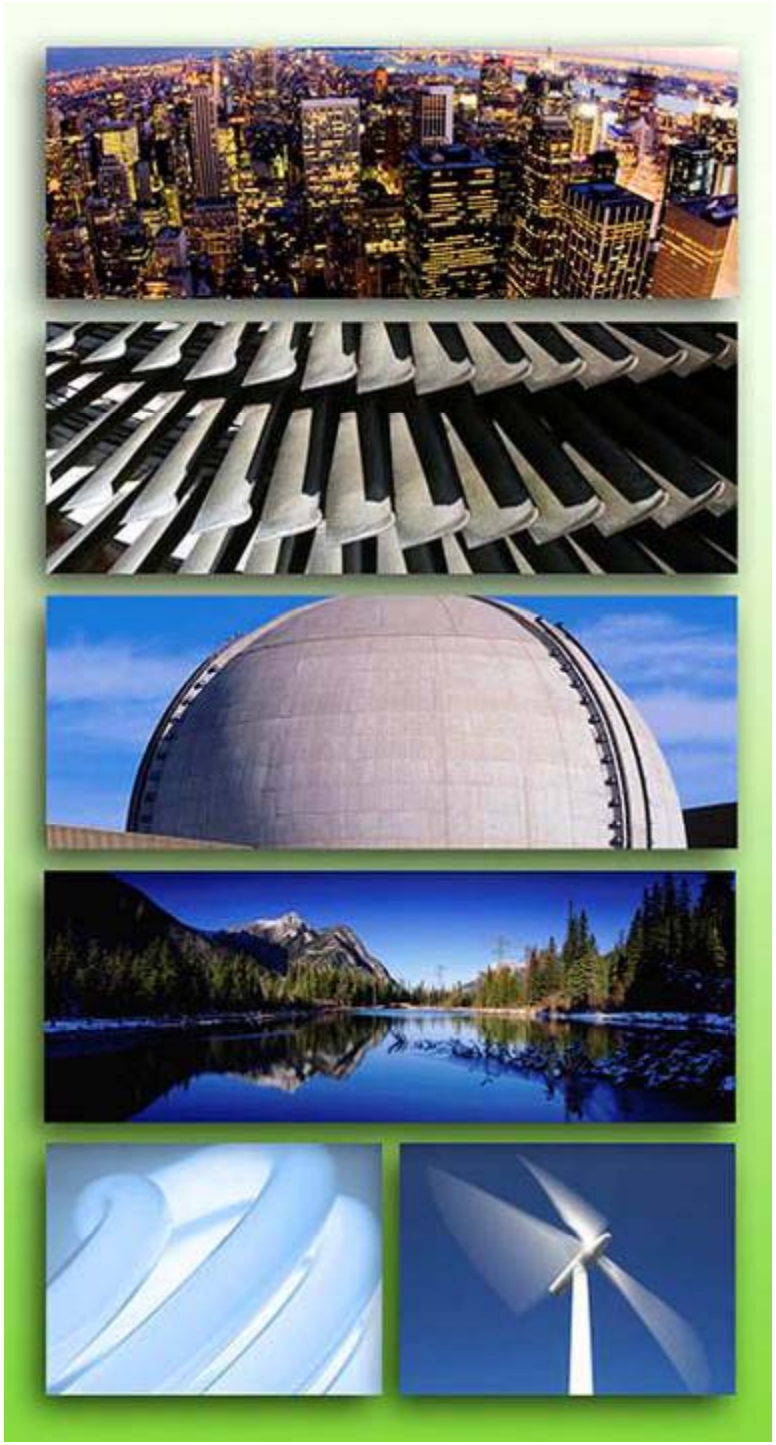

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The Significance of Halogenoxides for Mercury Wet Deposition in the U.S.

Arnout Ter Schure, PhD
Project Manager

2009 Mercury Science & Policy Conference

Chicago, IL, November 17-18, 2009

Presentation Outline

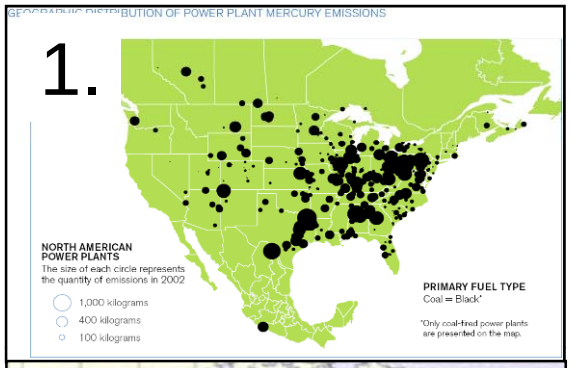
- Mercury Wet Deposition in US
  - What is the main source of mercury deposition in the US ?
    - Local Anthropogenic ($HgCl_2$?)
    - Oxidation of Global Background Pool (HgO ? , $HgBr_2$, Hg?)
  - Current models use:
    - Hg + OH , Hg + O_3
    - Product is HgO
  - BUT recent thermodynamic calculations suggest these reactions are less important: Oxidation mediated by halogen radicals (Br, I) is a possibility.
  - Test hypothesis in location with pronounced and continuous discrepancy: Gulf Coast

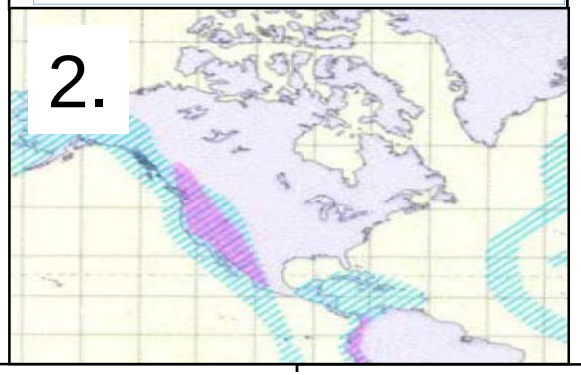
What is the main source?

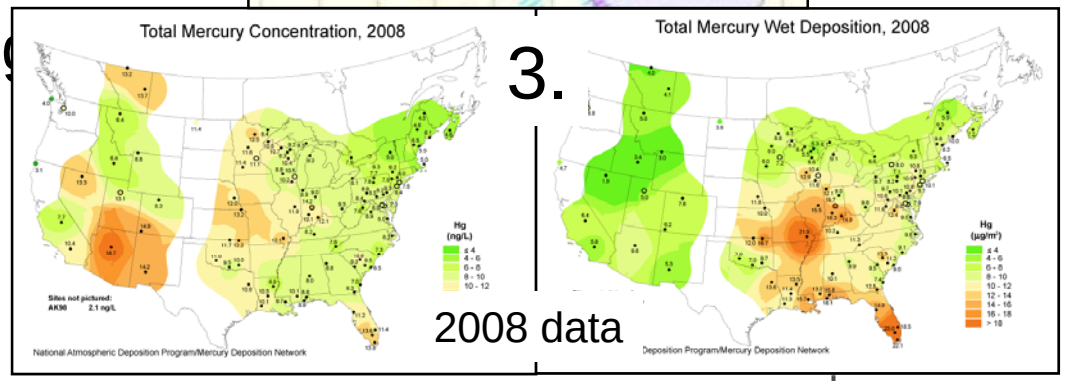
1. Most coal fired power plants are located ENE of Mississippi River.

2. Natural Hg sources are more widely distributed.

3. Conversely, measured Hg wet deposition fluxes (ng/m^2) and concentrations (ng/L) increase from NE to SE.







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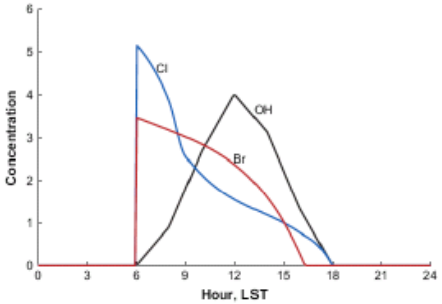
Laboratory Kinetics and Quantum Calculations

		ΔH [kJ/mol]	k [cm^3/molec/sec]	τ [days]
(R1)	$Hg^0 + O_3 \rightarrow HgO + O_2$	+93	<3E-20	>392
(R2)	$Hg^0 + OH \rightarrow HgO + H$	+415		
(R2a)	$Hg^0 + OH + M \rightarrow HgOH + M$	-40	<9E-14	>129
(R3)	$Hg^0 + Cl + M \rightarrow HgCl + M$	<<0	5.4E-13	1430
(R4)	$Hg^0 + Br + M \rightarrow HgBr + M$	<<0	1.1E-12	10
(R4a)	$Hg^0 + BrO \rightarrow HgO + Br$	+40	??	??
(R5)	$Hg^0 + I + M \rightarrow HgI + M$	??	??	??
(R5a)	$HgBr + I + M \rightarrow HgBrI + M$	??	??	??



- Ozone unlikely; OH is likely of minor importance.
- The rate of mercury oxidation appears dominated by halogen chemistry

Lifetime estimates based on: $[O_3]$ = 40 ppb; [OH] = [Br] = 10^6 molec/cm^3; [Cl] = 1.5 10^4 molec/cm^3

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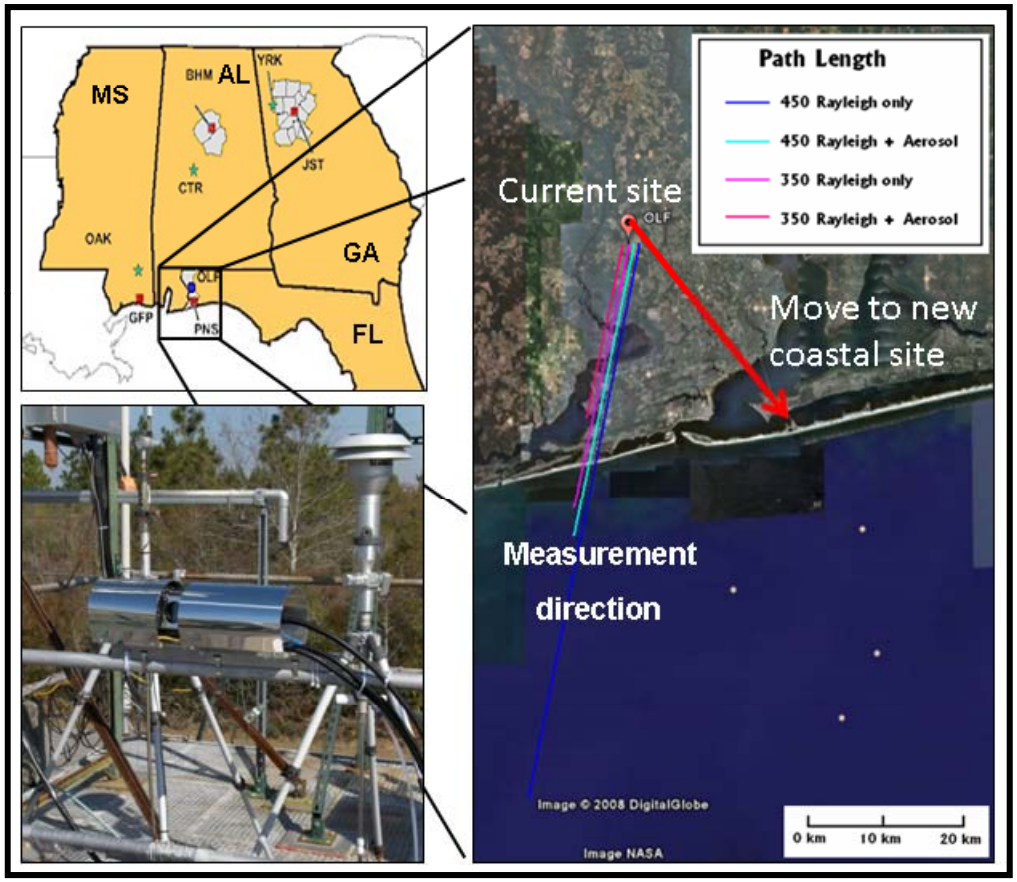
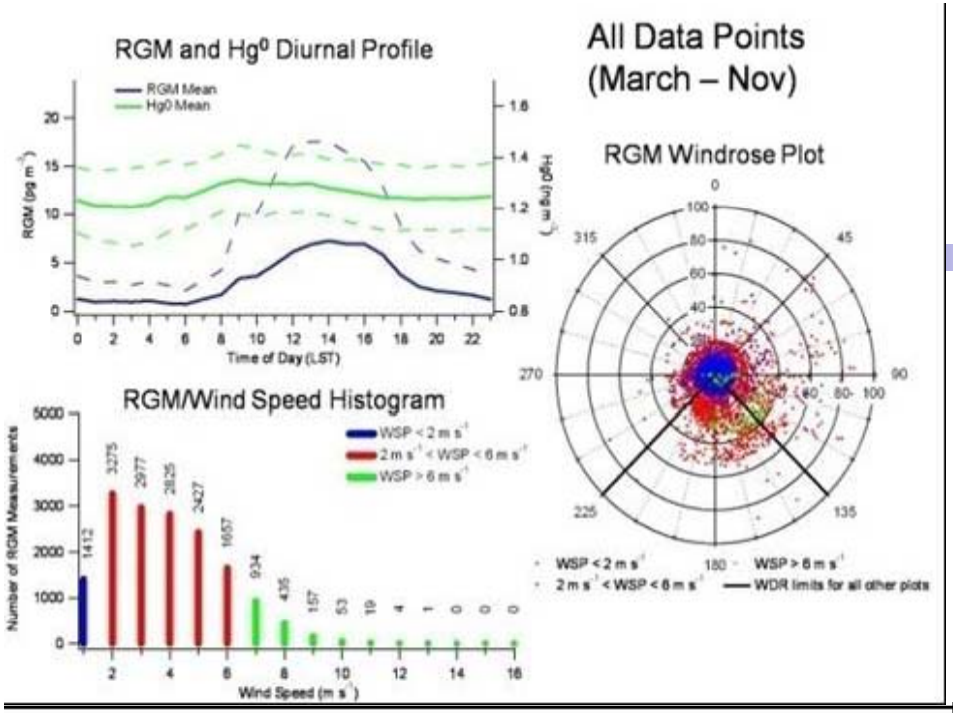
Coastal Atmospheric Halogen Oxides

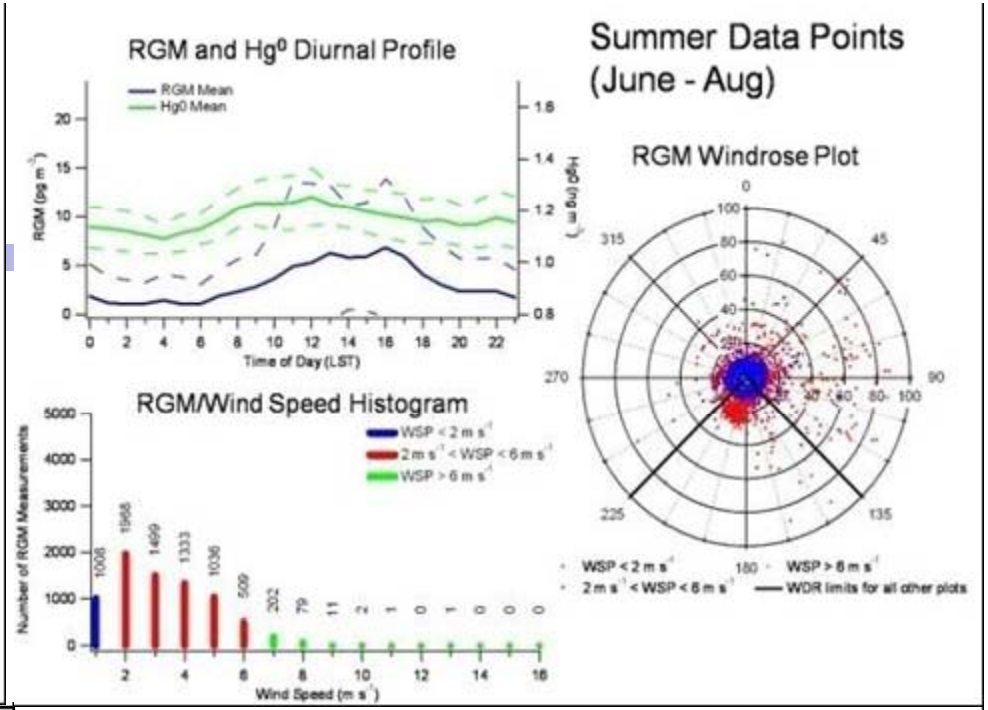


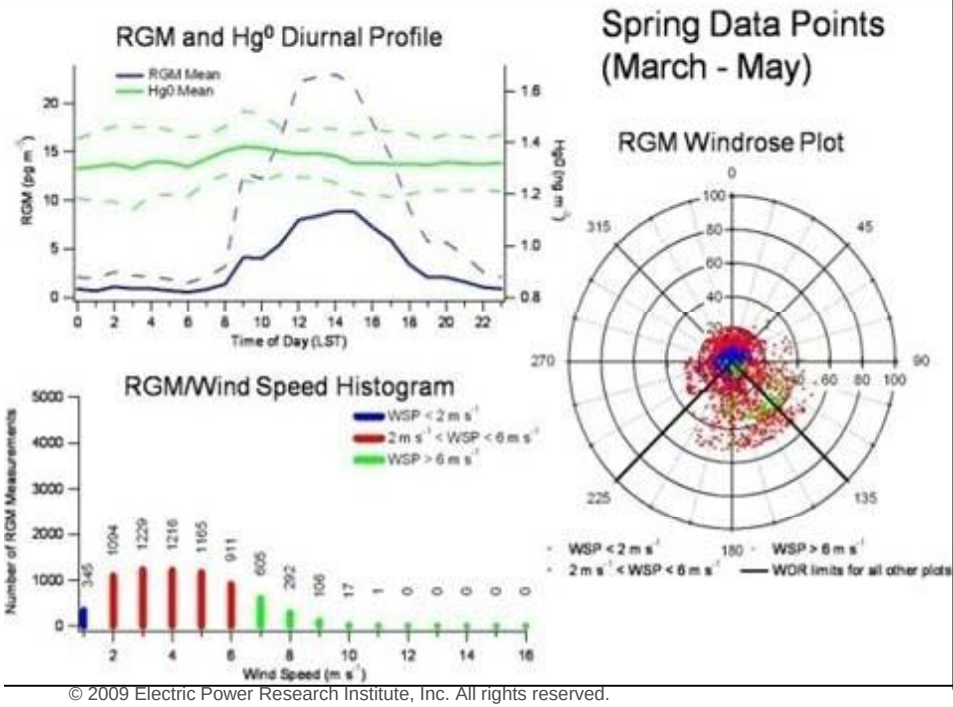
- What halogen species are present in the coastal environment?
- What are the background concentrations of halogen oxides?
- Do halogen oxides correlate with RGM, and wet deposition?

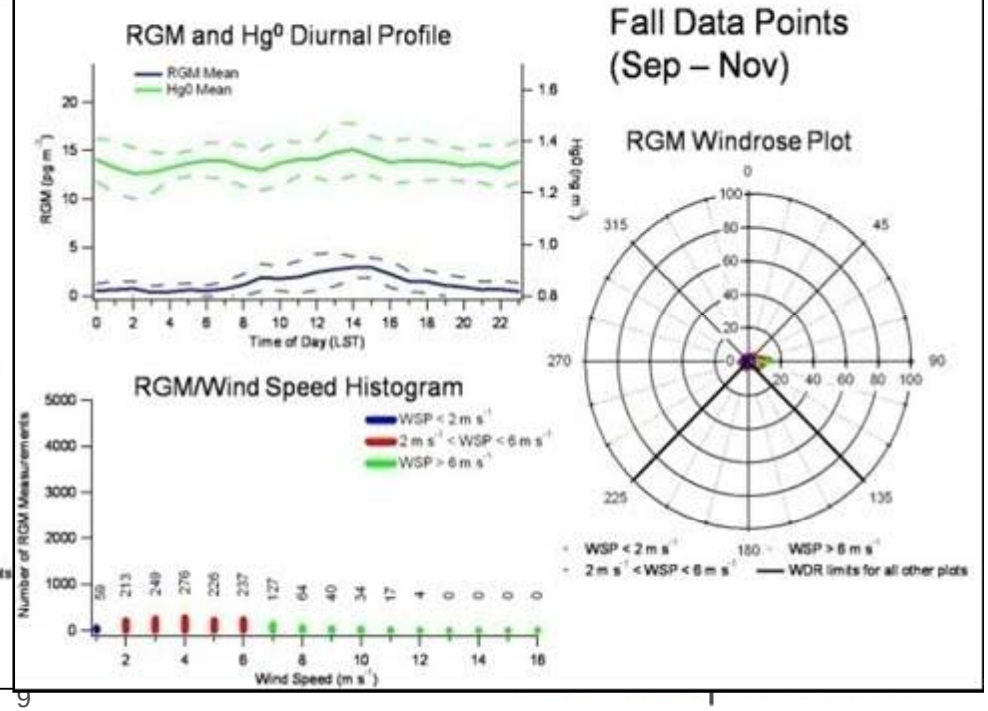
Halogen data

Species	Elevated NO_x (morning, ~5 ppb)	Low NO_x (afternoon, ~0.2 ppb)
Br	0.1 ppt	0.1 ppt
BrO	1 ppt (<5 ppt)	1 ppt (<5ppt)
IO	1 ppt (<2 ppt)	1 ppt (<2 ppt)
O_3	30 ppb	40 ppb
NO	2 ppb	0.15 ppb
NO_2	3 ppb	0.7 ppb
HO_2	10 ppt	100 ppt
HCHO	1.0 ppb	1.5 ppb
CHOCHO	150 ppt	300 ppt

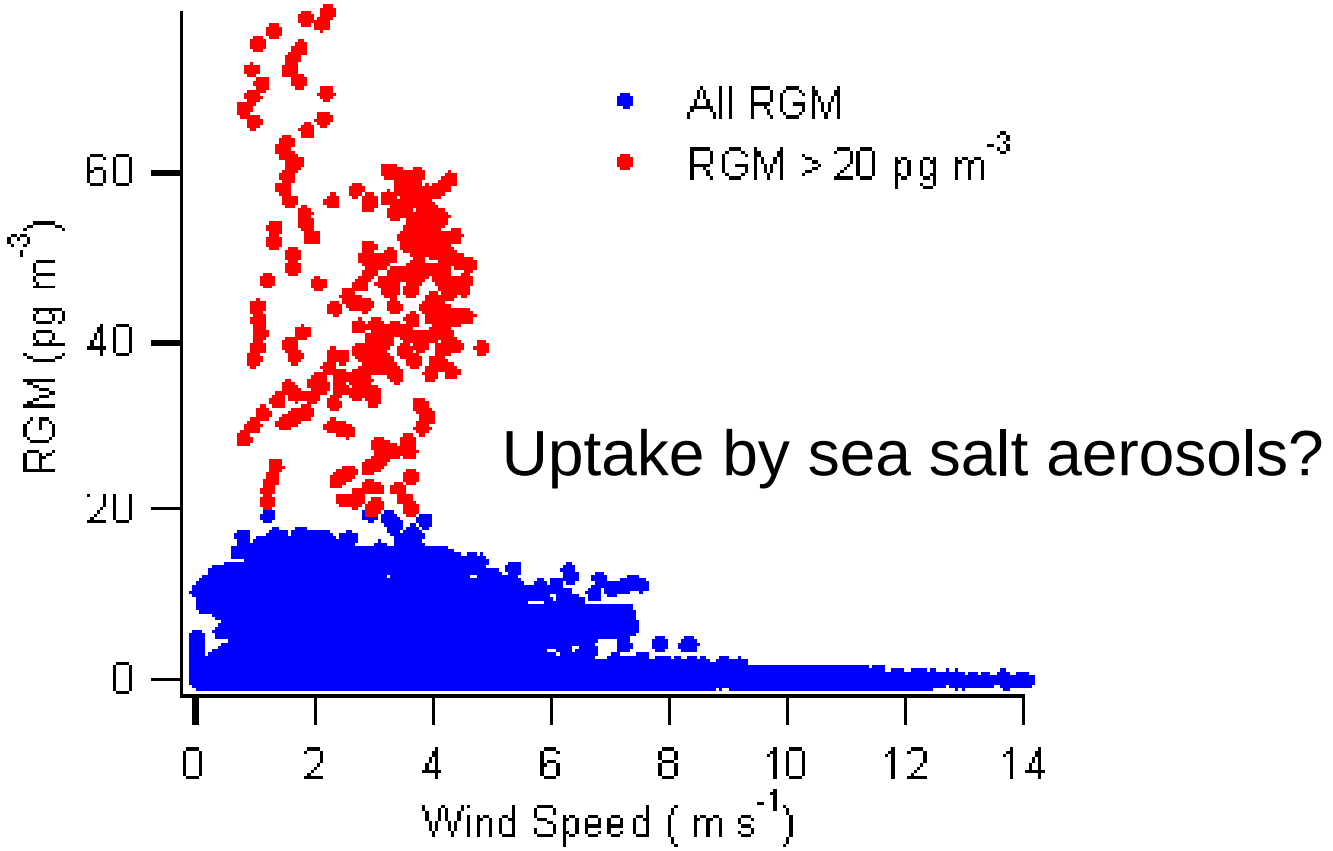








RGM vs Windspeed

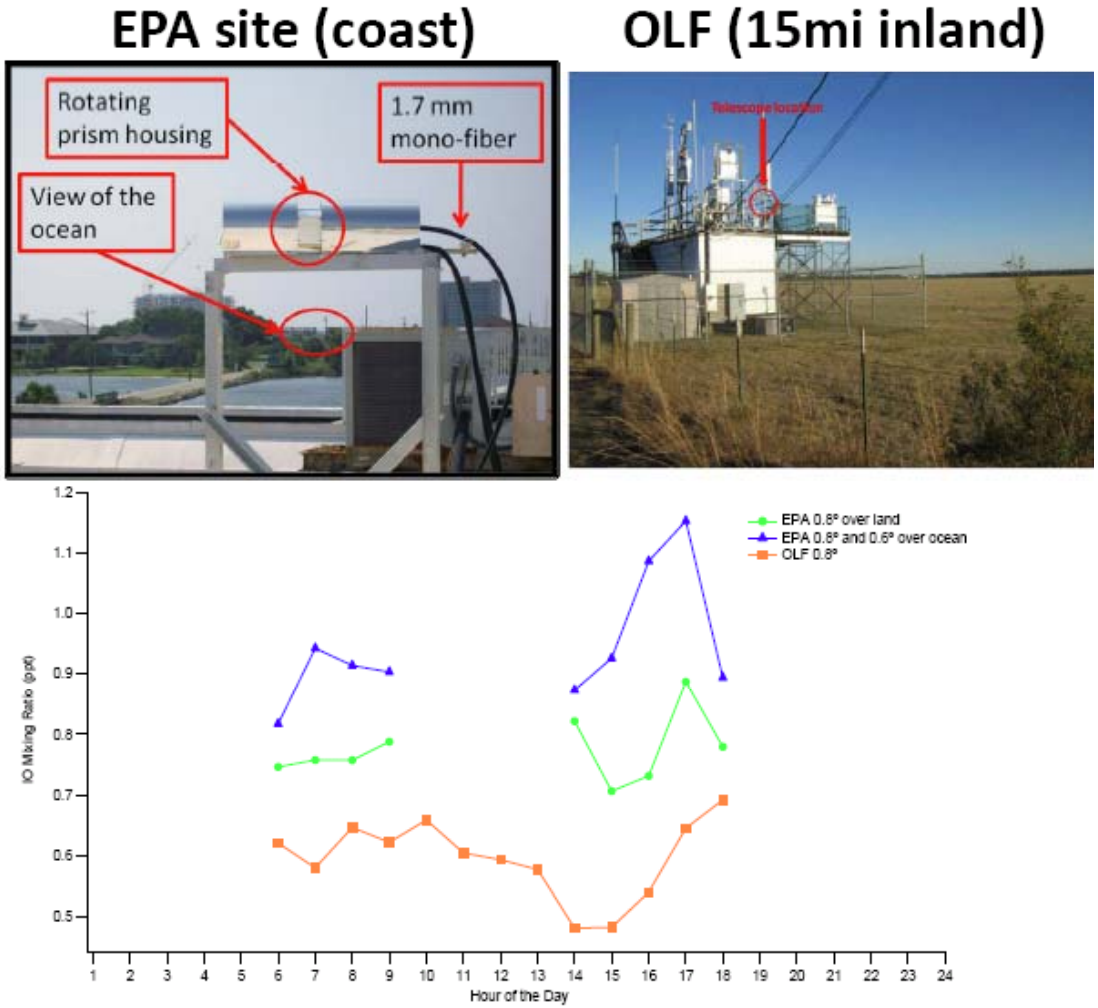


Combination of photochemical and meteorological (wind speed and wind direction) factors are at the core to explain events of elevated RGM (> 20 pg m-3) levels at OLF.

Summary Results Inland Station

- BrO not detect unequivocally; an upper limit of 1-4ppt from all data is estimated.
- IO present in small amounts: 0.5-1.5ppt, depending season.
- Glyoxal ($C_2H_2O_2$) also present: 0.2ppb.
- Formaldehyde (CH_2O) episodically detected: ~1.0 ppb.
- All constituents mainly detected at low altitudes (<2.5° above the horizon)
- Box model: >99% of chemically active forms of bromine are converted into inert species (HBr) within a minute and cannot survive transport from the coast to OLF.

Higher Levels of IO at New coastal site



Implications

Goodsite et al. 2007. Environ. Sci. Technol. 38, 1772-1776.

Direct effect → unimportant

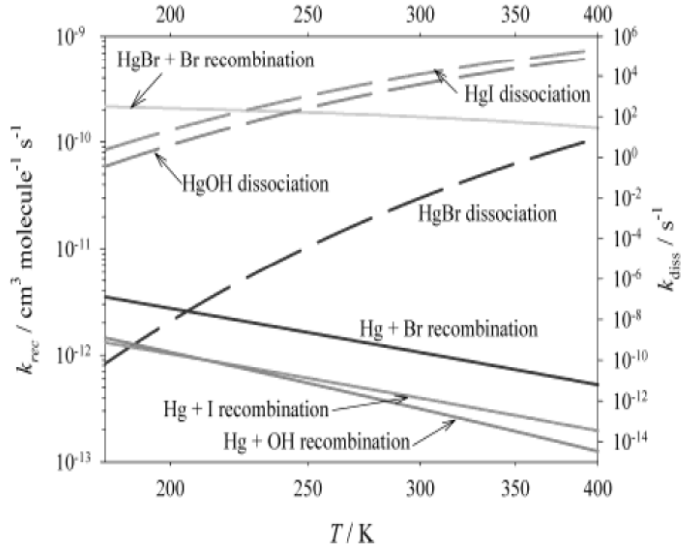


FIGURE 1. Rate coefficients calculated using RRKM theory, plotted as a function of temperature in Kelvin (*T*/K) for the recombination of Hg with Br, I, and OH and of HgBr with Br (solid lines, left-hand ordinate); and for the thermal dissociation of HgBr, HgI, and HgOH (broken lines, right-hand ordinate).

Calvert & Lindberg 2004. Atmos. Environ. 38, 5105–5116. Indirect effect → important

(b) Reaction of HgBr radicals

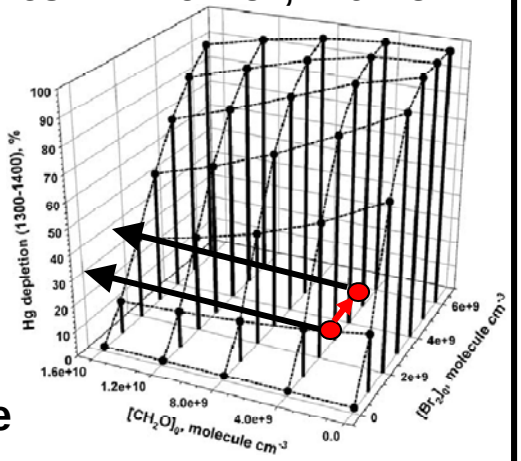
HgBr Reaction	Rate (molecule cm^{-3} s^{-1})	% of total HgBr reaction with X
HgBr → Hg + Br	1.09	−0.3
HgBr + OBr → BrHgOBr	1.84×10^2	76.4
(BrHgOBr + *hν* → Br + OHgBr)	(1.50×10^2)	2.7
HgBr + Br → BrHgBr	6.62	
HgBr + Cl → ClHgBr	3.8×10^{-4}	3.8×10^{-4}
HgBr + I → IHgBr	7.6	3.2
HgBr + OH → HOHgBr	1.16	0.5
HgBr + OCl → BrHgOCl	3.61	1.5
(BrHgOCl → BrHgO + Cl)	(7.39)	
HgBr + OI → BrHgOI	3.82×10^1	15.8
HgBr + HgBr → Hg_2Br_2	8.42×10^{-4}	7.0×10^{-4}

Calvert & Lindberg 2003. Atmos. Environ. 37, 4467–81.

"…gaseous mercury depletion rates are strongly dependent on …. reactive trace gases such as CH_2O" **This study:**

~1.0 ppb CH_2O and

~0.1 ppt Br_2 at inland site



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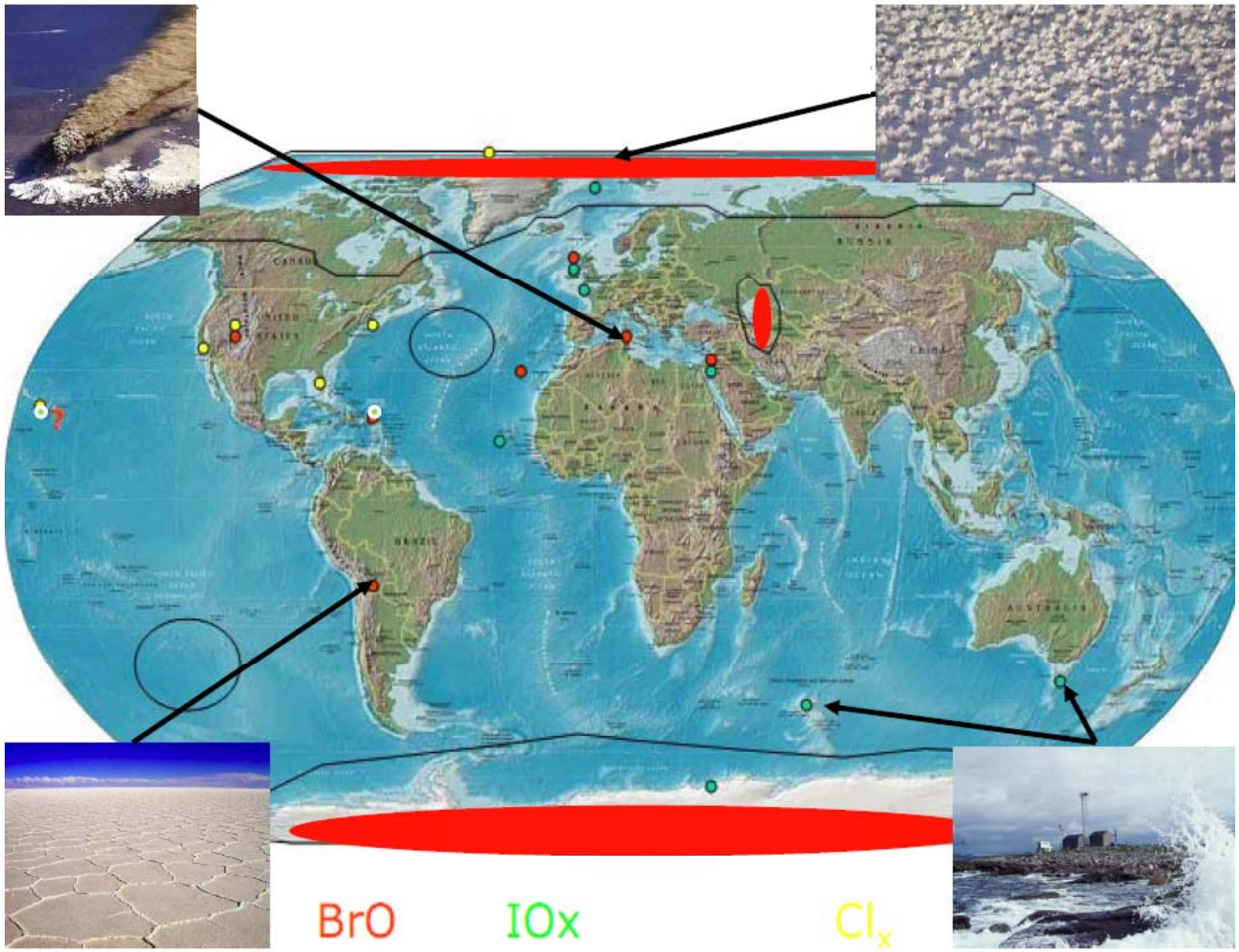
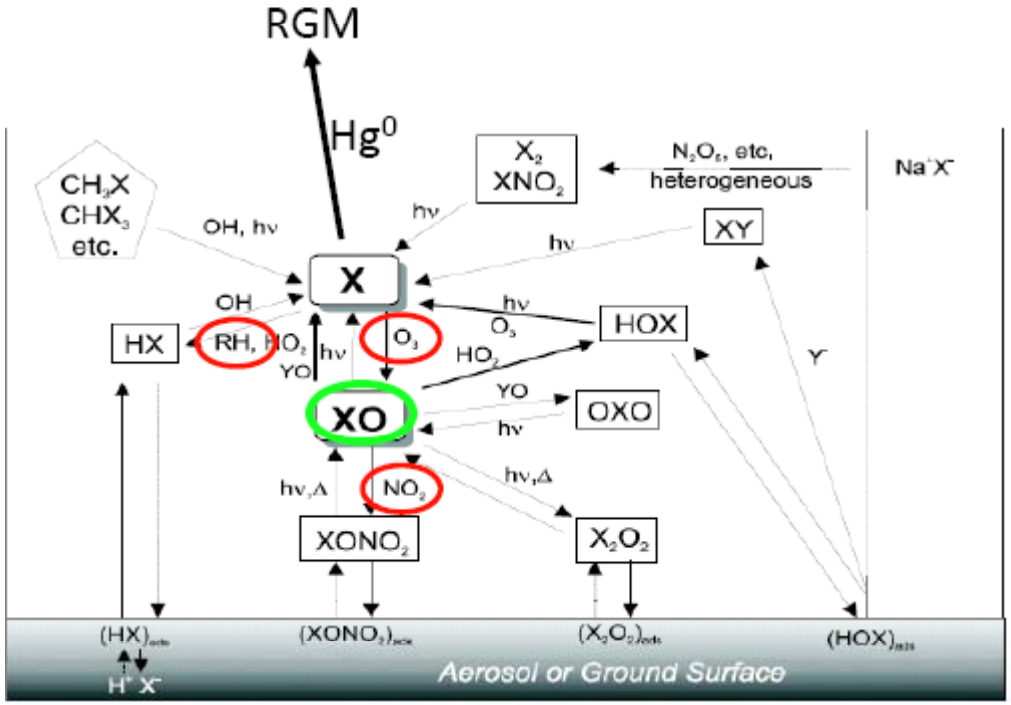
Halogen Measurements around the Globe

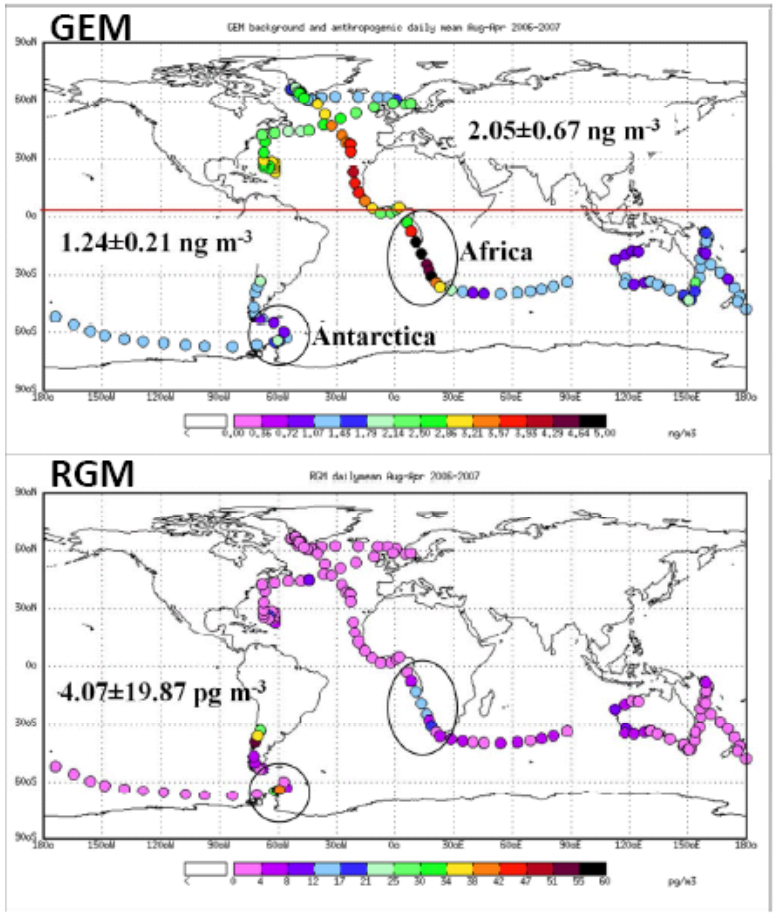


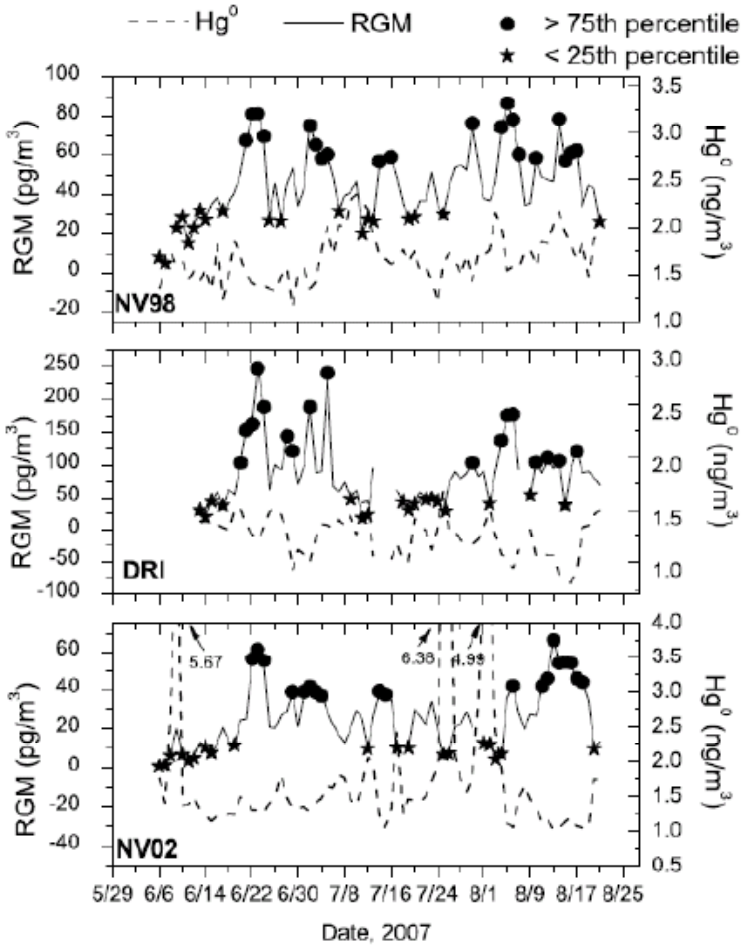
Halogen Chemistry in the atmosphere



- Oxidant levels determine the rate of mercury oxidation
- Competing NOx and HOx reactions to form inert reservoir species

Boundary Layer vs. Free Troposphere as Source for RGM?

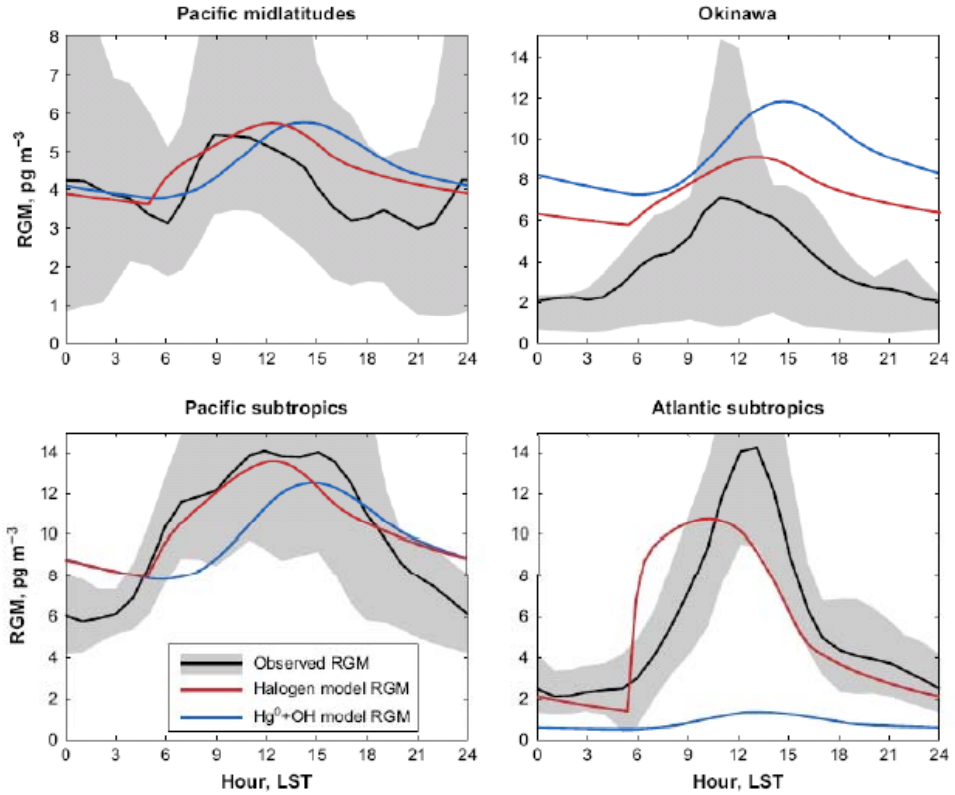




Skov et al. (2009), pers. comm.
RV Galathea: ½ month cruise (08-06 to 04-07)

Weiss Penzias et al. (2009), JGR, 114, D14302
Obrist et al. (2008), pers. comm.

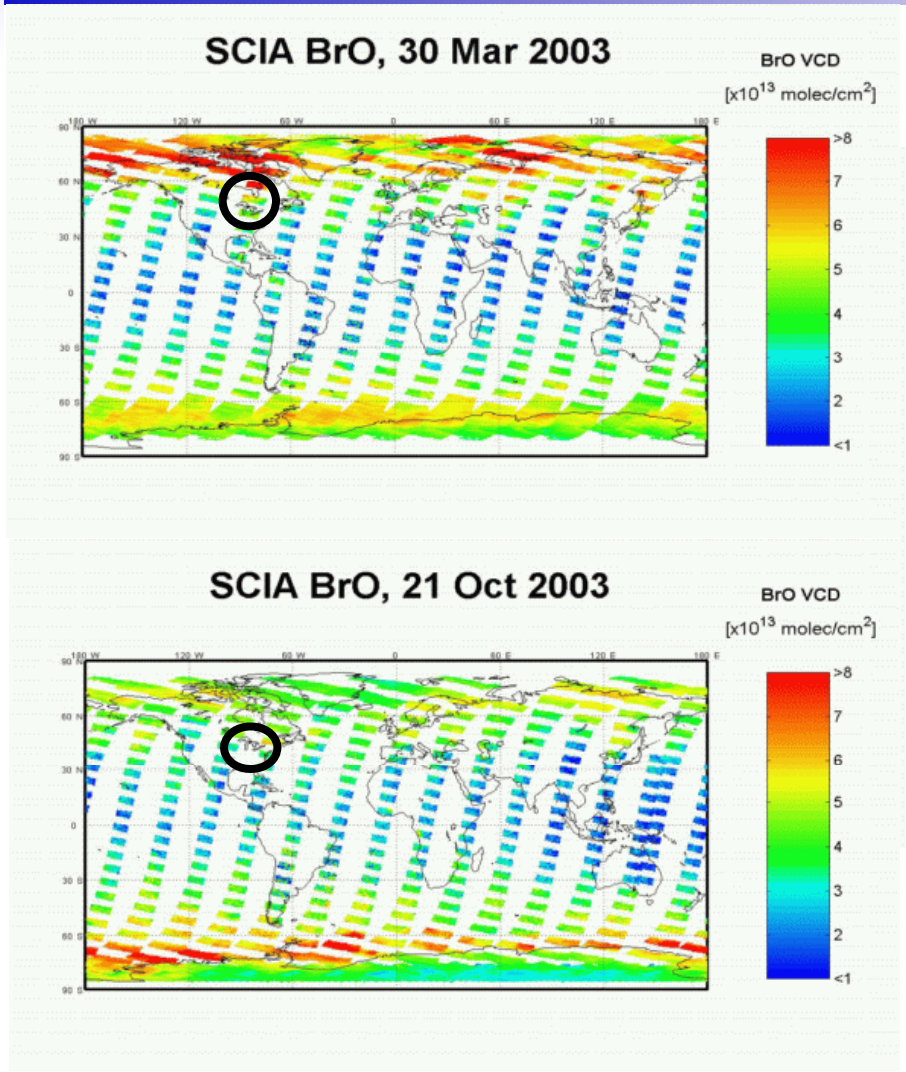
RGM diurnal cycle over the open ocean

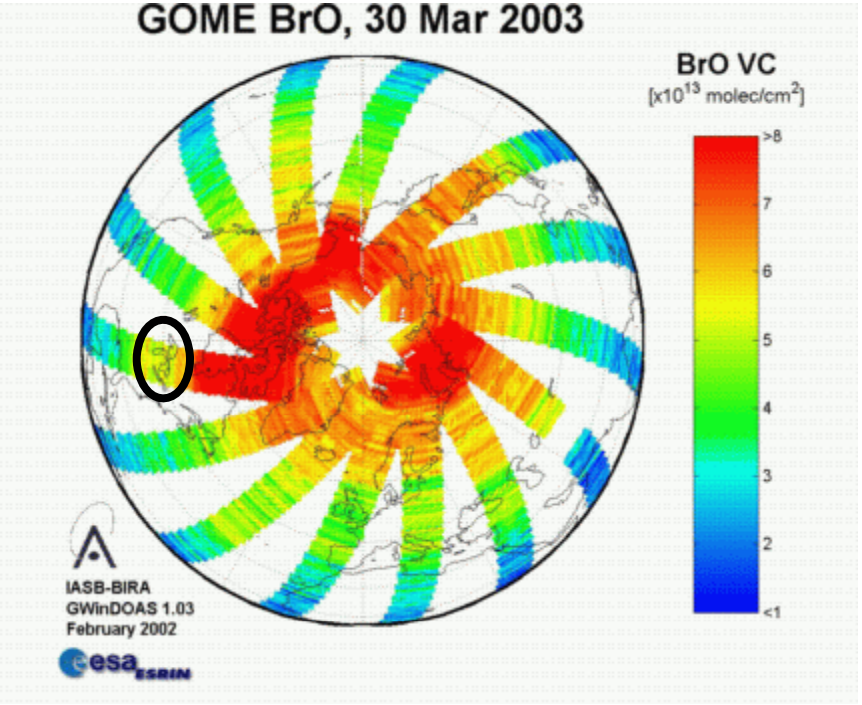


- Diurnal cycle is not explained by OH chemistry
- Halogen chemistry is needed to predict the observed dirunal cycle

Holmes et al. 2009, Atmos.Environ.

GOME and SCIAMACHY Satellite Data of BrO





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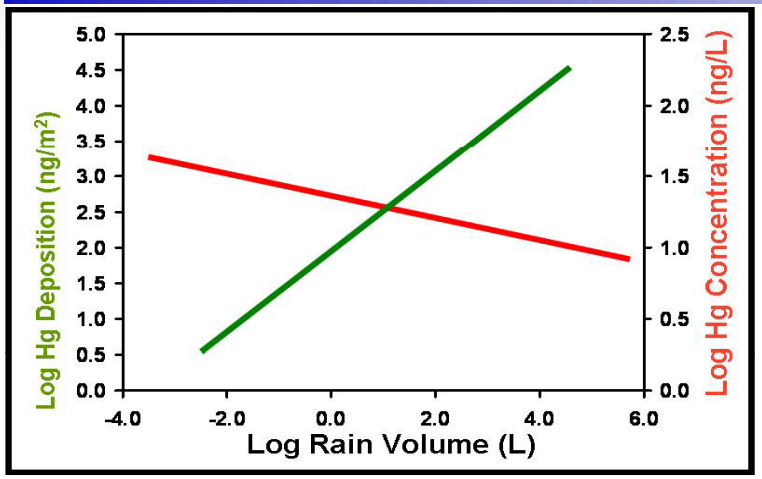
Summary, Implications and Conclusions

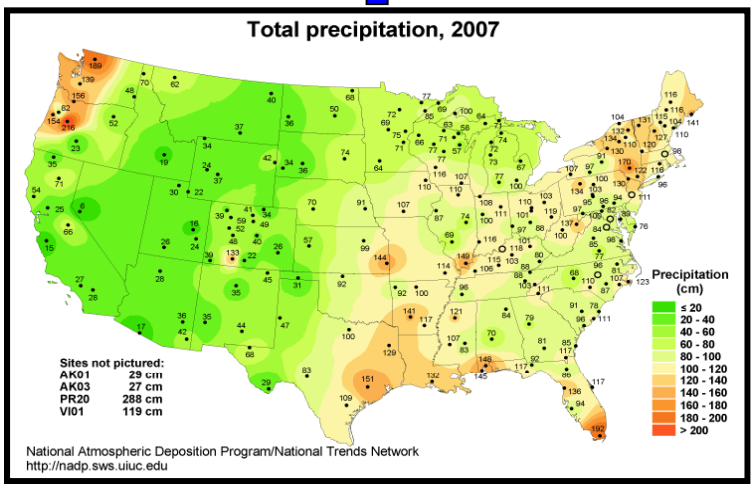
- Halogen chemistry improves fit between models and observations
  - Half life Hg^0
  - RGM's diurnal cycle (at least over the open ocean).
- Halogenoxides detected world wide in boundary layer.
- Halogens may play significant role in Hg oxidation along the Gulf Coast based on current observations.
- Satellites shows elevated BrO levels during spring time at higher latitudes (free troposphere); incl. The Great Lakes.
- Free troposphere important RGM pool and subsidence events can bring RGM to the surface.
- Currently no halogenoxide measurements in boundary layer above and around the great lakes.

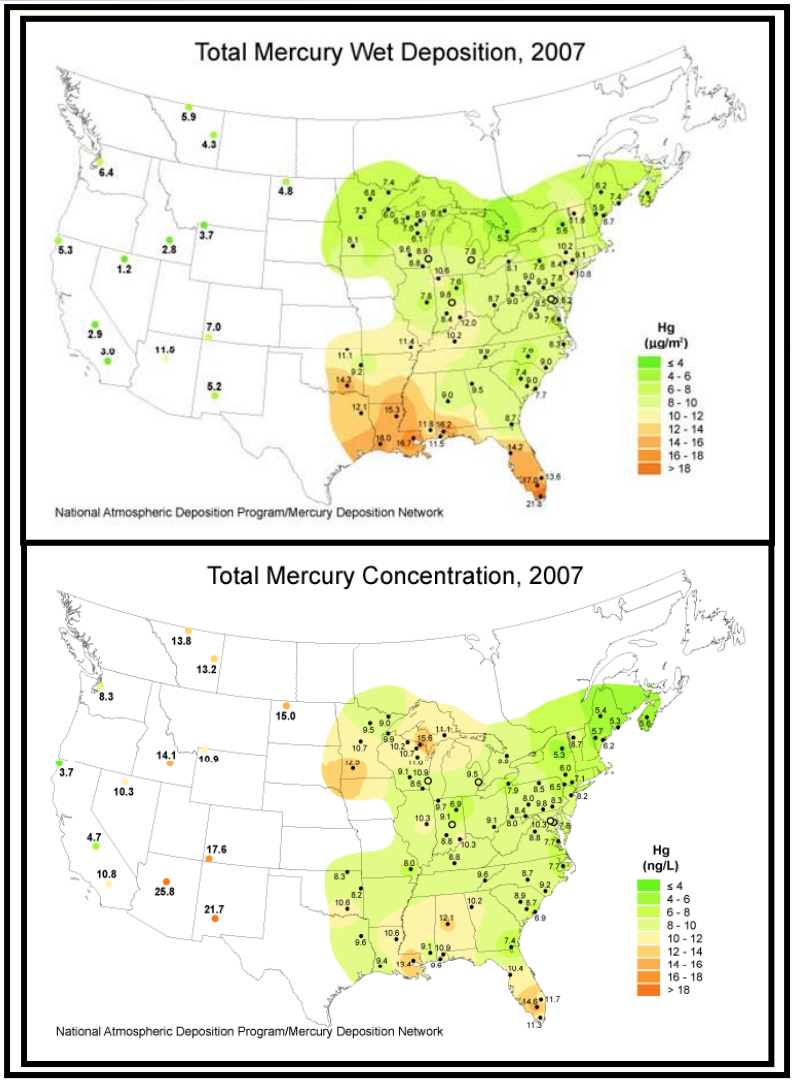
Questions?

Together…Shaping the Future of Electricity

Precipitation driven ? Reality check







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