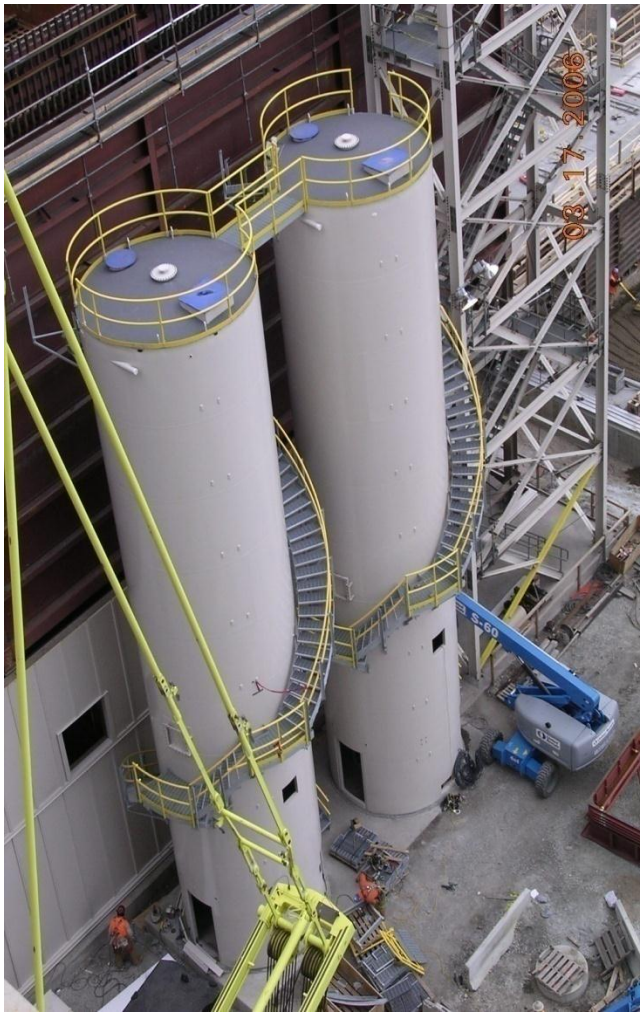

Mercury Control in the Boiler

Connie Senior

Reinhold NOx Roundtable
Columbus, Ohio
February 13-14, 2012

Motivation for This Presentation

- There's more than activated carbon, when it comes to mercury control in coal-fired boilers
- Chemistry of mercury in the boiler and the interaction of mercury with other control processes, like SCR, affect the performance of downstream mercury control from activated carbon injection or scrubbers
- Topics to be discussed: control of unburned carbon, halogen injection, impact of SCRs

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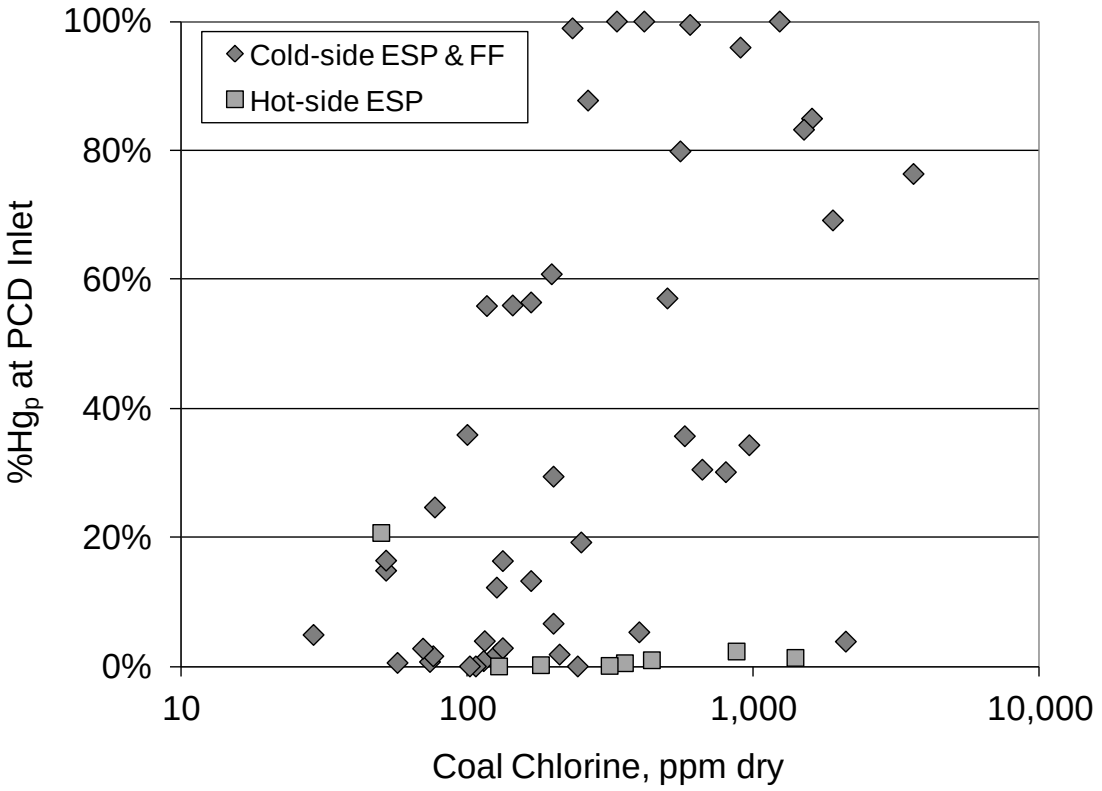
Hg Removal in the Boiler

- Hg isn't removed in the boiler
- *But*, some things that happen in the boiler affect how much mercury can be removed downstream
- How is Hg removed?
- Adsorption on particles (fly ash, sorbents) and removal in the particulate control device
- Absorption of oxidized mercury in scrubbers

Adsorption

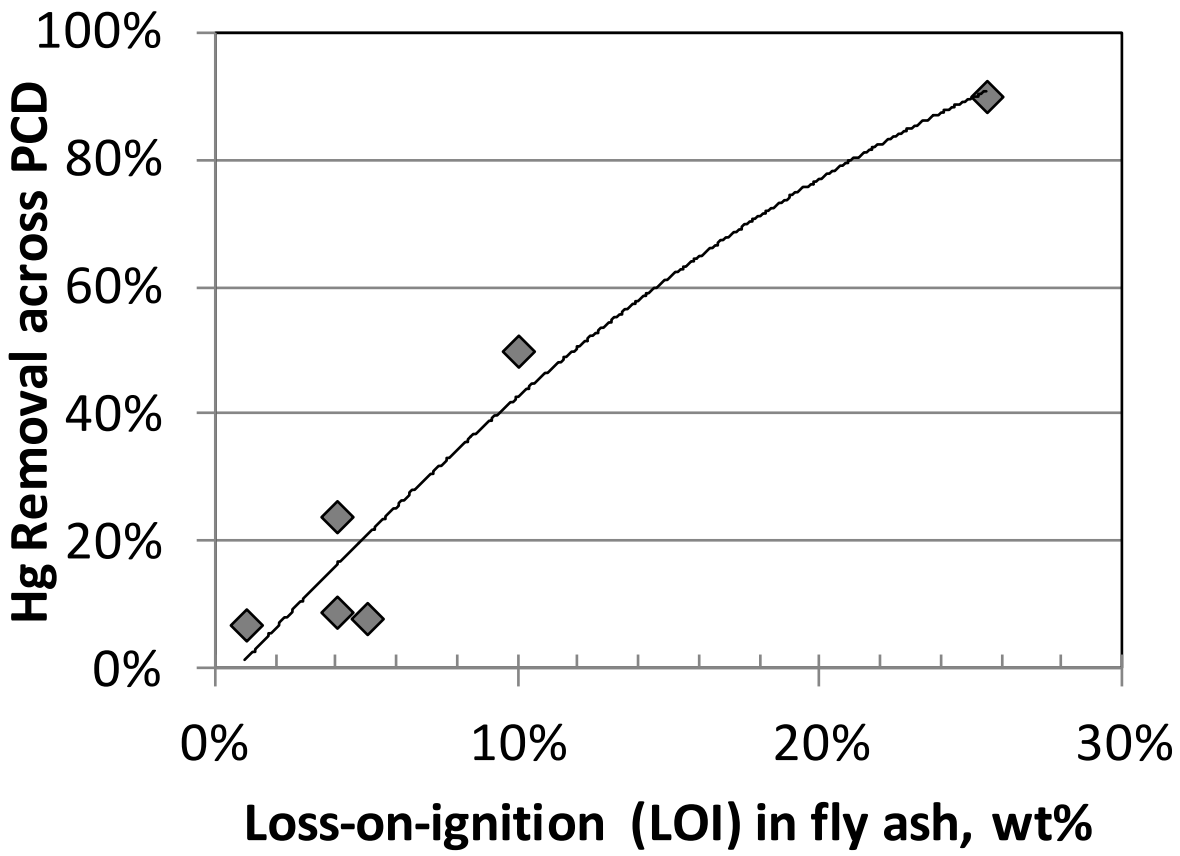
- How do we get more mercury onto particles?
- More halogens generally mean more particulate Hg
- Other factors:
  - Type of PCD
  - SO_3
  - Unburned carbon in ash



Source: 1999 ICR Data

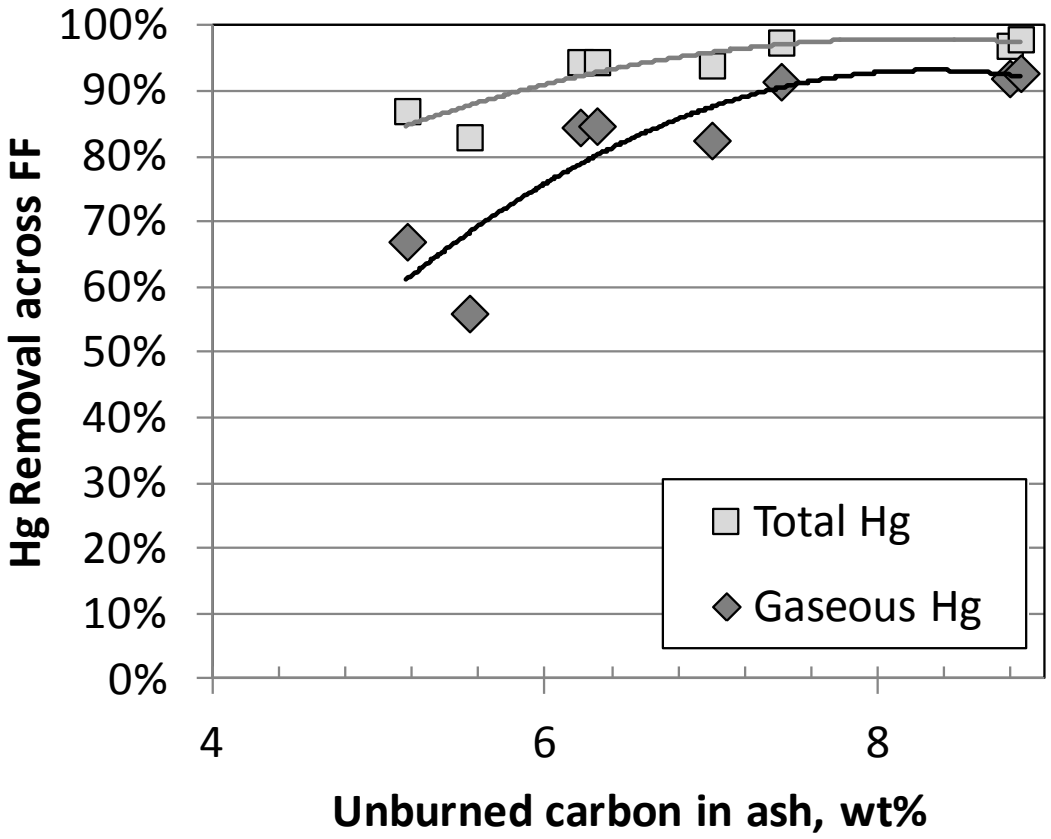
Unburned Carbon & ESPs

- Data from bituminous coals in pc-fired boilers



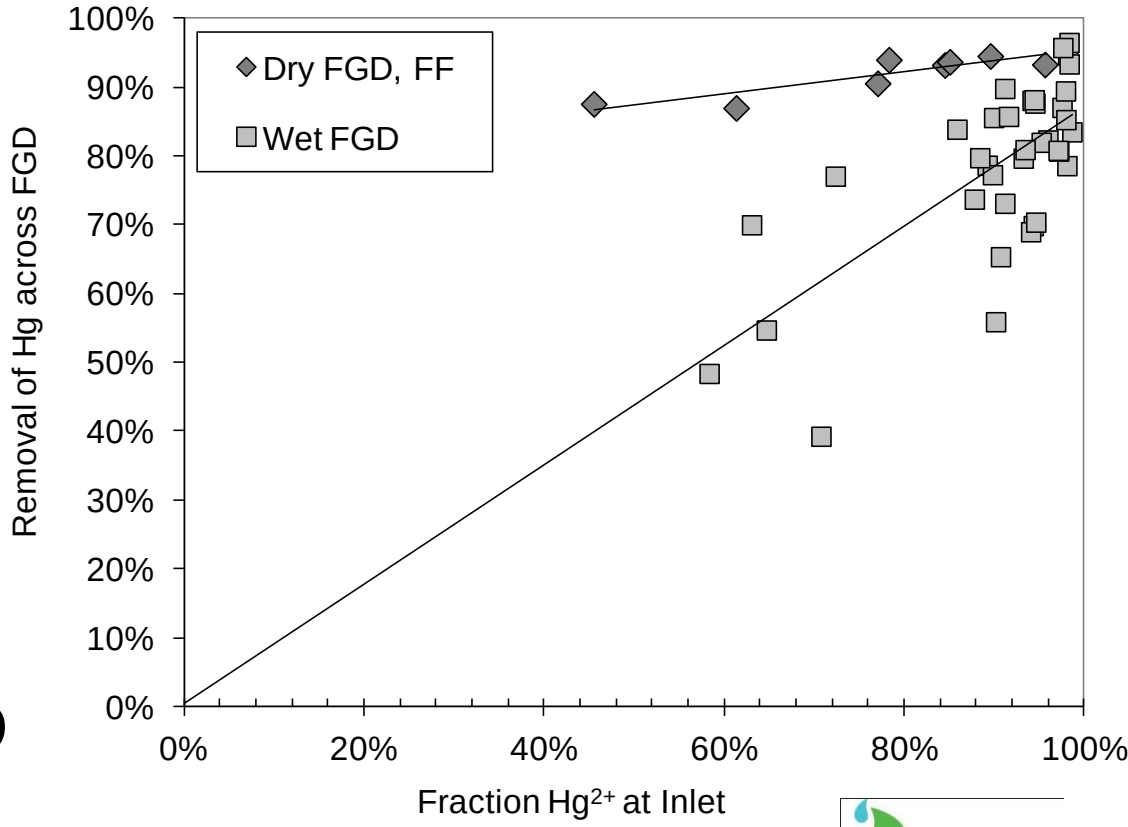
Unburned Carbon & Fabric Filter

- T-fired boiler with low-NOx combustion system, low-sulfur fuel
- Unburned carbon changed by changing combustion parameters



Absorption

- How do we get more Hg into the scrubber?
- Higher fraction of oxidized Hg at scrubber inlet => higher Hg removal
- Factors:
  - Halogen in fuel
  - Re-emission of Hg^0 in wet FGD

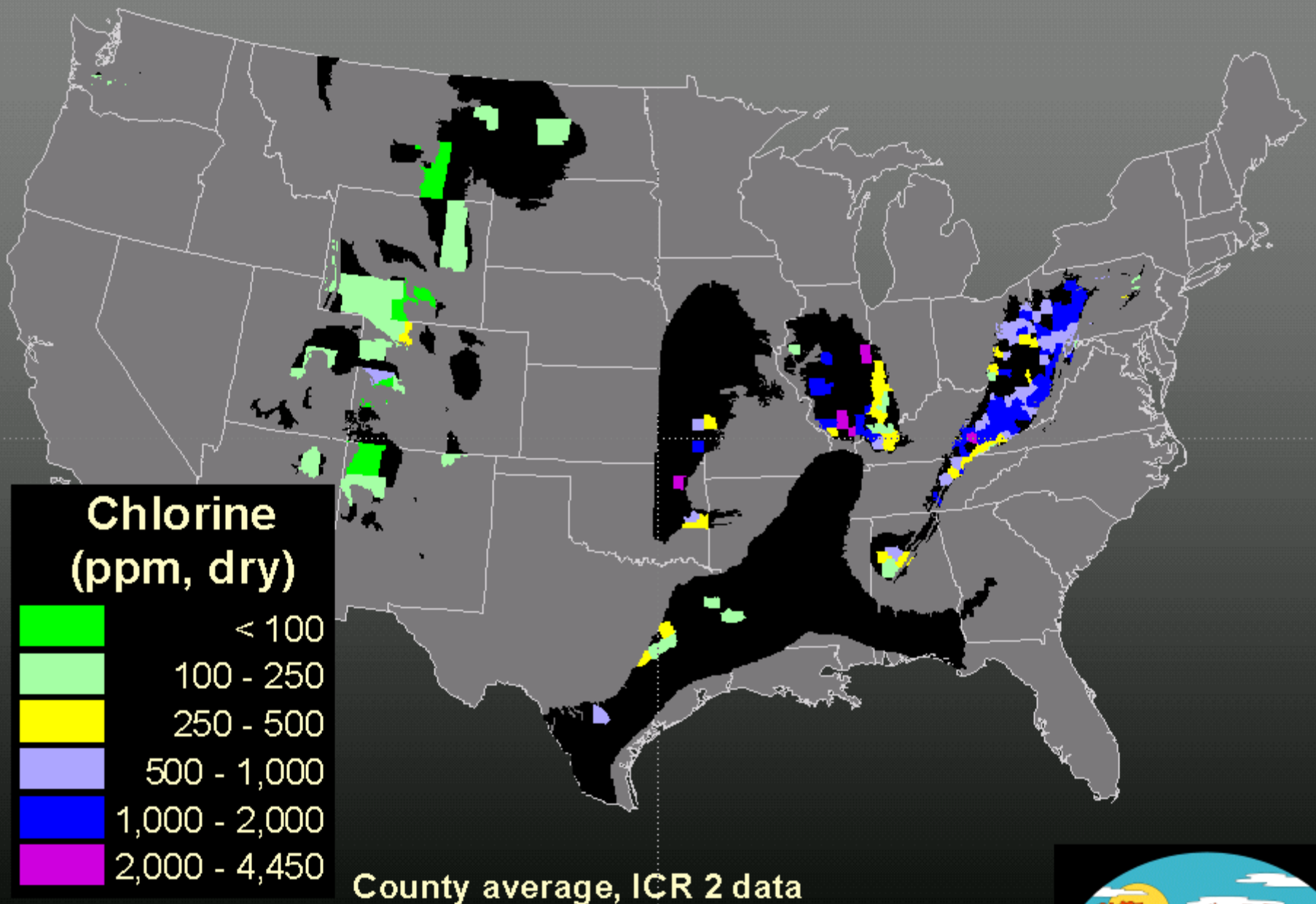


Source: NETL, EPRI demos

Why Add Halogens?

- Adding halogens to fuel or flue gas:
  - Halogen content of US coals varies widely

Chlorine in Coal

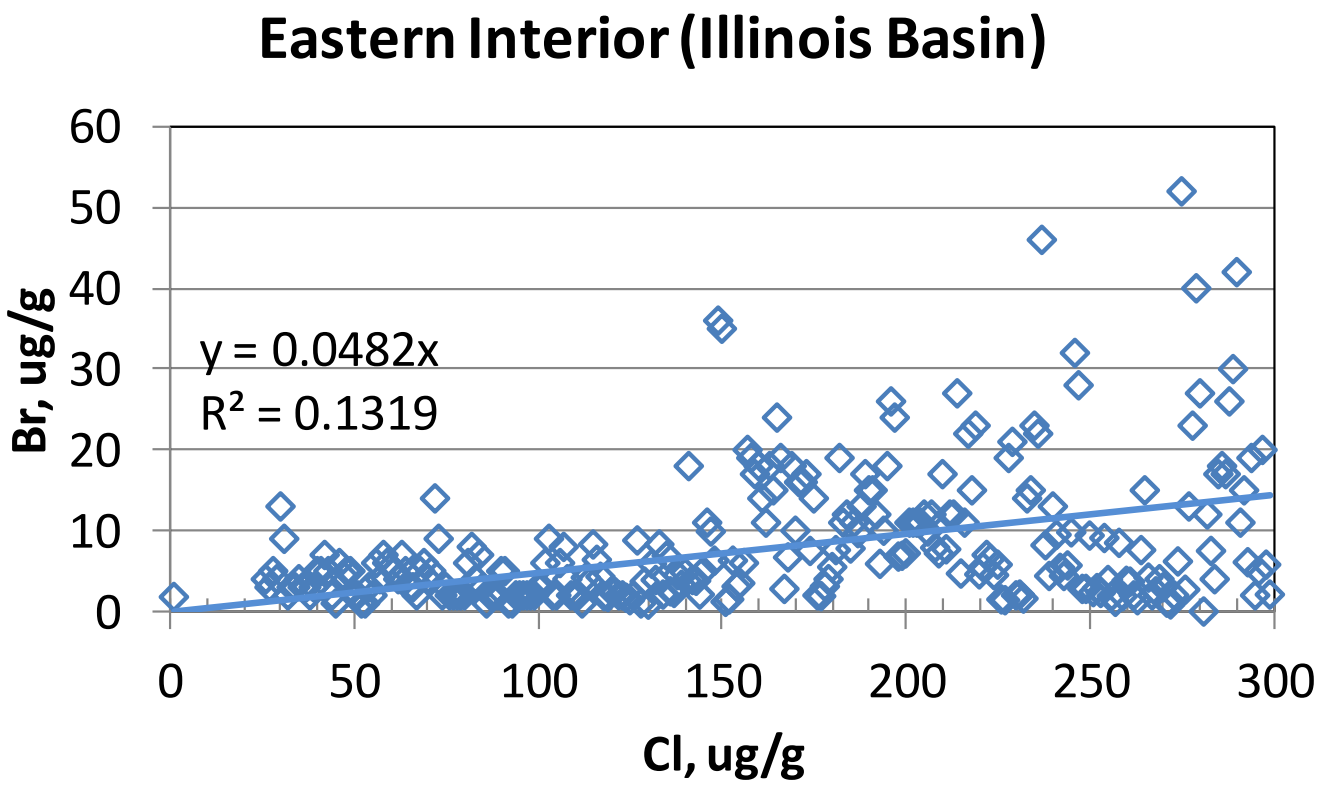


http://ugs.utah.gov/emp/mercury/index.htm

UTAH GEOLOGICAL SURVEY

Why Add Halogens?

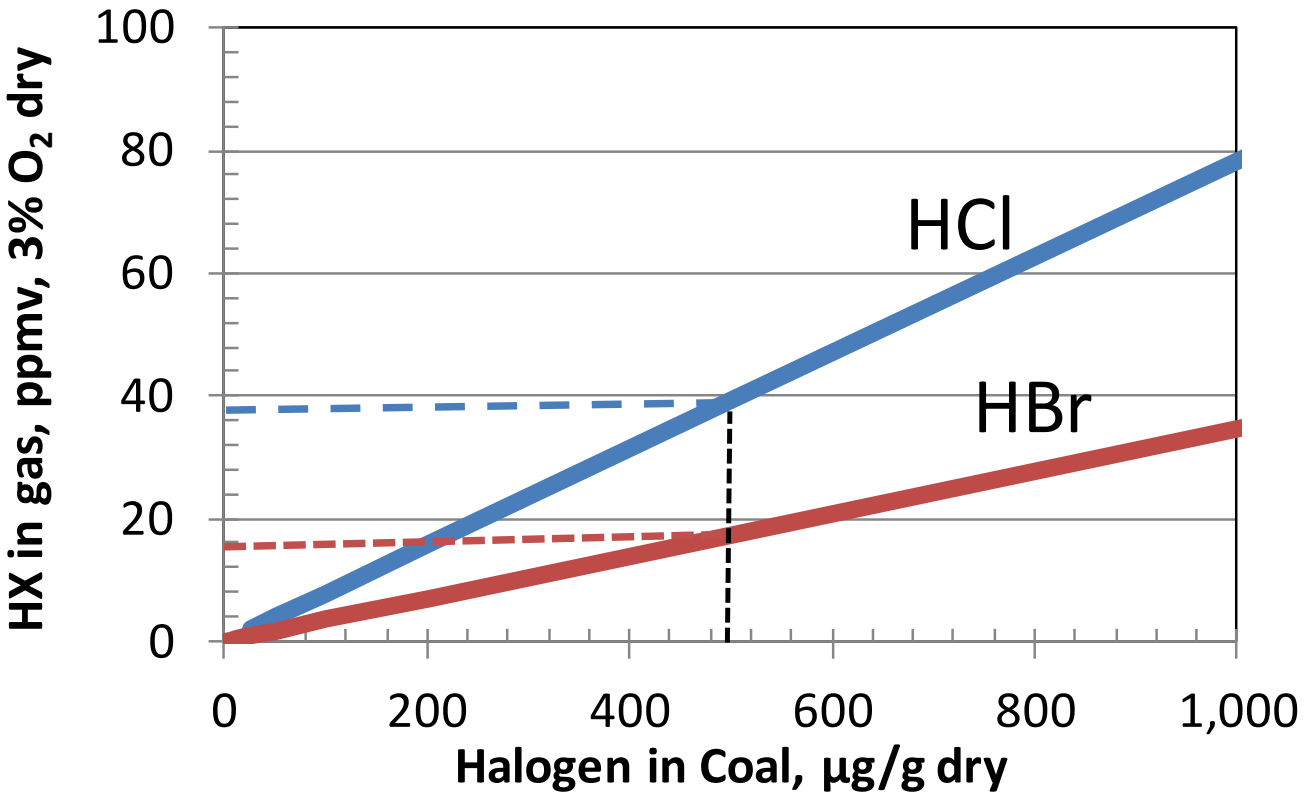
- Adding halogens to fuel or flue gas:
  - Halogen content of US coals varies widely
    - Bromine content typically 1% to 4% of chlorine content



Source: USGS COALQUAL database

Why Add Halogens?

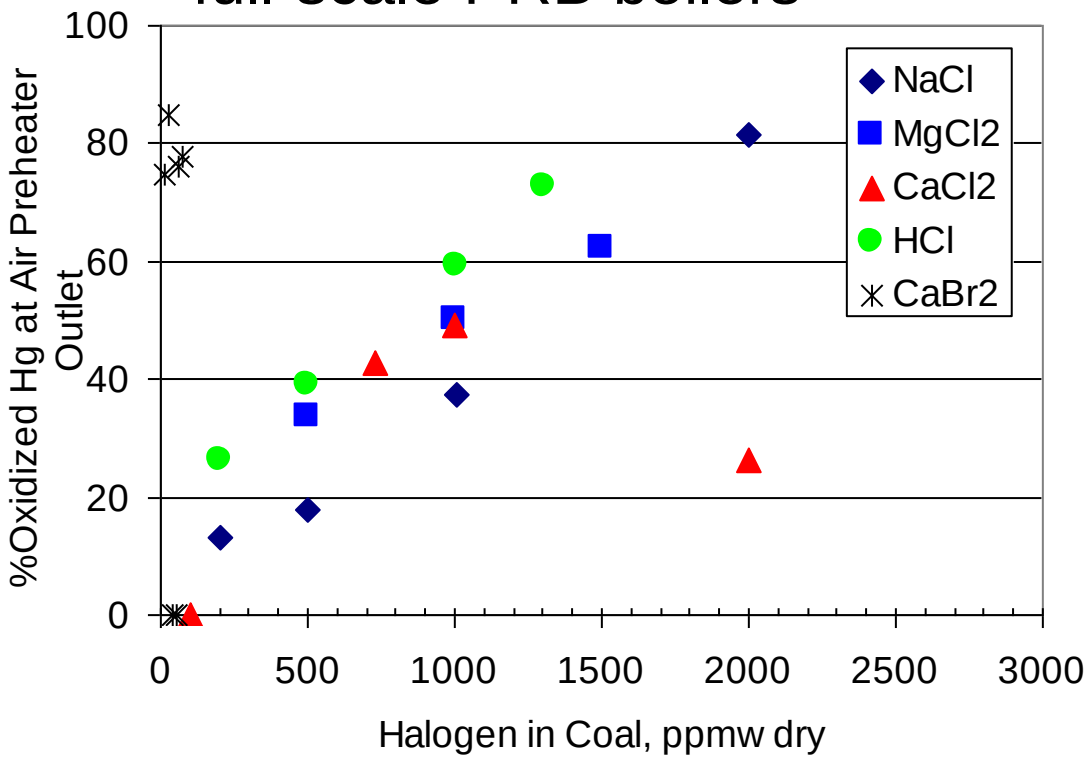
- Adding halogens to fuel or flue gas:
  - 500 ug/g Cl in coal = ~40 ppmv HCl in flue gas
  - 500 ug/g Br in coal = ~17 ppmv HBr in flue gas



Why Add Halogens?

- Adding halogens to fuel or flue gas:
  - Halogen content of US coals varies widely
  - Oxidation of Hg and capture of Hg on fly ash enhanced with additions of halogens, like Cl and Br

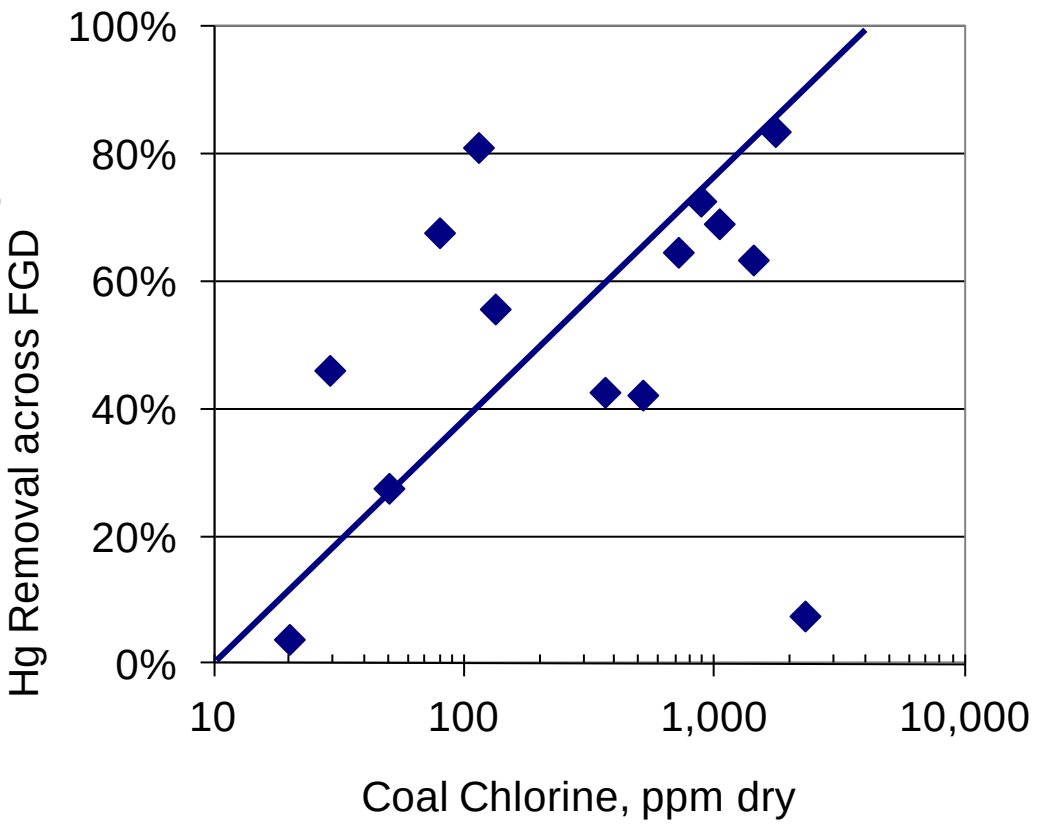
Halogen addition at various full-scale PRB boilers



Source: Dombrowski et al., 2006

Why Add Halogens?

- Adding halogens to fuel or flue gas:
  - Halogen content of US coals varies widely
  - Oxidation of Hg and capture of Hg on fly ash enhanced with additions of halogens, like Cl and Br
  - Many plants' APCDs can take advantage of native capture



Source: 1999 ICR

Summary: Why Add Halogens?

- Adding halogens to fuel or flue gas:
  - Halogen content of US coals varies widely
  - Oxidation of Hg and capture of Hg on fly ash enhanced with additions of halogens, like Cl and Br
  - Many plants' APCDs can take advantage of native capture
- Adding halogens to activated carbon increases the ability to capture elemental Hg in low-halogen flue gas

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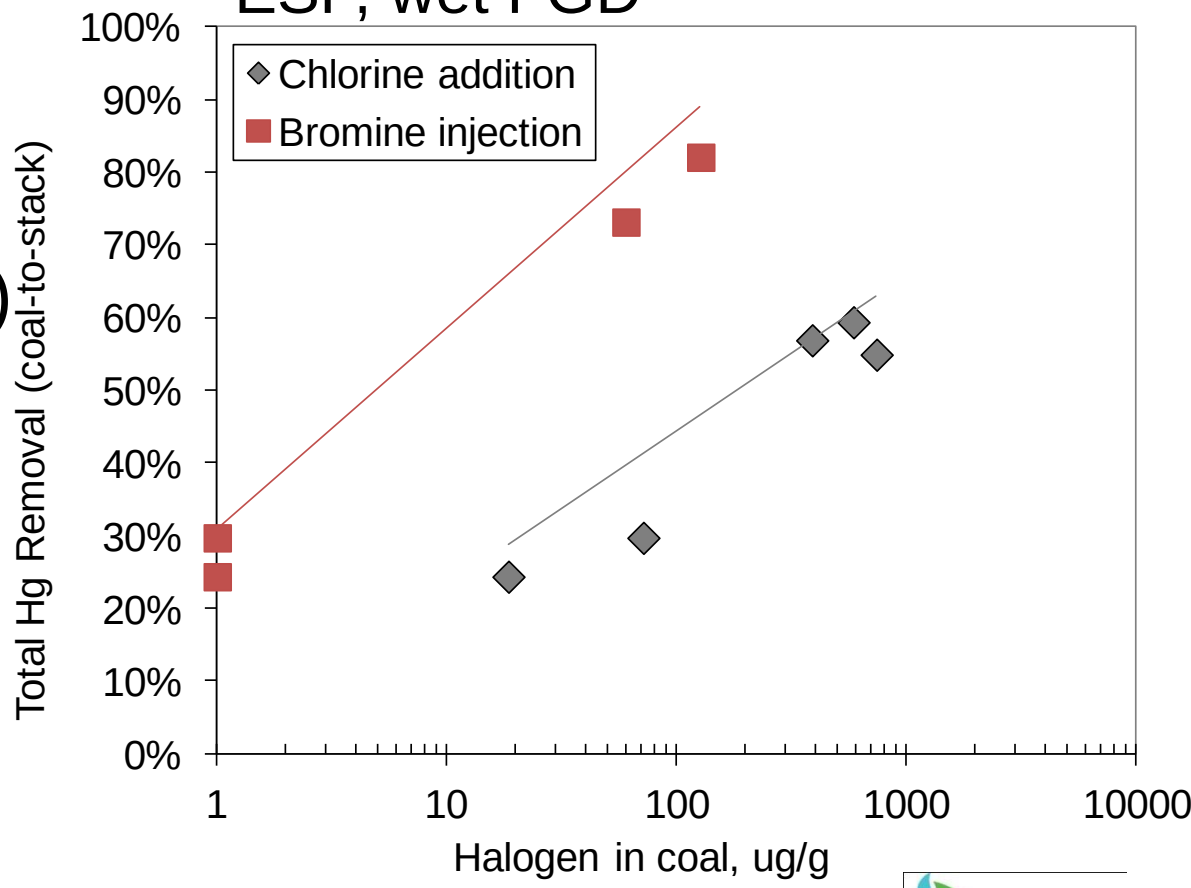
How Effective Are Halogens?

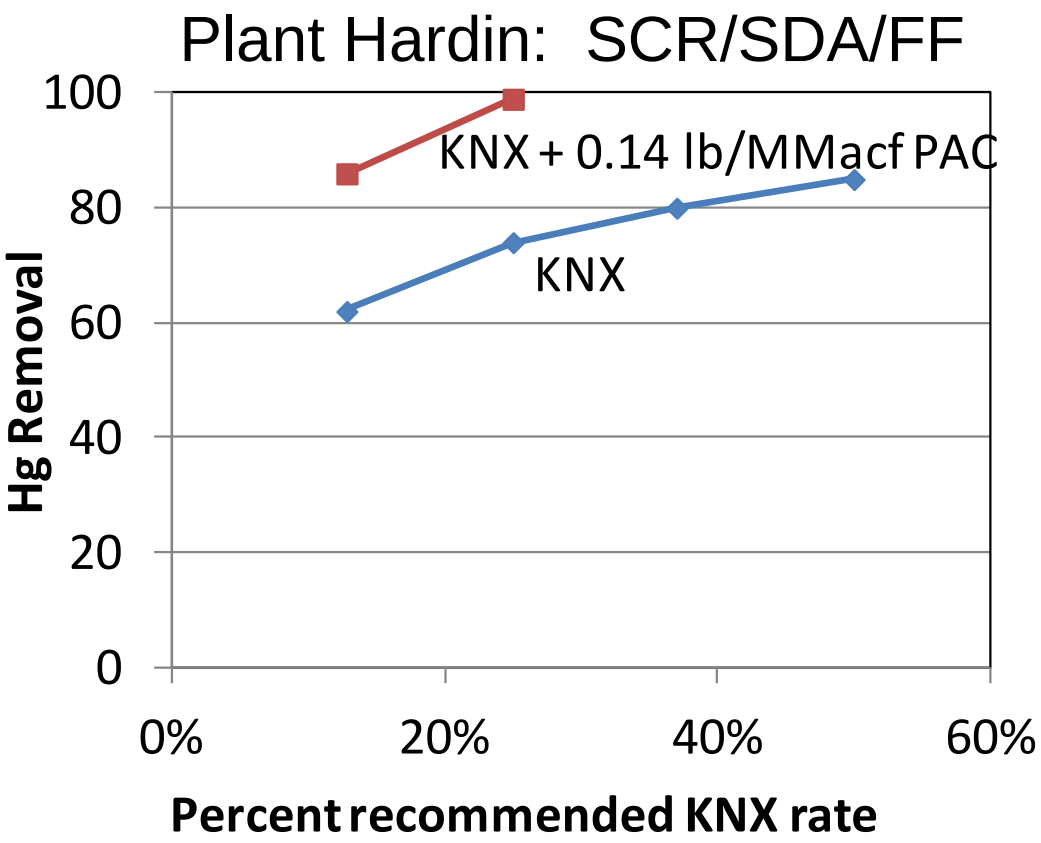
- Halogens increase oxidized mercury: Br more effective than Cl (on an equal mass basis)
- Increased Hg removal across scrubbers

Monticello: PRB/lignite, ESP, wet FGD



How Effective Are Halogens?

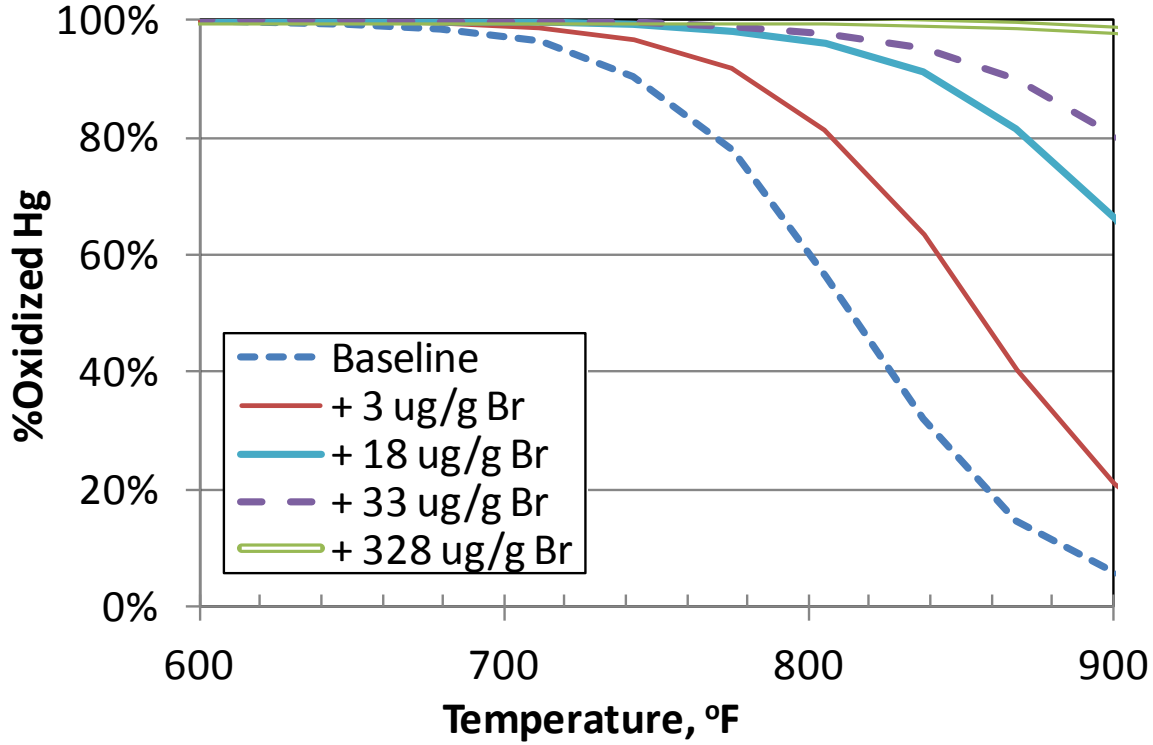
- Halogens increase oxidized mercury: Br more effective than Cl (on an equal mass basis)
- Increased Hg removal across scrubbers
- Halogens increase effectiveness of PAC



Source: DOE/EPRI sampling campaigns

Effect of SCRs on Added Halogens

- Catalysts drive reactions toward equilibrium
  - Results will be catalyst-specific
- Adding Br to the fuel makes the shift to Hg^{2+} take place at higher temperatures (than Cl)



Equilibrium modeling of Plant Miller data of Berry *et al.*

Effect of SCRs on Added Halogens

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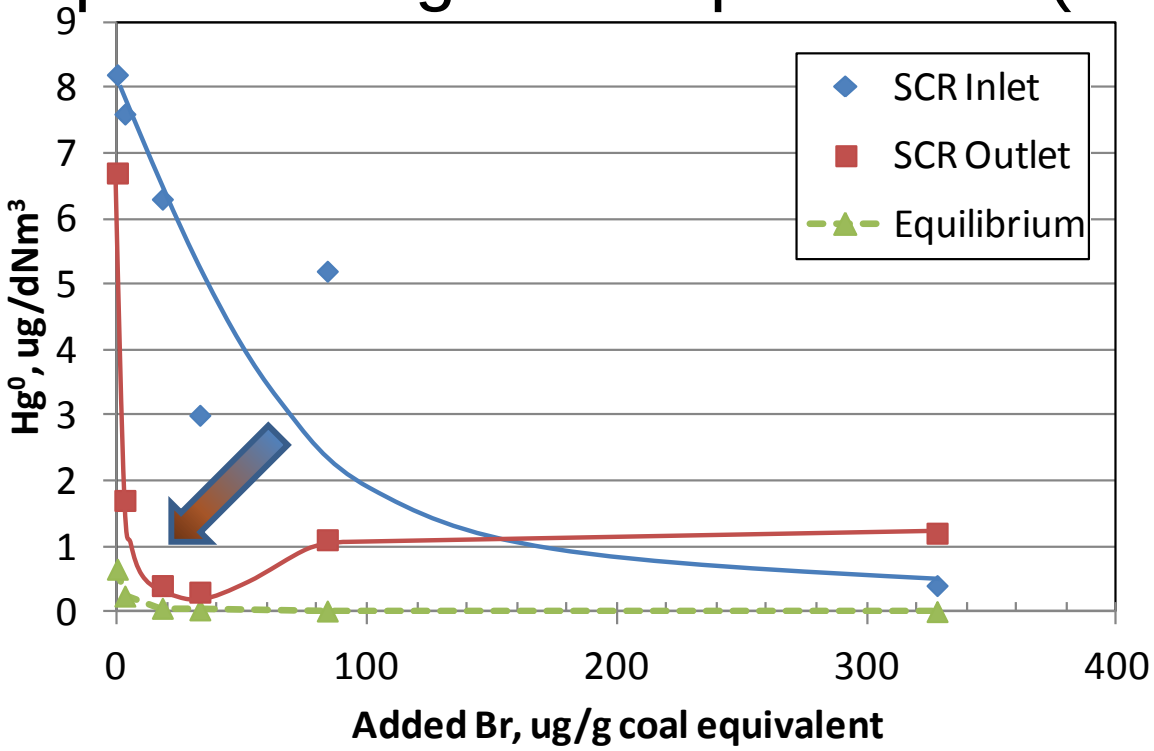

Comparison of Plant Miller data of Berry *et al.* with calculated equilibrium

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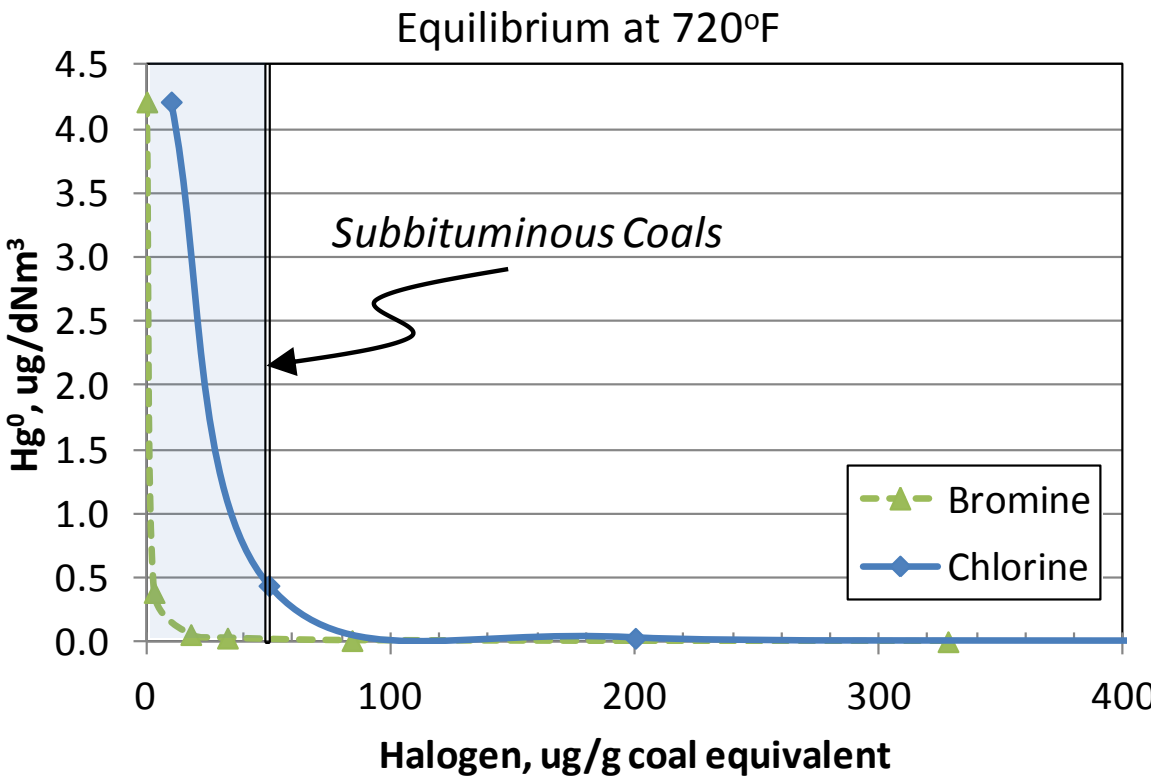
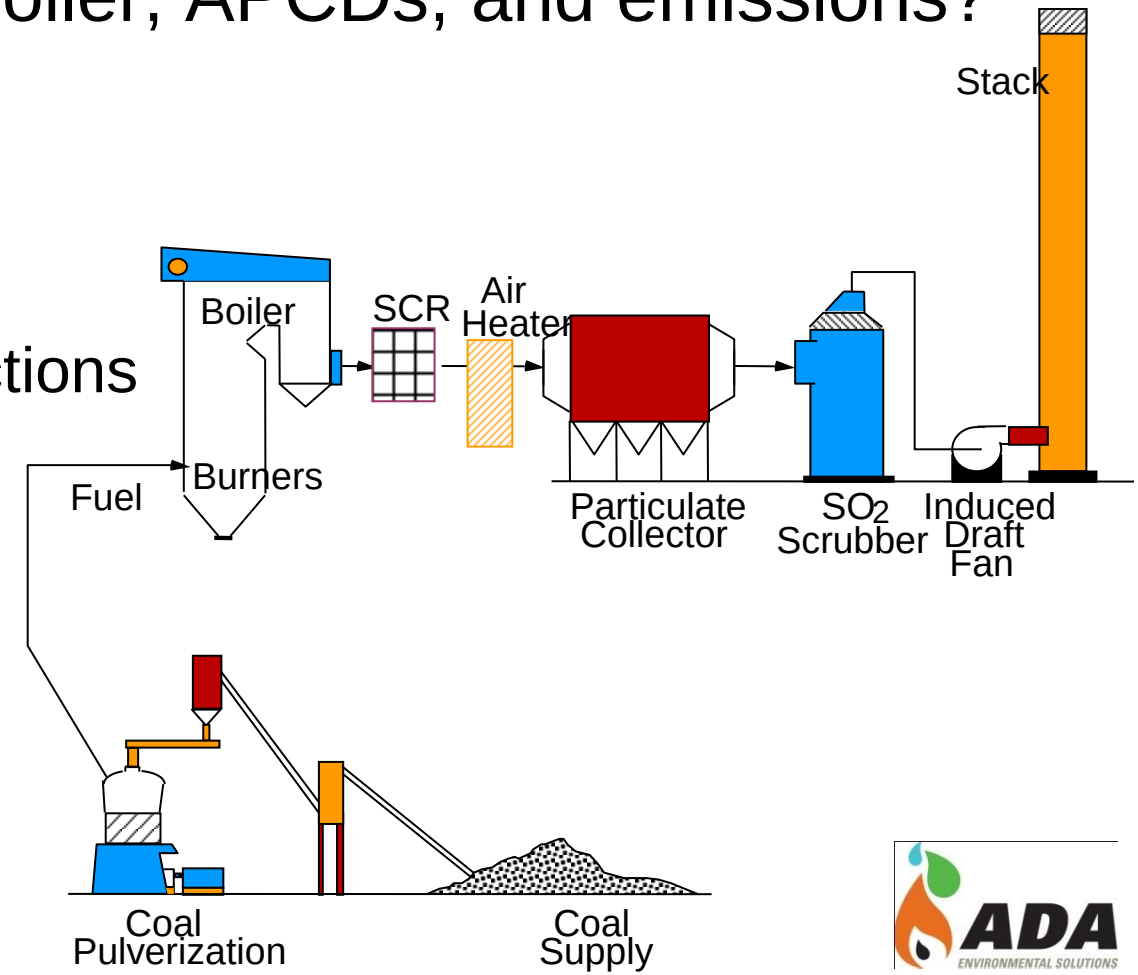
Effect of SCRs on Added Halogens

- Bromine is more efficient (equal mass basis) than chlorine at oxidizing Hg across SCRs
  - Results will be catalyst-specific
  - Subbituminous (low-chlorine) coals only



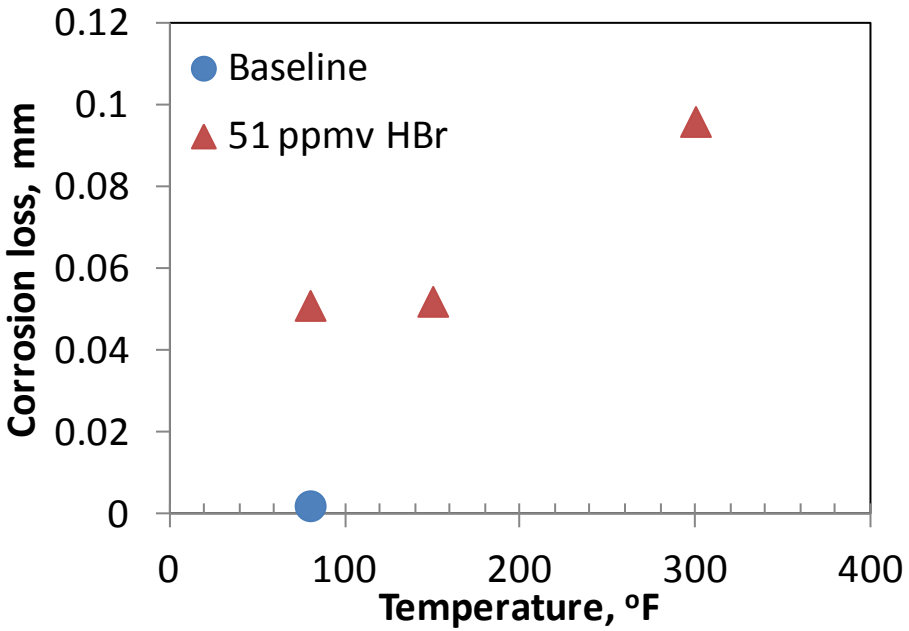
Fate and Impacts of Halogens

- What are the potential impacts of halogen addition on the boiler, APCDs, and emissions?
  - Corrosion
  - Fly ash
  - Stack emissions
  - Scrubber interactions



Corrosion in Flue Gas

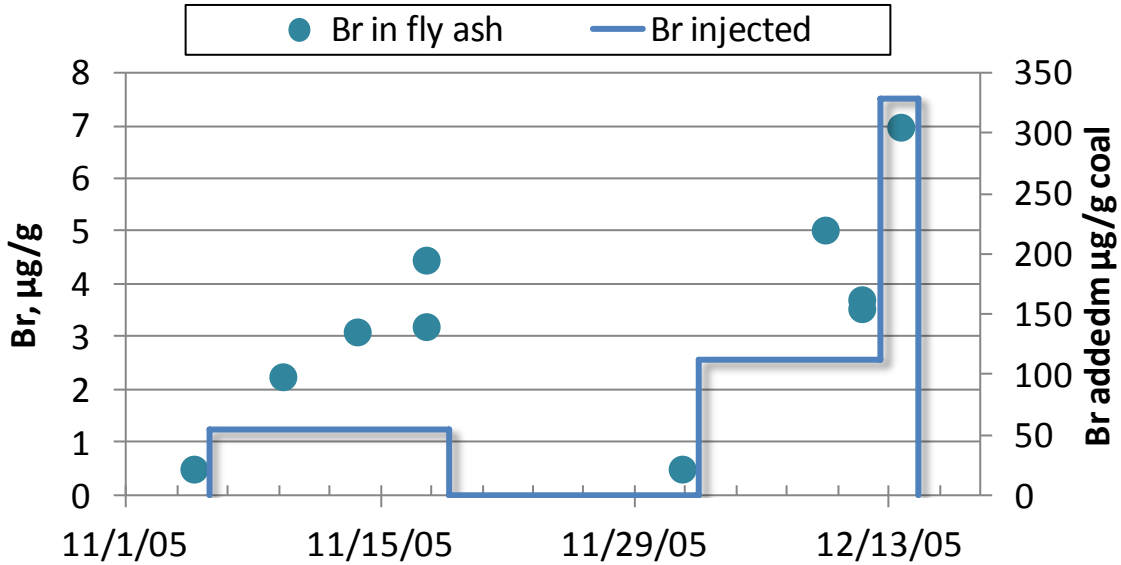
- Chlorine corrosion in furnaces can occur for very high levels of chlorine in coal (> 2000 µg/g)
  - Bromine addition at much lower concentrations
- Indirect evidence that HBr might be more corrosive than HCl at flue gas temperature
- No direct comparison, but HBr corrosion higher than baseline (no HBr) in simulated flue gas (6-month study)



Zhuang et al., 2009

Bromine Addition: Fly Ash Impacts

- Bromine additive or brominated PAC results in increase in Br in fly ash
- Example: Br injection at Monticello (C-ESP)



Bromine injection at Monticello (EERC, URS data)

Bromine Addition: Fly Ash Impacts

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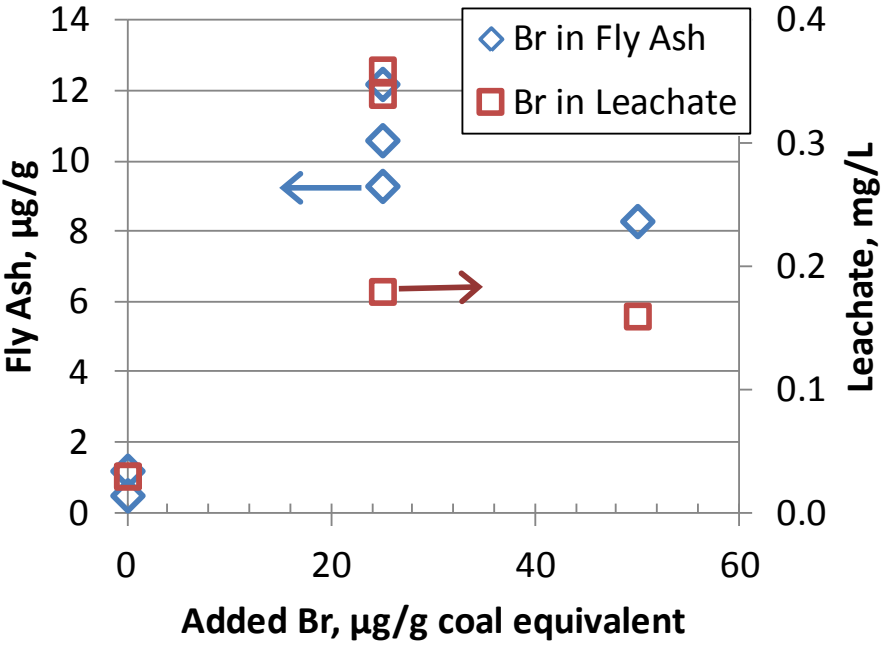
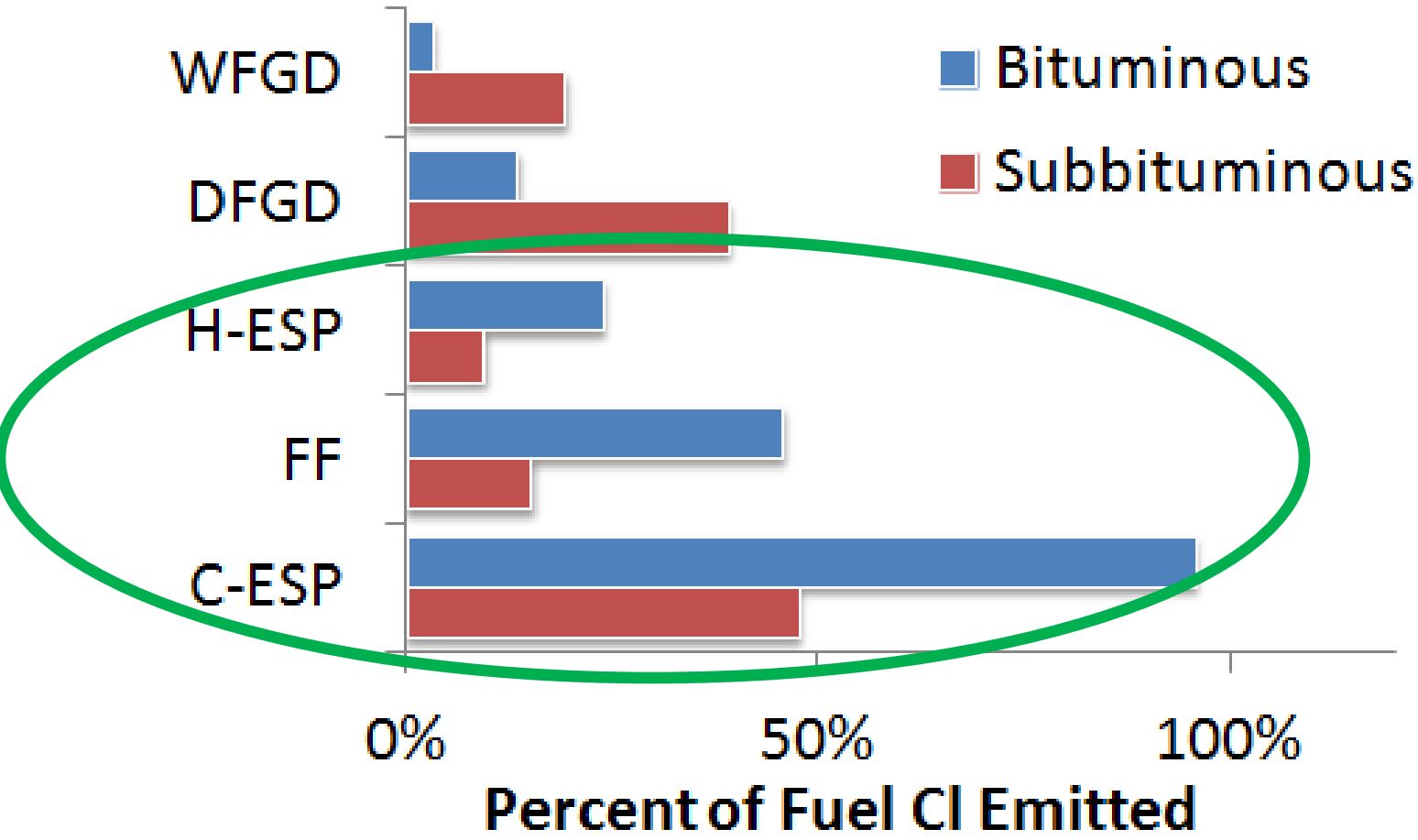
- Example: Br injection at Plant Miller (PRB, C-ESP)



- According to the authors:
  - Hg concentration in fly ash didn't increase with Br injection
  - 1% of Br captured by fly ash
  - 50% of Br on fly ash leached in SPLP test

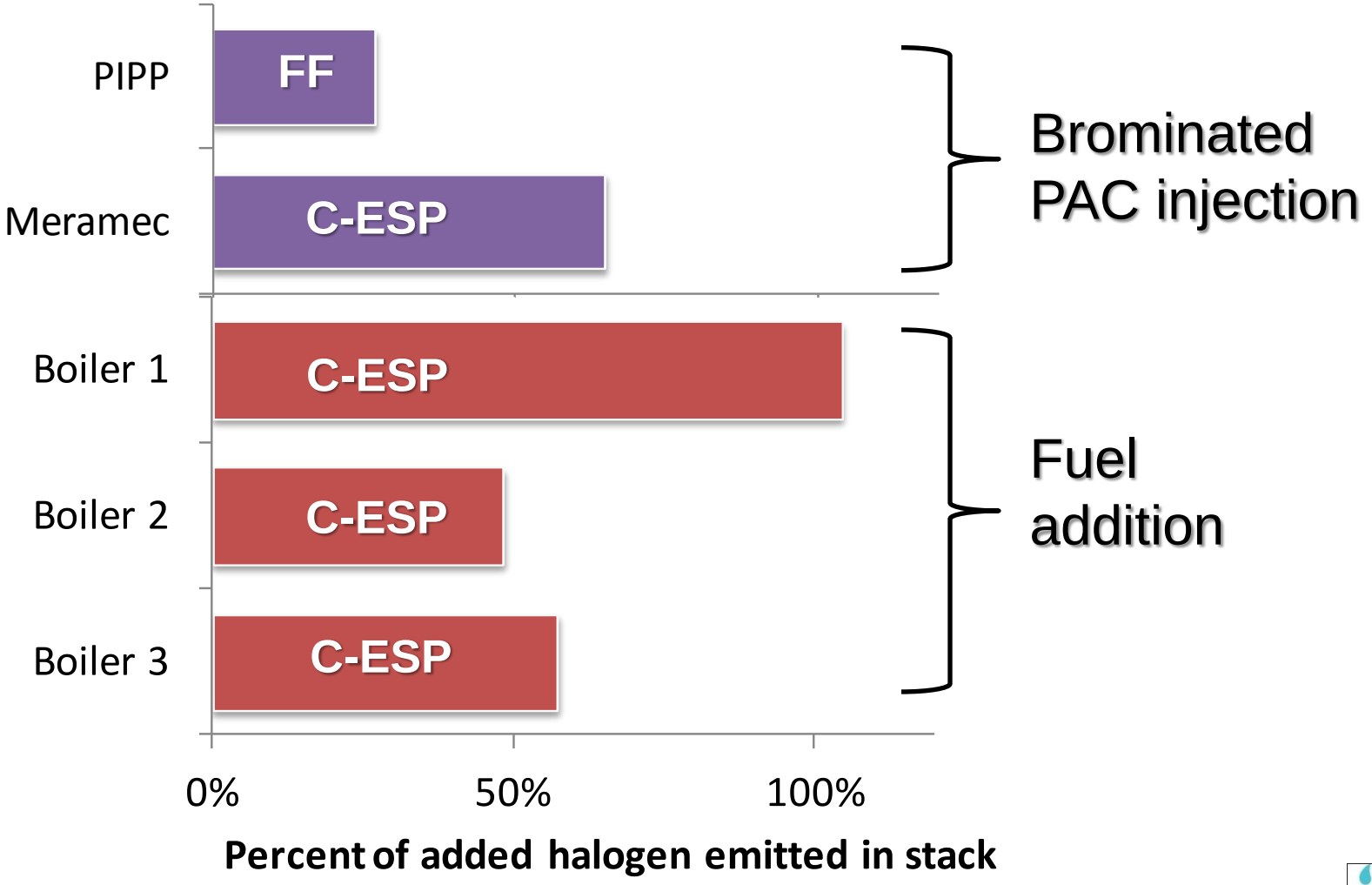
Dombrowski et al., 2008

Chlorine Emission from APCDs



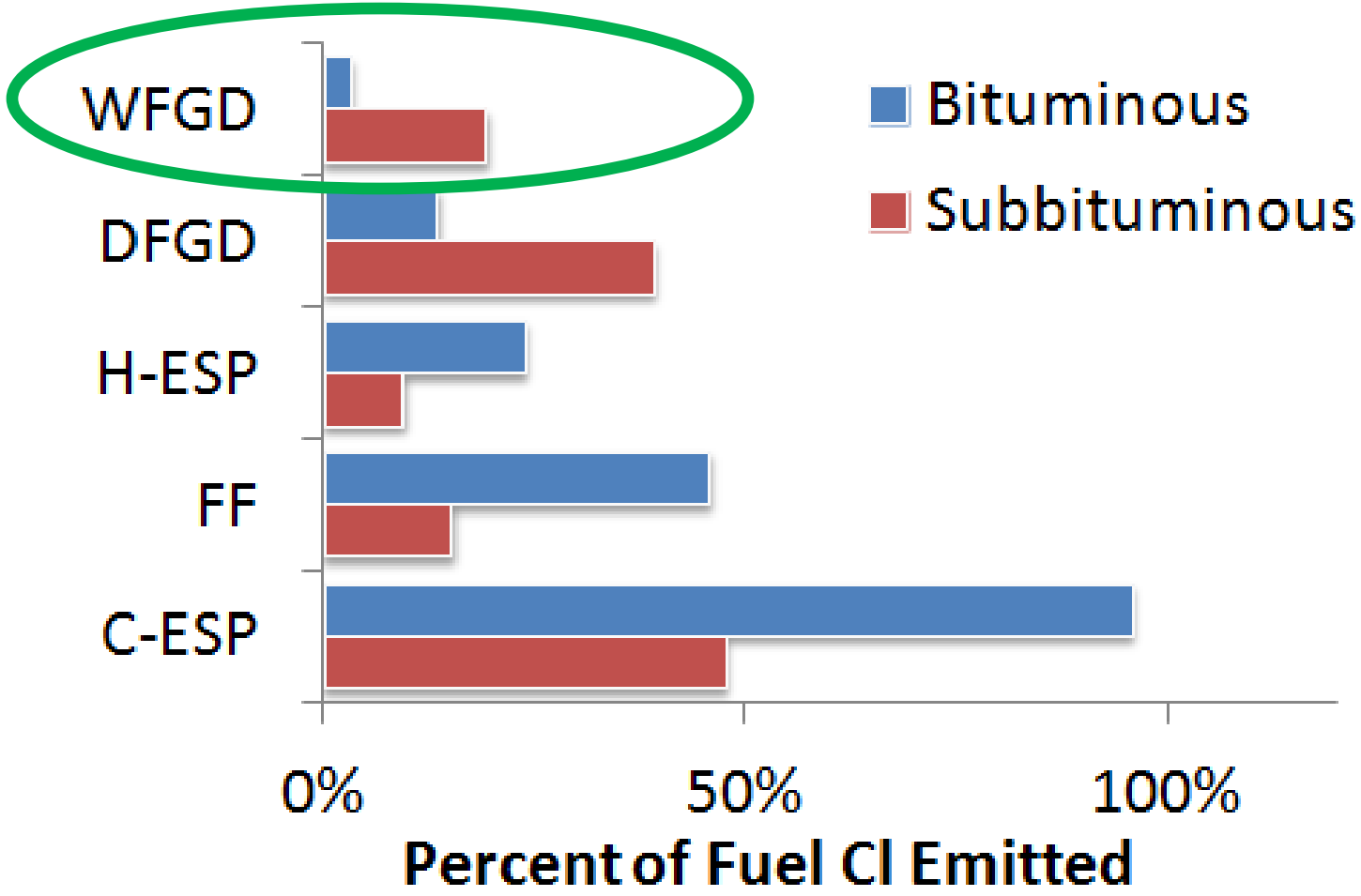
Source: 2010 ICR

Bromine Emission from APCDs



All boilers are pulverized coal, burning subbituminous coal

Chlorine Emission from APCDs



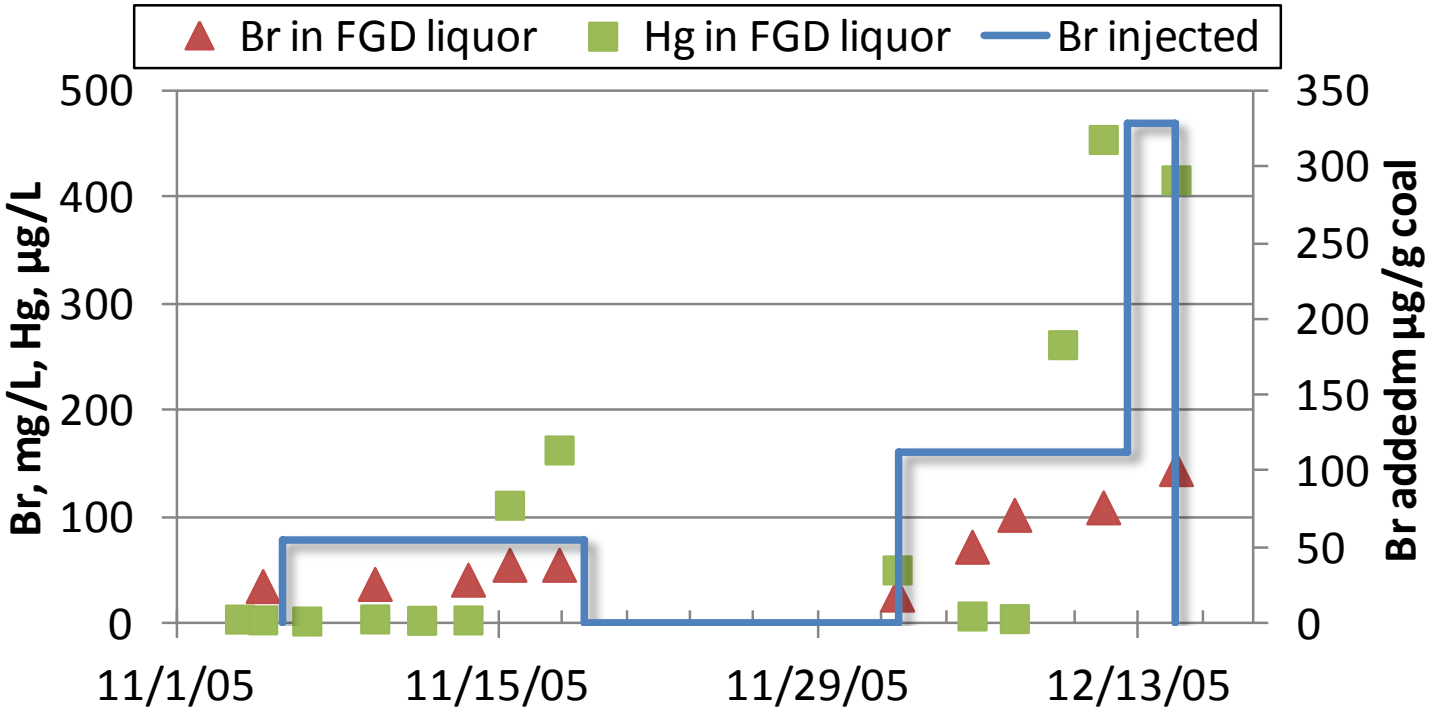
Source: 2010 ICR

Halogens in Wet Scrubbers

- Adding halogens (Cl or Br) increases oxidized Hg, which increases capture of Hg in scrubber
- Wet FGD scrubbers remove halogens efficiently
  - Average Cl removals for wet FGDs (2010 ICR): 81% for subbituminous, 97% for bituminous
  - Removal of Br at Plant Miller wet FGD: 94-96% (Dombrowski et al., 2008)
- Halogens build up in wet scrubber liquor

Halogens in Wet Scrubbers

- Halogens and Hg build up in wet scrubber liquor… slowly, depending on scrubber design



Bromine injection at Monticello (EERC, URS data)

Halogens and Wet Scrubbers

- Increased Cl, Br concentration in scrubber liquor can decrease Hg re-emission

Halogens and Wet Scrubbers

- Recent observations (Air Quality VIII) that Br addition to the fuel increases Se in scrubber liquor

Data from bituminous site with C-ESP, wet FGD

	Se in fly ash, µg/g	% Se capture by fly ash	Se in FGD liquor, µg/L
Baseline	24	70%	300
Br addition	10	20%	4900

(Dombrowski et al., 2011)

  - Less uptake of Se by fly ash means more Se enters FGD

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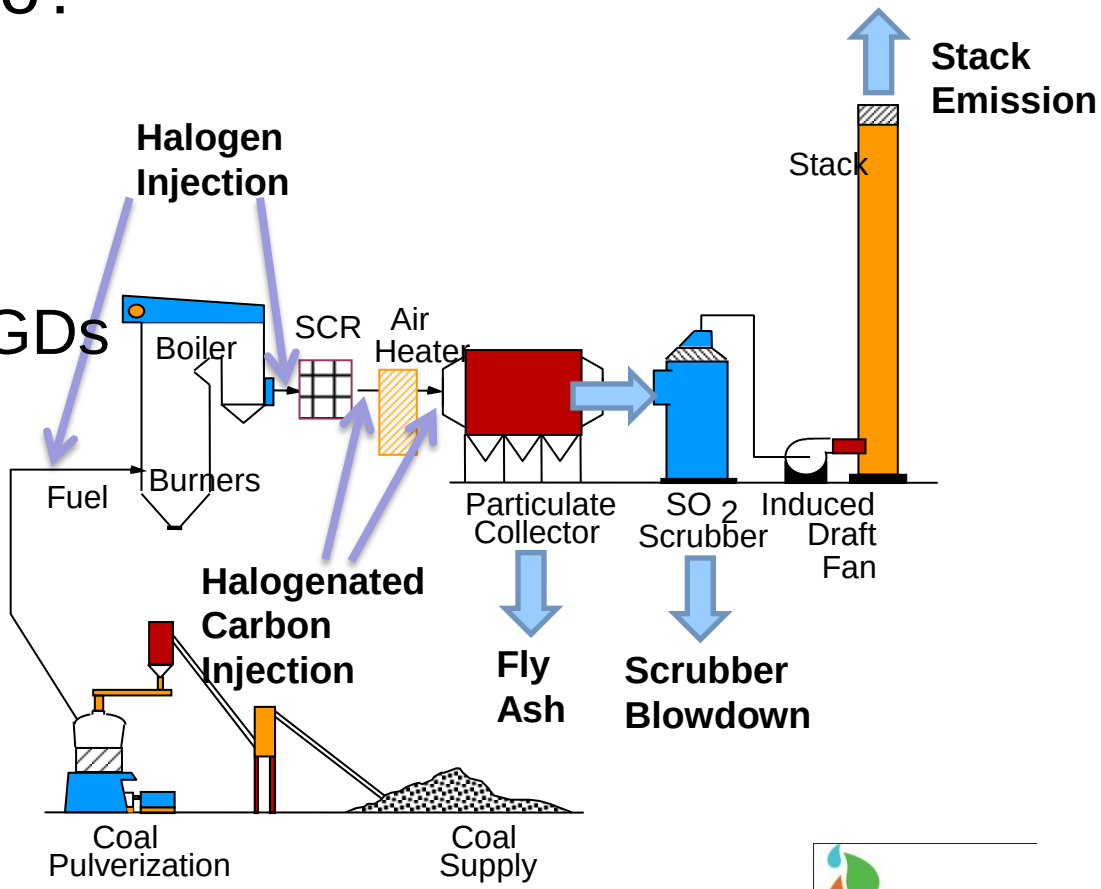
Halogens Summary

- Halogen fuel/flue gas additives OR halogenated PAC
- Where do halogens go?
  - Some removal in particulate control devices
  - Efficient removal in FGDs
- Br is “new kid on the block” – information needed:
  - Corrosion
  - Multi-media fate
  - Trace metal interactions



Hg Removal in the Boiler

- How is Hg removed?
- Adsorption on particles (fly ash, sorbents) and removal in the particulate control device
- Absorption of oxidized mercury in scrubbers
- How can we improve removal by what happens in the boiler?
  - Increase unburned carbon – if you can
  - Consider adding more halogens if
    - There's enough LOI, but halogens are low
    - There's a scrubber
  - Keep SO_3 low post-APH

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Questions?

ADA: Innovate, Develop, Commercialize