Dissolved Metals Concentrations in FGD Wastewater Correlate with FGD Oxidation State

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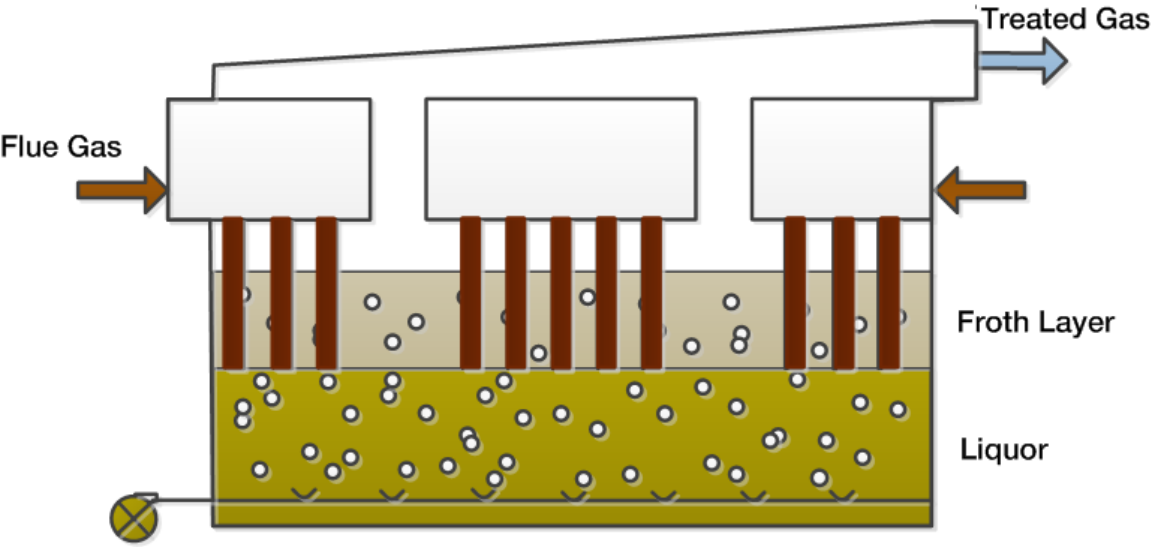
Role of FGD Liquor Chemistry



FGD Liquor Chemistry

- SO_2 Control
- Gypsum Size Distribution
- Corrosion
- Hg Reemission
- Waste Water Composition

Complex System

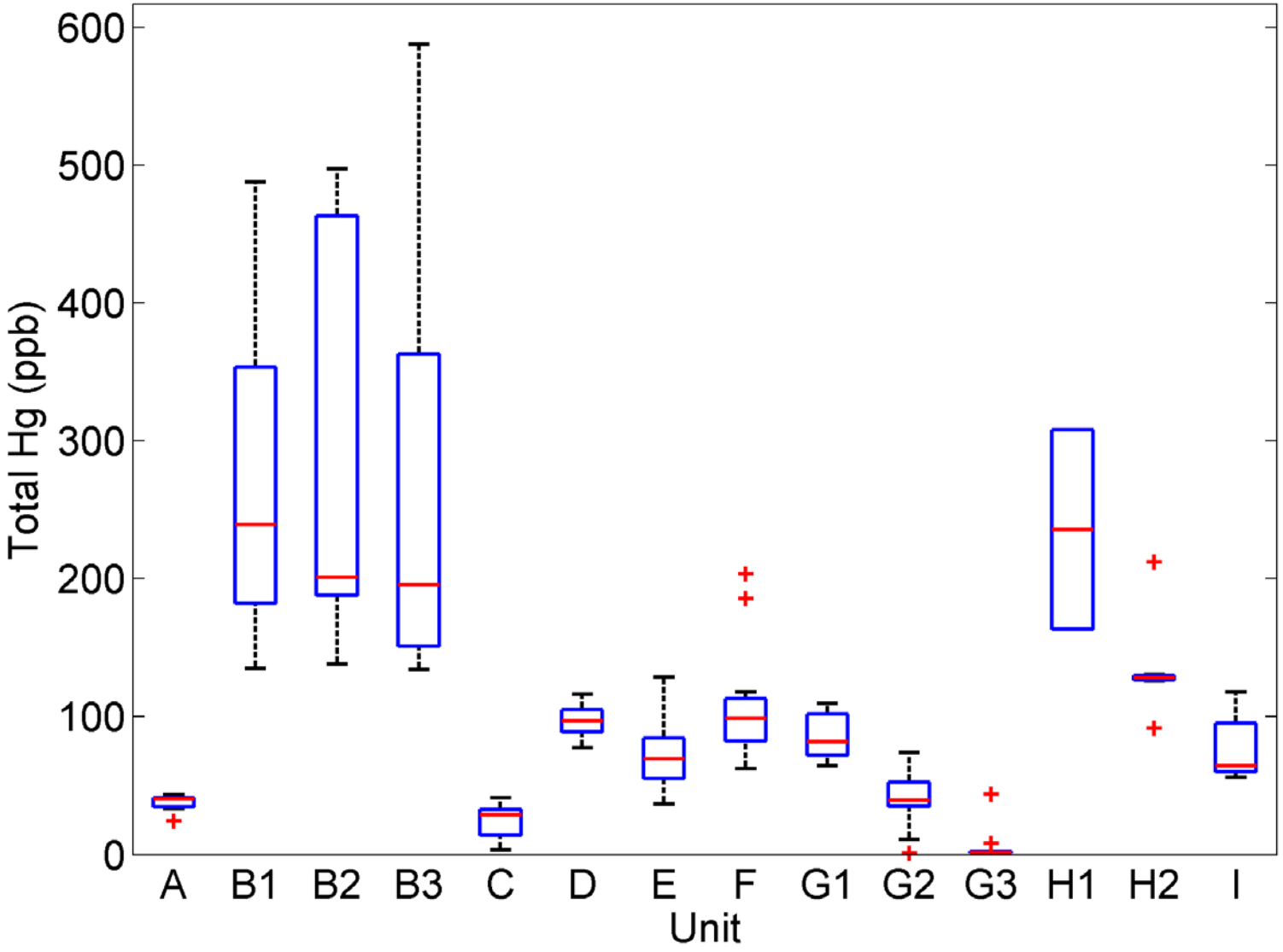
- FGD Liquor Chemistry
  - FGD technology
  - FGD operation: oxi air flow, level
  - Flue gas: Sulfur, NO_x, Cl, Hg, Se, ash
  - Limestone trace species
- Difficult to recreate in laboratory
- Differs between ‘sister’ units

Survey of FGD Liquors

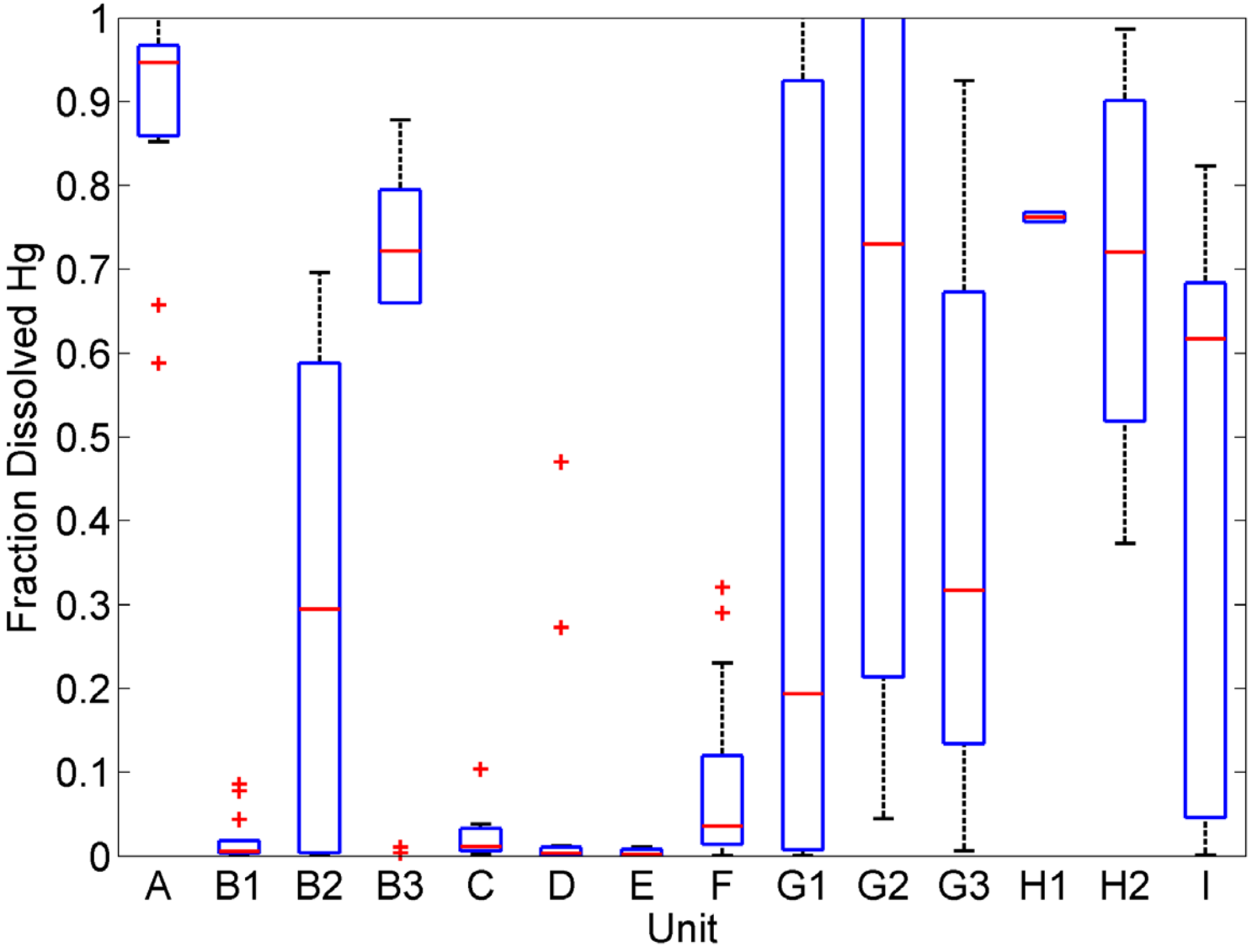
- 14 Southern Company coal-fired units
  - Eastern Bit. and PRB coals
  - Chiyoda and Advatech FGD Technologies
  - Multiple sources of limestone

- 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.

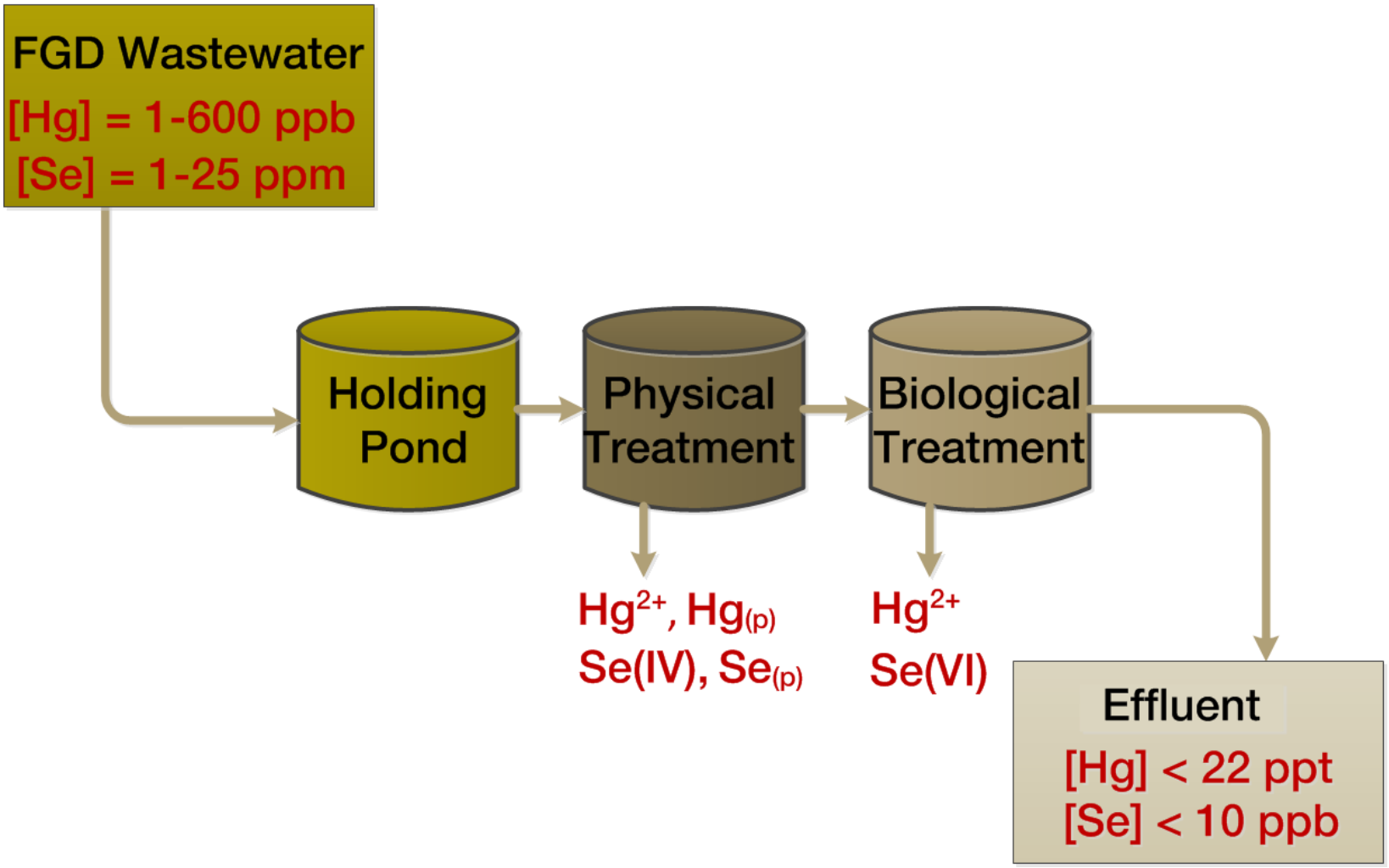
Variable Total Hg



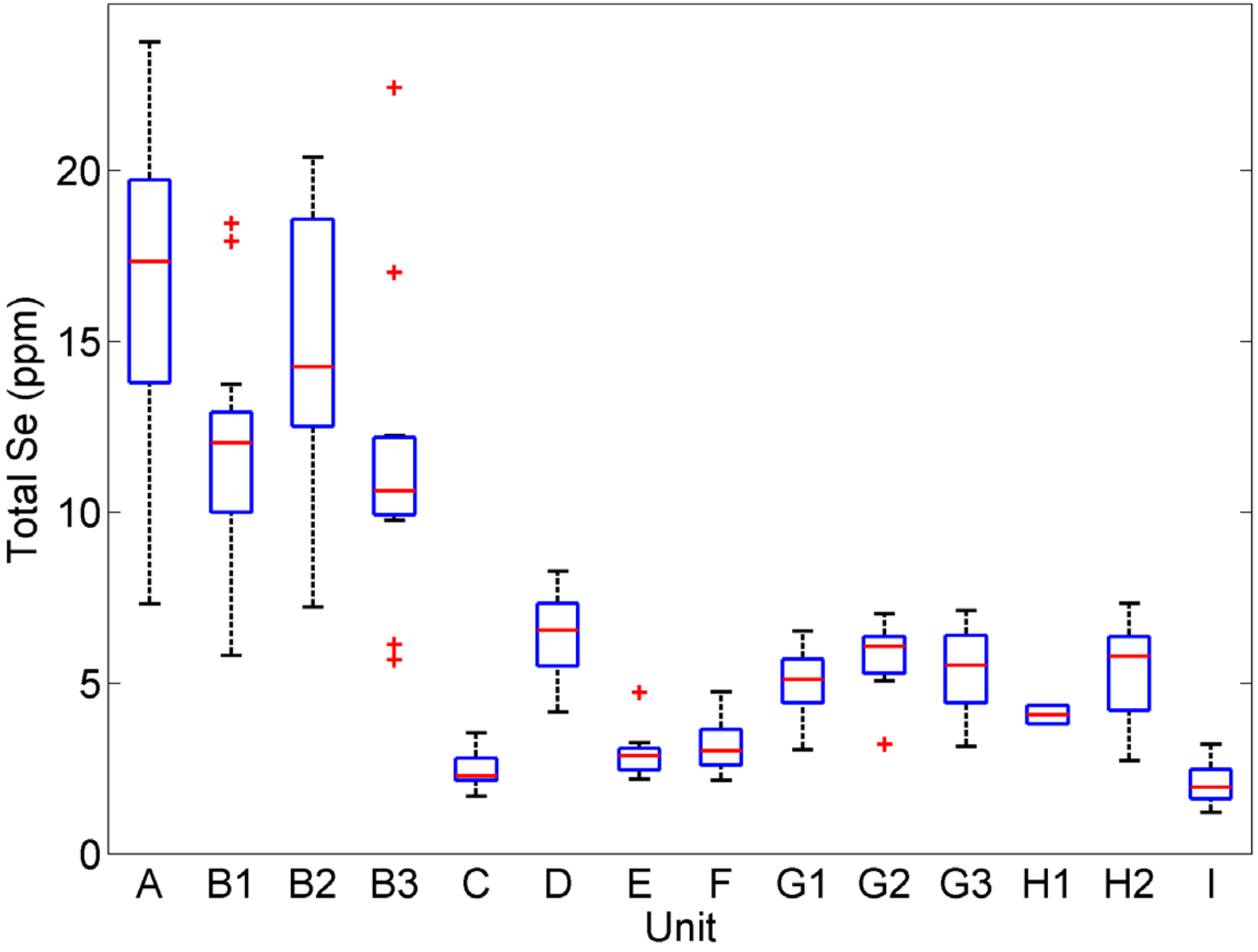
Variable Dissolved Hg



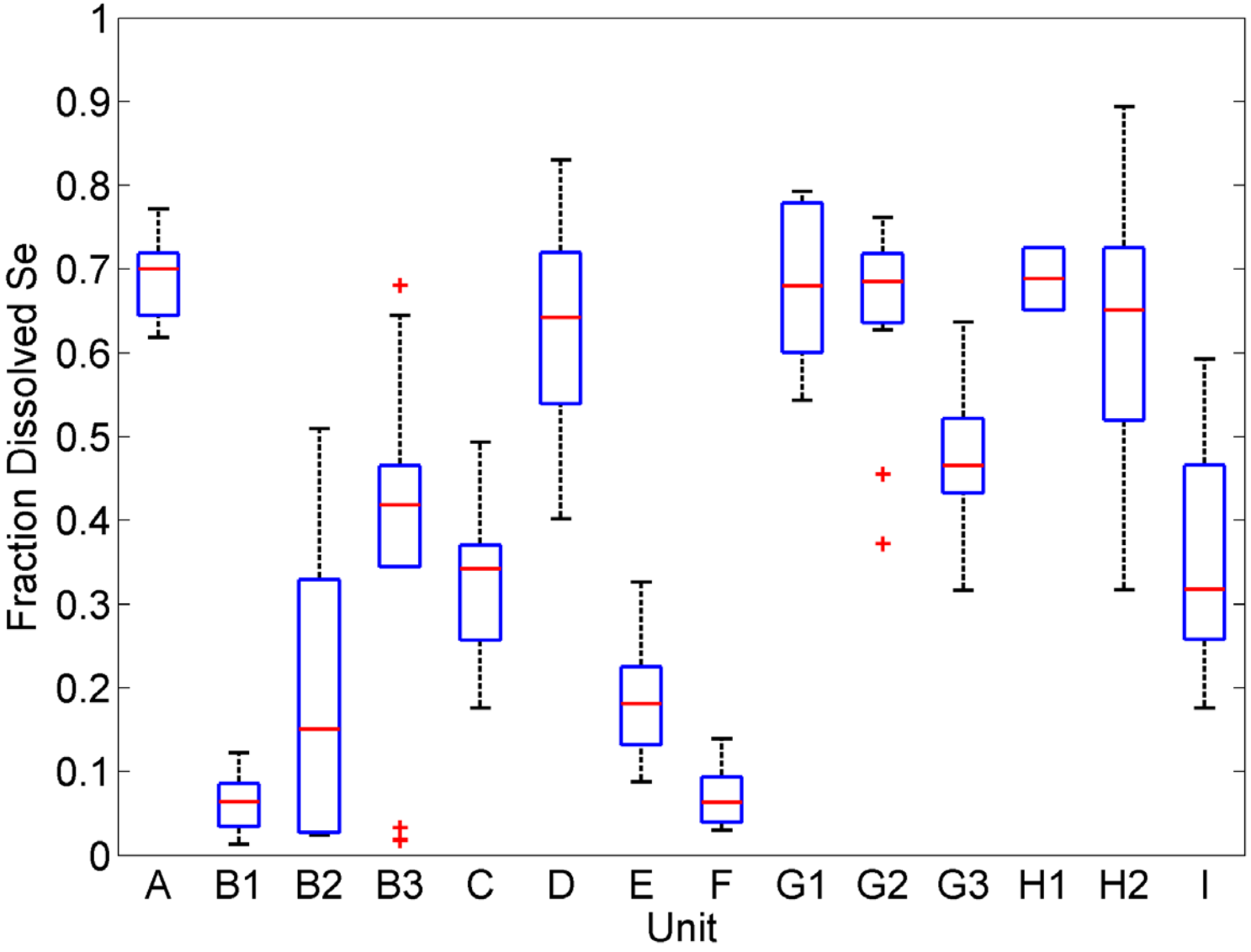
FGD Wastewater Treatment



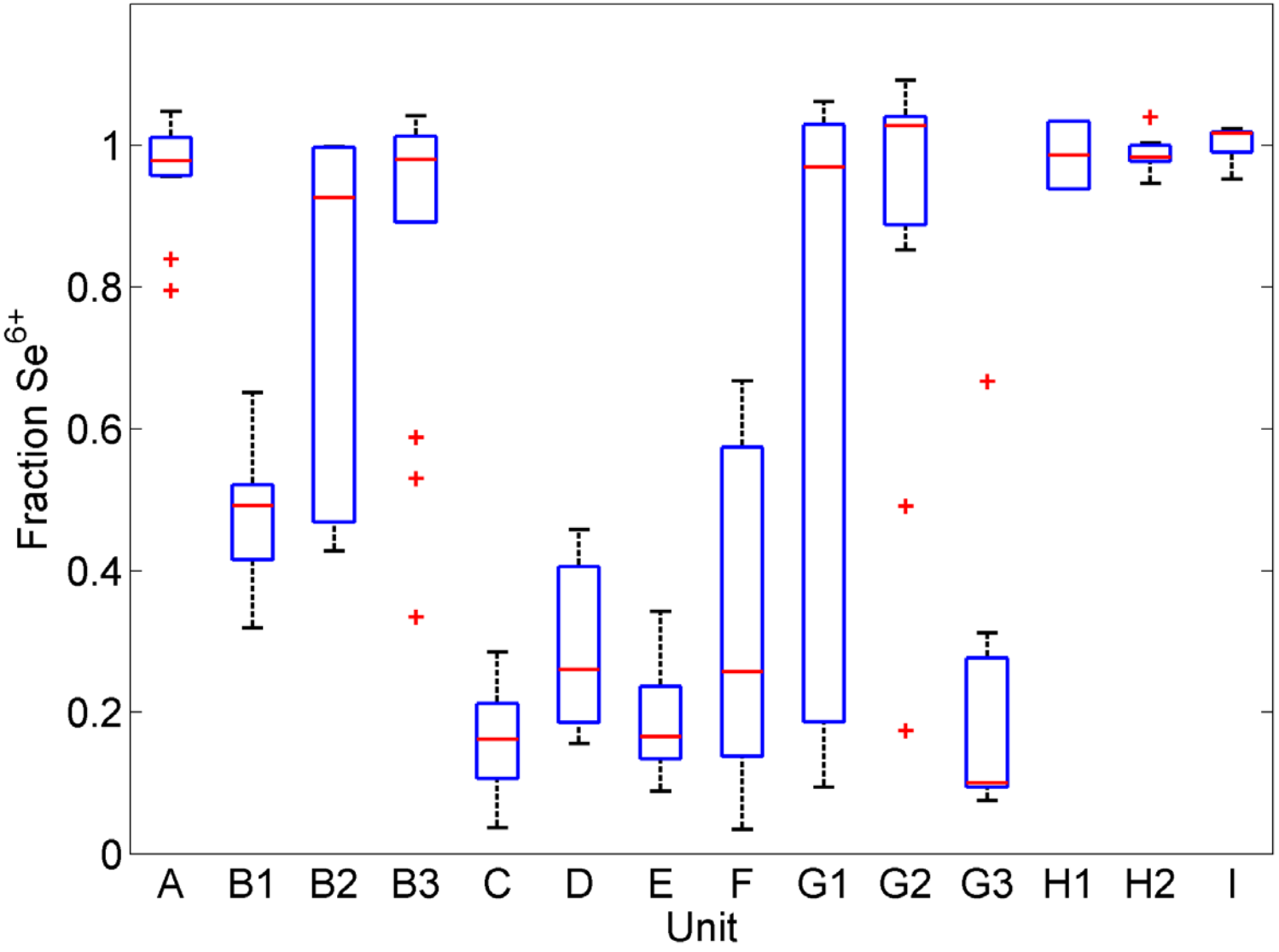
Variable Total Se



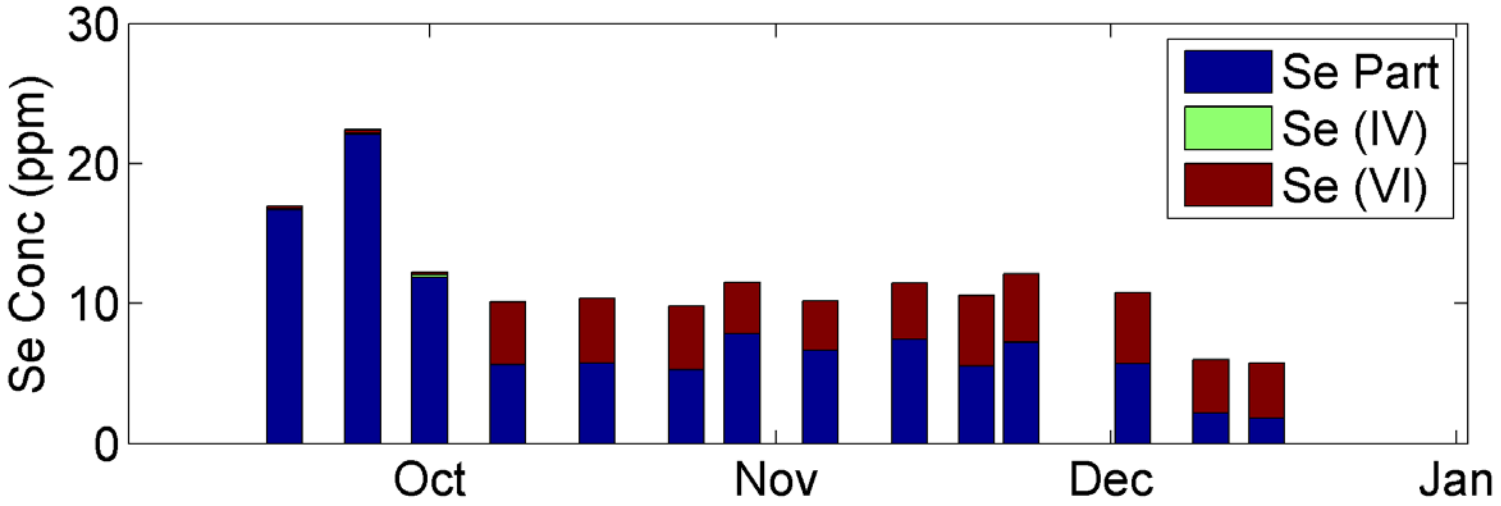
Variable Dissolved Se

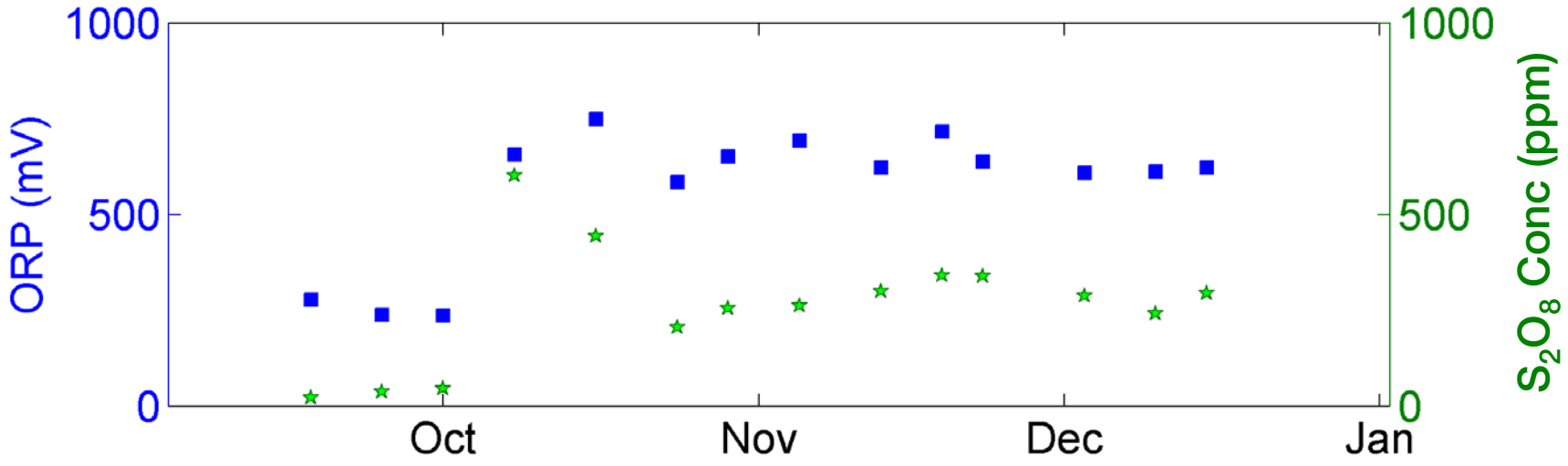


Variable Se Speciation

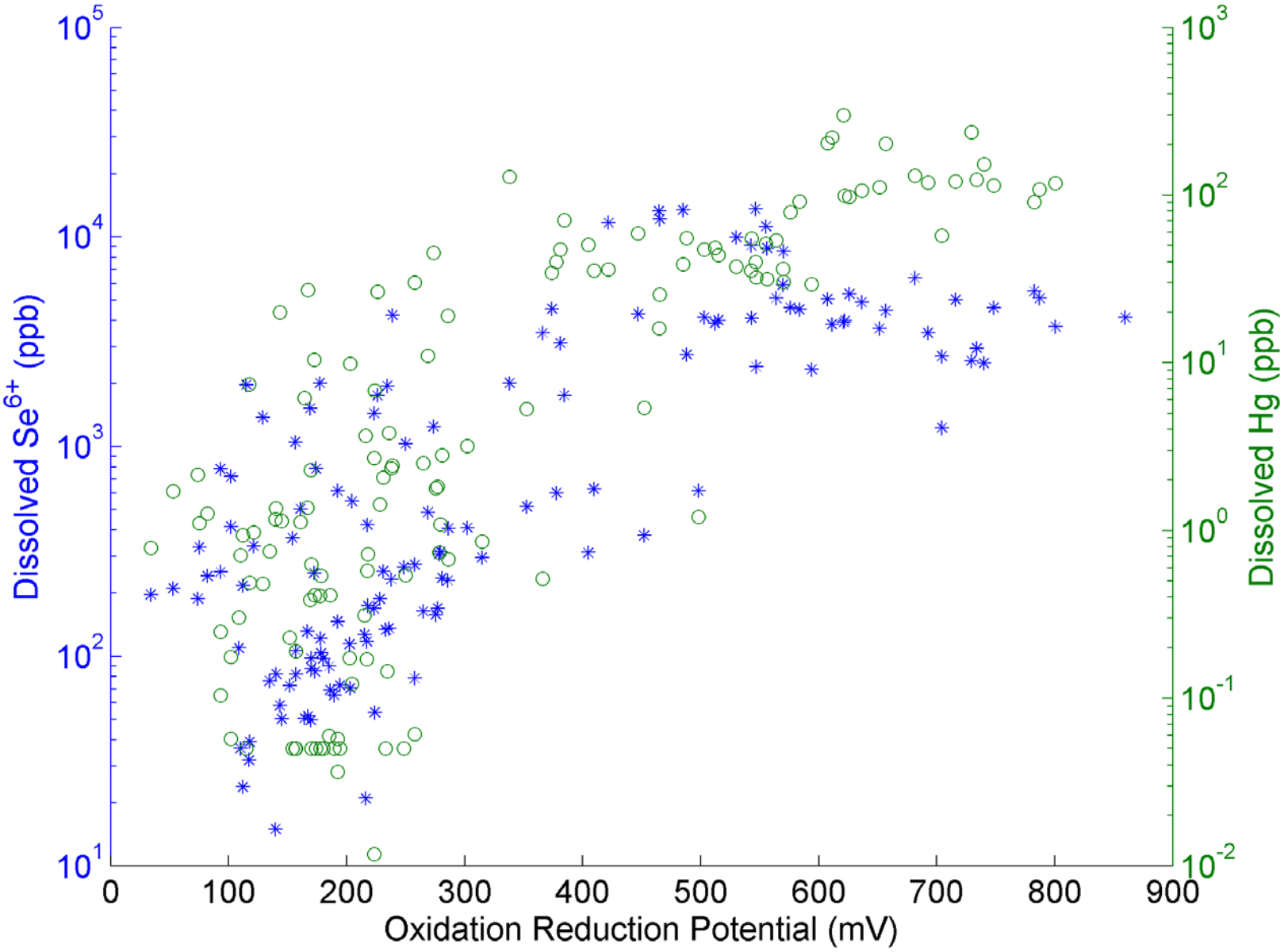


Variable Se Speciation – Unit B3



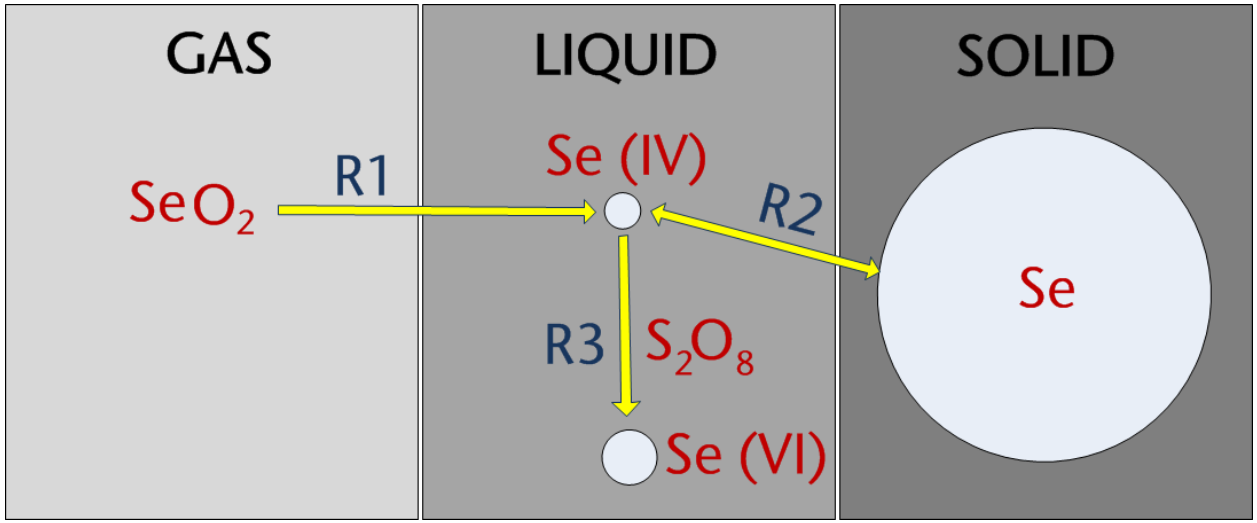


Role of ORP

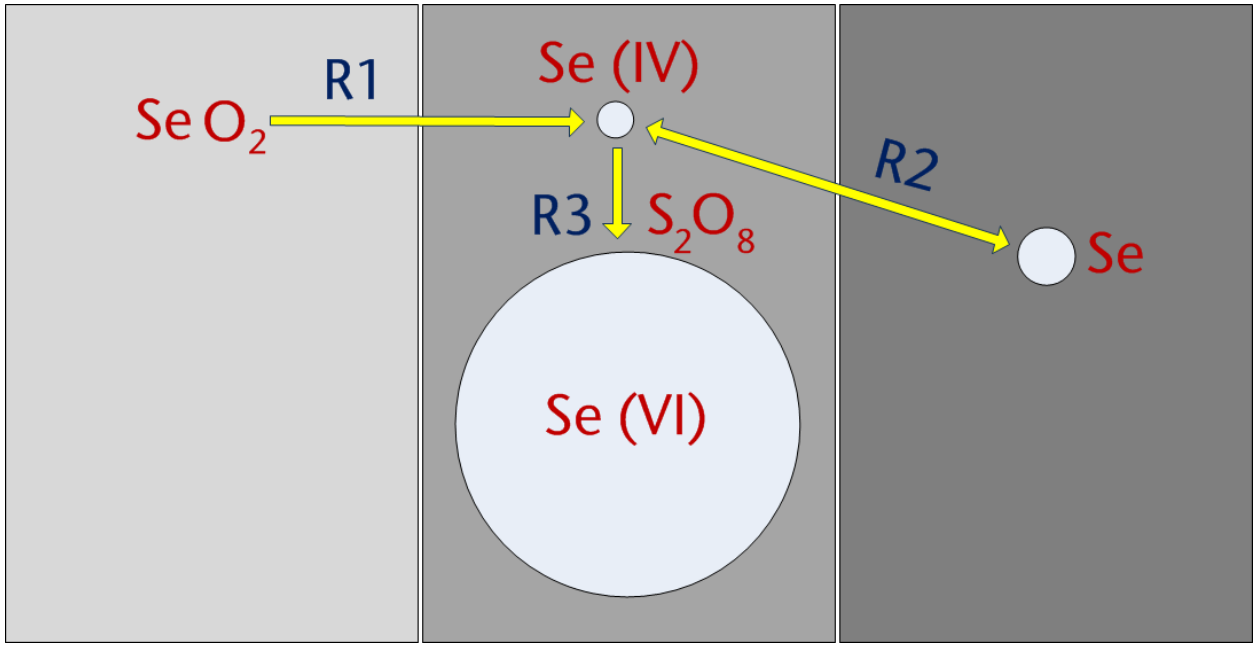

Dissolved Se6+ (ppb)
Dissolved Hg (ppb)
Oxidation Reduction Potential (mV)
10^5
10^4
10^3
10^2
10^1
10^3
10^2
10^1
10^0
10^-1
10^-2
0
100
200
300
400
500
600
700
800
900

Selenium Chemistry

Low ORP



High ORP



Next Steps

- Integrate concurrent plant data
  - Load, opacity, coal analyses, etc.
  - FGD level, flow, oxidation air, etc.
  - SO_2 and Hg CEMS
- Hypothesis testing by
  - Event time series
  - Correlation across data set
- Example hypotheses
  - Range of ORP for good SO_2 control
  - ORP vs. dissolved Se by FGD technology

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

Acknowledgements and Contact

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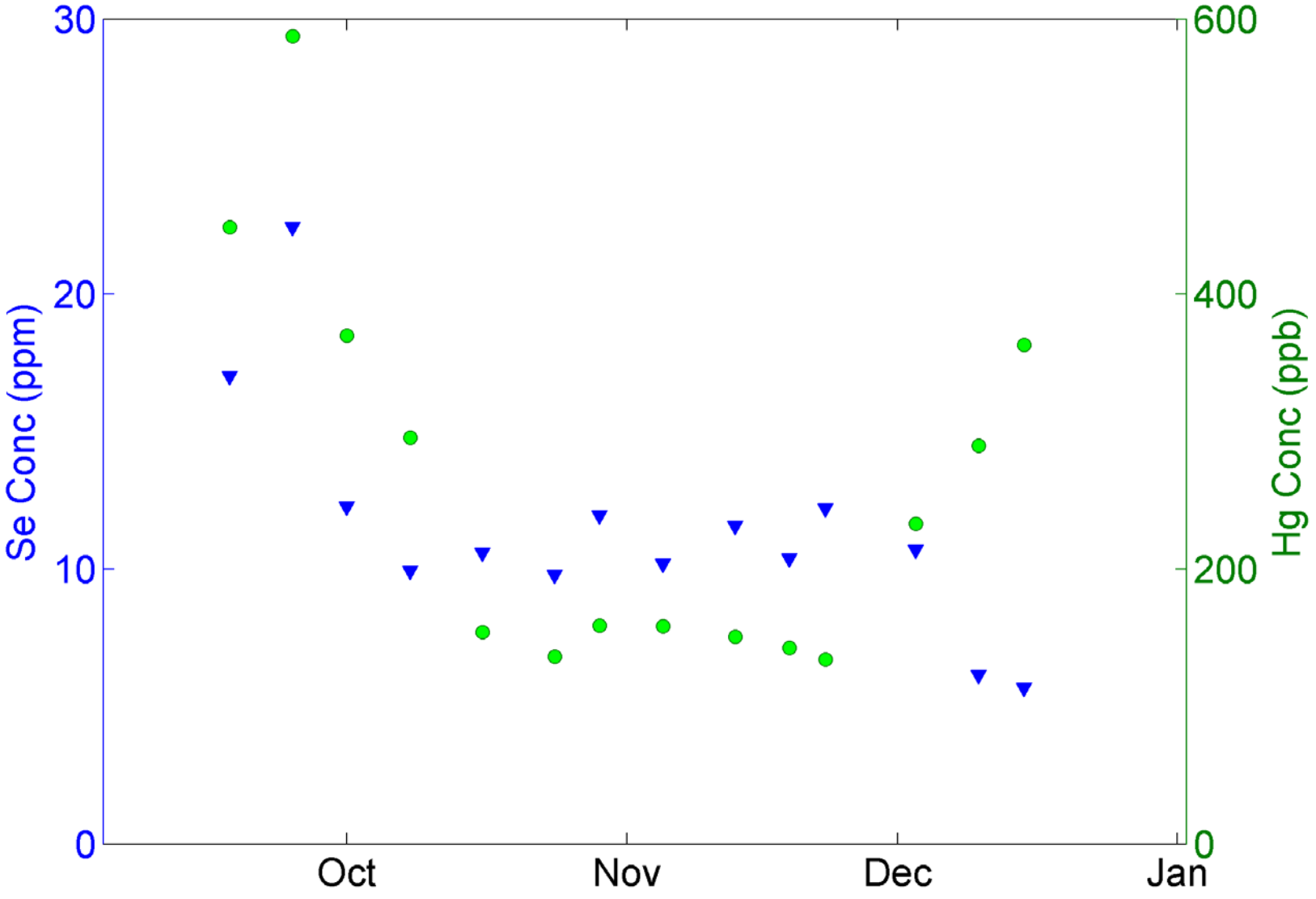
Variable Se and Hg – Unit B3



Wastewater Motivation

Effluent Limits for FGD WW Based on the Performance of Physical-Chemical Treatment Followed by Biological Treatment

U.S. Environmental Protection Agency
Office of Water, Engineering and Analysis Division
August 11, 2011

Pollutant	Daily Max. Limit	Monthly Avg. Limit
Mercury (ng/L)	55	22
Selenium (µg/L)	19	10