The Impact of Hg Control Technologies on Mobility Pathways of Hg, Ni, As, Se, Cd and Pb from Coal Utilization Byproducts

Carl E. Hensman, Amy L. Dahl, B. Doreen McIntosh, Lucas T. Hawkins, Philip I. Kilner, Josie M. Hein - Frontier Geosciences Inc.

Eric. M. Prestbo – Tekran Corporation

Cindy Gilmour - Smithsonian Environmental Research Center

Lynn Brickett – US DOE - NETL

US DOE Contract DE-AC26-05NT42110

Contacts

- Principal Investigator
  - Carl E. Hensman – carlh@frontiergeosciences.com
- Project Coordination
  - Amy L. Dahl – AmyD@frontiergeosciences.com
- US DOE NETL Project Manager
  - Lynn Brickett - Lynn.Brickett@NETL.DOE.GOV

- Frontier Front Desk – 206-622-6960

Overview

- Background and current state
- Total captured
- Thermal release
- SPLP leaching
- Microbial mobility

Background and current state

- The CUBs being tested are generated from NETL mercury control projects
  - Some of the technologies may deposit additional quantities of mercury onto the CUBs
- 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.
- Currently – the study is ~50% complete
  - 135 separately collected samples
  - 15 separate locations
  - ~8000 analysis
- Individual pathway studies are not designed to be directly interpreted in cross-comparison
  - Looking at the studies to indicate the impact of different Hg control technologies (Hg-CT) on CUBs across different facilities under the same experimental protocol.

Facility Summary (discussed today)

Facility	Sample	Sample Location	Fuel	Load (MW)	Hg-CT
A	Ash	Surge Silo	PRB	360	Halogenated ACI
B	Ash	ESP Hopper	FUL	220	ACI + Proprietary
C	Ash	Spray Dryer Hopper	FUL	400	ACI + Proprietary
D	Ash	Fabric Filter Hopper	FUL	400	ACI + Proprietary
E	Fly Ash	ESP	Bit. Blend	60	Halogenated ACI
F	Fly Ash	Hopper	PRB/TL Mix	Not Given	Halogen Injection
G	Fly Ash	Hopper	LSEB	Not Given	ACI
H	Fly Ash	Hopper	PRB	Not Given	ACI

Sample collection and distribution

- Samples delivered from source
  - 3 from a Baseline operation period
  - 3 from the Hg-CT operation period
- Received, photographed and stored
  - Singular location, uniquely for this project
  - Temperature (daily) and ambient Hg (quarterly) monitored
- Sample sub-sampled by one individual
  - Frontier established protocols
- Sub-samples distributed
- Triplicates taken by study group

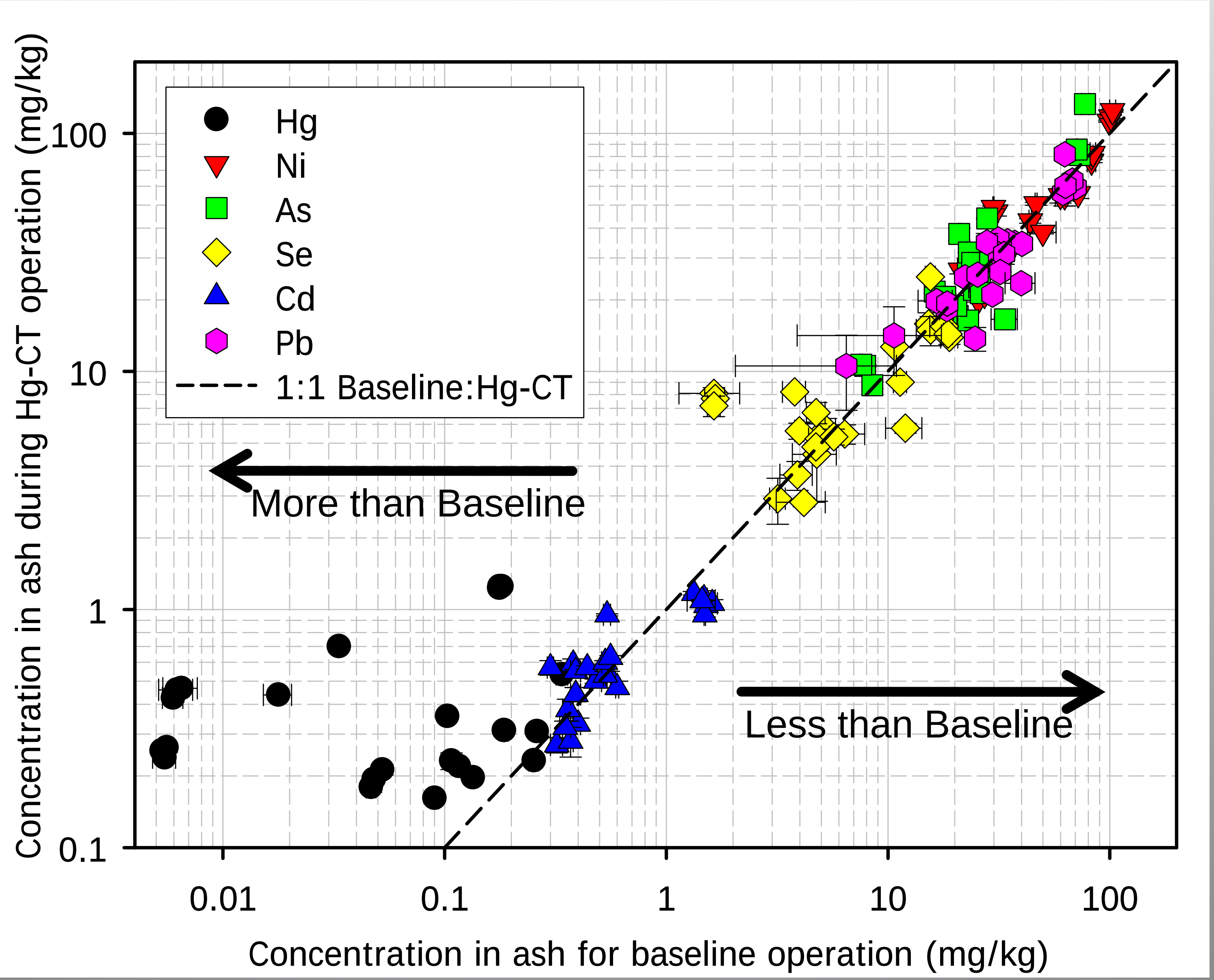
Total in Ash

- HNO_3/HCl/HF bomb digest with evaporative reflux with HNO_3 for removal of insoluble fluorides
- Hg analysis by CV-AFS
- Ni, As, Se, Cd, Pb analysis by ICP/MS

Total in ash

- ‘Baseline’
  - 3 samples at 3 time periods
- Hg-CT
  - 3 samples at 3 time periods
- Minimum of triplicates of each sample
  - Thermal requires 3 sub-samples and 3 analytical runs at the instrument of each sub-sample of each sample (total of 9 per sample)

Total target metals in ash



Total target metals in ash

$$Ratio = \frac{[Hg-CT]_{Average}}{[Baseline]_{Average}}$$

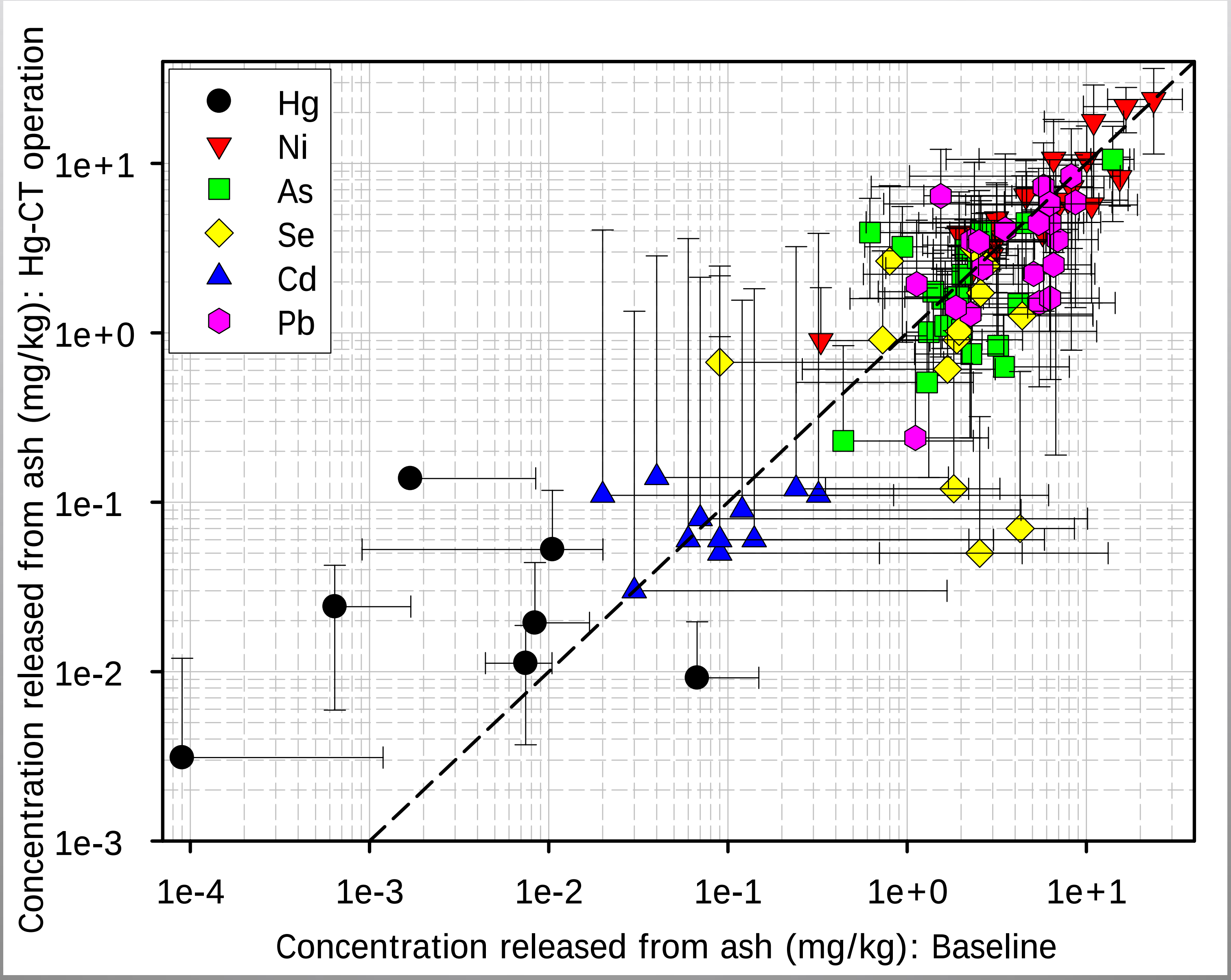
Facility	Hg	Ni	As	Se	Cd	Pb
A	7	1	1	1	1	1
B	2	1	1	1	2	1
C	46	1	1	1	1	1
D	72	1	1	1	1	1
E	4	1	1	5	1	1
F	2	1	1	1	1	1
G	1	1	1	1	1	1
H	27	1	1	1	1	1

Thermal release from ash

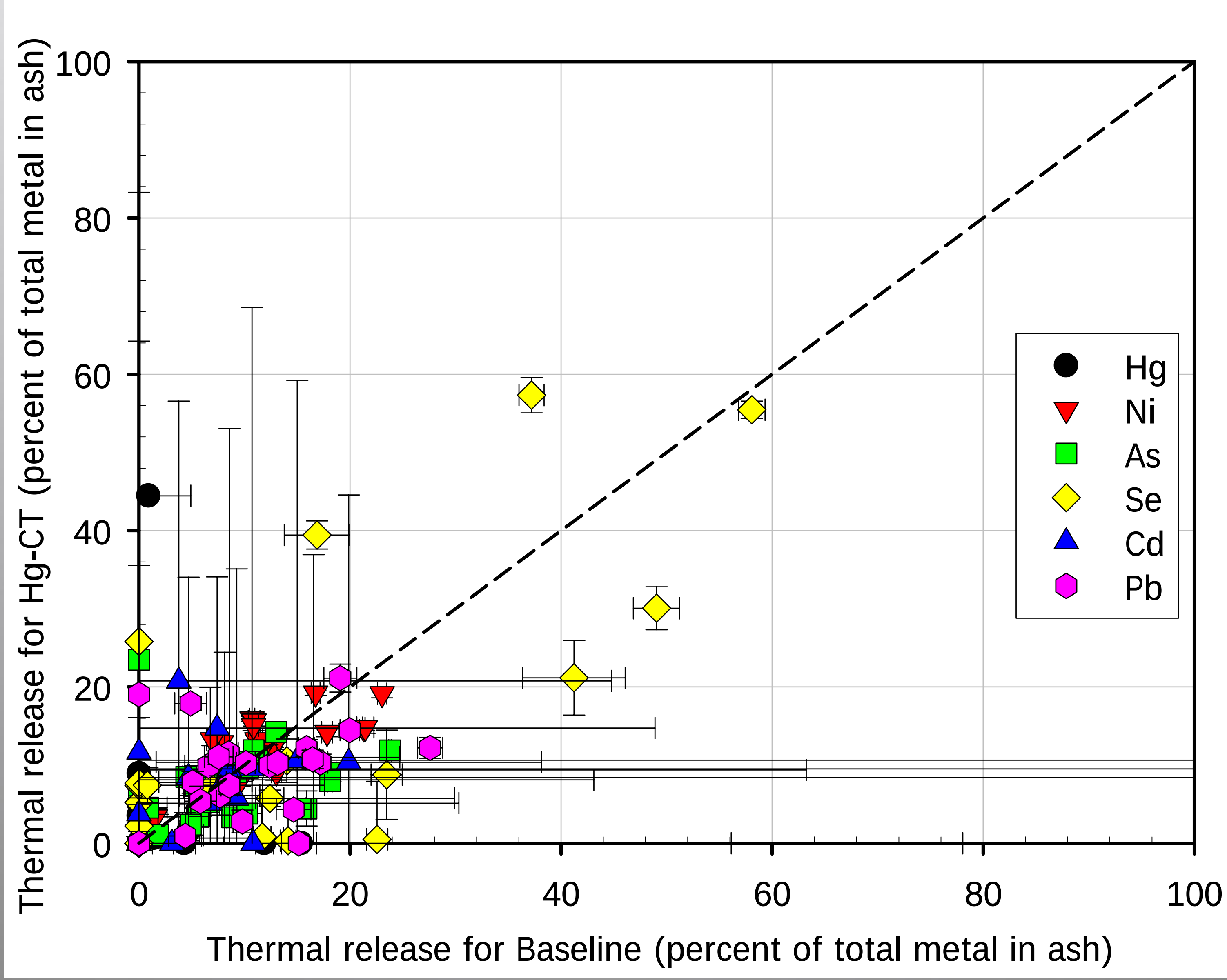
Final Use	Method	Temperature	Time	Support
Soil fill / Landfill	Low-flow heated chamber	40°C	30 days	Glass plate
Asphalt / Wallboard	Tube Furnace	190°C	60 min	Glass plate
Cement	Tube Furnace	1200°C	5 minutes	Glass plate

EGS™

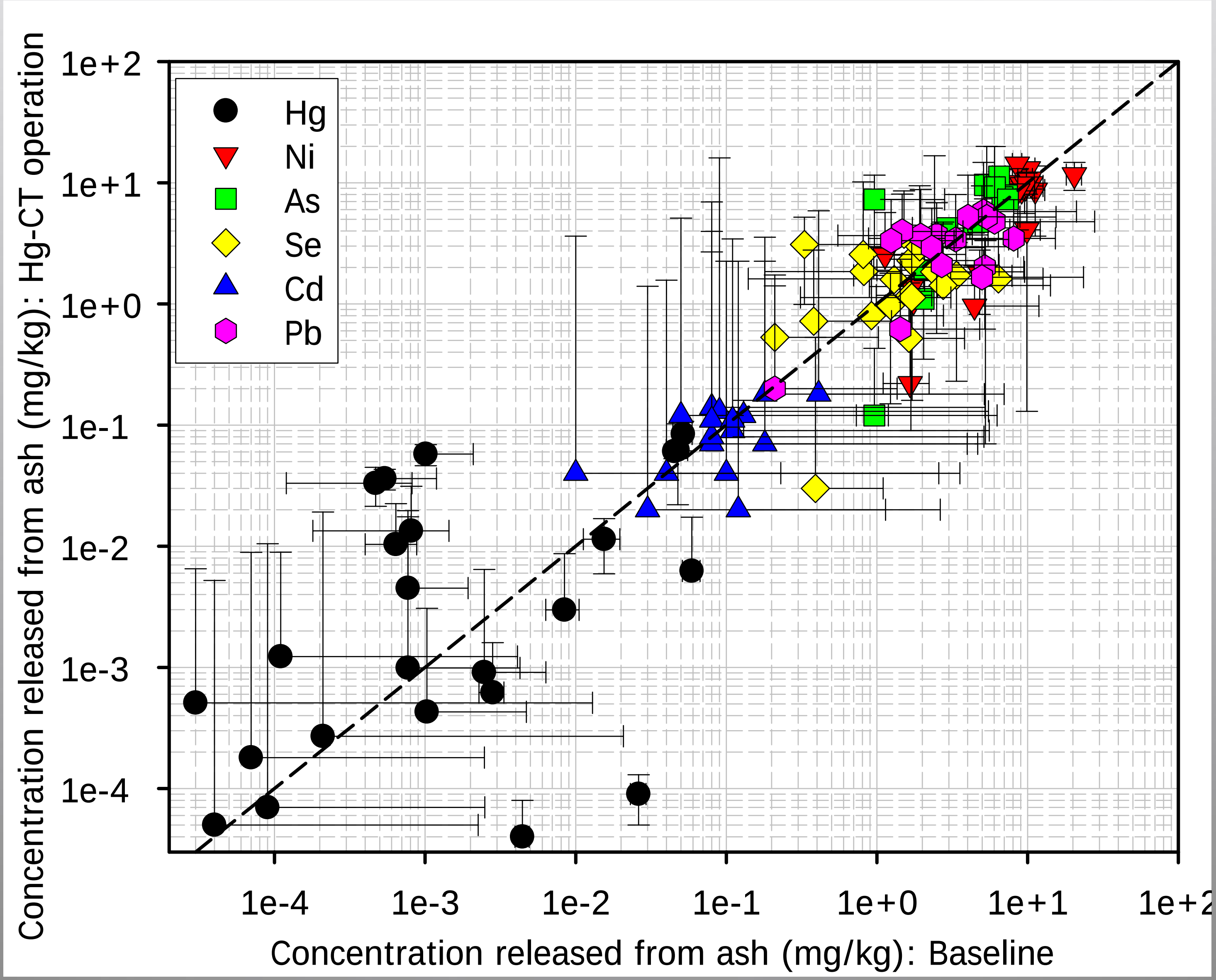
Thermal release 40°C over 30 Days



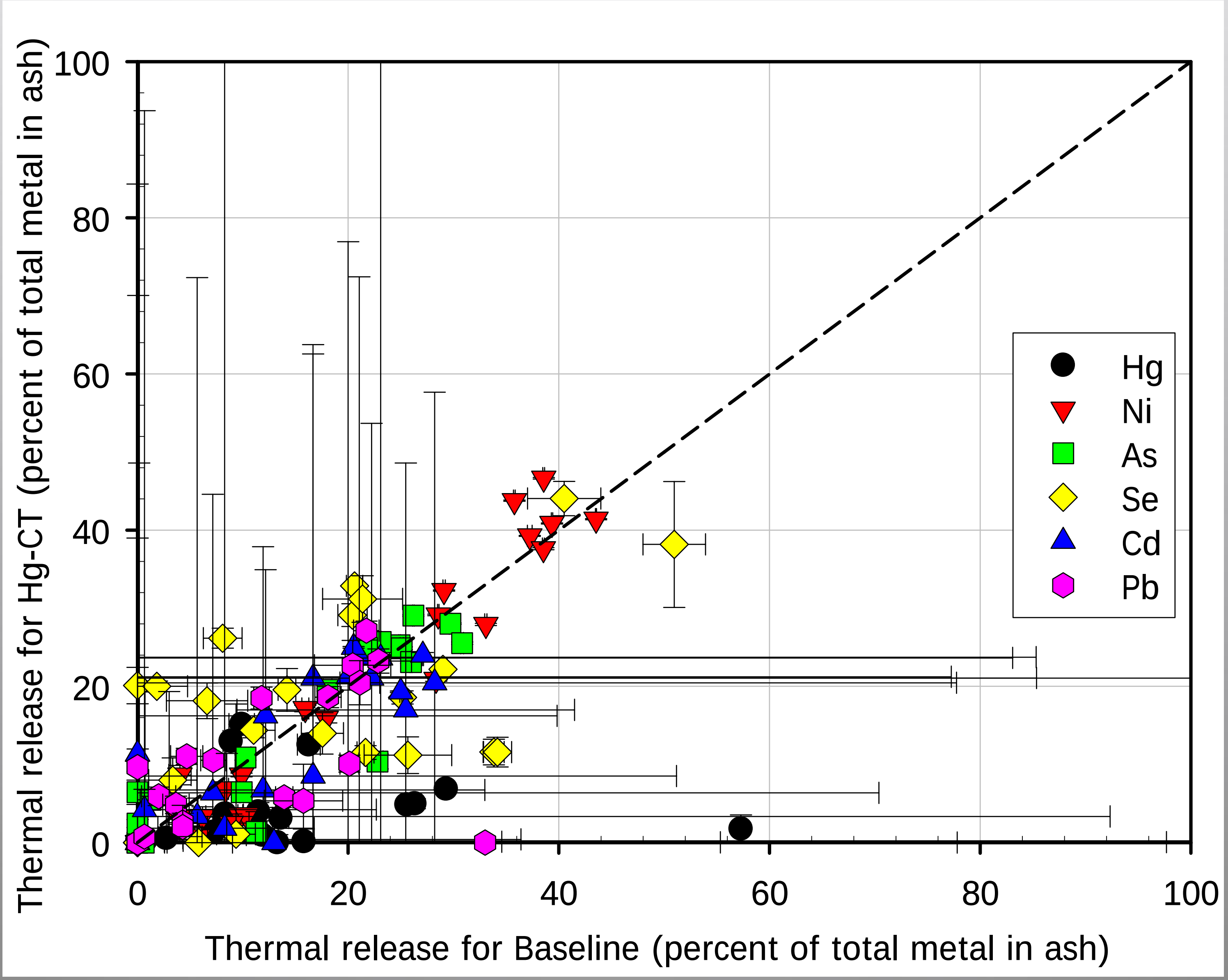
Thermal release 40°C over 30 Days



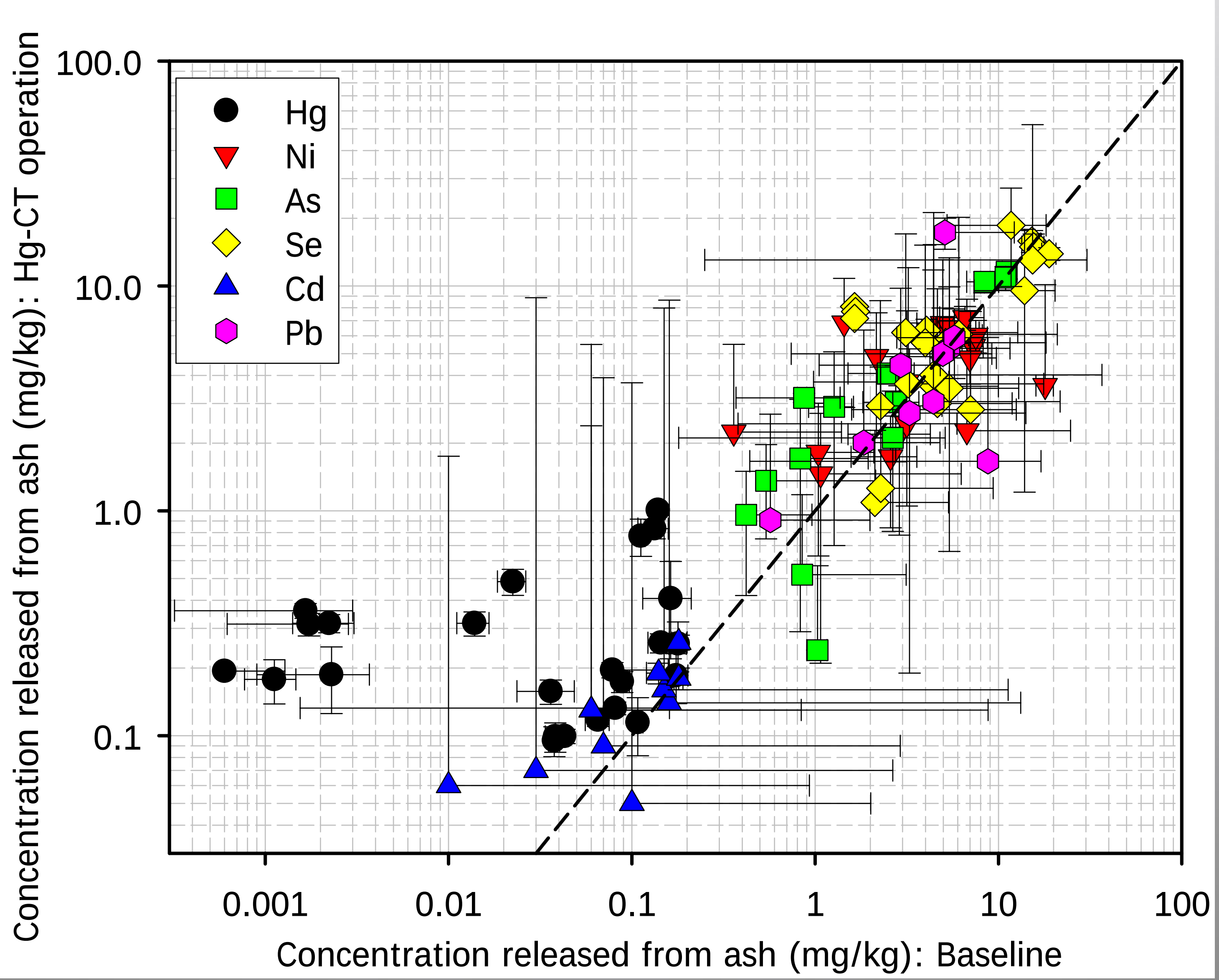
Thermal release 190°C over 1 hour



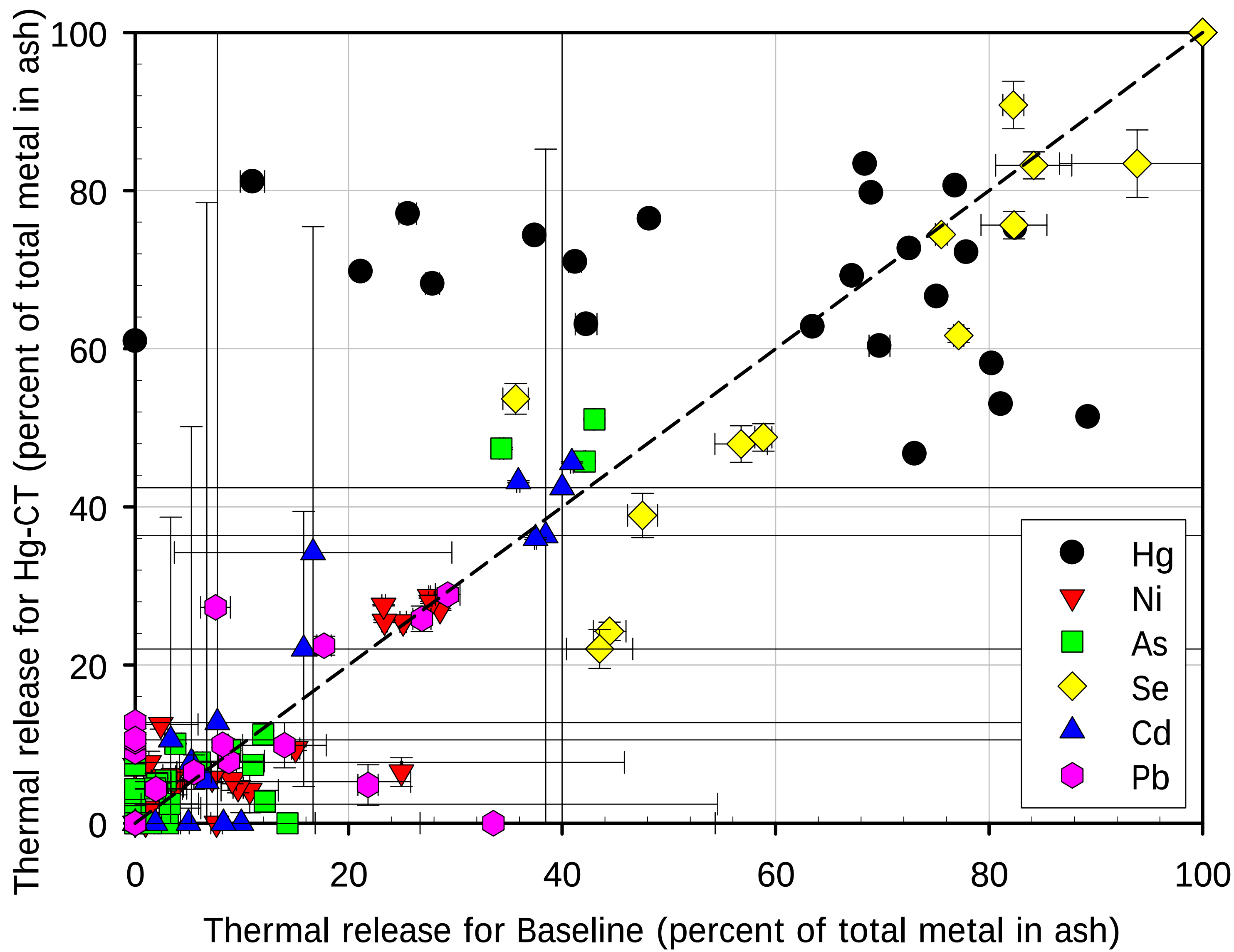
Thermal release 190°C over 1 hour



Thermal release 1200°C over 5 minutes



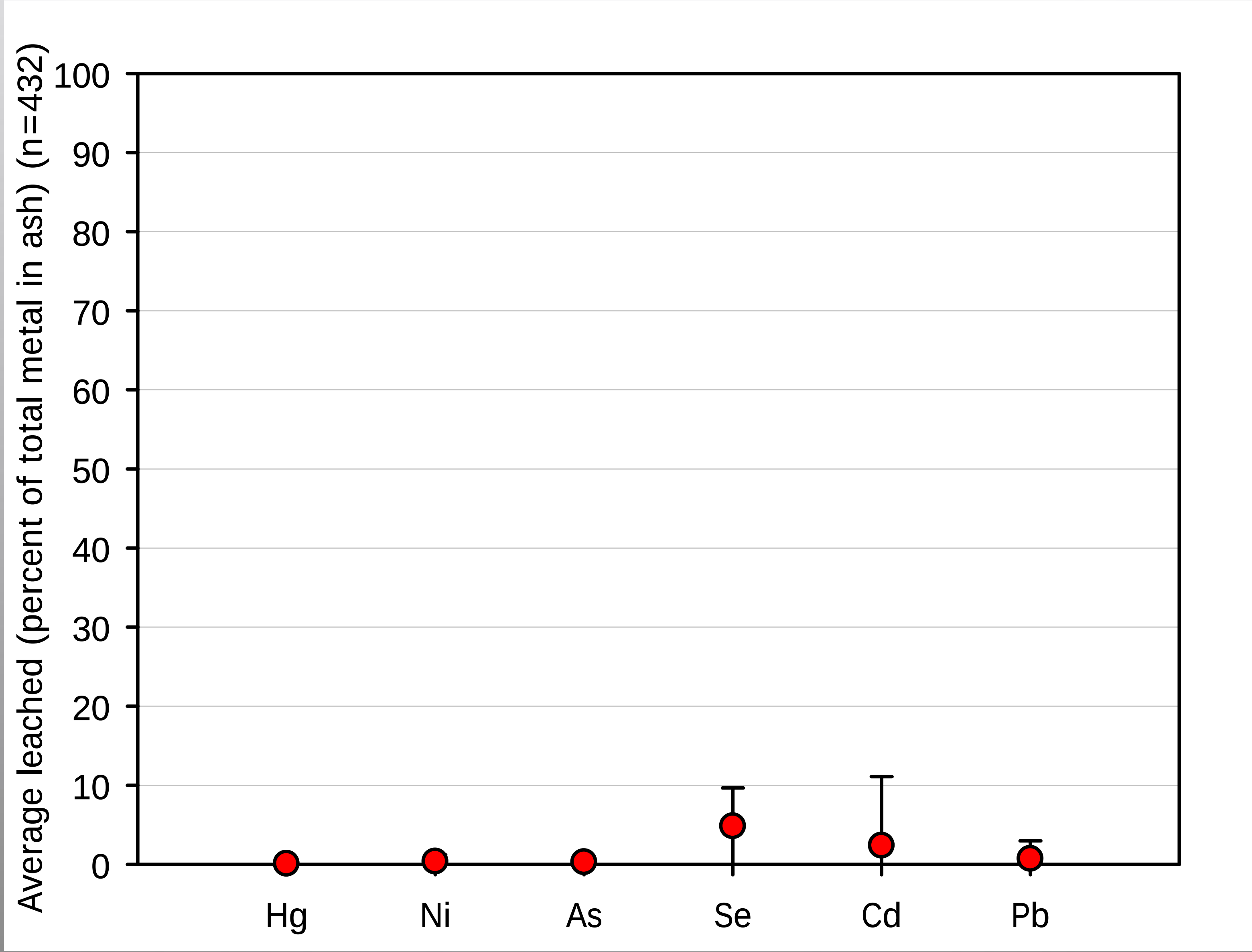
Thermal release 1200°C over 5 minutes



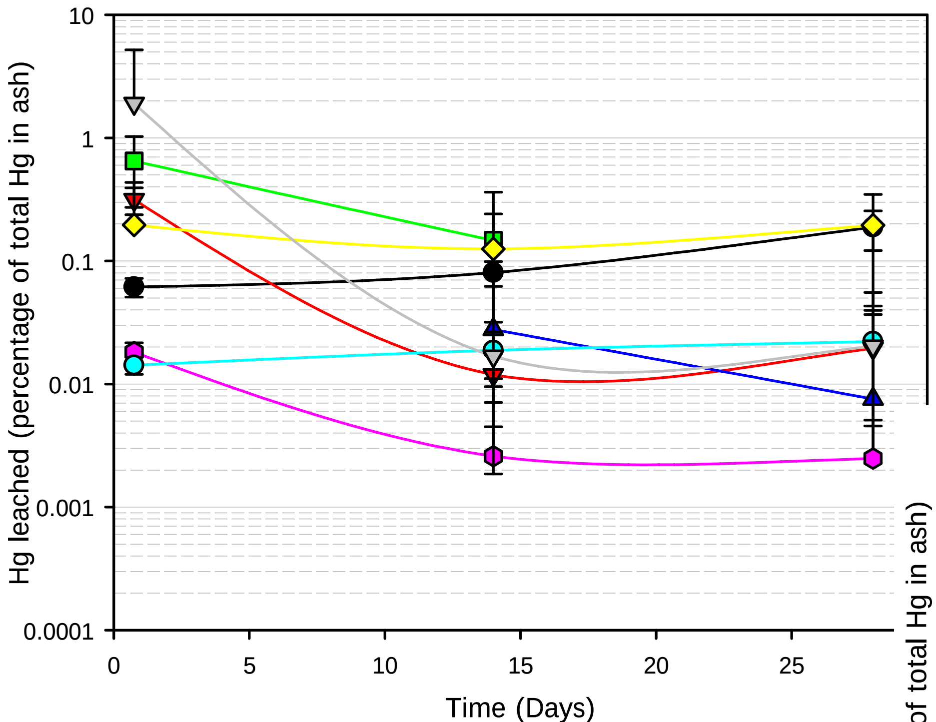
SPLP Leaching

- 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 leaching

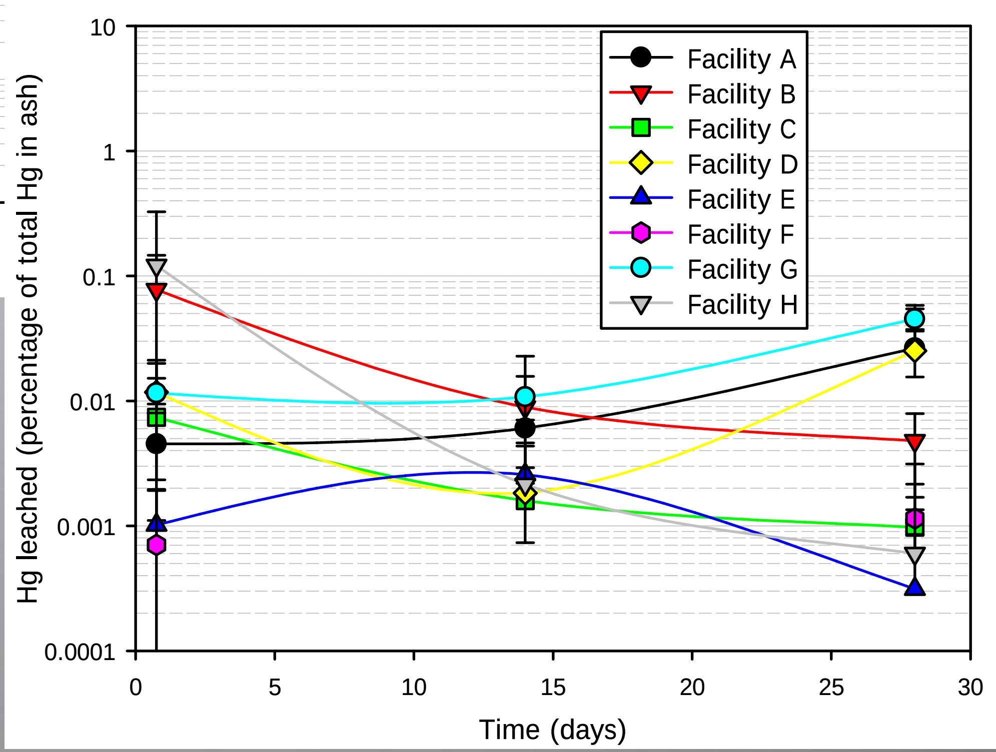


SPLP leaching - Mercury

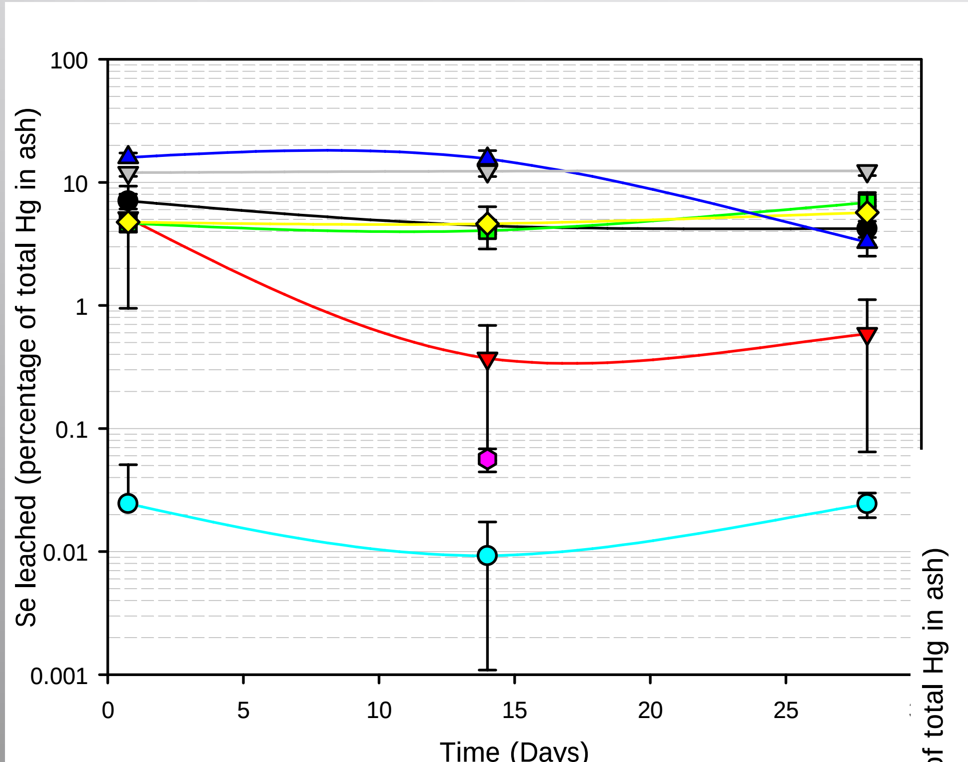


Baseline

Hg-CT

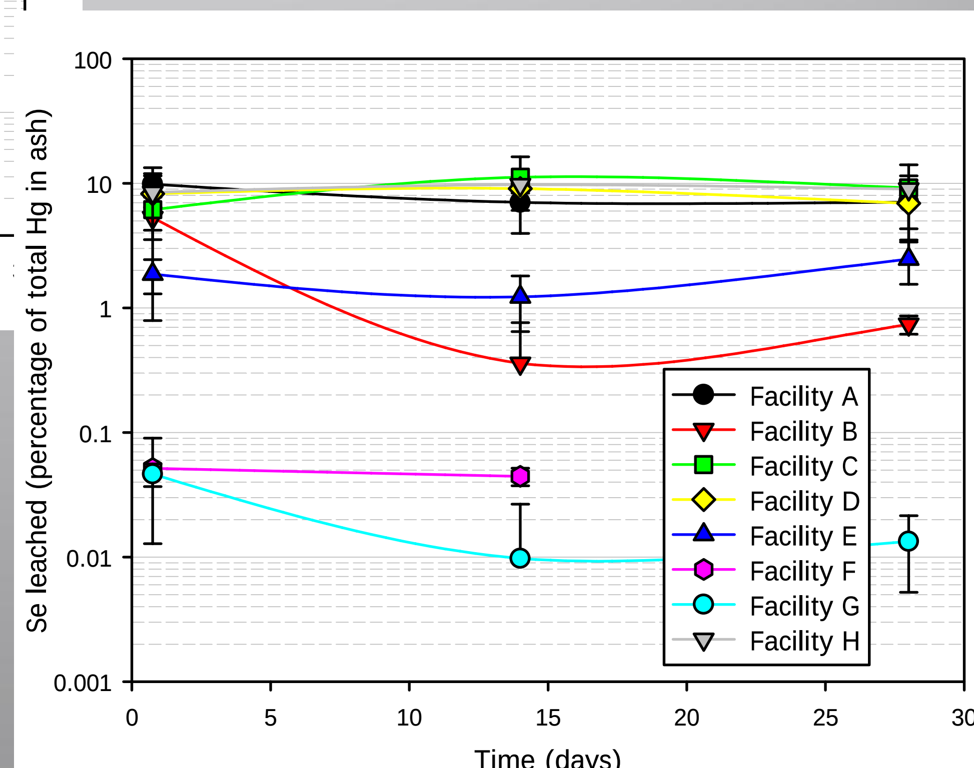


SPLP leaching - Selenium



Baseline

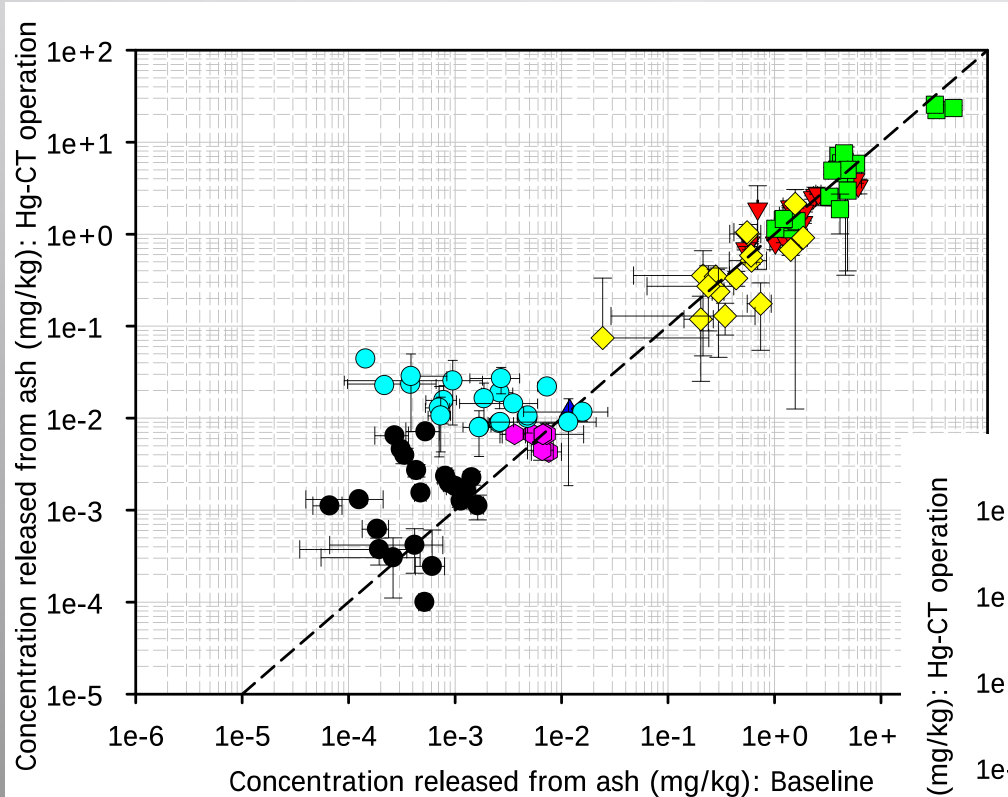
Hg-CT



Microbial mobility

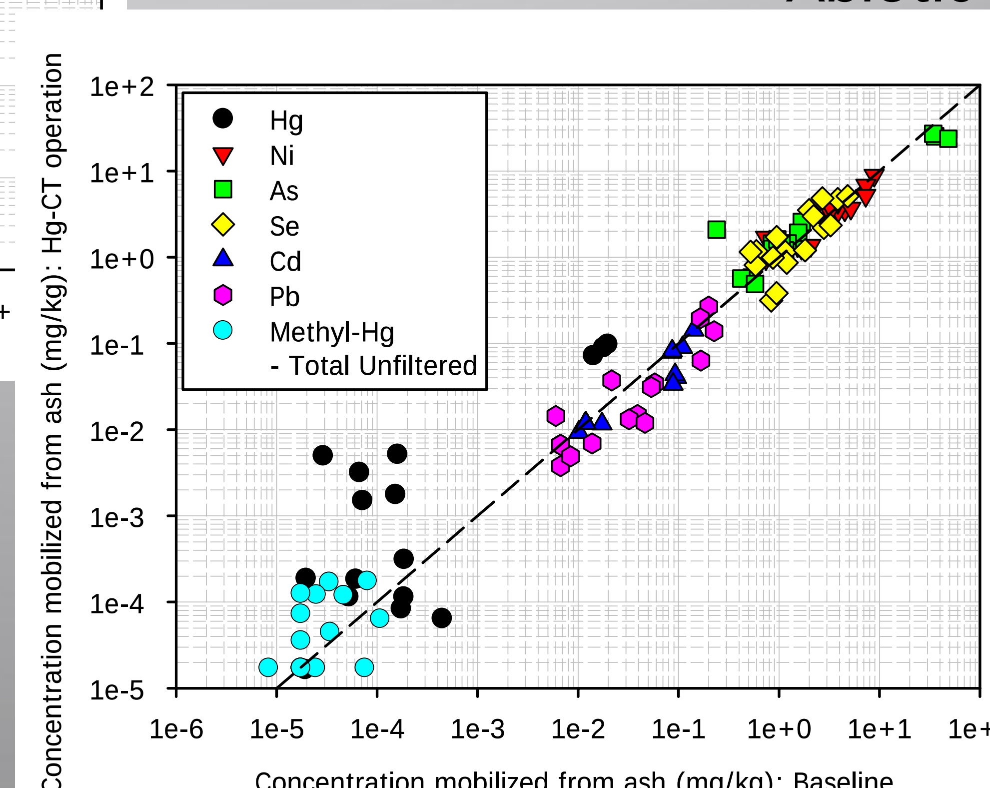
- Potential for metal dissolution, volatilization and methylation by microorganisms
- Using a batch reactor – anoxic conditions
- Hg-methylating bacterium - sulfate-reducing bacterium *Desulfobulbus propionicus*
- Ideal methylating medium
  - Worse-case methylation potential

Microbial mobility

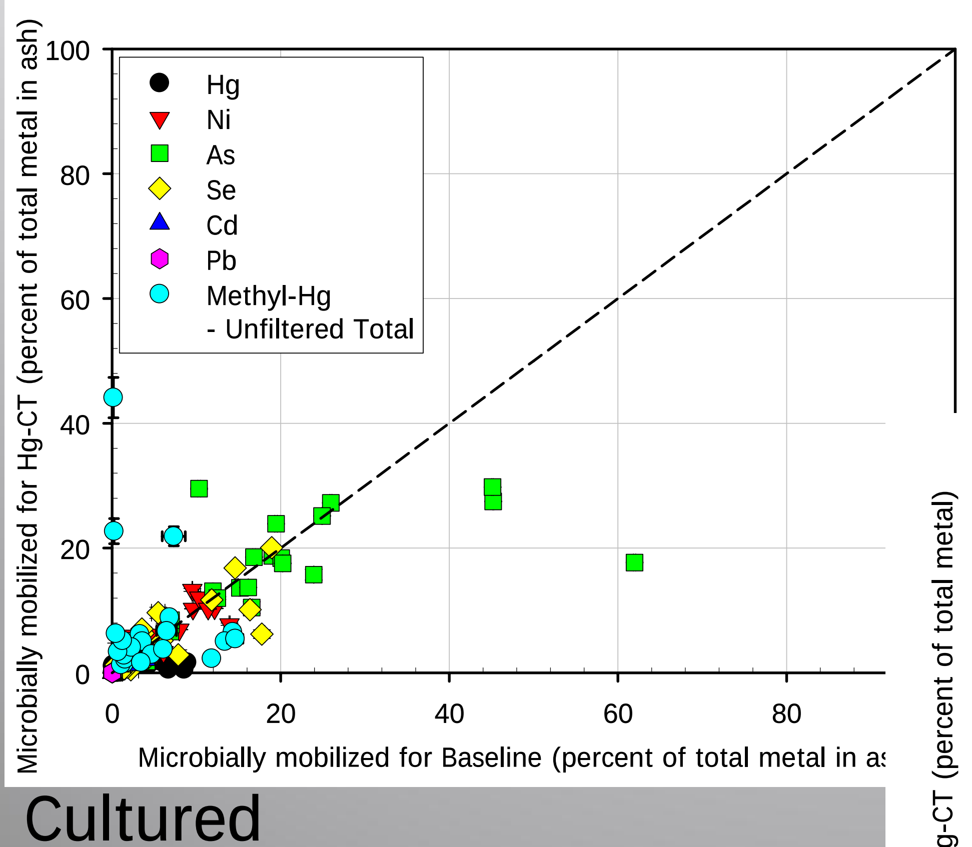


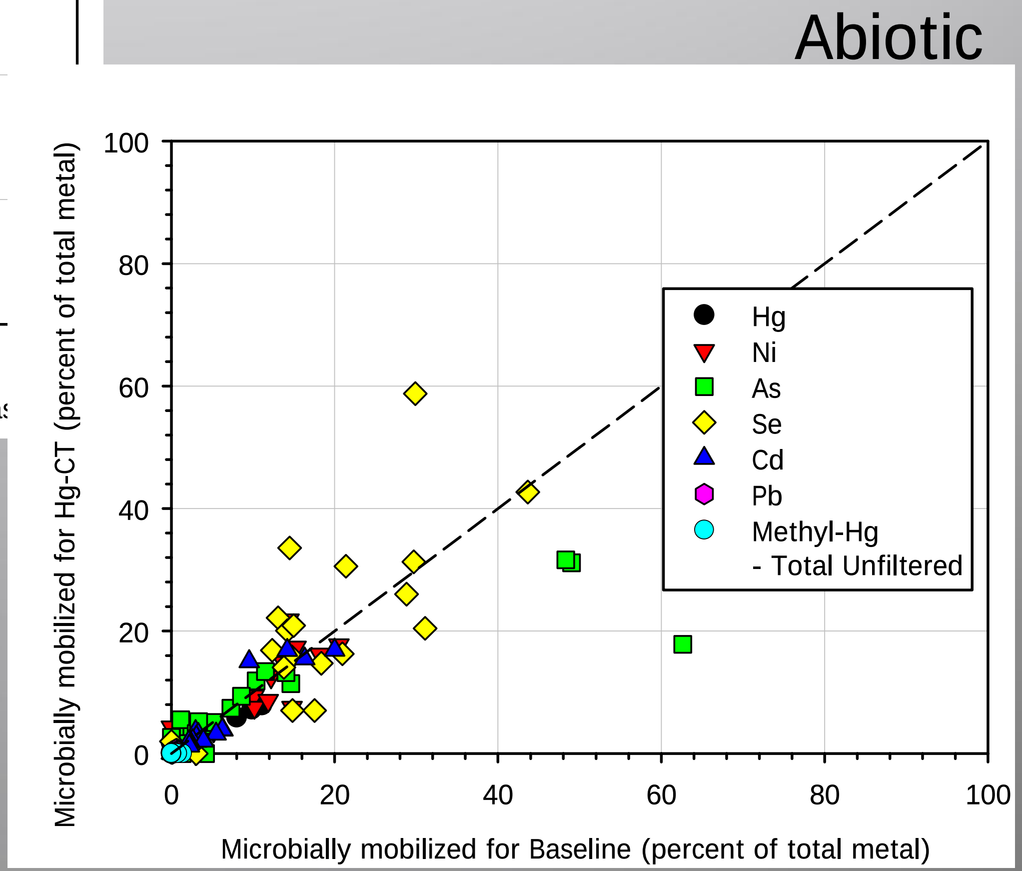
Cultured

Abiotic



Microbial mobility





Microbial mobility

$$Ratio = \frac{[Cultured]_{Average}}{[Abiotic]_{Average}}$$

Facility		Methyl-Hg	Hg	Ni	As	Se	Cd	Pb
A	Baseline	33	0.08	0.2	3	0.2	0.1	0.2
	Hg-CT	151	0.02	0.2	2	0.3	0.3	0.5
B	Baseline	261	68	0.6	13	0.08	2	2
	Hg-CT	622	16	0.5	4	0	1	0.6
C	Baseline	17	5	0.7	3	0.4	1	1
	Hg-CT	480	1	0.7	2	0.3	1	1
D	Baseline	129	3	0.4	4	0	0.9	0.5
	Hg-CT	238	2	0.6	7	0	2	3
E	Baseline	nc	nc	nc	nc	nc	nc	nc
	Hg-CT	nc	nc	nc	nc	nc	nc	nc
F	Baseline	132	11	0.9	1	0.4	0.1	0.03
	Hg-CT	153	16	0.9	1	0.2	0.1	3
G	Baseline	493	1	0.7	1	0.9	1	0.2
	Hg-CT	177	2	0.6	1	0.05	1	0.2
H	Baseline	148	16	2	5	1	0.1	0.1
	Hg-CT	253	2	2	2	1	0.2	0.2

Summary – Under conditions studied

- There is a general increase in the amount of Hg found in the ash collected from the facilities, during Hg-CT operation
  - More Hg is from in the ash collected at the FF than the SDA
  - All other metal don't exhibit increased concentration in the ash, except for Se at Facility E
- 40°C over 30 days
  - Hg is stabilized in the ash by the Hg-CT
  - Se appears to be the most volatile target metal
- 190°C over 1 hour
  - Most metals are not stabilized in the ash by the Hg-CT, except the FF collected ash of Facility D
- 1200°C over 5 min
  - Up to 100% Se is thermally released from ash
  - Up to 80% Hg is thermally released from ash
  - Up to 50% As is thermally released from ash
  - Up to 40% Cd is thermally released from ash
  - Up to 30% Ni and Pb are thermally released from ash

Summary – Under conditions studied

- Leaching is minimal (<1%) for Hg
  - Hg-CT reduces Hg leaching further (<0.1%)
- Most easily leached metal is Se, followed by Cd
  - Even so the ash leaches <10% Se from the ash
- Microbial activity increases Methyl-Hg for all ash tested
  - Under ideal methylating conditions. Actual disposal environment would need to be simulated for true methylation potential
- Microbial activity decreases Cd and Pb mobility
  - Total dissolved Hg mobility is decreased, but most likely due to Methyl-Hg production (association to particulates)