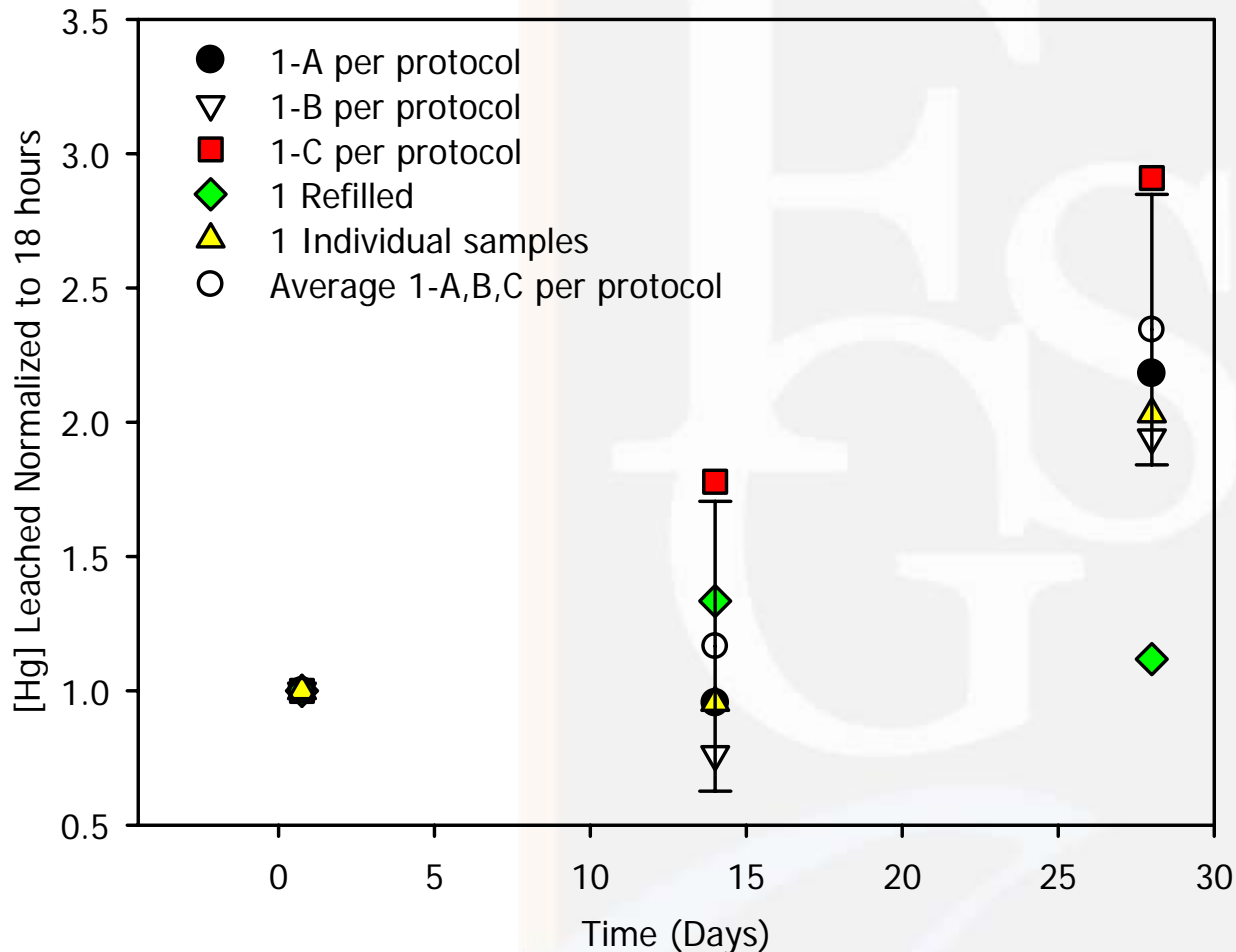
- To date 48 Samples for leaching
- In triplicate = 144 samples
- Per tumbler = 3 trips (9 samples) + 3 controls
- 2 tumblers
- ~1 month of tumbling
- ~8 months for completion

Analysis at 0.75, 14 and 28 days

If a separate bottle was used for each analysis event, completion of current samples ~2 years



# SPLP Operational Considerations



## Per protocol

60 mL removed @ 18 hours and 14 days

## Refilled

60 mL removed and replaced with fresh leachate

## Individual

Each sampling event had a separate sample bottle

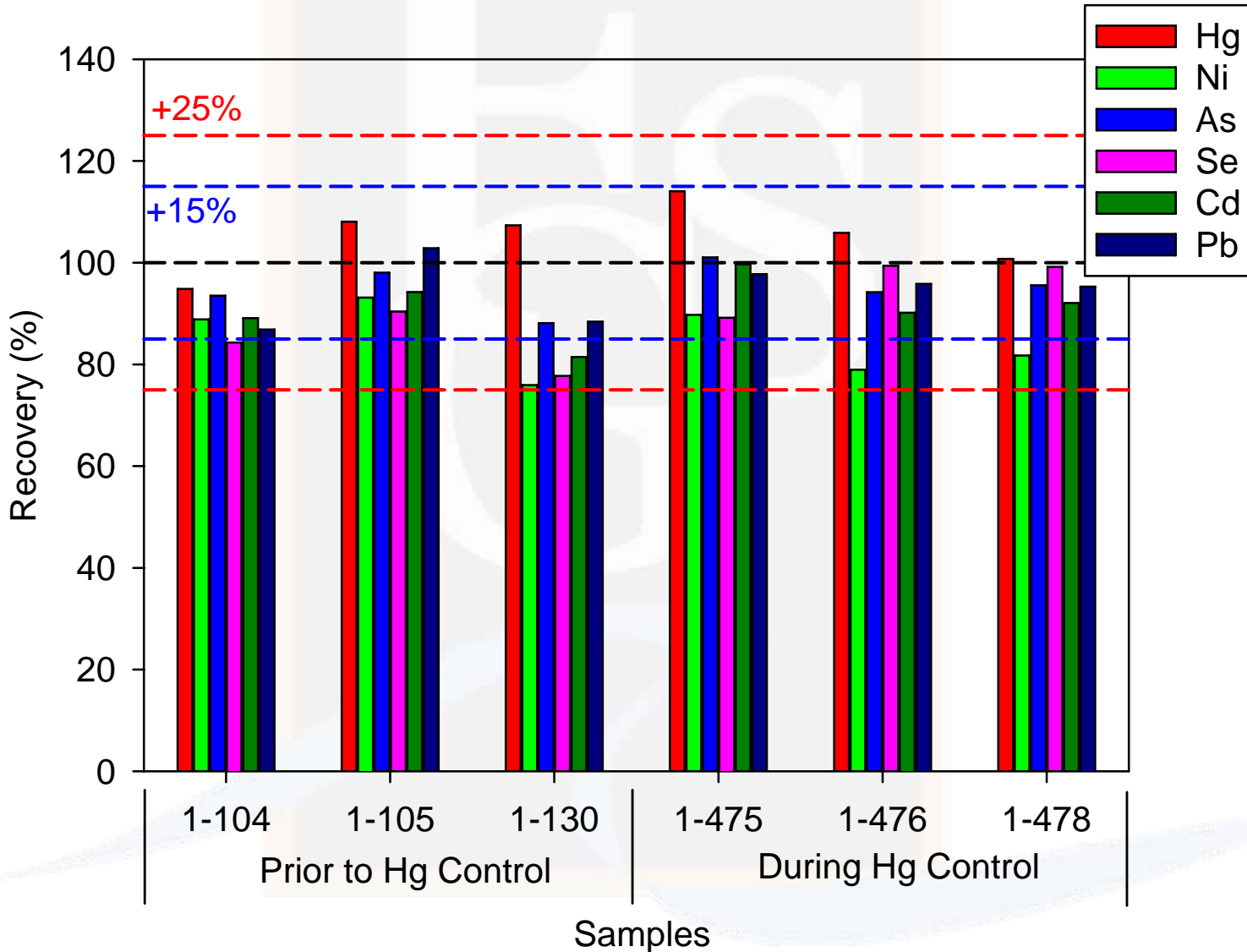
## Other notes

Amount of solid removed during sampling event was negligible

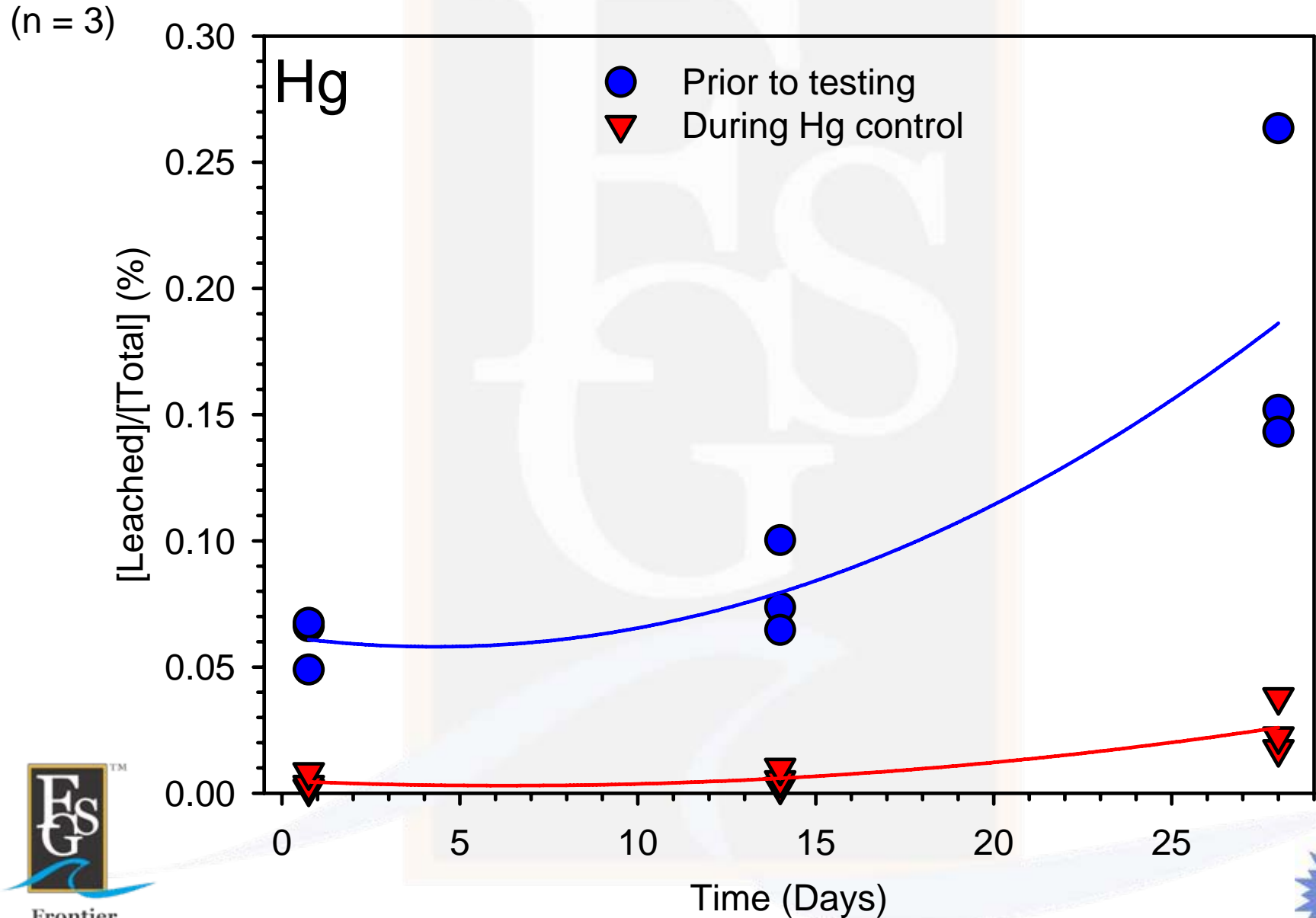


# Leaching Mass Balance

$[\text{Metal leached} + \text{Metal in leached solid}] / [\text{Total Metal}]$

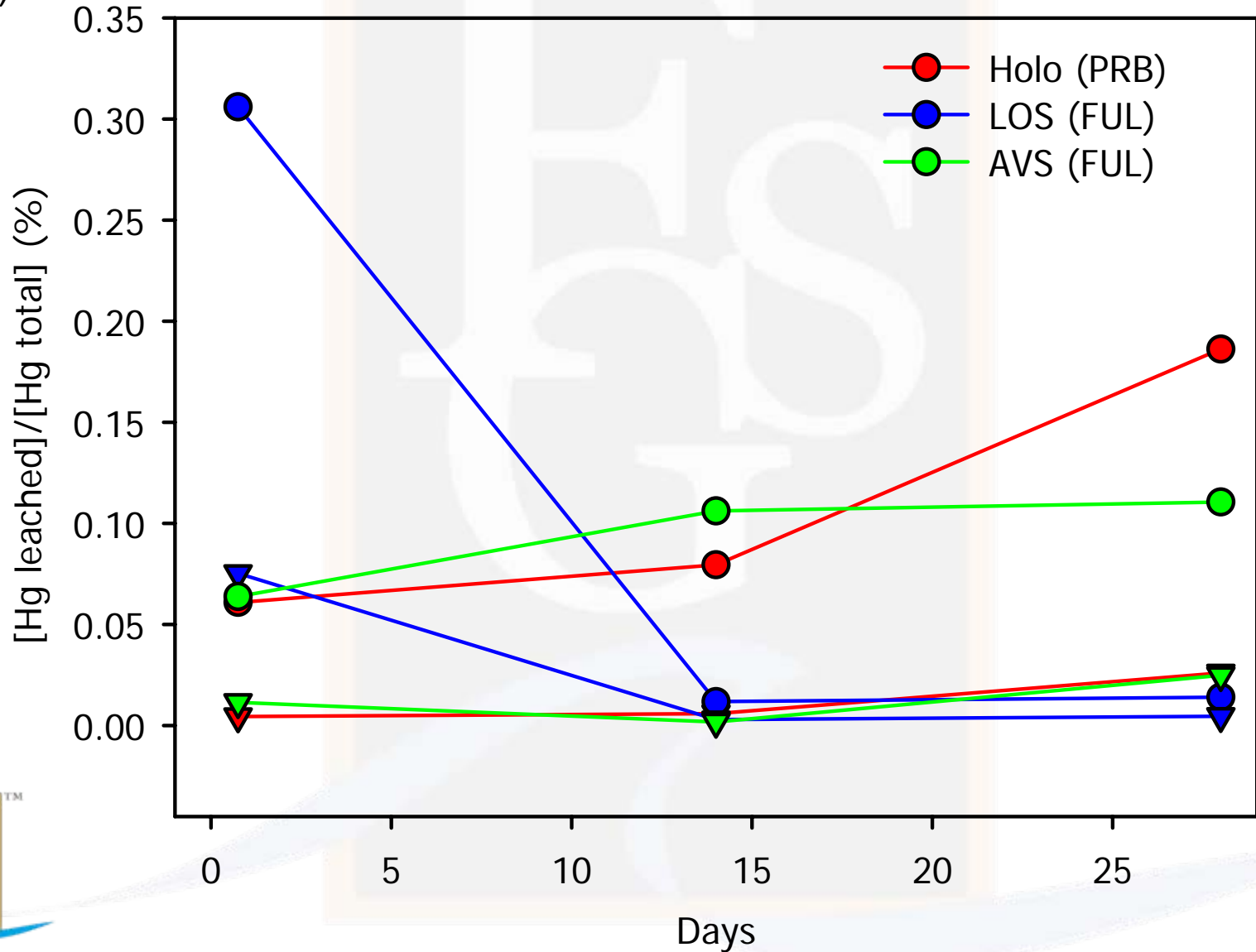


# Leaching – Fly Ash, Halogenated ACI, PRB



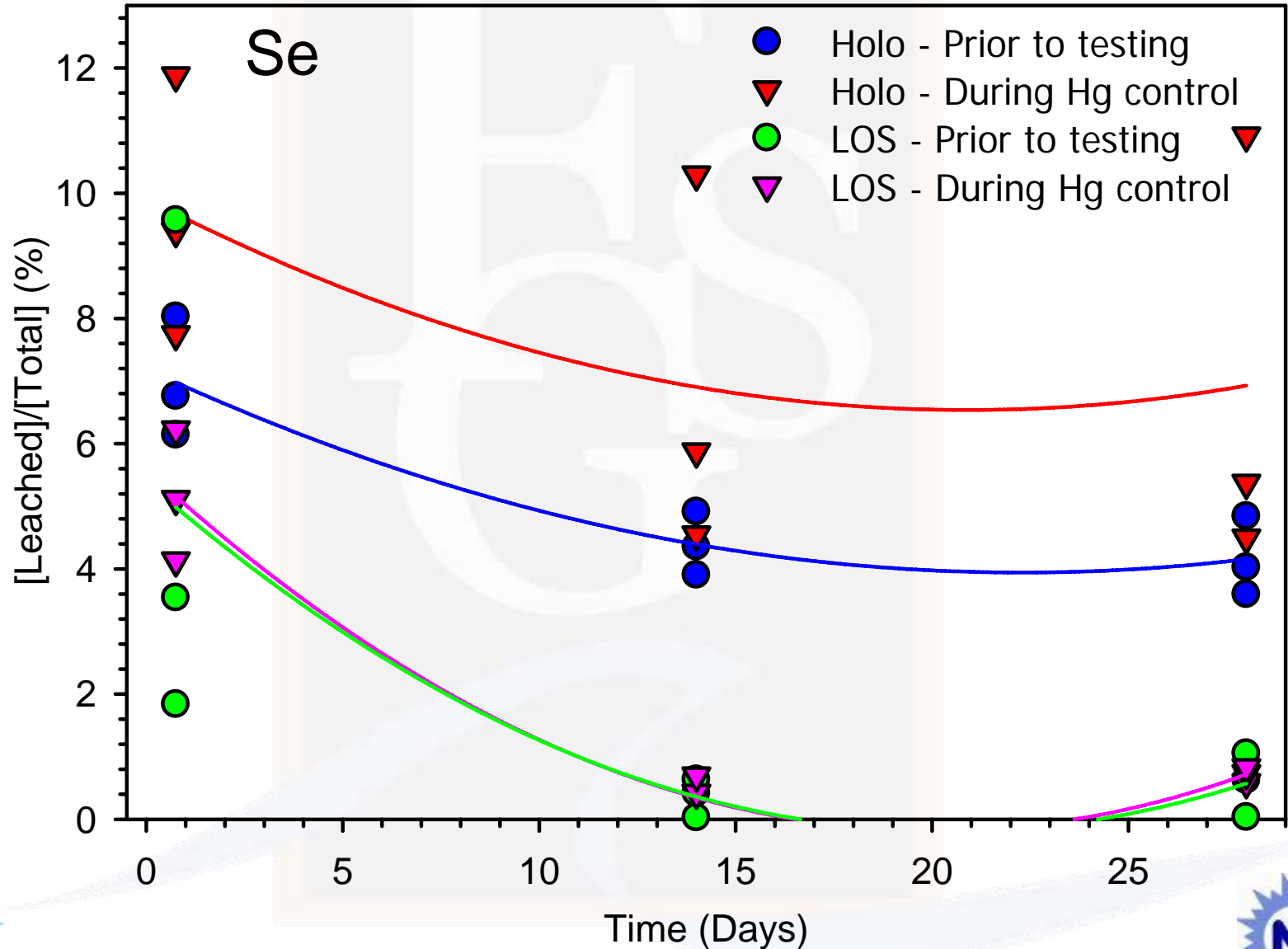
# Leaching Studies

(n = 9)



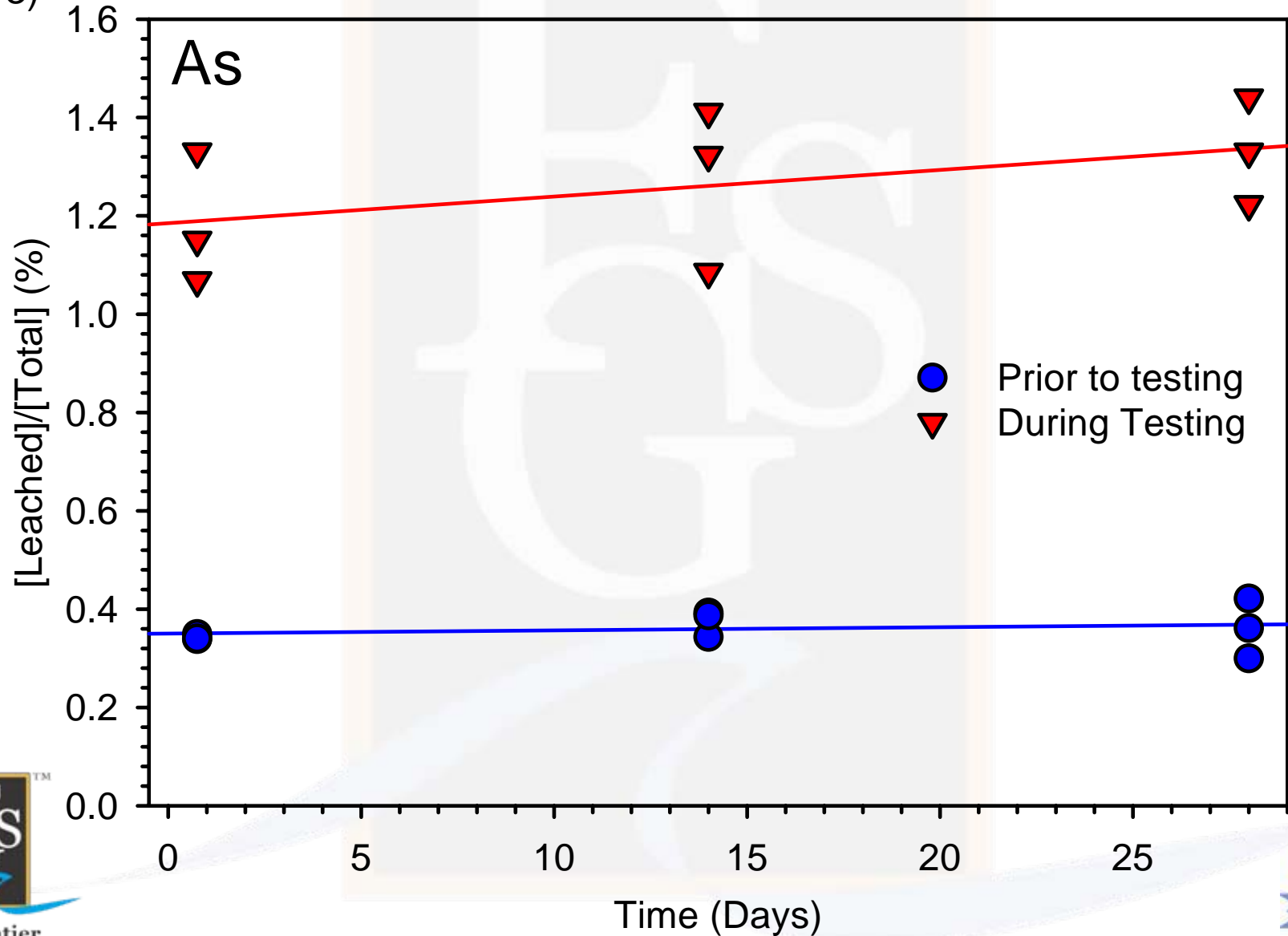
# Leaching – Fly Ash, Halogenated ACI, PRB

(n = 3)



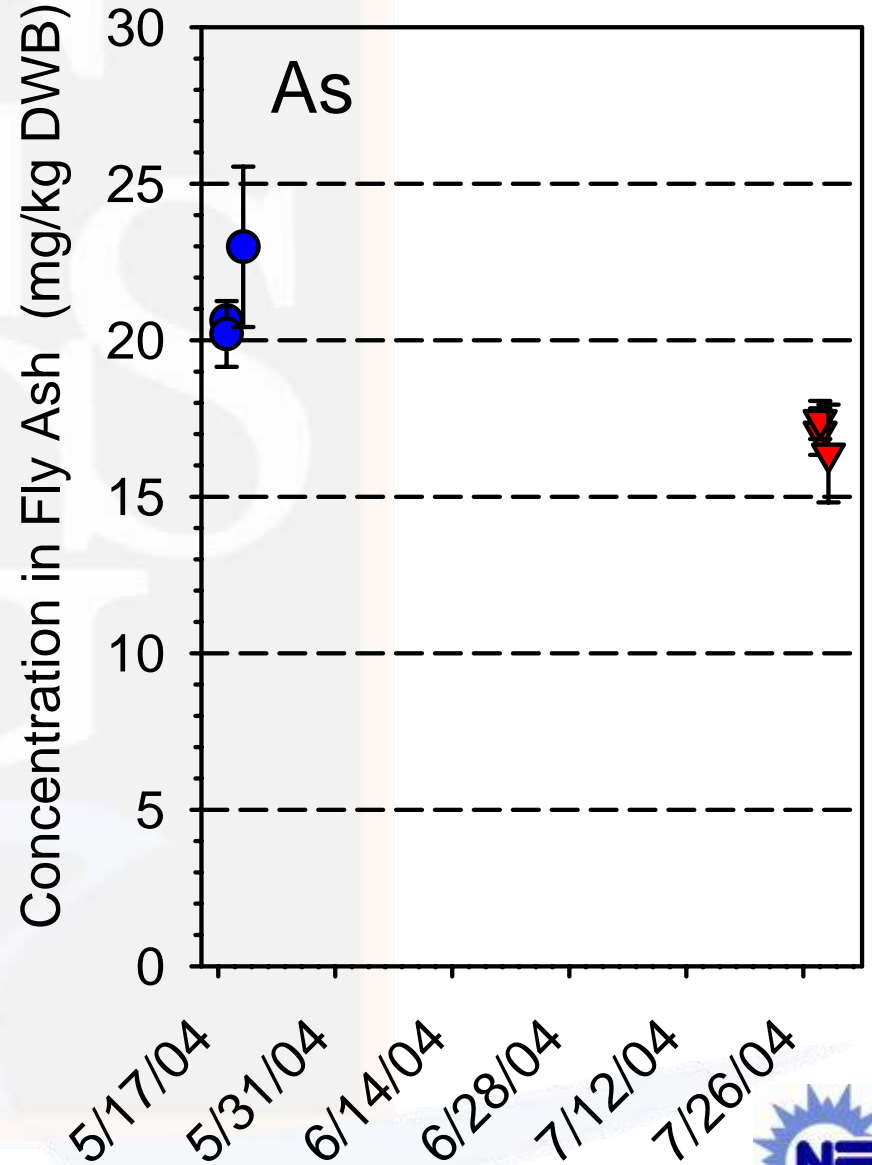
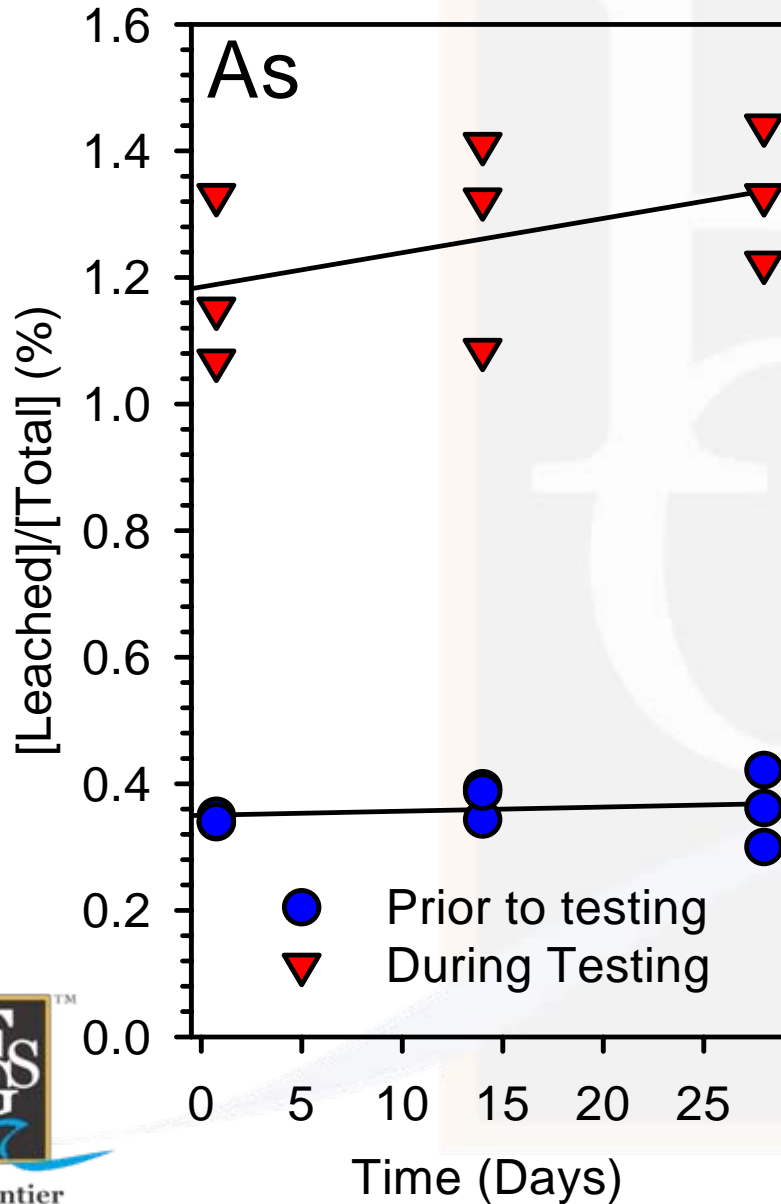
# Leaching - Fly Ash, Halogenated ACI, PRB

(n = 3)



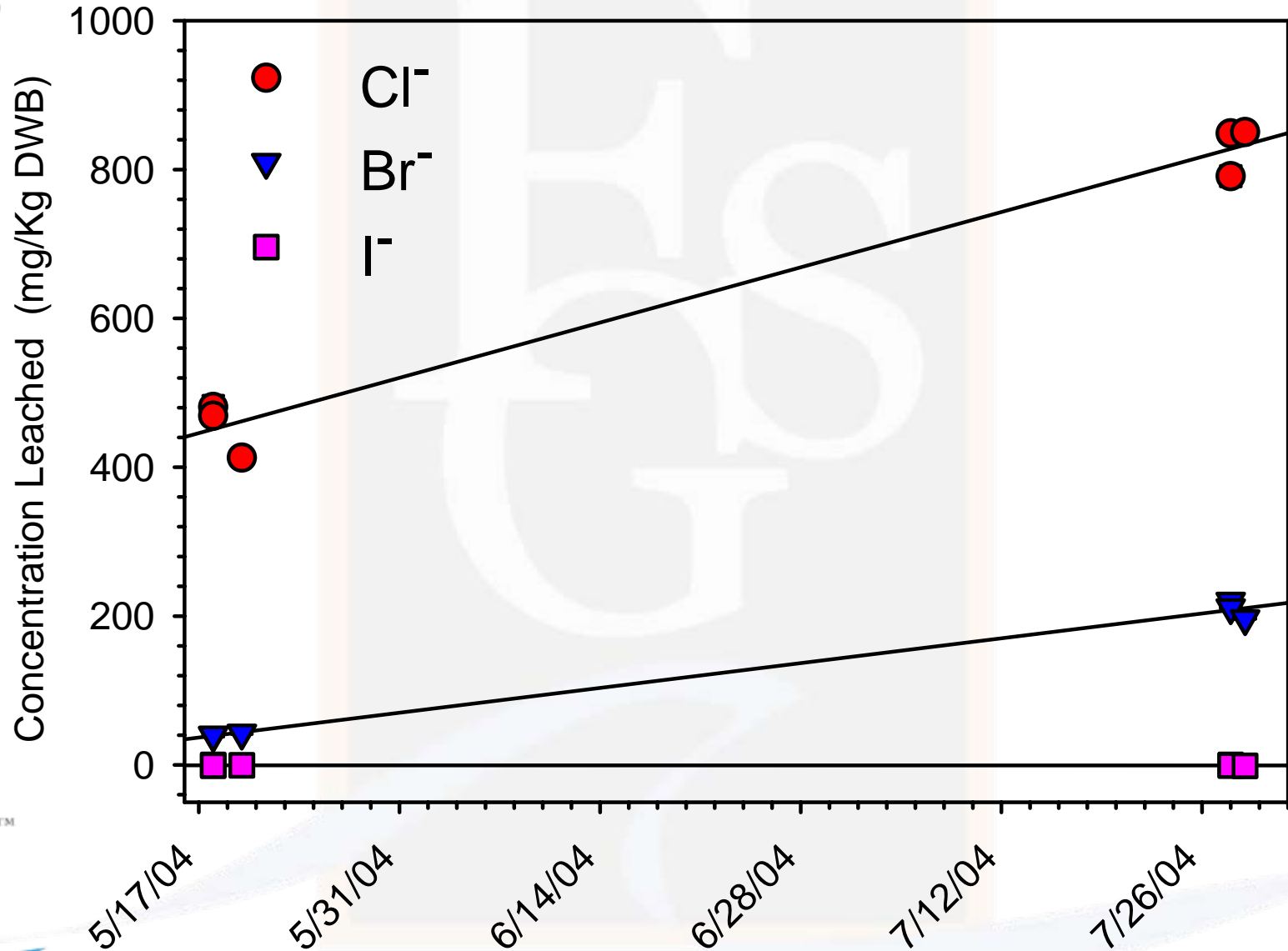


# Leaching - Fly Ash, Halogenated ACI, PRB



# Halides – SPLP Leaching Protocol

(n = 3)



# CUBs – Thermal Release Protocol

- Low Temperature Solids
  - biologically active landfills 35 – 45 °C
  - embankment temperatures 30 – 40 °C
  - US rolling traffic 21 – 40 °C
- Low Temperature FGD Liquids
  - mercury lost in sampling handling and transport
- Mid Temperature FGD solids
  - wallboard production - calcining
    - >128 °C to promote release of water
    - <163 °C to prevent anhydrous calcium sulfate formation
- Mid Temperature Fly ash
  - asphalt production 125 – 190 °C
- High Temperature Fly ash
  - cement production - calcining 1400 °C

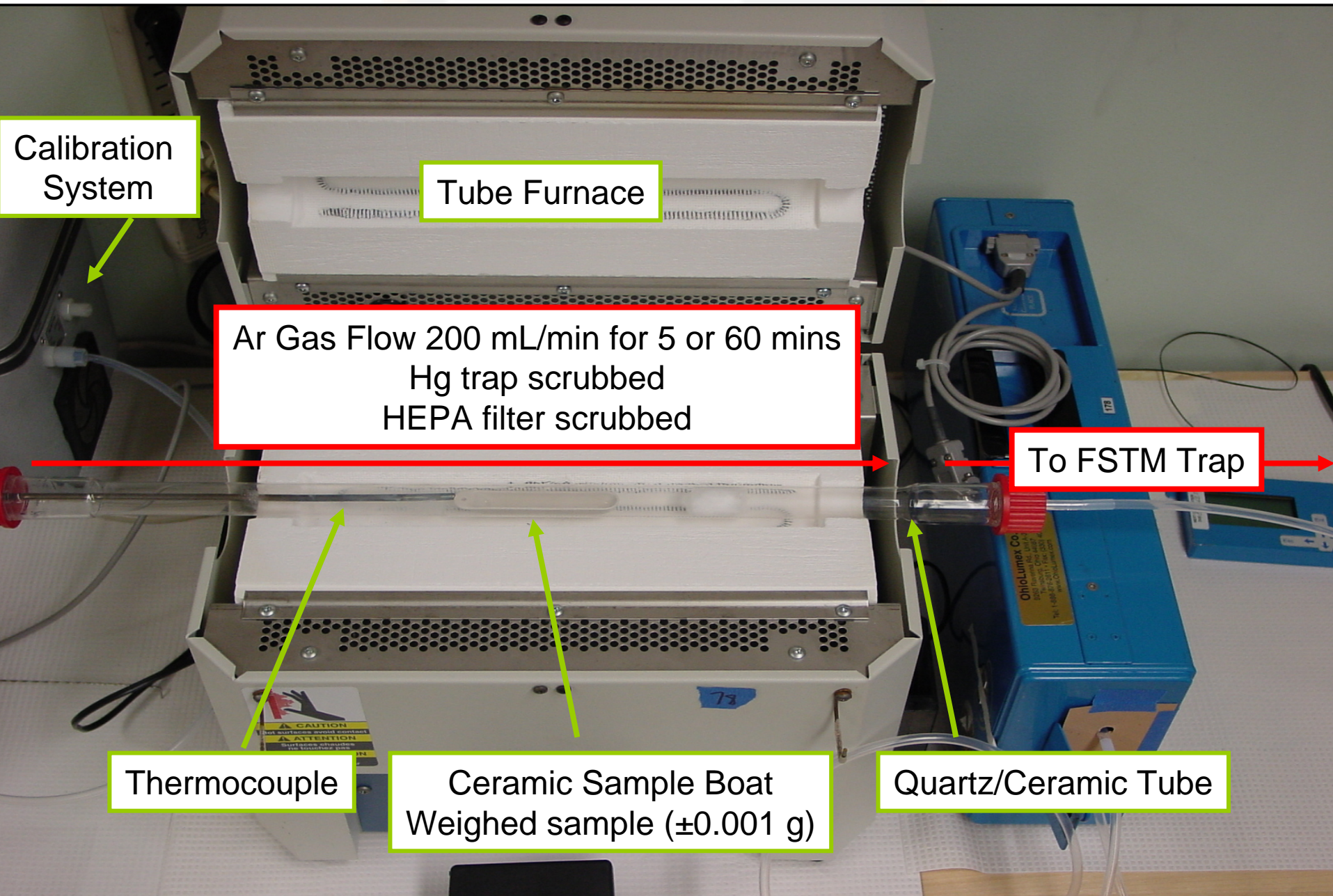


# Low Temp Study – 40 °C for 30 days

Nothing released of statistical significance to date



# CUBs – Mid and High Temperature



Calibration System

Tube Furnace

Ar Gas Flow 200 mL/min for 5 or 60 mins  
Hg trap scrubbed  
HEPA filter scrubbed

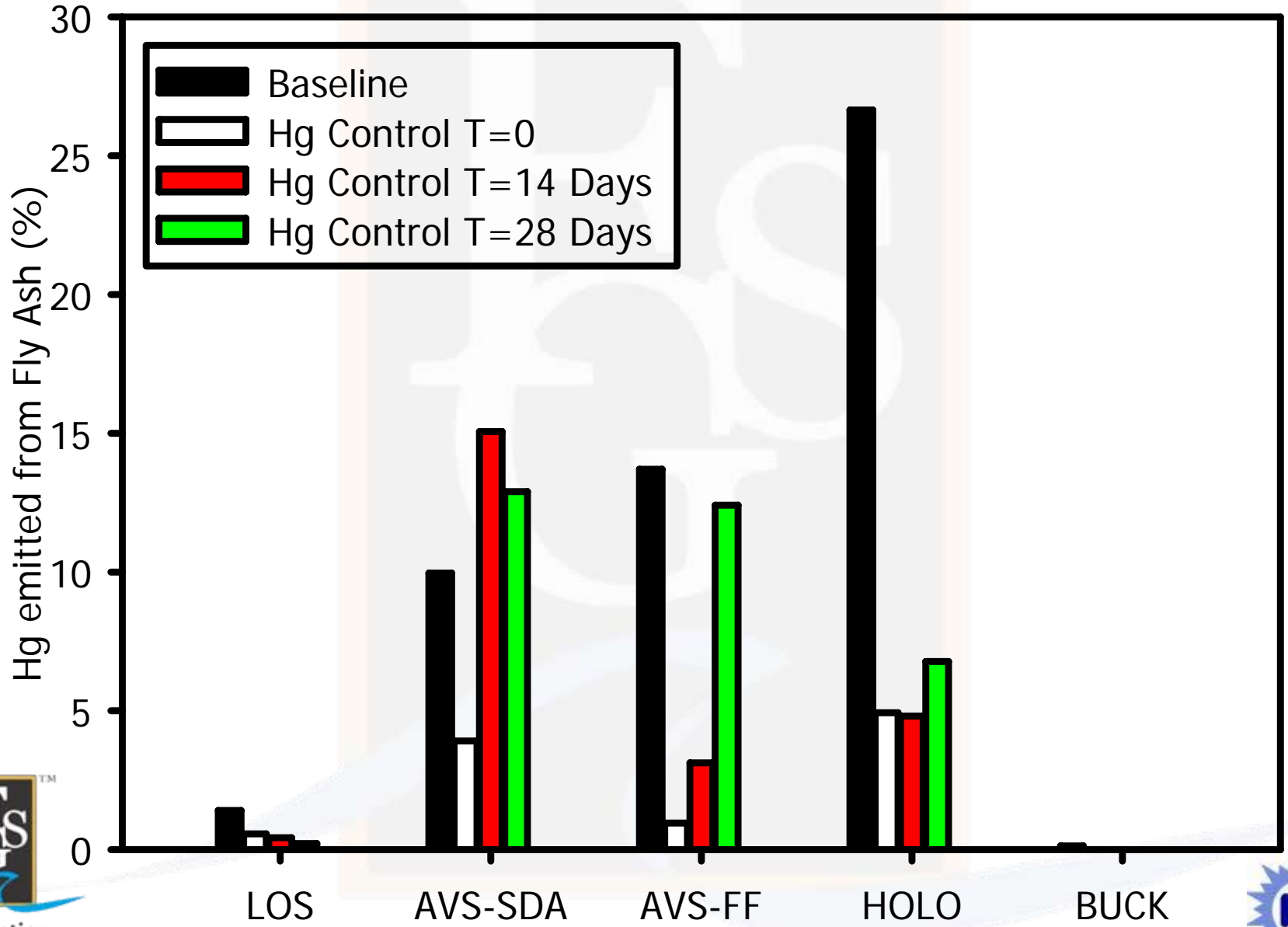
To FSTM Trap

Thermocouple

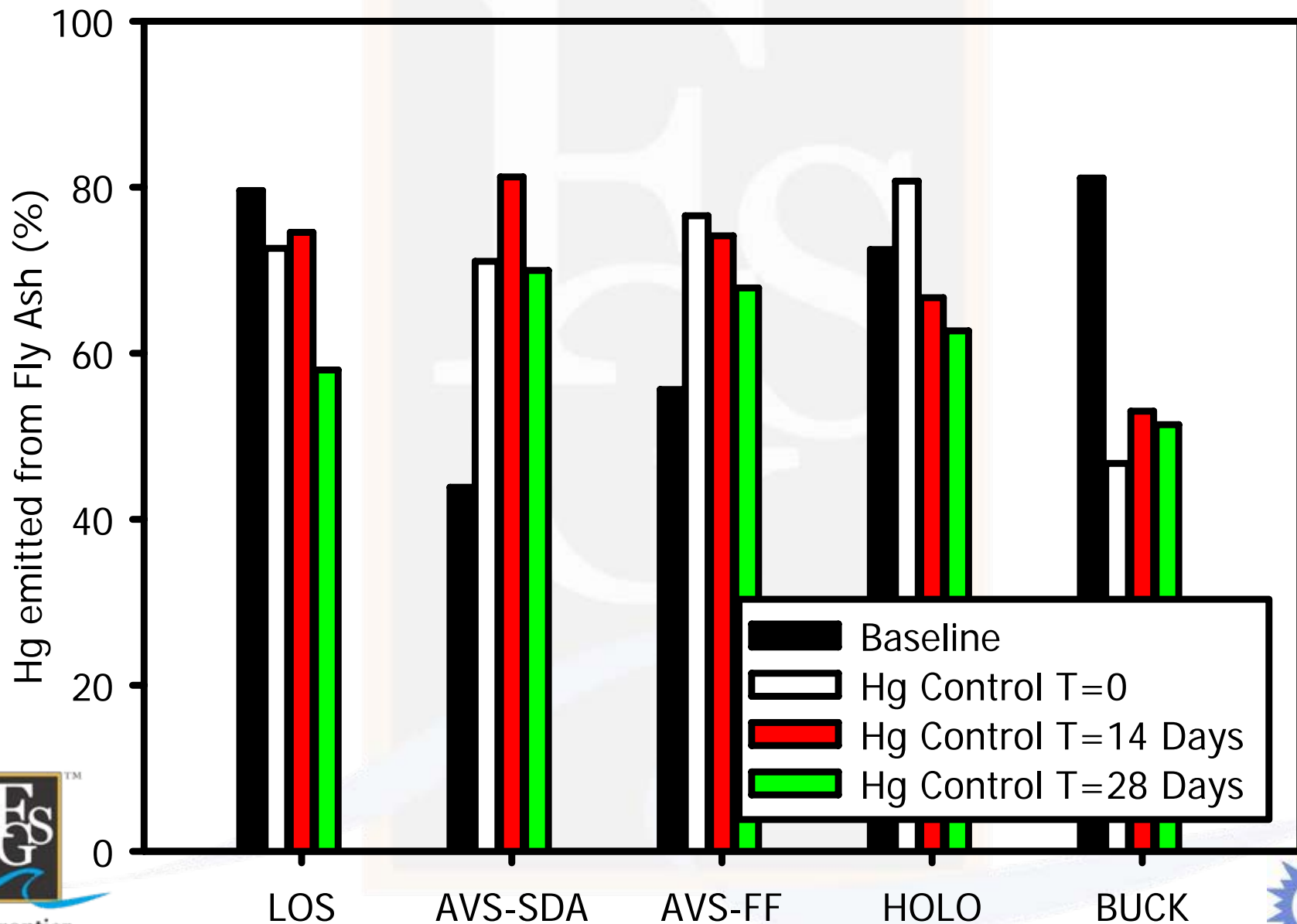
Ceramic Sample Boat  
Weighed sample ( $\pm 0.001$  g)

Quartz/Ceramic Tube

# Mid-Temp Study – 190 °C for 1 hour



# High-Temp Study – 1200 °C for 5 mins



# Trace Metals Emission

## Summary - Data is still being reviewed

Halogenated ACI in BUCK Unit (Bitumous blend) shows lowest TM emission except for As. It is the only location, to date, that shows significant emission at high temp for As.

## For the other locations analyzed to date:

Ni consistently shows emission loses ~20-30% for both mid and high temp

As typically does not show emission loses

Se typically shows emission loses ~100% at high temp and ~20% at mid temp

Cd consistently shows emission loses ~20-30% for high temp

Pb typically does not show emission loses



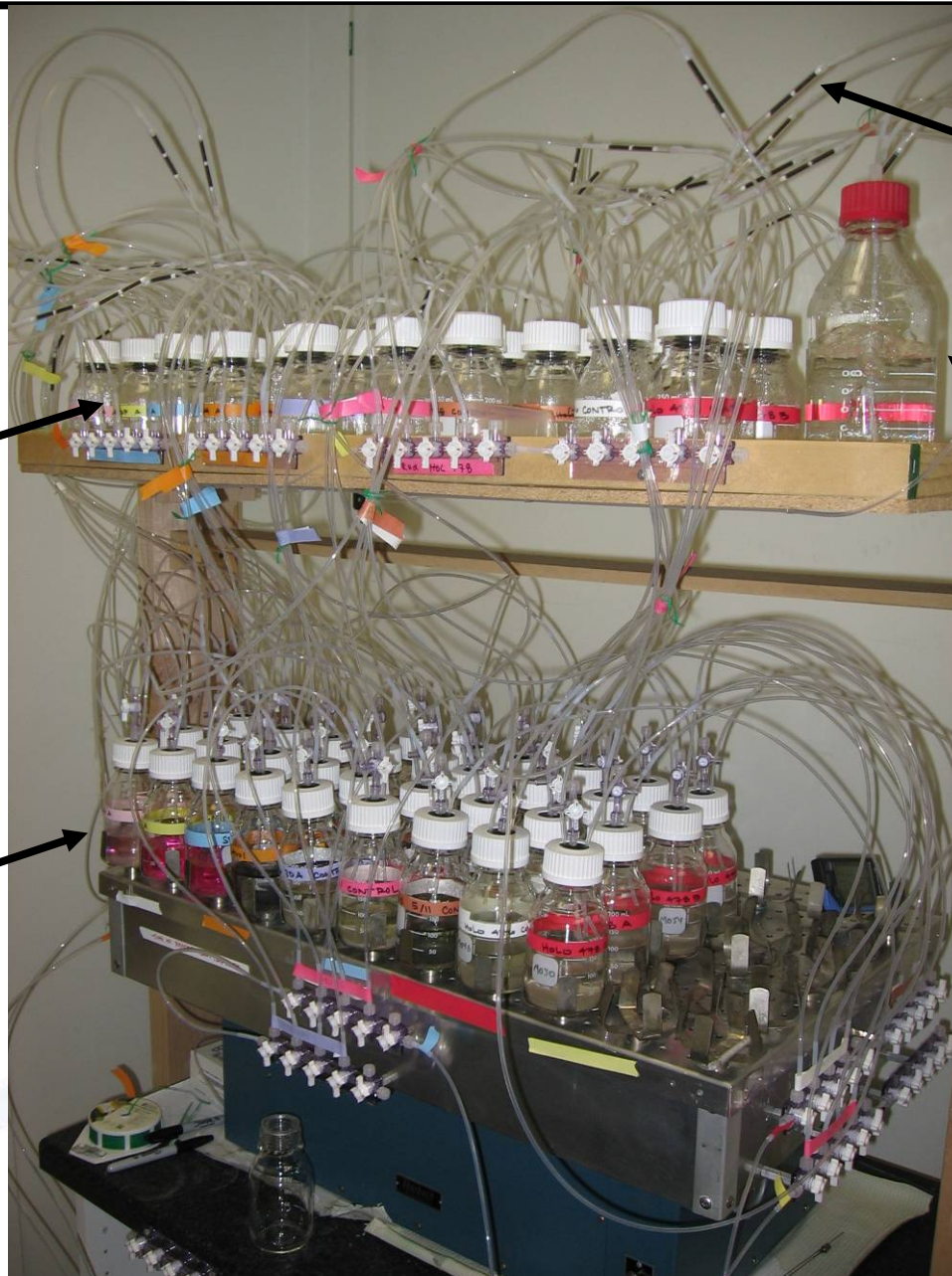


# Observation at High Temp

- At 1200 °C a few samples will glassify and fuse in the sample boat
- Dropping to 900 °C solves this problem
  - Should still see full thermal release of Hg, other metals are being investigated
- Appears to be related to the amount of injected carbon in the fly ash



# Microbial Studies



Modified  
M-29 Traps

FSTM Traps





Humidifier

Reaction Vessels



# Current Status

Location	Total Metals	Volatility	Microbial	Leaching	Halides
Leland Old Station	Completed	Completed	In process, report Apr 07	Completed	Completed
Holcomb	Completed	Completed	In process, report Apr 07	Completed	Completed
Meramec	Completed	Test not authorized	Test not authorized	Test not authorized	Test not authorized
Monroe	Completed	Test not authorized	Test not authorized	Test not authorized	Test not authorized
Buck, Unit 6	Completed	Completed	In process, report Jan 07	Completed	Completed
St. Clair, Unit 1	Completed	Test not authorized	Test not authorized	Test not authorized	Test not authorized
Antelope Valley Station, SDA	Completed	Completed	In process, report Apr 07	Completed	Completed
Antelope Valley Station, FF	Completed	Completed	In process, report Apr 07	Completed	Completed
Monticello	Completed	Completed	Test not authorized	Completed	Completed
Monticello (FGD Solids)	In process, report Jan 07	In process, report Jan 07	In process, report Apr 07	Completed	Completed
Monticello (FGD Liquids)	In process, report Jan 07	In process, report Jan 07	Test not authorized	Test not authorized	In process, report Jan 07
Yates	Completed	Completed	Completed	Completed	Test not authorized
Stanton	Completed	In process, report Jan 07	In process, report Apr 07	In process, report Jan 07	In process, report Jan 07

 Test not authorized  
 Completed  
 In process, report Jan 07  
 In process, report Apr 07

70 samples and ~4500 analyses to date