Mercury Hot Topic Hour
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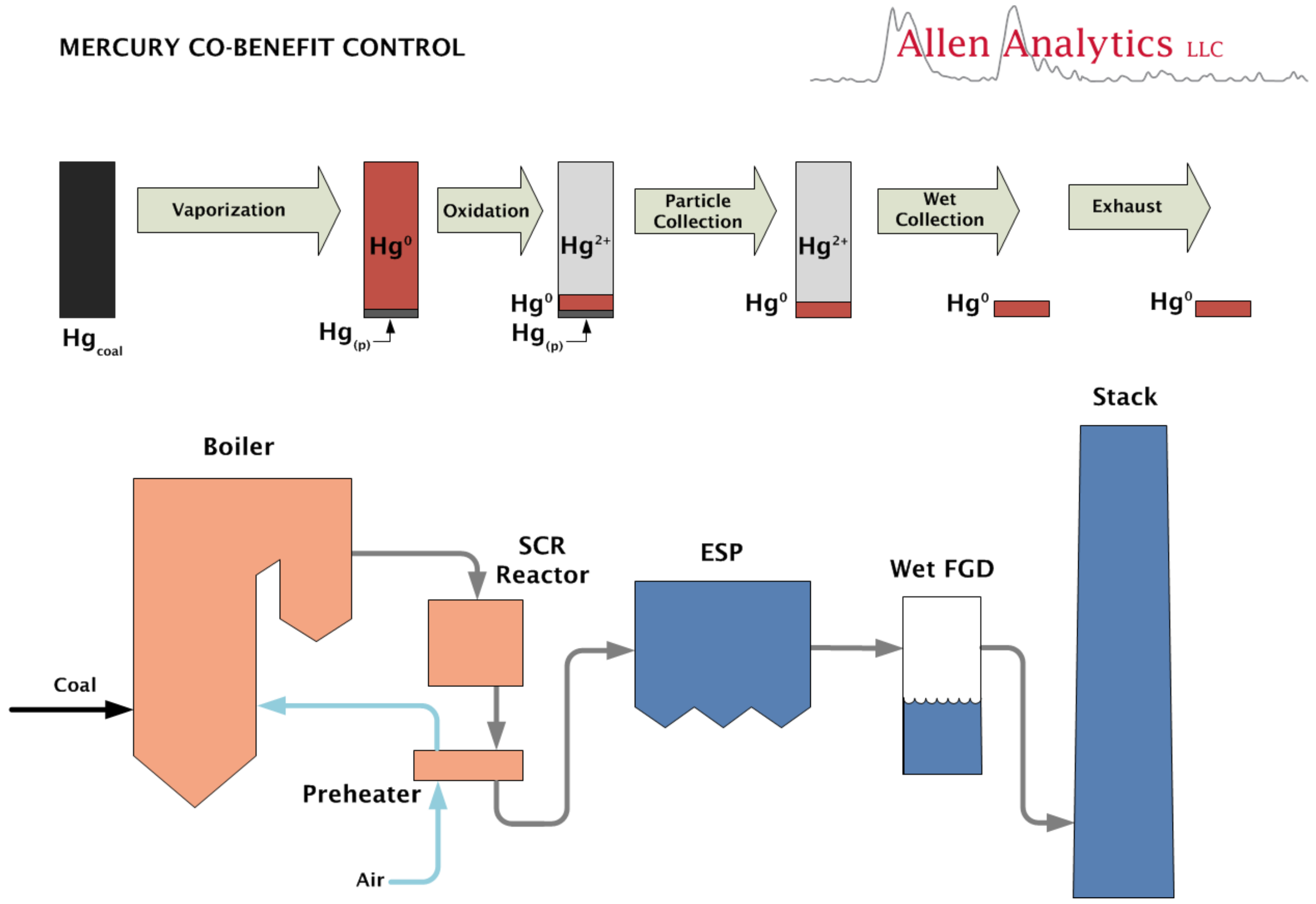
Lessons from Forty Plant-Months of “Co-Benefit” Mercury Abatement Using Existing Pollutant Control Equipment, J. O. Allen, M. B. Looney, and C. A. Tyree, EUEC 2011

Dissolved Metals Concentrations in FGD Wastewater Correlate with FGD Oxidation State, J. O. Allen and C. A. Tyree, Paper #99 MEGA Symposium 2012

Two Surveys

- Hg Emissions and Process Variables
  - 11 flagship coal-fired units
  - 347 plant-months of data
  - What are Hg emissions with existing equipment?
- Trace Metals in FGD Liquor and Process variables
  - 14 flagship coal-fired units
  - 4-months of weekly sample collection
  - What are trace metal concentrations in FGDs?

Hg Oxidation and Wet Capture



- Processes across multiple units that are largely unengineered and uncontrolled for Hg

Hg Emission Survey Method

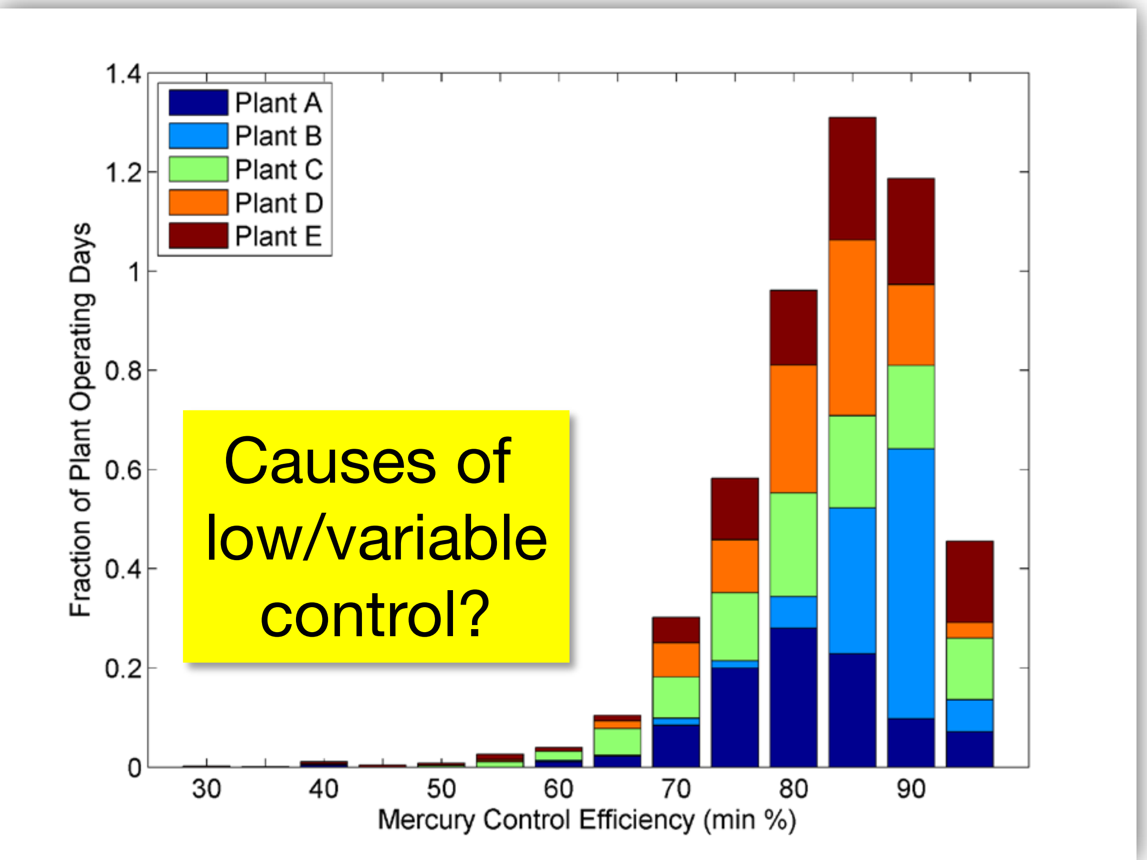
- Retrieve operational and emissions data
  - Approx. 40 variables for each plant: Boiler, SCR, ESP, wFGD, CEMS
  - 347 plant-months of data in 2009 - 2011
  - 1-min data, ~$6x10^8$ data points
  - Hg and Cl inputs from coal deliveries
- Robust quality assurance
  - Inspected every data point
  - Screened CEMS calibrations
  - Compared high emission events with plant logs
- Retrospective Data Analysis
  - Develop physically consistent explanations
- Evaluate MATS Compliance Strategies

Co-Benefit Hg Control

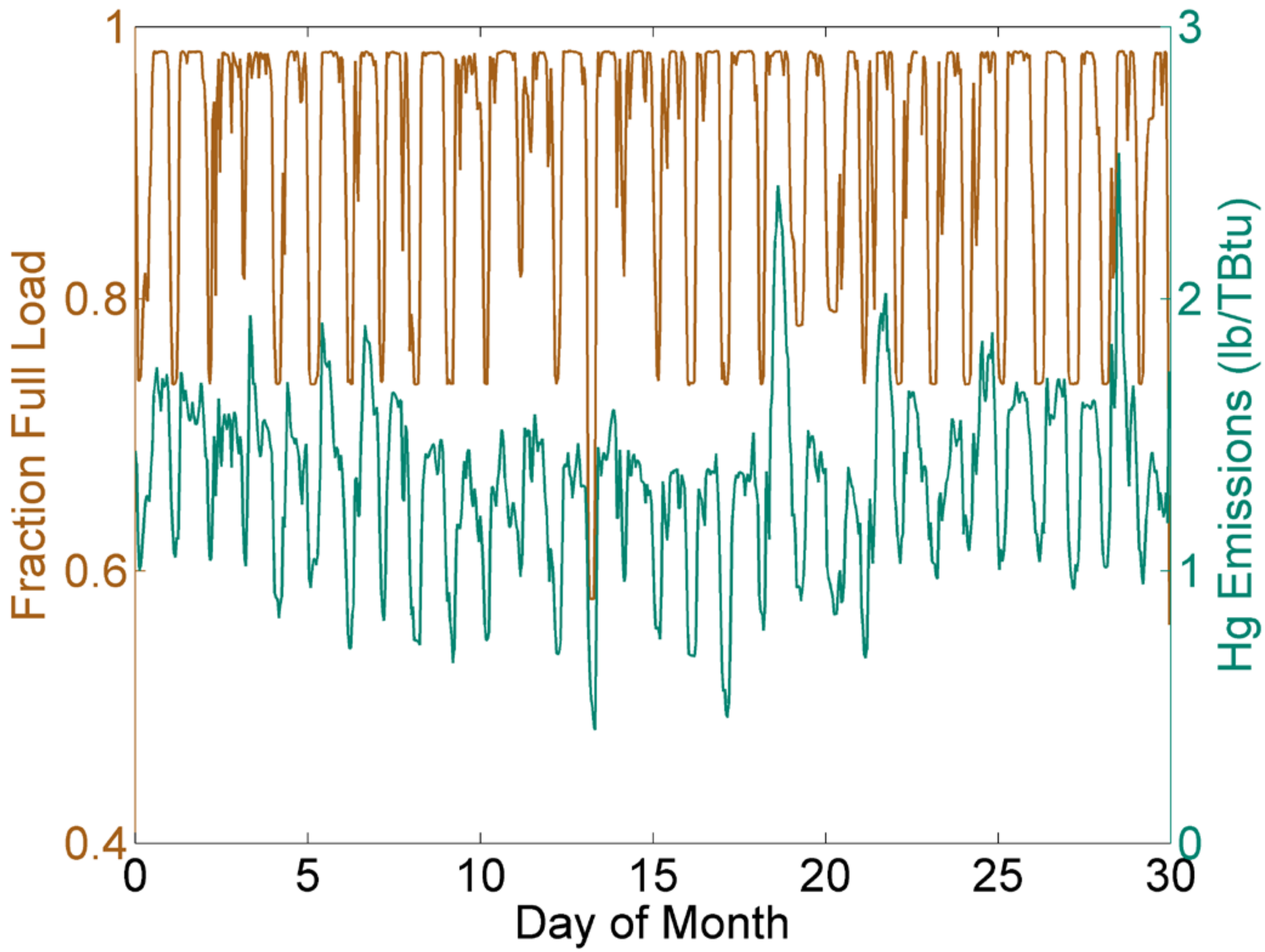
Five Flagship Coal-Fired Units, 2009-2010
Single Boiler with SCR, cold-side ESP, wet FGD
Central Appalachian Eastern Bituminous coals

Hg Control

- Average 85.5%
- > 90% on 34% of study days
- < 80% on some days for every plant

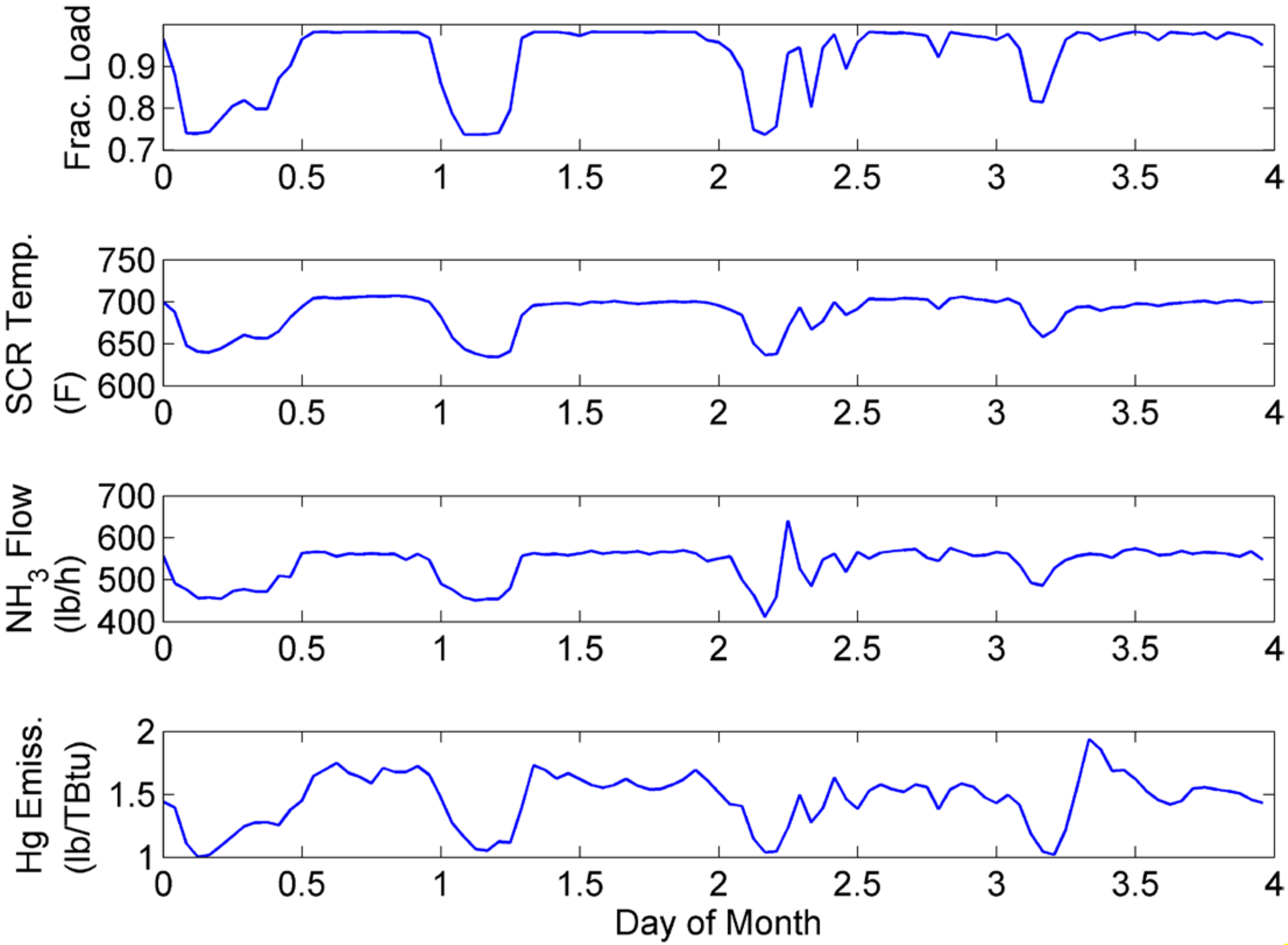


Hg Control Varied with Load



Load affects downstream AQCS; likely Hg oxidation in SCR

Load Affected SCR Operation



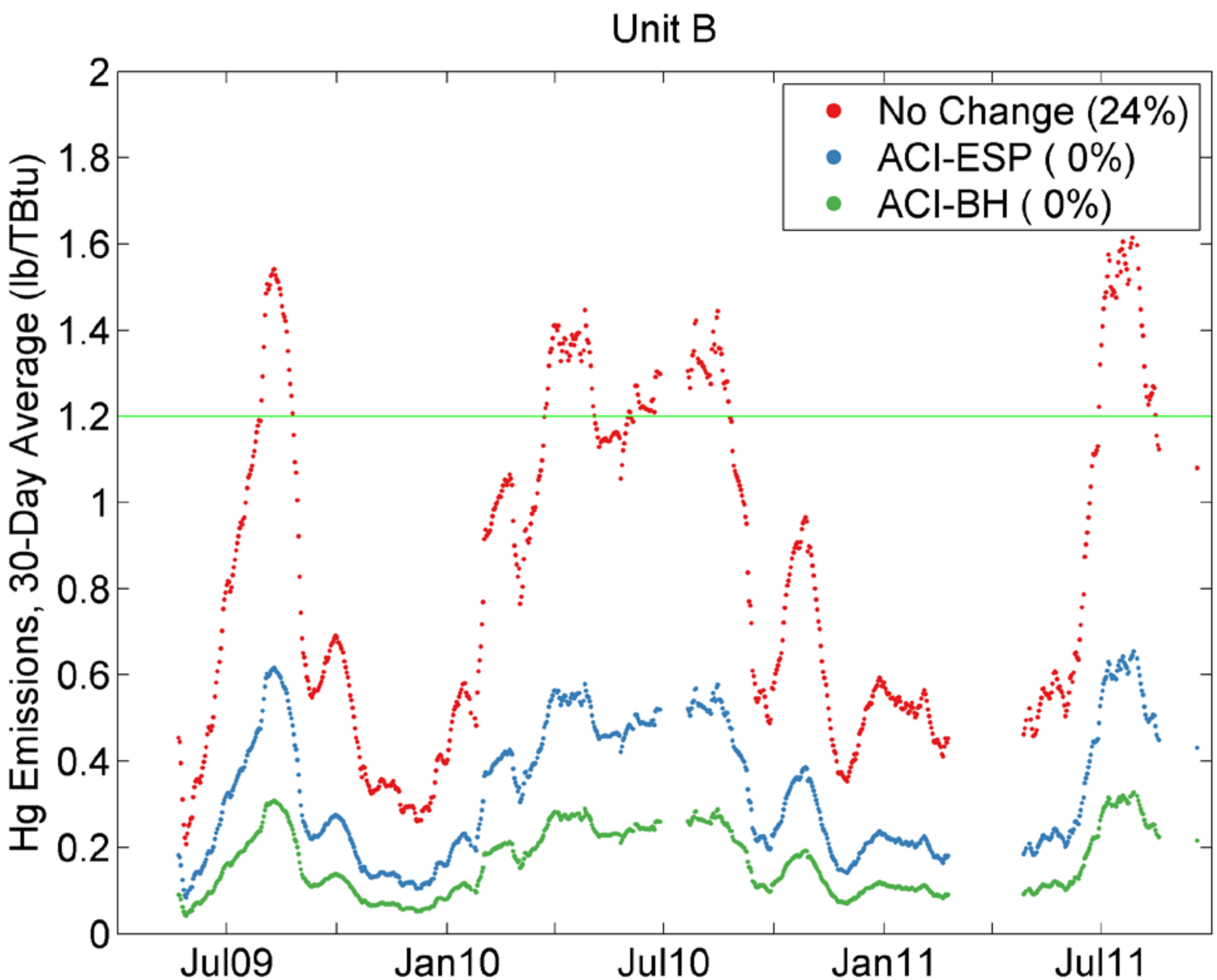
We suggest that Hg oxidation decreases at full load due to:
↓ residence time, ↑ NH_3 flow, ↑ SCR temperature

MATS Compliance Strategy

Unit		Hg Emission Average (lb/TBtu)				
	N 30-d Averages	Frac > Limit	Mean	99^{th} Prctile	Max	Min Ctrl
A	360	0.20	0.76	1.61	1.69	0.29
B	724	0.24	0.83	1.58	1.64	0.27
C	915	0.26	0.92	1.90	1.92	0.38
D	883	0.33	0.97	1.61	1.98	0.39
E	695	0.91	2.97	9.35	9.55	0.87
F	922	0.05	0.79	1.34	1.47	0.18
G	600	0.17	0.81	1.43	1.45	0.17
H	739	0.37	1.15	2.02	2.12	0.43
I	439	0.11	0.68	1.79	1.83	0.34
J	780	0.04	0.71	1.29	1.35	0.11
K	666	0.14	1.00	1.35	1.38	0.13

All units had mean emissions < 1.2 lb/TBtu,
but exceeded 30-d average for at least 4% of days.

MATS Compliance Strategy for Unit B



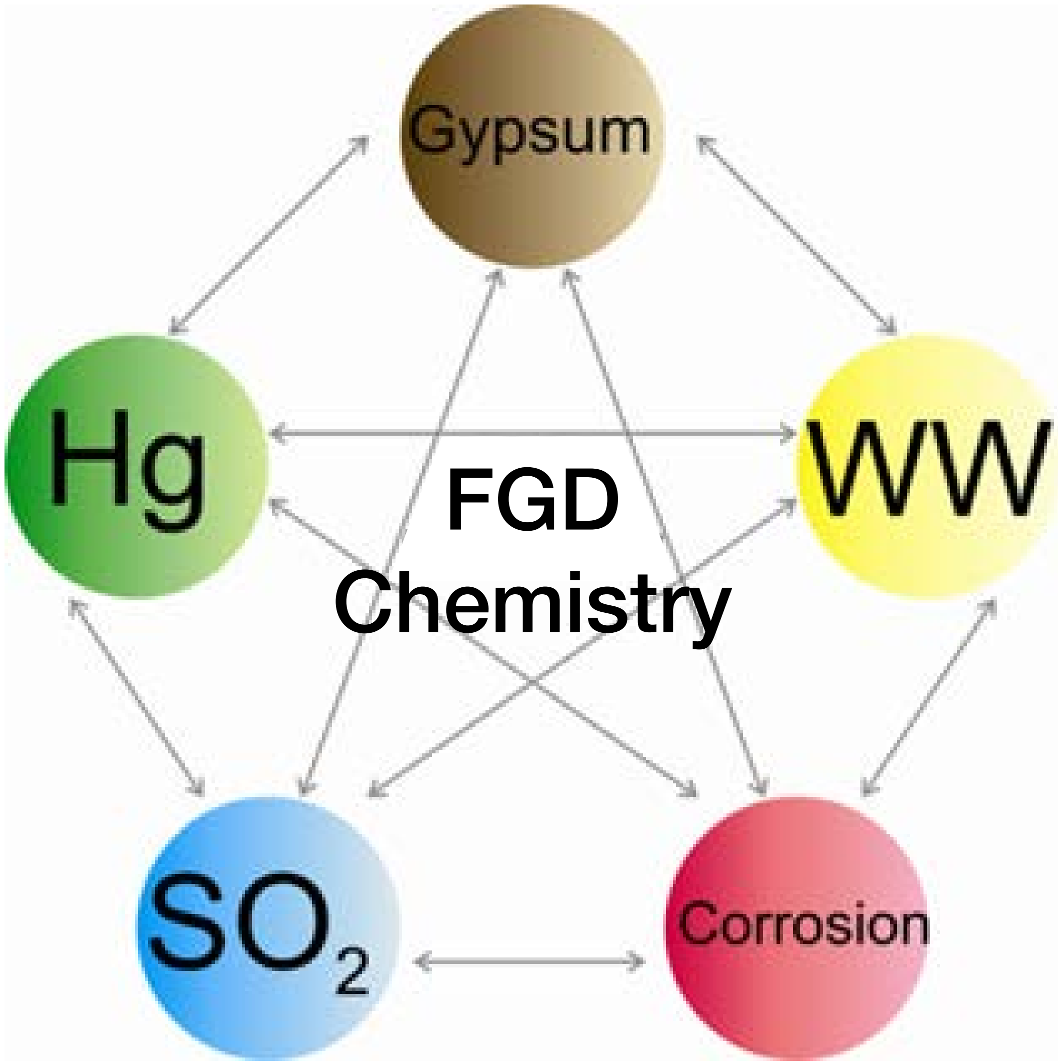
Show historical emissions with control options.

Survey of FGD Liquors

- 14 flagship coal-fired units
  - Eastern Bit. and PRB coals
  - Chiyoda and Advatech FGD Technologies
  - Multiple sources of limestone

- Limestone and FGD liquor samples collected weekly for 4 months; analyzed for
  - pH, ORP, $S_2O_8^{2-}$, Cl^-, Br^-, NO_3^-
  - Ca, Mg, Fe, Mn, Hg, etc.
  - Speciated Se.

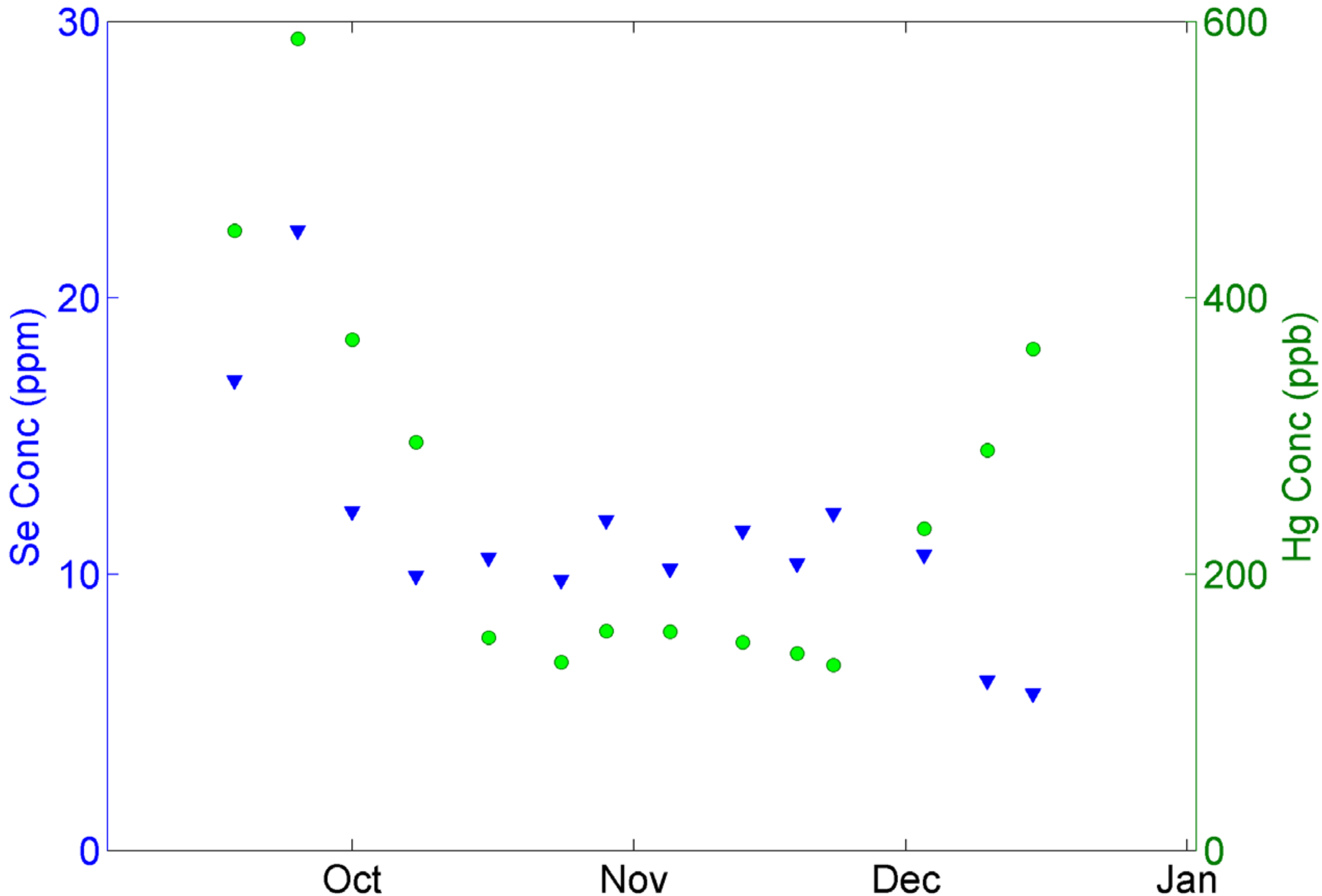
Central Role of FGD Chemistry



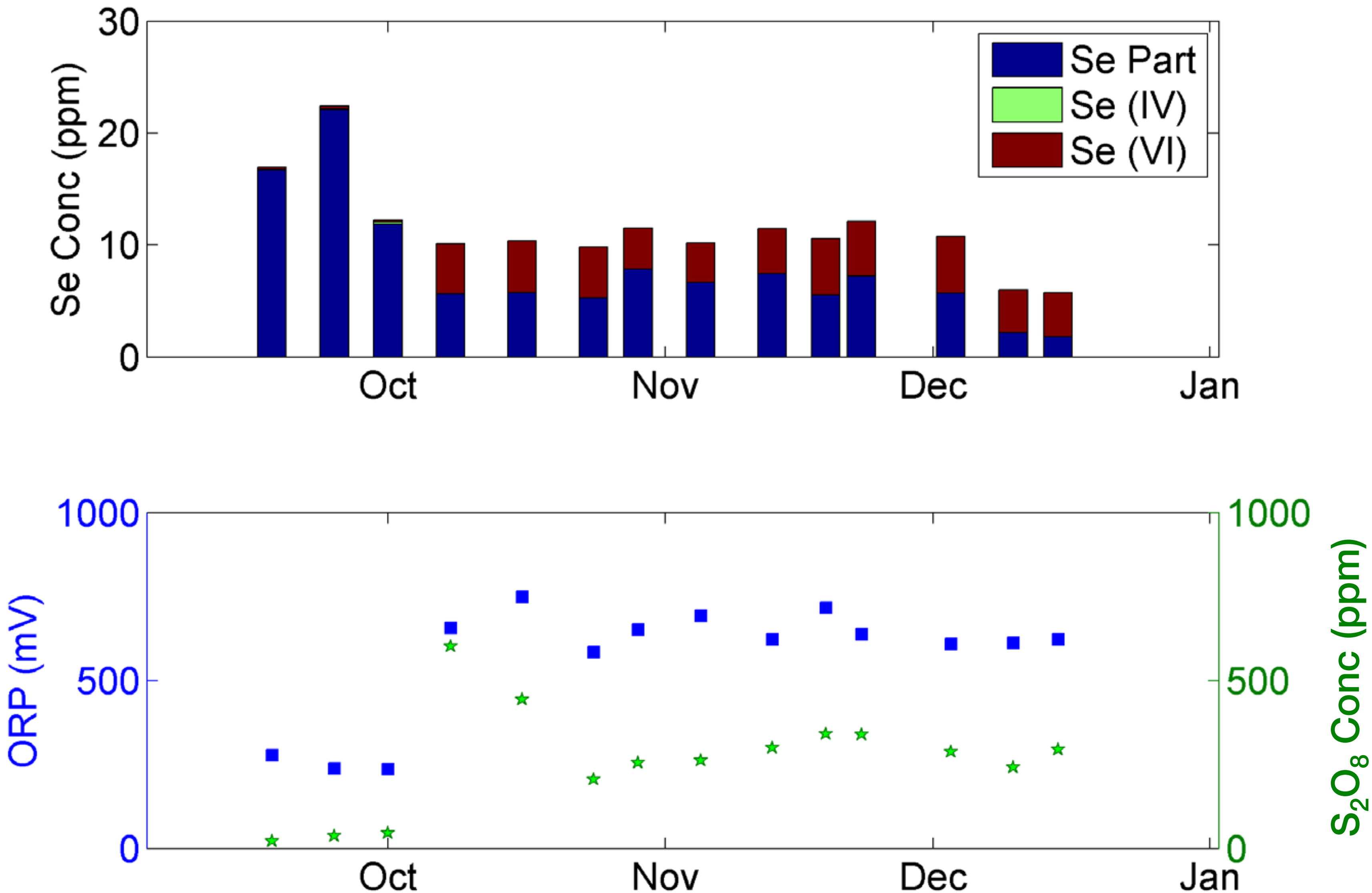
Complex System

- FGD Liquor Chemistry
  - FGD technology
  - FGD operation: oxi air flow, level
  - Flue gas: Sulfur, NO_x, Cl, Hg, Se, ash
  - Limestone trace species
- Difficult to recreate in laboratory
- Differs between ‘sister’ units

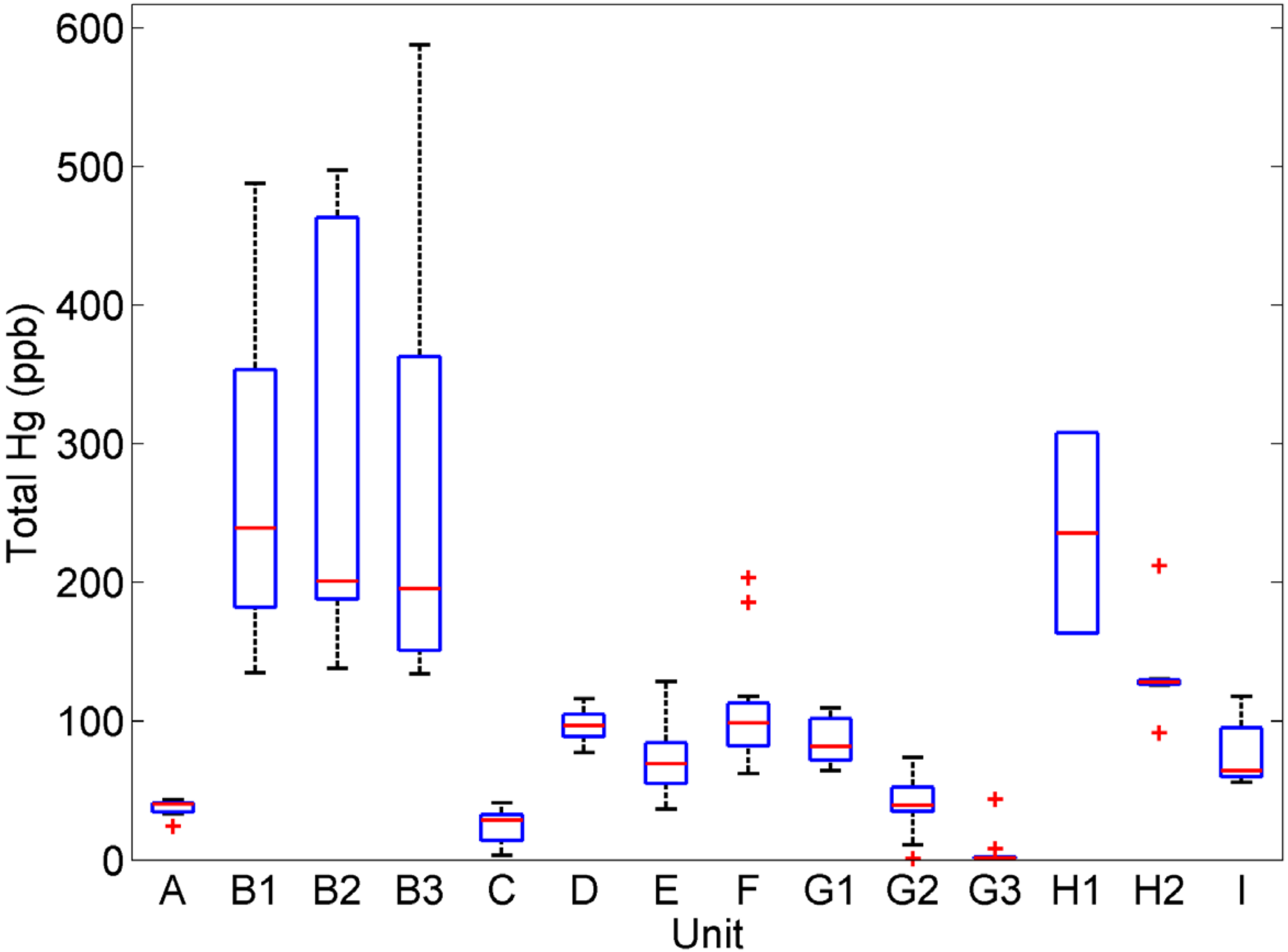
Variable Se and Hg – Unit B3



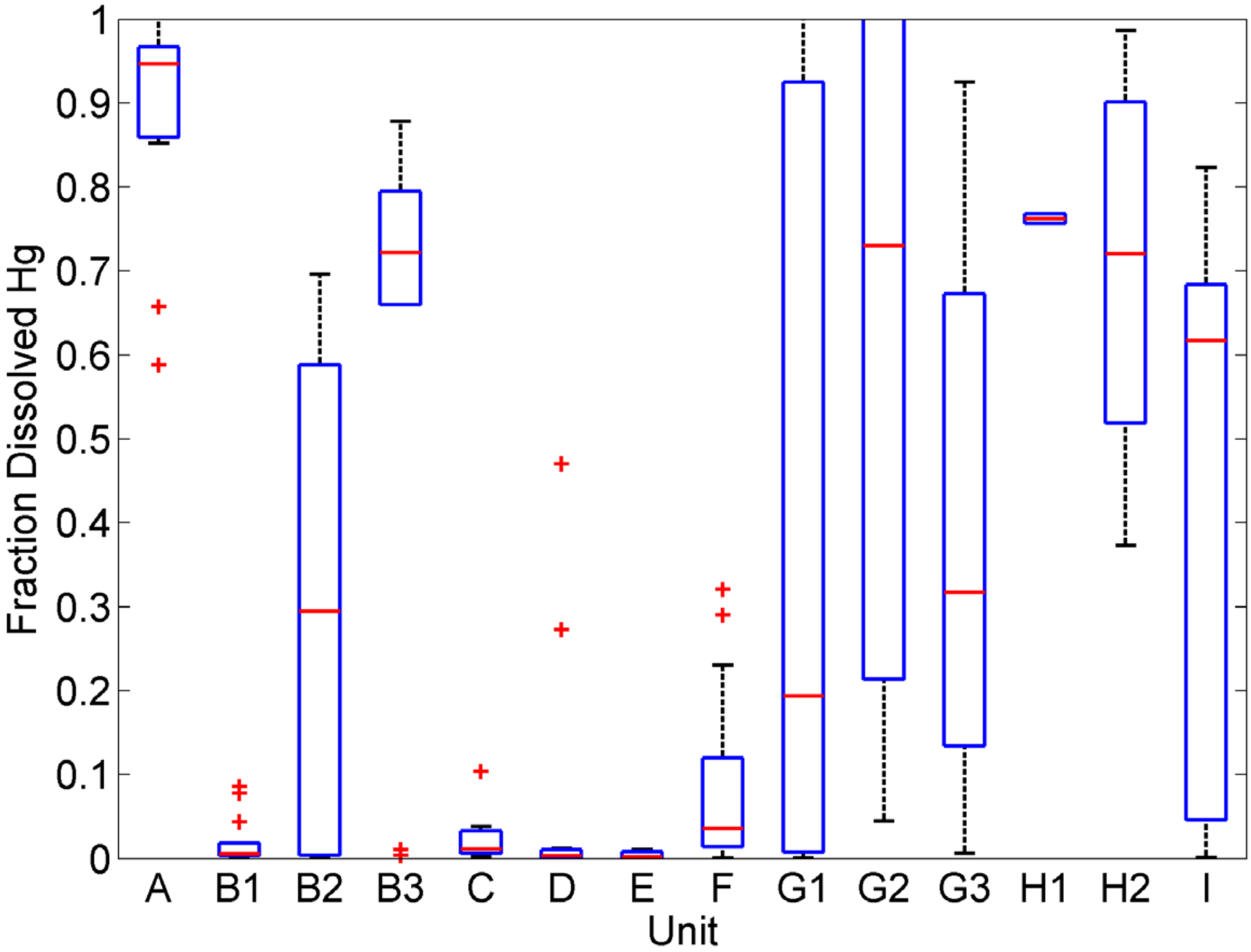
Variable Se Speciation – Unit B3



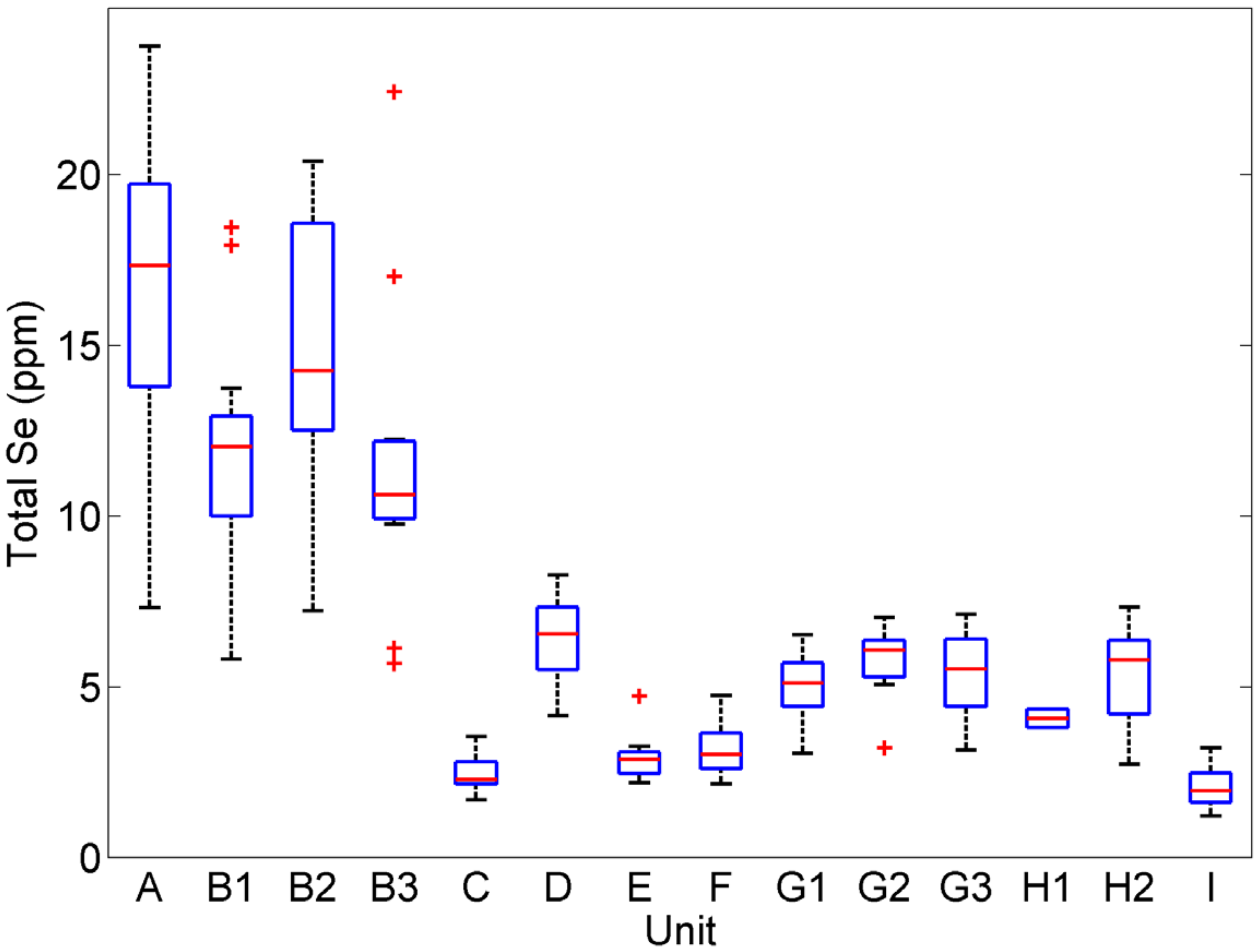
Variable Total Hg



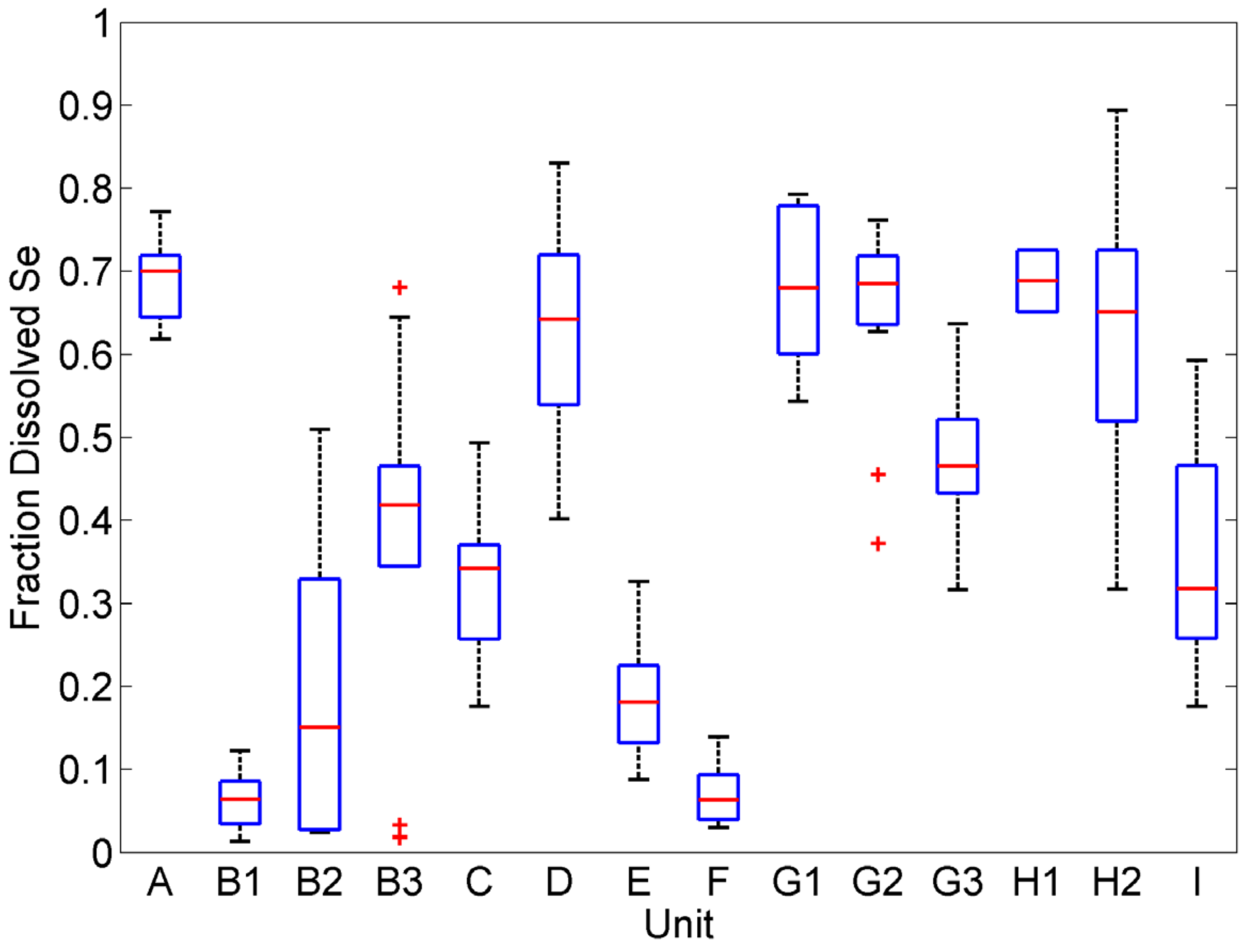
Variable Dissolved Hg



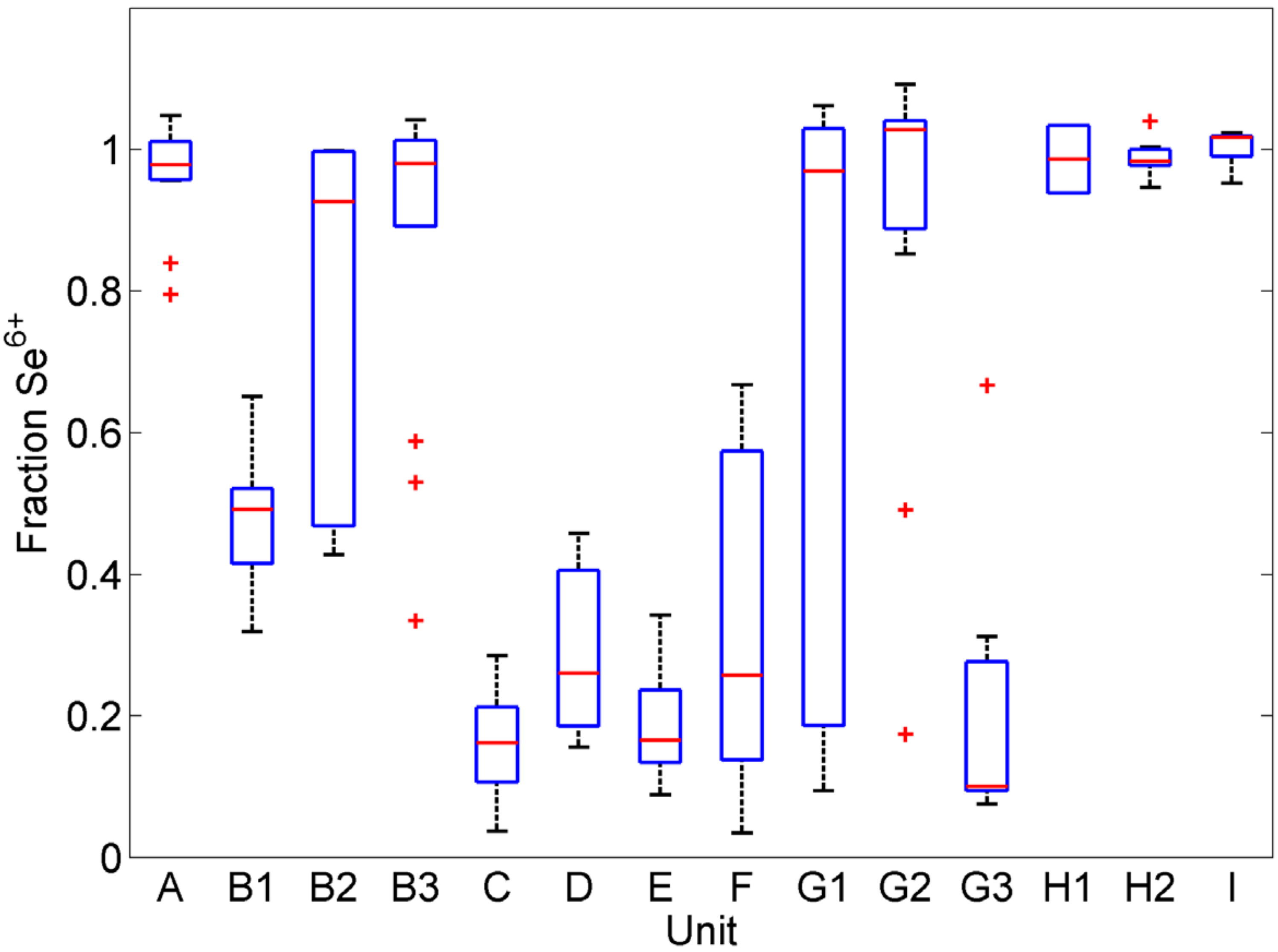
Variable Total Se



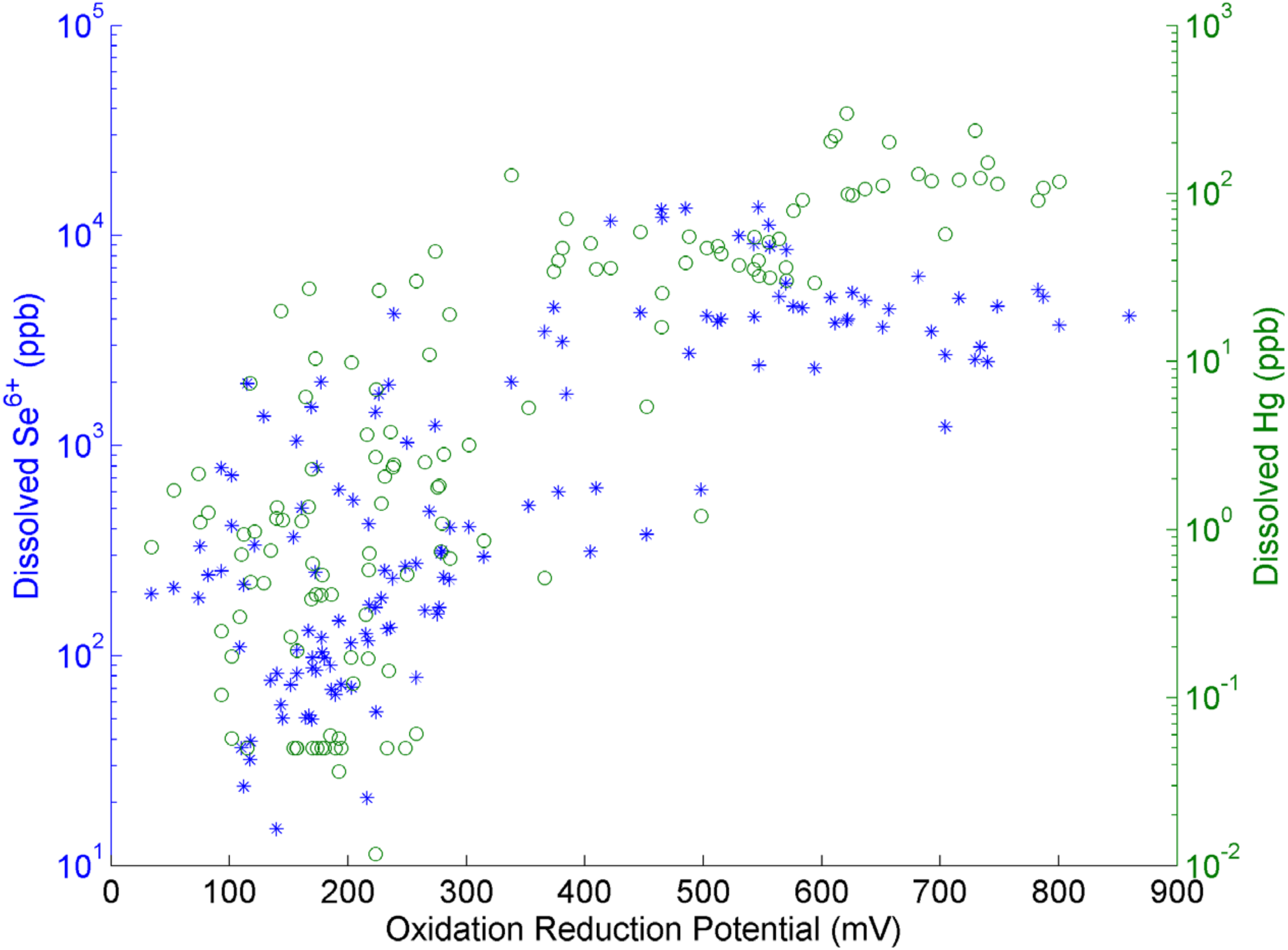
Variable Dissolved Se



Variable Se Speciation



Role of ORP

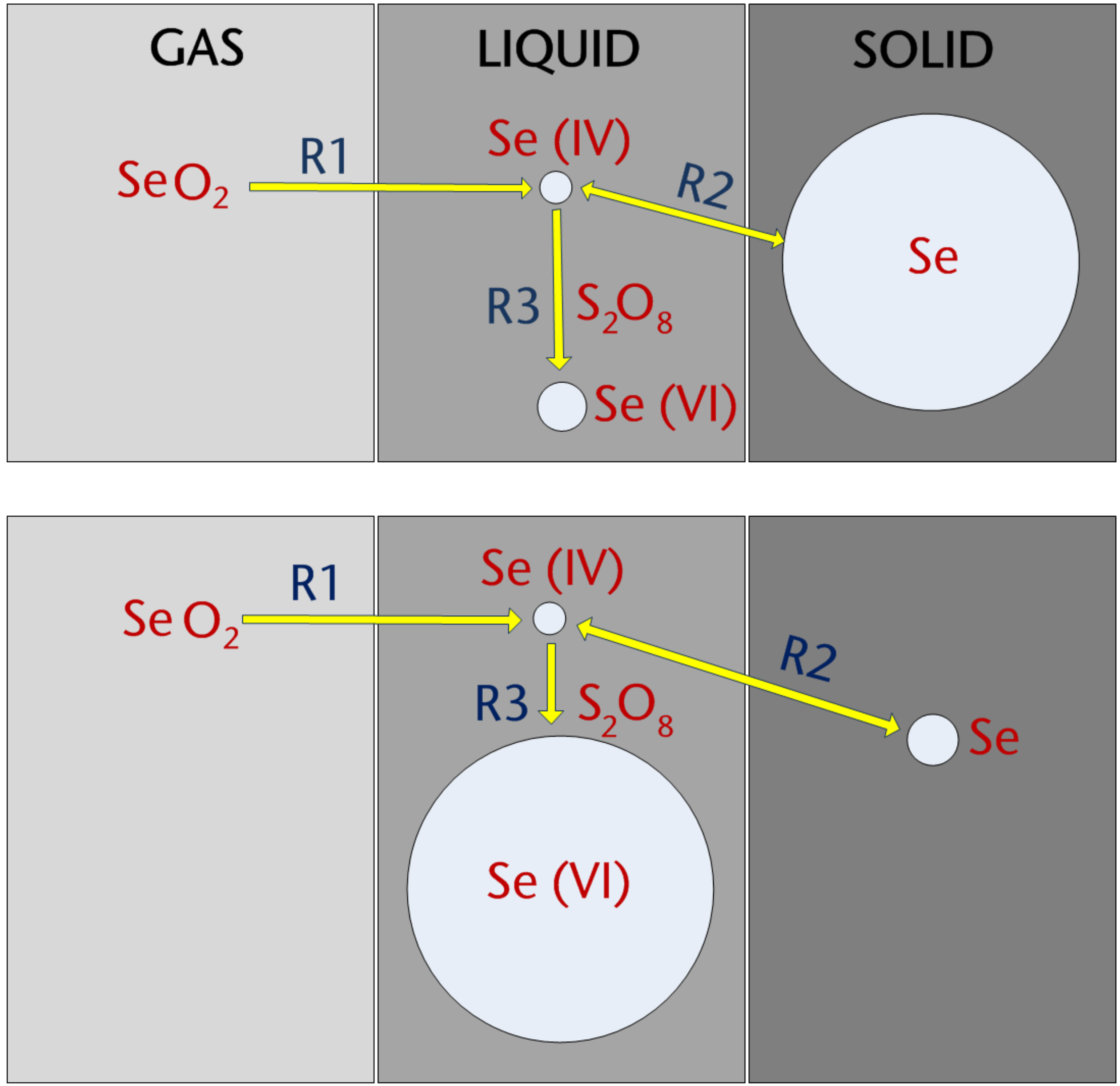


Dissolved Se^{6+} (ppb)
Dissolved Hg (ppb)
Oxidation Reduction Potential (mV)
10^5
10^4
10^3
10^2
10^1
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
0 100 200 300 400 500 600 700 800 900

Selenium Chemistry

Low ORP

High ORP



Conclusions

- Large survey of FGD liquor chemistry
- Oxidation state is not controlled; ORP varies in the range 30-1,000 mV
- Trace metal concentrations vary
  - Hg: 0 – 100 ppb
  - Se: 80 – 15,000 ppb
  - Se(VI): 15 – 13,500 ppb
- Dissolved [Hg] and [Se] correlated with ORP