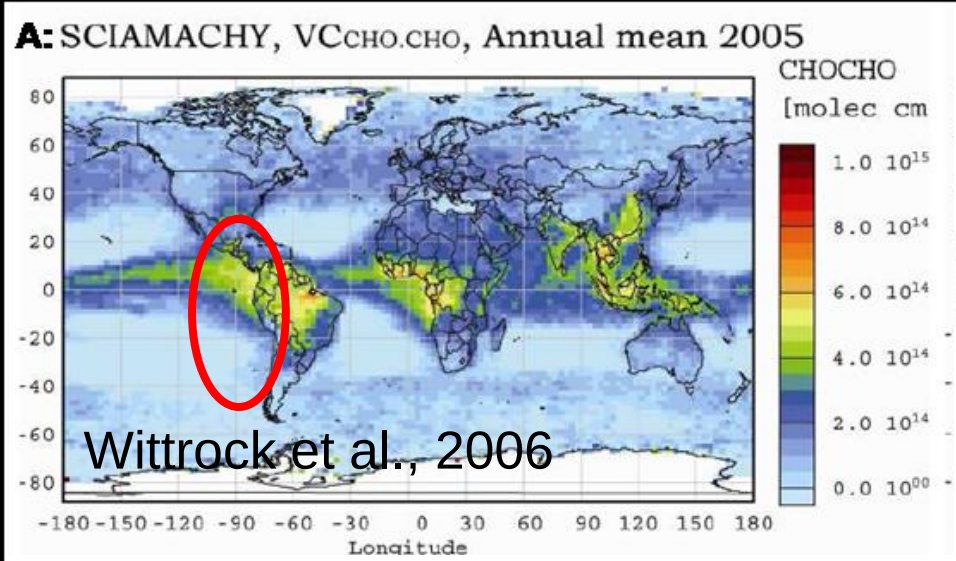
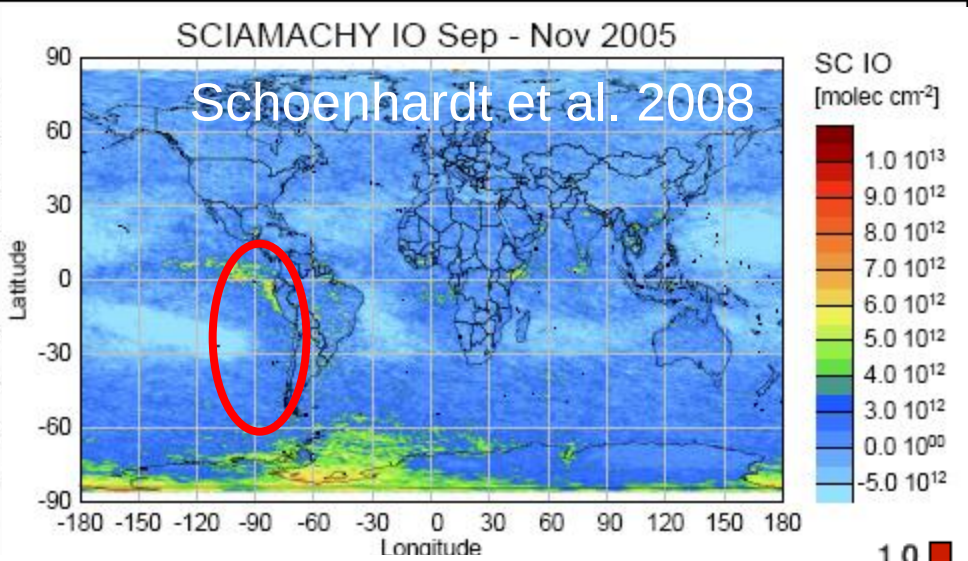

TORERO 2012
Tropical Ocean tRoposphere Exchange of Reactive halogen species and Oxygenated VOC

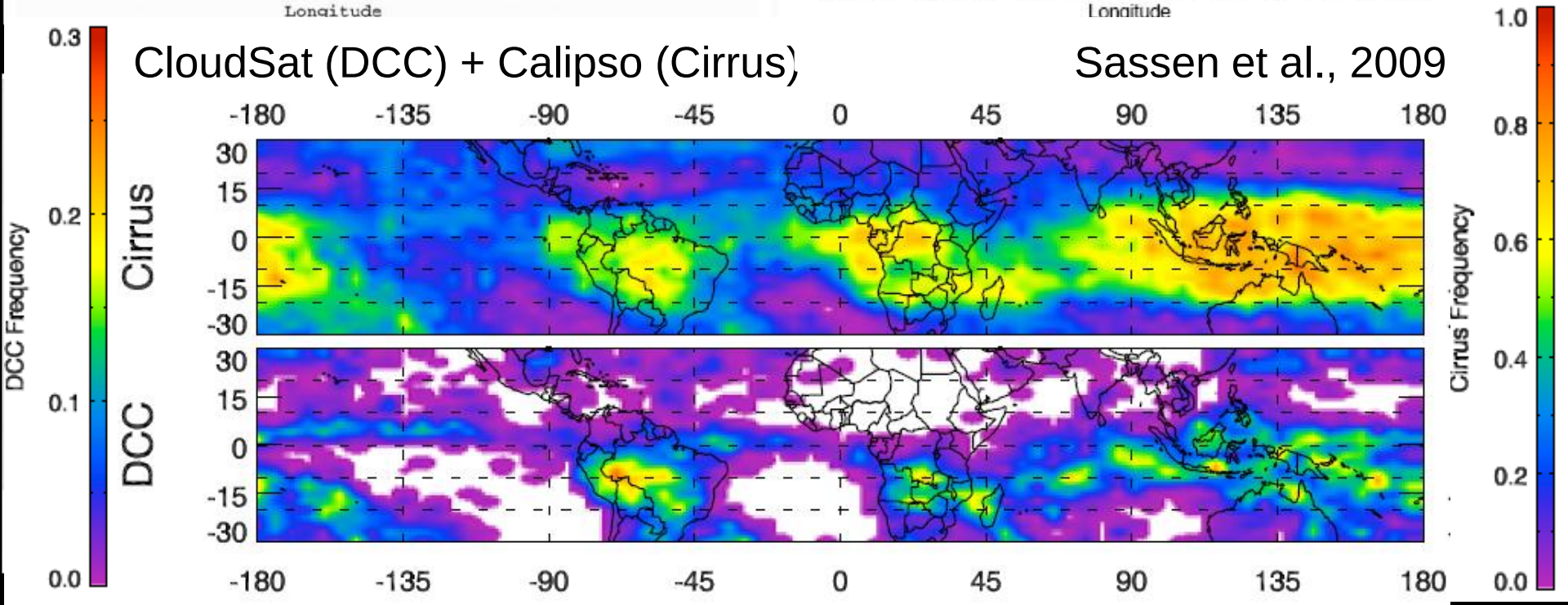
Scientific Objectives

- Halogen Chemistry: from surface waters to the free troposphere
  - Halogens and organic carbon modify oxidative capacity, and affect the lifetime of climate active gases (O3, DMS, CH4)
  - Bromine can modify mercury
- Satellites: provide information on global scales, shape our view about sources

TORERO study area







Glyoxal: A smoking gun for other OVOCs

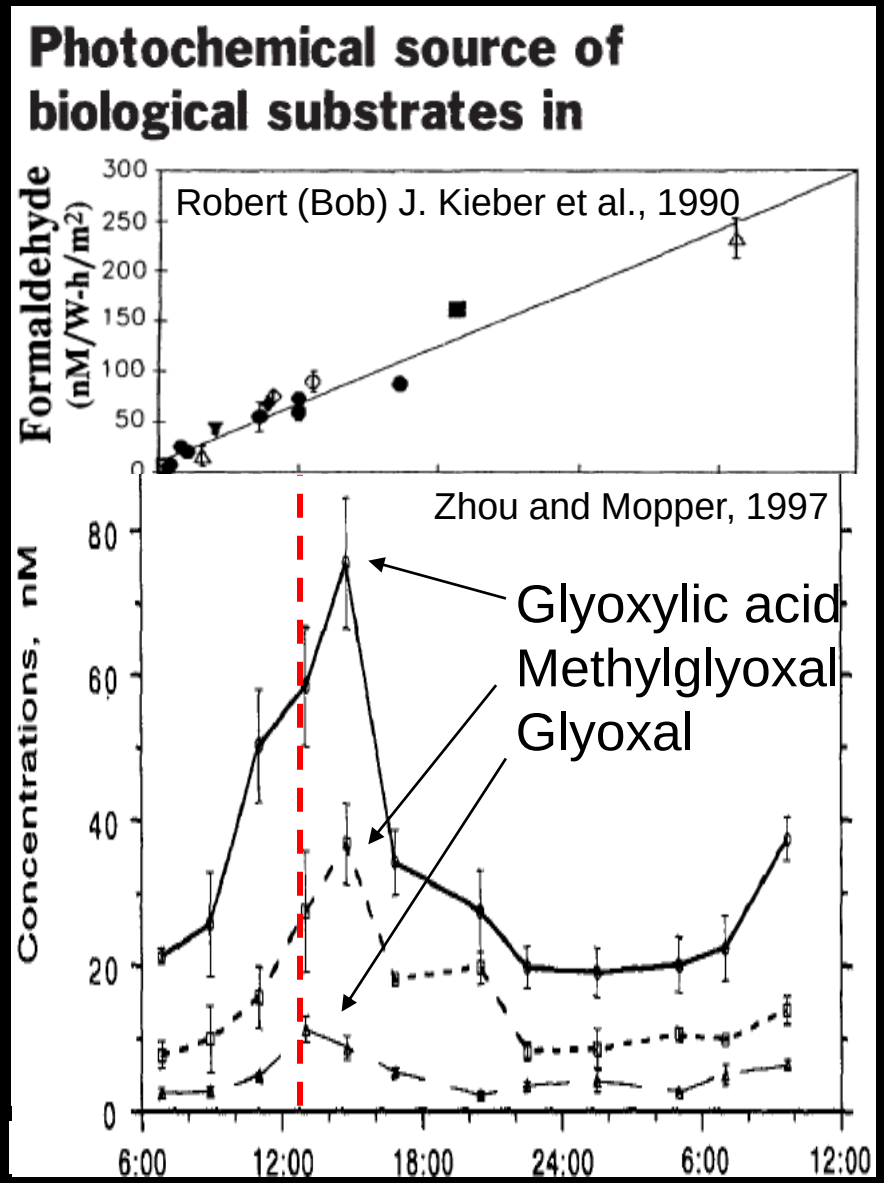
Table III. Typical Carbonyl Concentrations in Clean Marine Air, and Predicted and Measured Concentrations in Surface Open Ocean Seawater

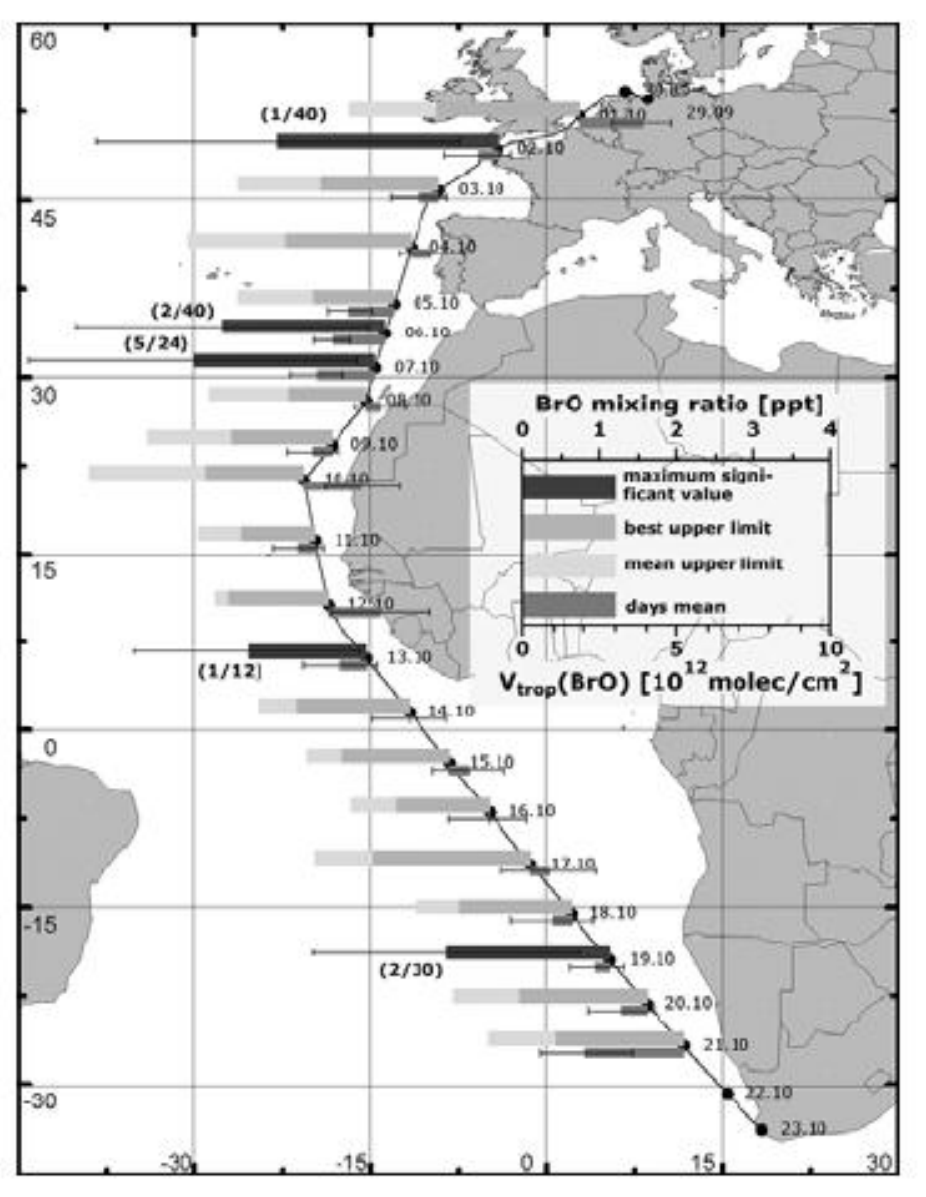
compounds	concn in air,[a] ppb	predicted concn in seawater,[b] nM	measured concn in seawater,[c] nM
formaldehyde	0.4	1500	2–40
acetaldehyde	0.3	4	2–15
propanal	0.1	1	0.4–3
butanal	0.08	0.5	0.3–2
pentanal	0.1	0.5	0.2–5
hexanal	0.1	0.3	0.2–0.6
heptanal	0.1	0.2	0.2–0.5
octanal	0.1	0.1	0.2–0.7
nonanal	0.15	0.06	0.2–1
decanal	0.1	0.02	0.2–0.8
benzaldehyde	~0.01	0.3	ND[c]
acetone	0.3	10	3–50
butanone	0.05	0.8	0.5–2
glyoxal	0.08	30000	0.5–5
methylglyoxal	~0.01	300	0.1–1.5

[a] Typical carbonyl concentrations in the air over open Caribbean Sea and Sargasso Sea. [b] Predicted concentrations in seawater in equilibrium with atmosphere: $[R'R''CO] = K^*P$ at 25 °C. [c] Carbonyl concentrations measured in South Sargasso Sea surface water. ND, not determined.

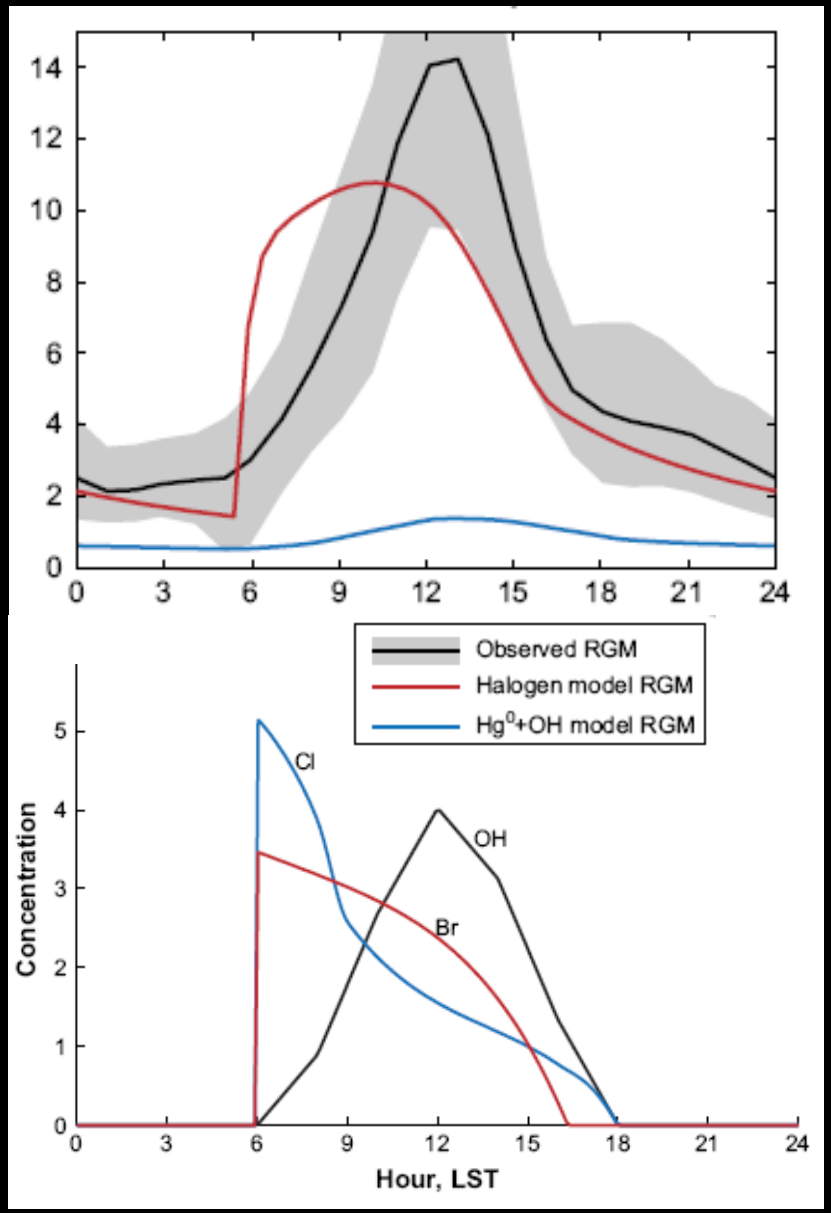
Zhou and Mopper, 1990, EST, 24, 1864

Glyoxal over the Sargasso Sea
(80 ppt during the day)



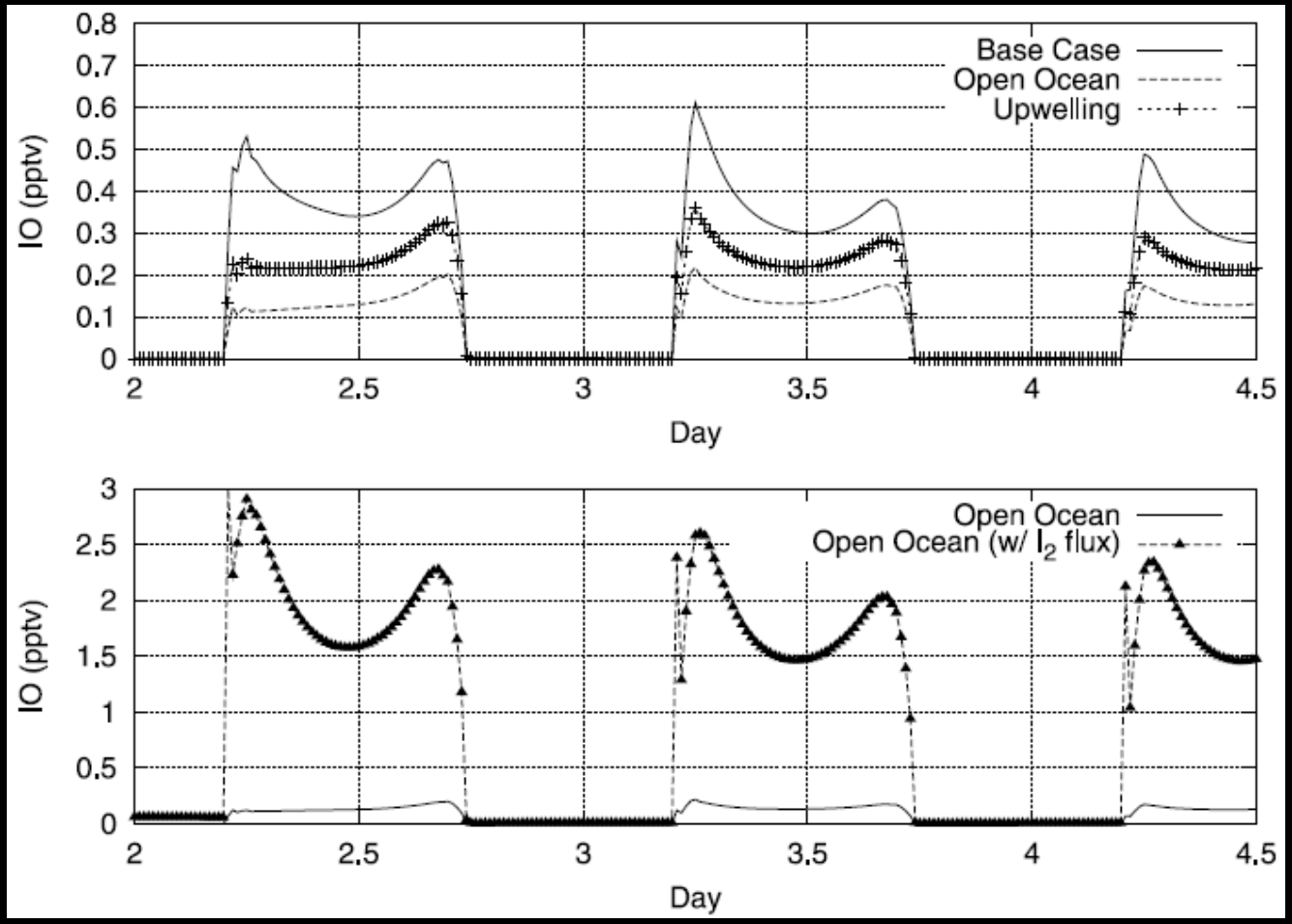


Leser et al., 2003



Holmes et al., 2009; Geos-Chem:
~ 2ppt BrO under most conditions

Reactive Iodine Species



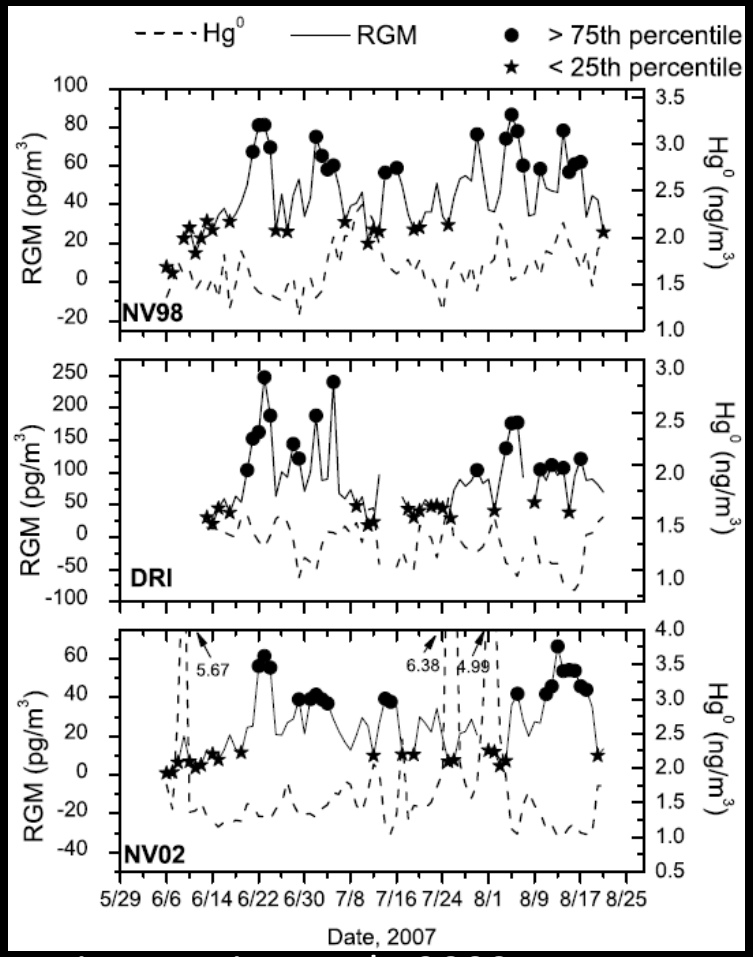
only organic iodine gases as iodine precursors (biological source)

organic iodine ("open ocean") and additional flux of I_2

Jones et al., 2010; Mahajan et al., 2010

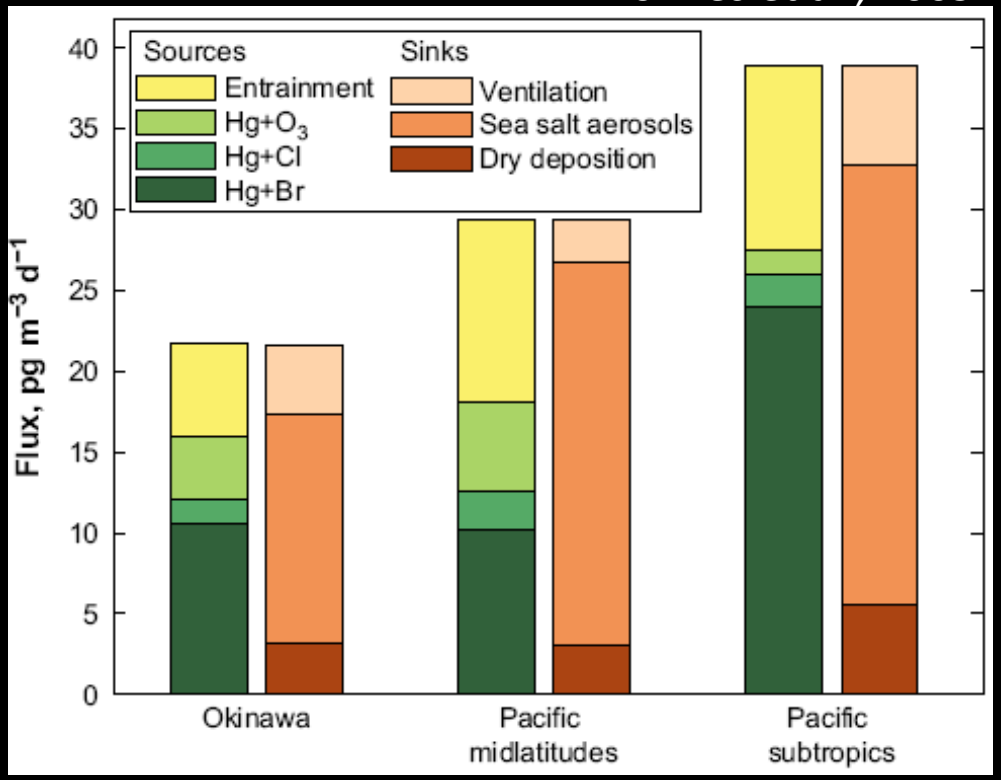
- Organic precursors alone are not sufficient.
- An inorganic iodine precursor?

Atmospheric Mercury



Weiss-Penzias et al., 2009

Holmes et al., 2009



$$\mathrm{Hg^0 + Br \xrightarrow{M} HgBr} \qquad 1.1 \times 10^{-12}\,(T/298)^{-2.37}$$

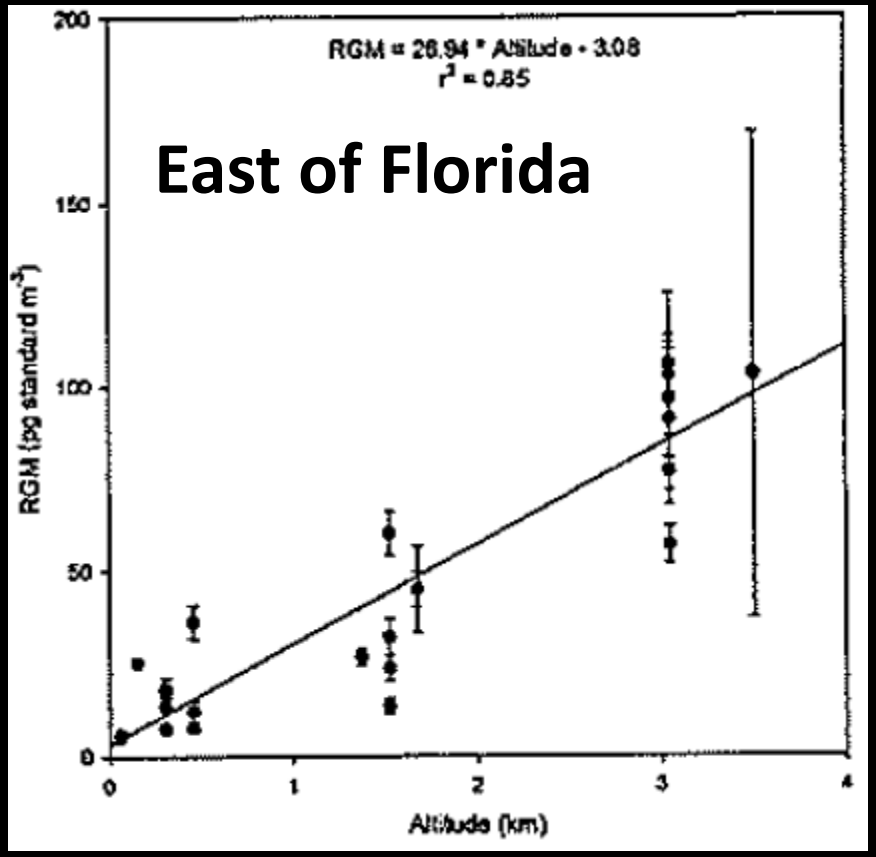
$$\mathrm{HgBr \xrightarrow{M} Hg^0 + Br} \qquad 1.2 \times 10^{10}\exp(-8357/T)$$

$$\mathrm{HgBr + Br \xrightarrow{M} HgBr_2} \qquad 2.5 \times 10^{-10}\,(T/298)^{-0.57}$$

Is there a pool of reactive gaseous mercury, RGM, in the FT?

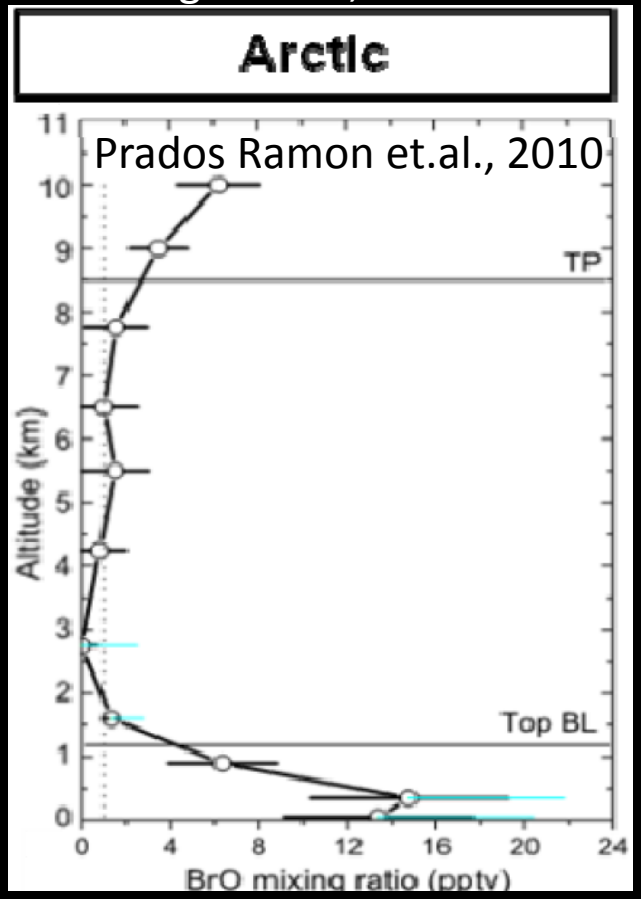
Is there a hemispheric Br atom background in the FT?

Atmospheric Mercury



Landis et al., 2005

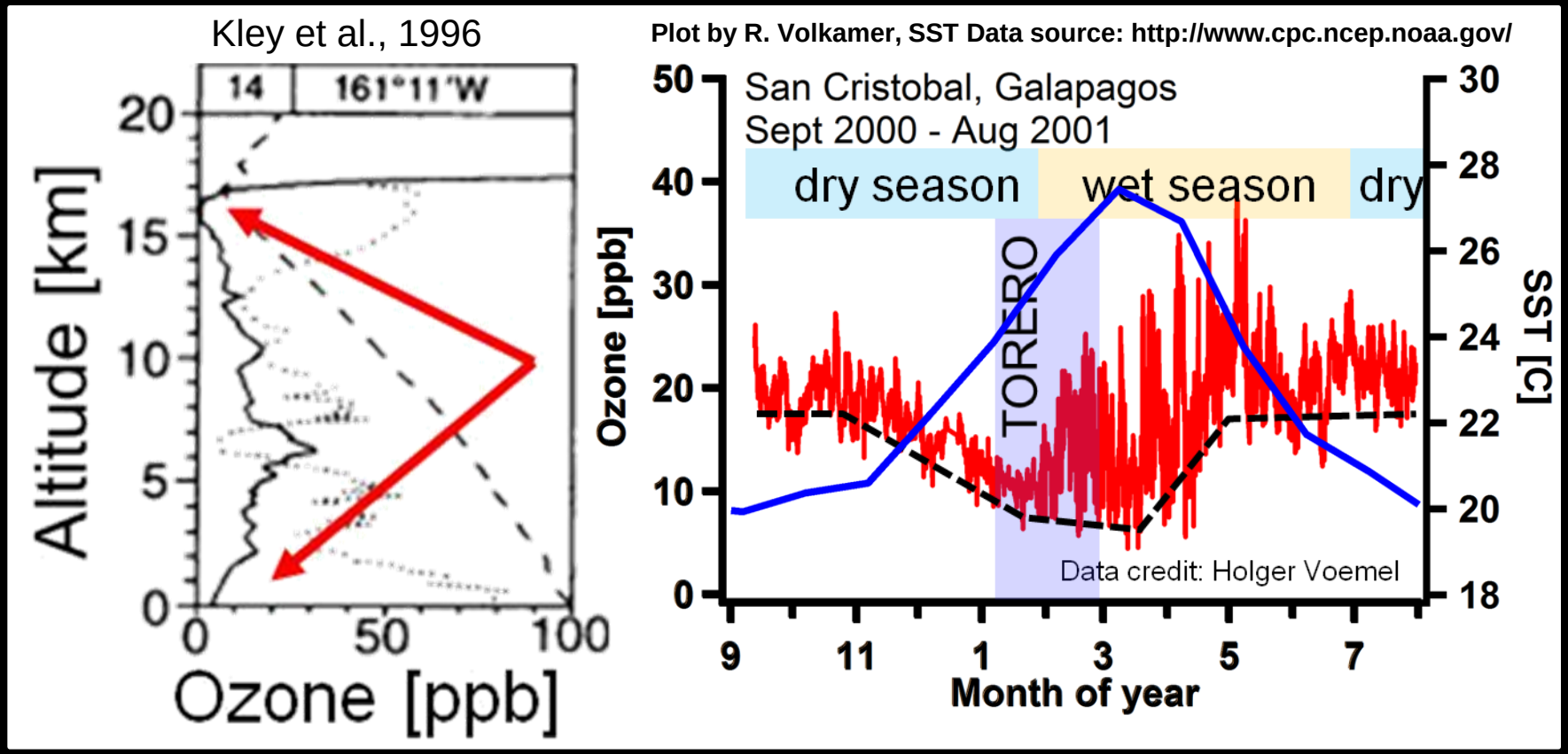
Fitzenberger et al., 2000



- Many high-altitude particles contained Hg! (Murphy et al., 1998)
- Few RGM measurements available in the FT.
- BrO ubiquitous in the FT? Uncertainties remain...

Fitzenberger et al., 2000; van Roozendael et al., 2002; Ebinghaus et al., 2002; Salawitch et al., 2005; Theys et al., 2007; Prados-Ramon et al., 2010; Heue et al., 2010; Coburn et al., 2011

TORERO timing



- Pronounced annual ozone cycle (min <10 ppb) at Galapagos (right)
- Vertical distribution could be suggestive of deep convective transport
- Is low O3 in MBL controlled by changes in chemistry or transport?
- SST link may point to relevance of surface ocean dynamics?