The Ocean in near Equilibrium with Respect to Atmospheric CH_3Br

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- Dr. Jim Butler and Dr. Steve Montzka
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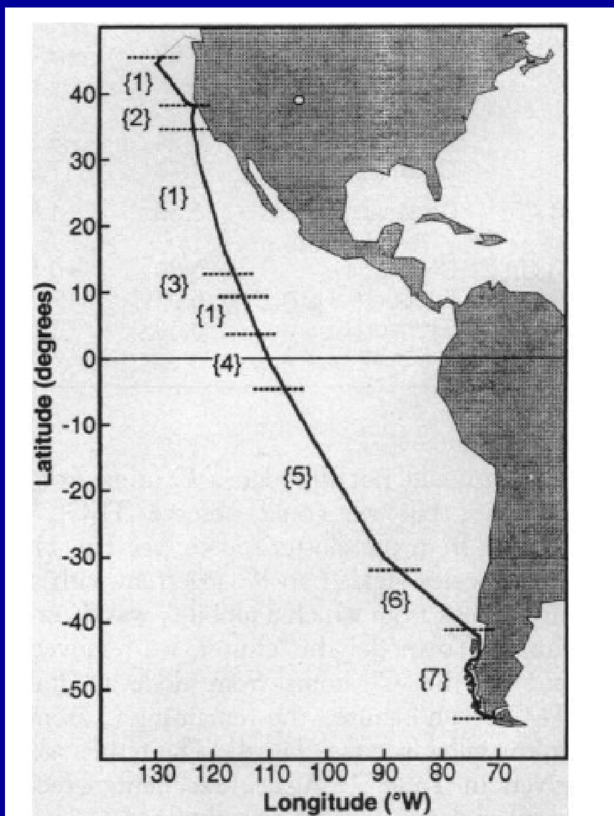
- The captains and crews of the R/V Thomas Thompson and FS Polarstern.

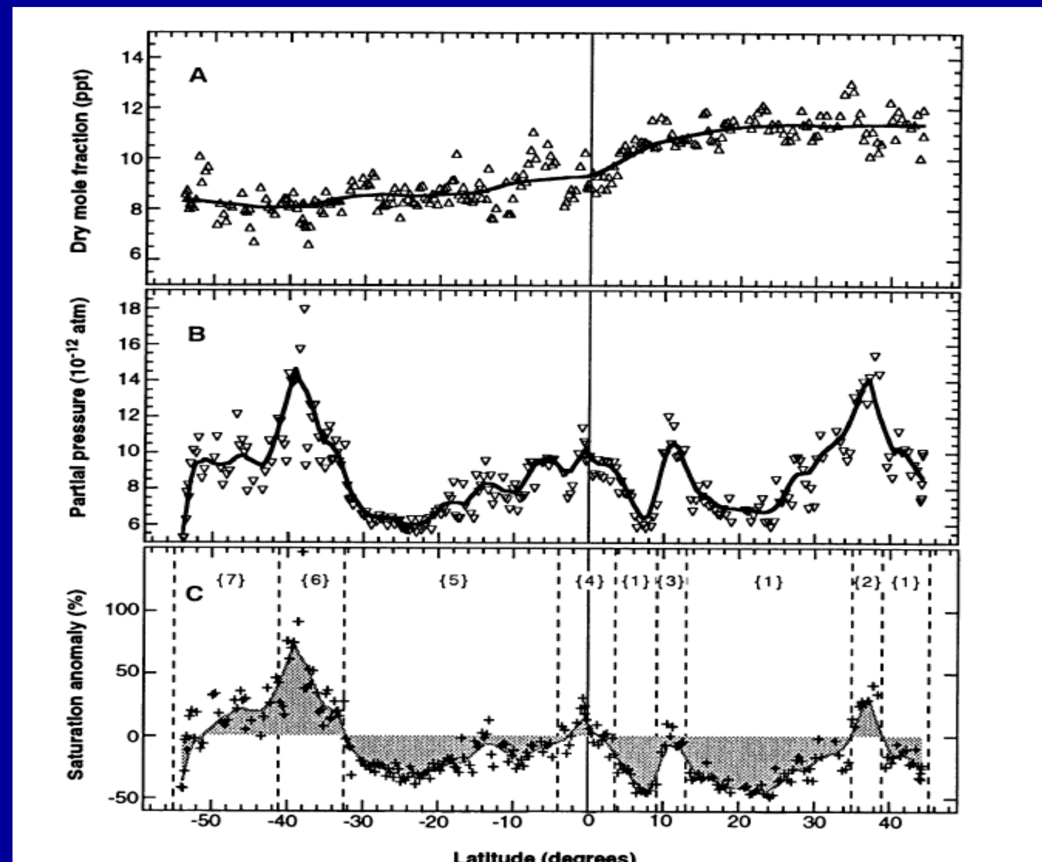
A Net Sink for Atmospheric CH_3Br in the East Pacific Ocean

Jürgen M. Lobert, James H. Butler, Stephen A. Montzka, Laurie S. Geller, Richard C. Myers, James W. Elkins

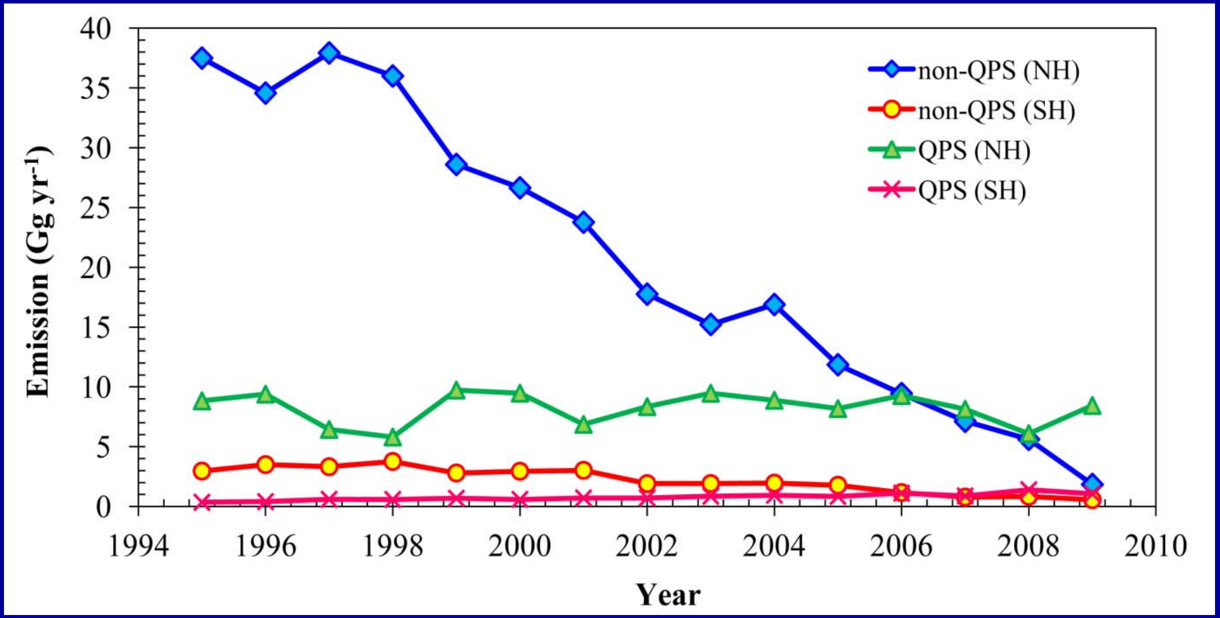
BLAST I, 1994

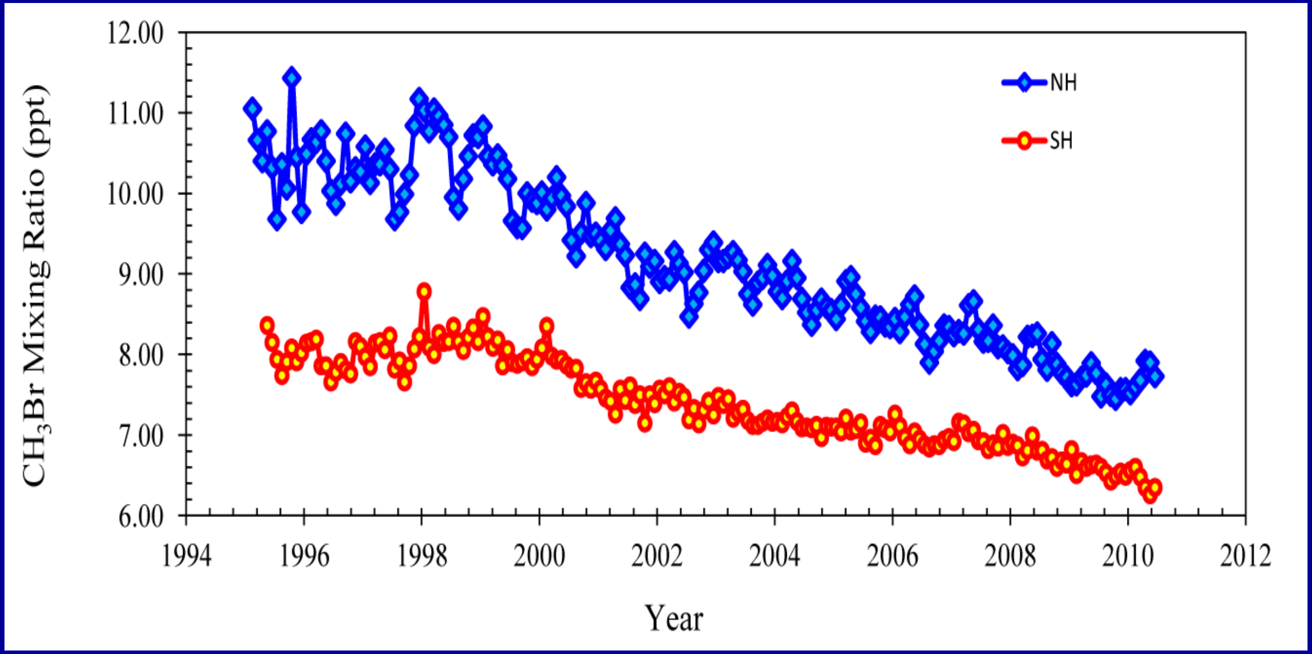
Published in Science in 1995





Phase-Out





Atmospheric Observations from NOAA/ESRL Global Monitoring Division

NOAA/ESRL GMAC 2012

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Buffering Effect of the Ocean

GEOPHYSICAL RESEARCH LETTERS, VOL. 21, NO. 3, PAGES 185-188, FEBRUARY 1, 1994

The potential role of the ocean in regulating atmospheric CH_3Br

James H. Butler

Climate Monitoring and Diagnostics Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colorado

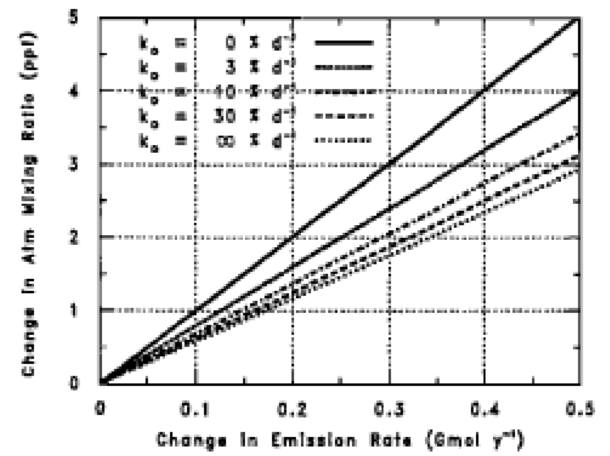
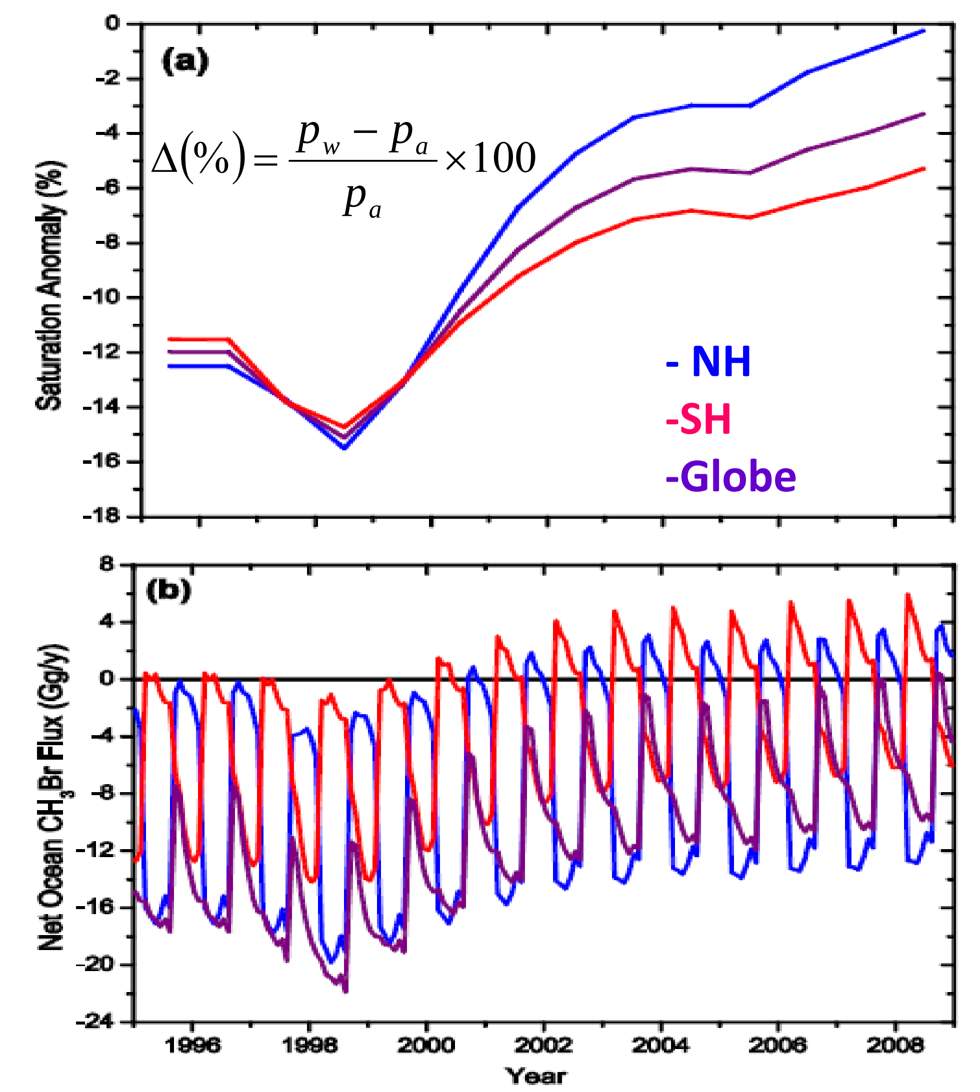


Fig. 2. Steady-state change in atmospheric mixing ratio (ppt) resulting from a changes in anthropogenic emission rate (Gmol y^{-1}). Curves are calculated from equation 12, with the current best estimates for k_a, k_1, and k_2 as given in Table 1, and allowing k_o to vary from 0 to ∞ (R = 0 to 1). The curve for $k_o = 0$ represents no oceanic loss, whereas for $k_o = \infty$ the oceanic degradation rate is infinitely fast.

Ocean should become less undersaturated as atmospheric concentration decreases

Recent Models Predicted Less Negative Saturation State



1996:

$\Delta(\%)$ = -11.7%

Net sea-to-air flux:

-14 Gg yr^{-1}

2007:

$\Delta(\%)$ = -6.0%

Net sea-to-air flux:

-6.6 Gg yr^{-1}

Yvon-Lewis et al., 2009, ACP

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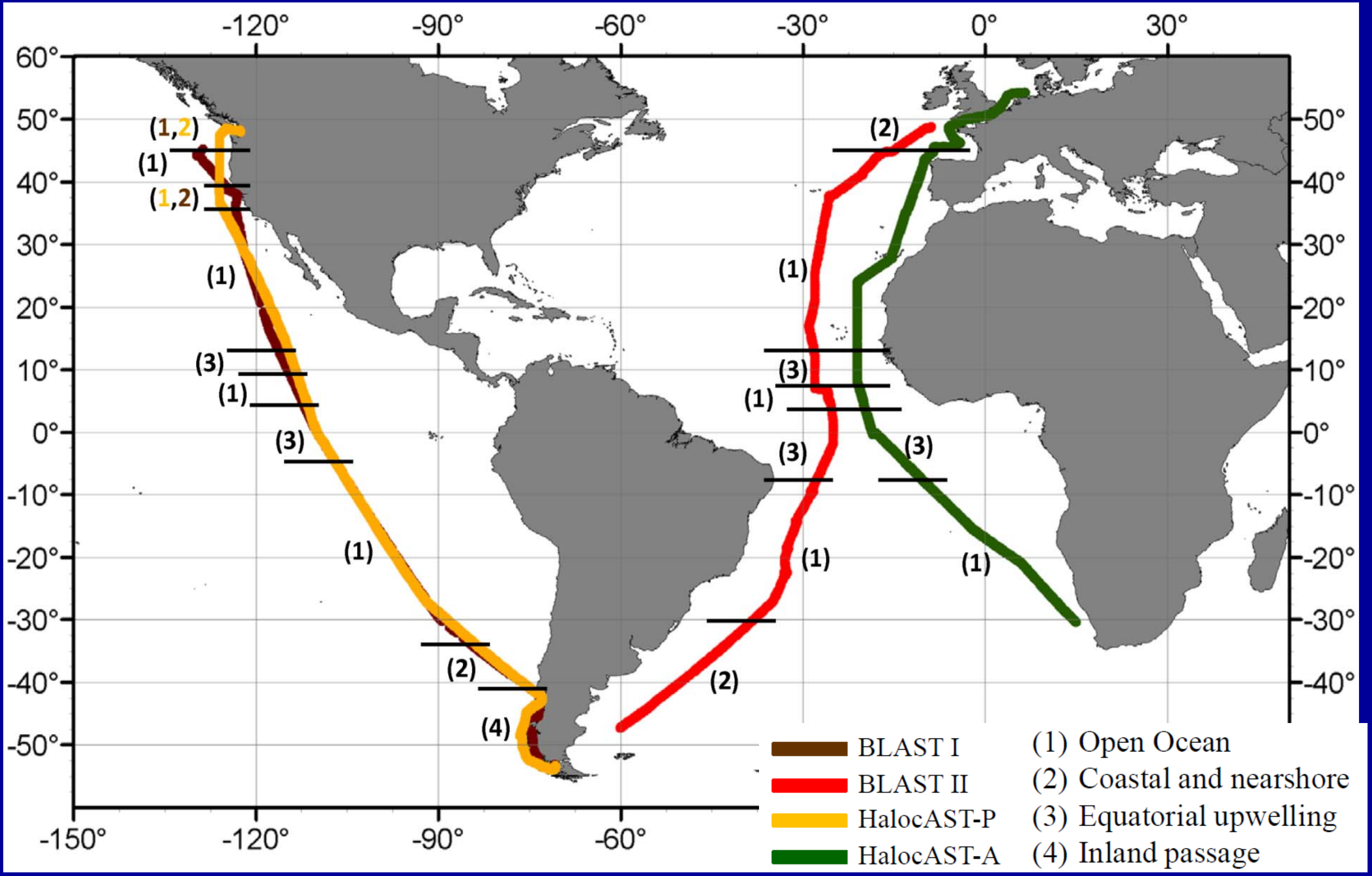
Halocarbon Air-Sea Transect s– Pacific and Atlantic



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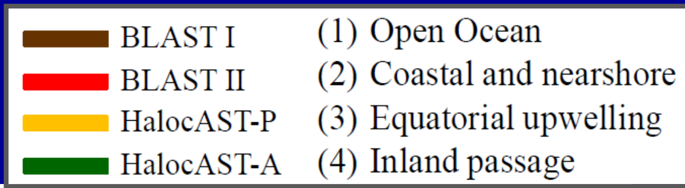
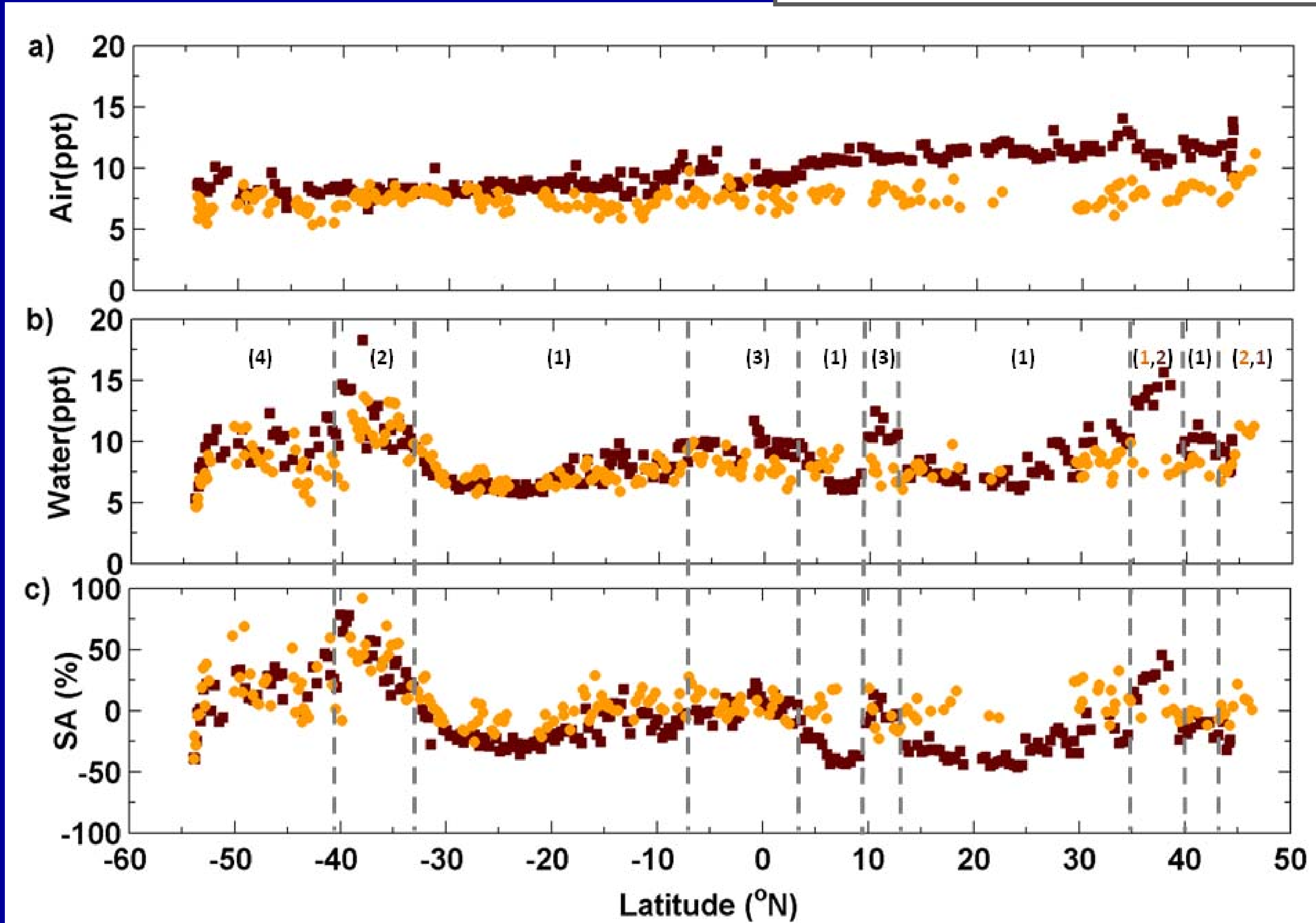
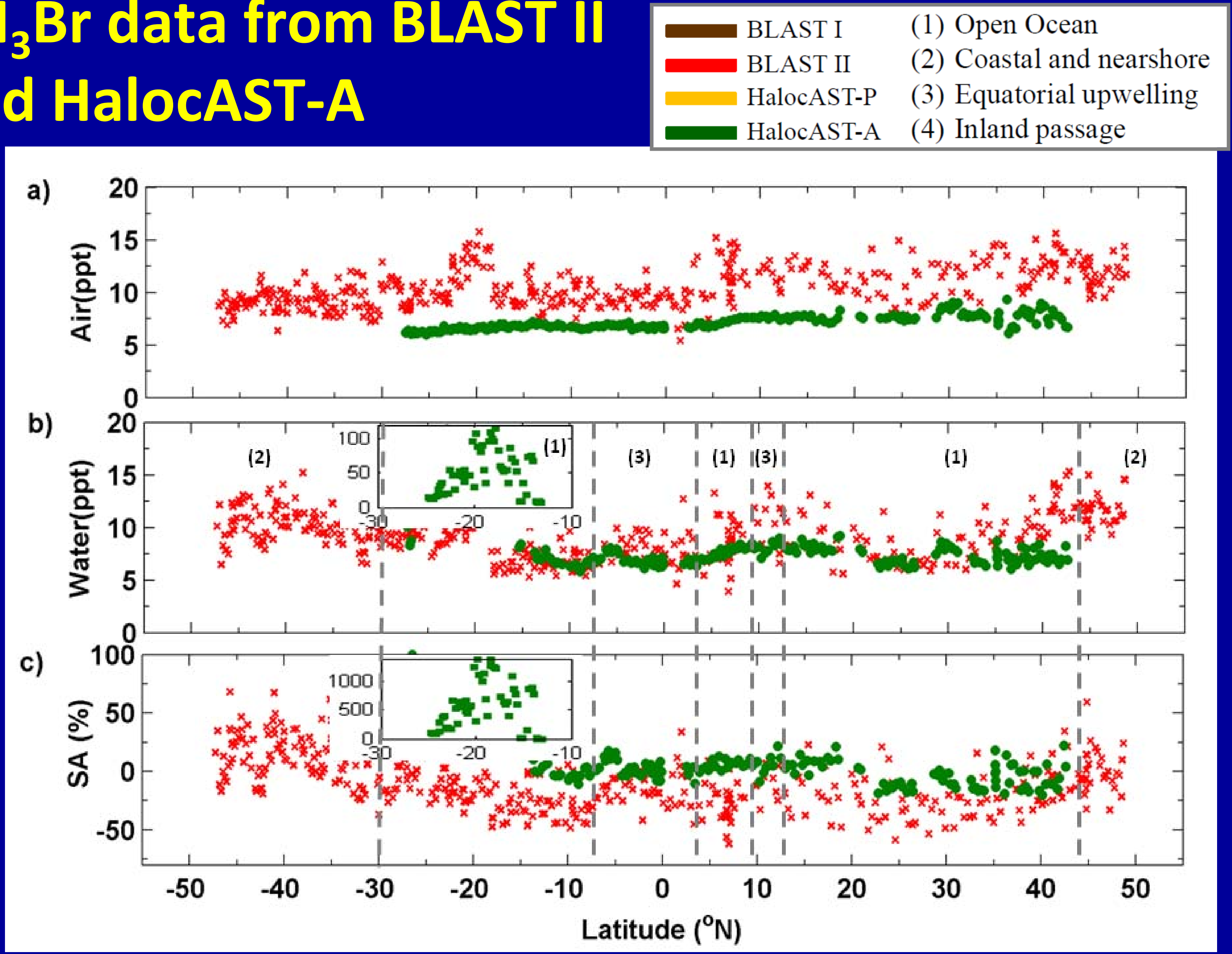
CH_3Br data from BLAST I and HalocAST-P





Hu, et al., Submitted, GBC

CH_3Br data from BLAST II and HalocAST-A



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Global Extrapolation

Region	Area Weighting Factor	Δ_{CH3Br} (%)	Flux (Gg yr^{-1})	Production (Gg yr^{-1})
Open Ocean	0.8	0.3	-0.05	1.2×10^2
Coastal	0.1	29.5	2.6	15
Upwelling	0.1	2.4	0.09	21
Global (HalocAST)		**3.4**	**2.6**	**1.5×10^2**
Global (BLAST)		**-15.7**	**-12.6**	**1.5×10^2**

Problems with global extrapolation of fluxes:

- Extrapolated fluxes may be biased by regional saturation anomalies or regional in-situ wind speeds.

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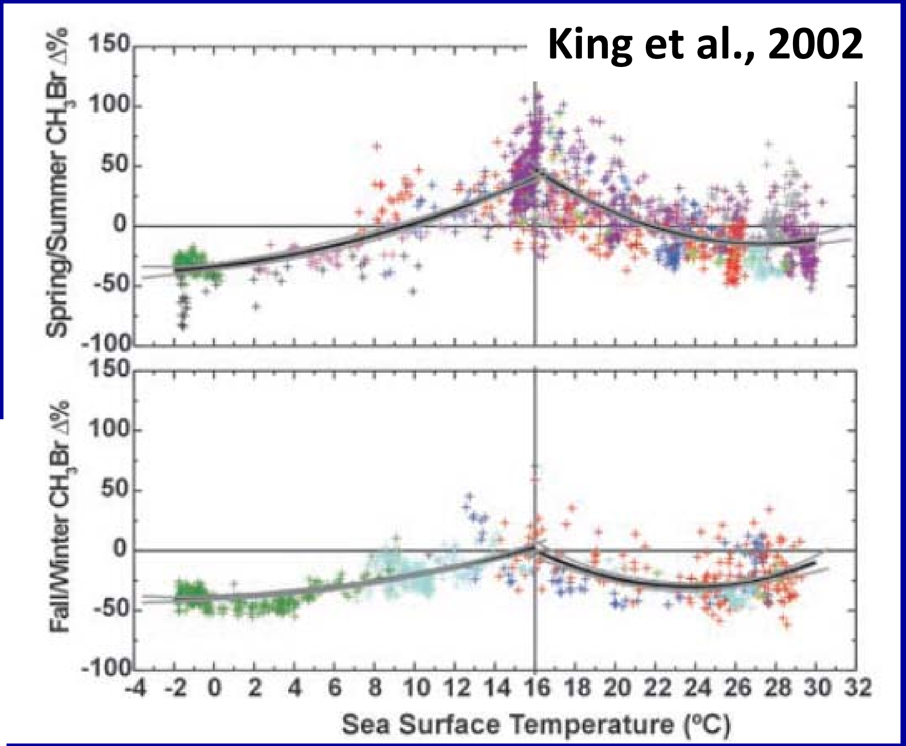
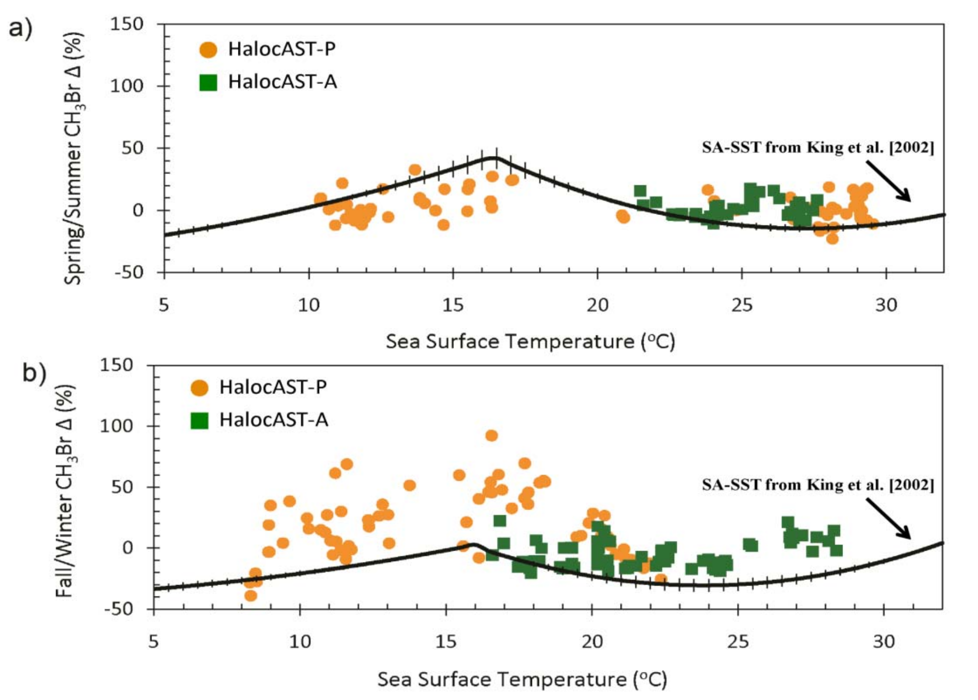
Δ(%) - SST relationships before the phase-out is no longer valid

Δ(%) - SST relationships before the phase-out

$$F = k_w H \frac{\Delta}{100} p_a$$





Δ(%) - SST relationships and HalocAST data

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Net Flux (F) = Emission (E) – Uptake (U)

18 year record of atmospheric CH_3Br from NOAA/ESRL GMD

$$U = f\left(p_a, k_{bio}, windspeed, SST, Sal, MLD\right)$$

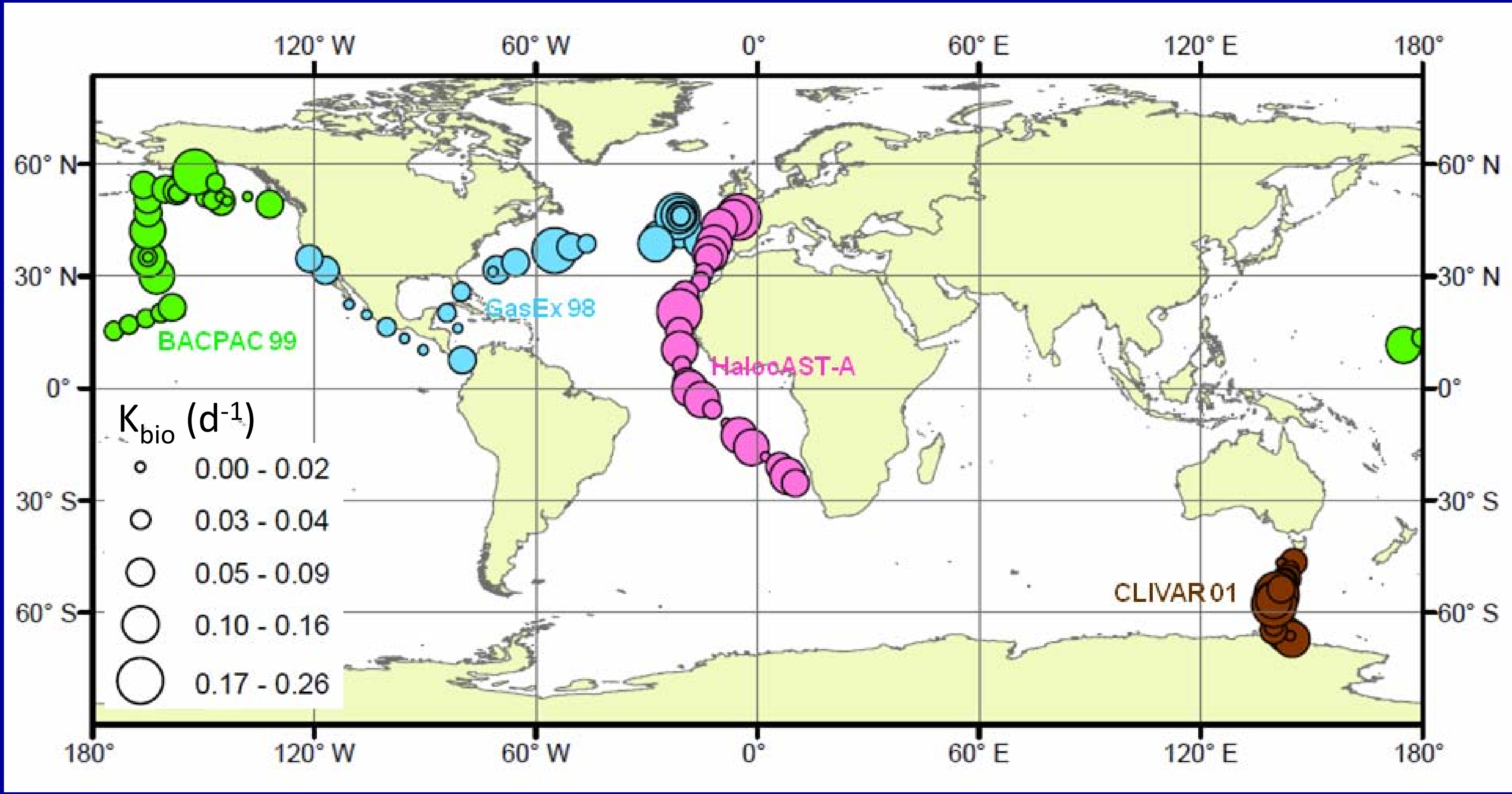
Measured before and after phase-out

DS279: $1^o \times 1^o$ gridded datasets of wind speed, SST, Sal, MLD

$$E = f\left(P, k_{bio}, windspeed, SST, Sal, MLD\right)$$

$$P = f\left(p_a, k_{bio}, SST, WindSpeed, Sal, MLD\right)$$

Biological Degradation Rate Constants



- No significant difference between degradation rate constants observed in the northeastern Atlantic during GasEx 98 and HalocAST-A.
- Global mean biological degradation rate constant = 0.05 (±0.01 S.E.) d^{-1}.

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1º x 1º Ocean Model

The old 1º x 1º Ocean Model (e.g. Yvon and Butler, 1996; King et al., 2002; Yvon-Lewis et al., 2009)

- Used Wanninkhof [1992].
- Did not include separate coastal rates and used only open ocean values for production rates, biological degradation rate constants, etc.

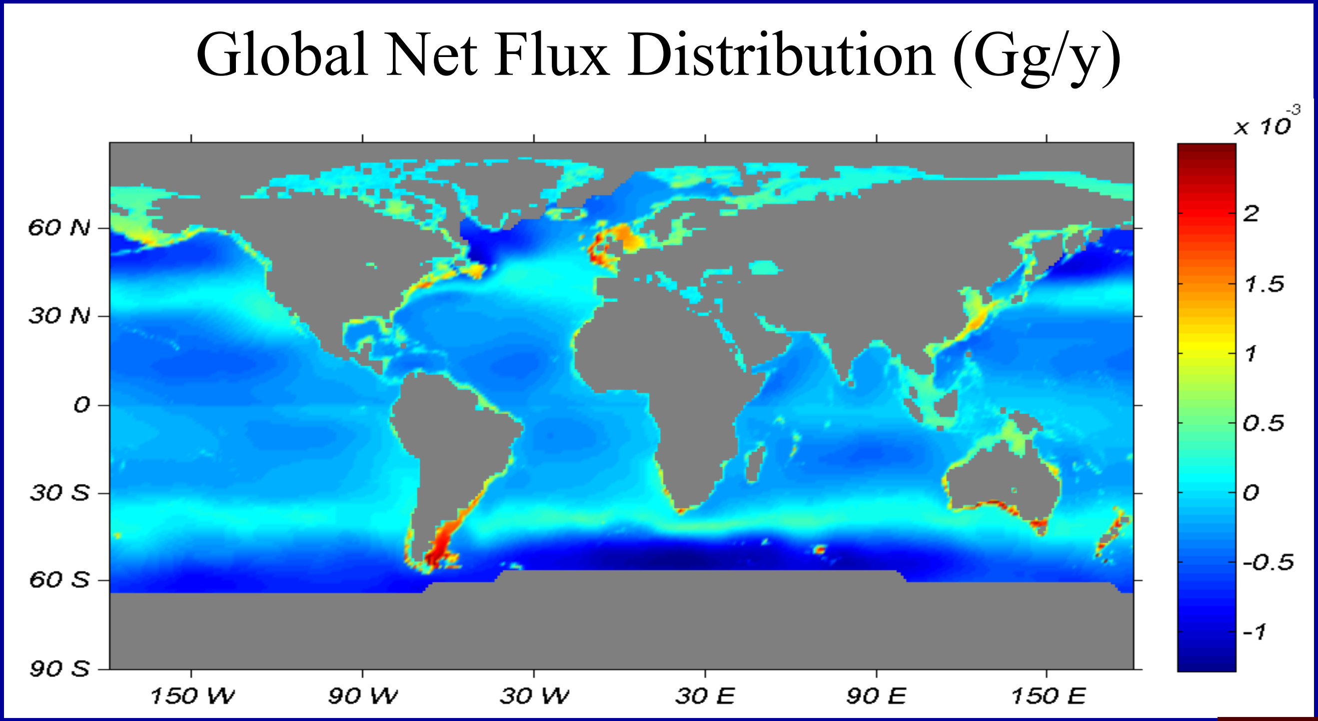
Revised 1º x 1º Ocean Model

✓Uses Sweeney et al. [2007].

✓ Includes rates for both the coastal and open ocean regions.

Before the CH_3Br Phase-Out

	Emission (Gg/y)	Uptake Rate (Gg/y)	Net Flux (Gg/y)
Global Ocean (W92)	**42**	**-56**	**-14**
Global Ocean (S07)	**31**	**-41**	**-10**
Global Ocean (S07 +)	**34.2**	**-41.1**	**-6.9**
Coastal Ocean	4.6	-2.4	2.2
Open Ocean	29.6	-38.7	-9.1



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At the End of the non-QPS Phaseout (2010)

	Emission (Gg/y)	Uptake Rate (Gg/y)	Net Flux (Gg/y)
Global Ocean (Cruise Data Extrapolation)	**?**	**?**	**2.6**
Coastal Ocean	?	?	2.6
Open Ocean	?	?	0
Global Ocean (Model)	**34.2**	**-31.5**	**2.7**
Coastal Ocean	4.6	-0.8	3.8
Open Ocean	29.6	-30.7	-1.1

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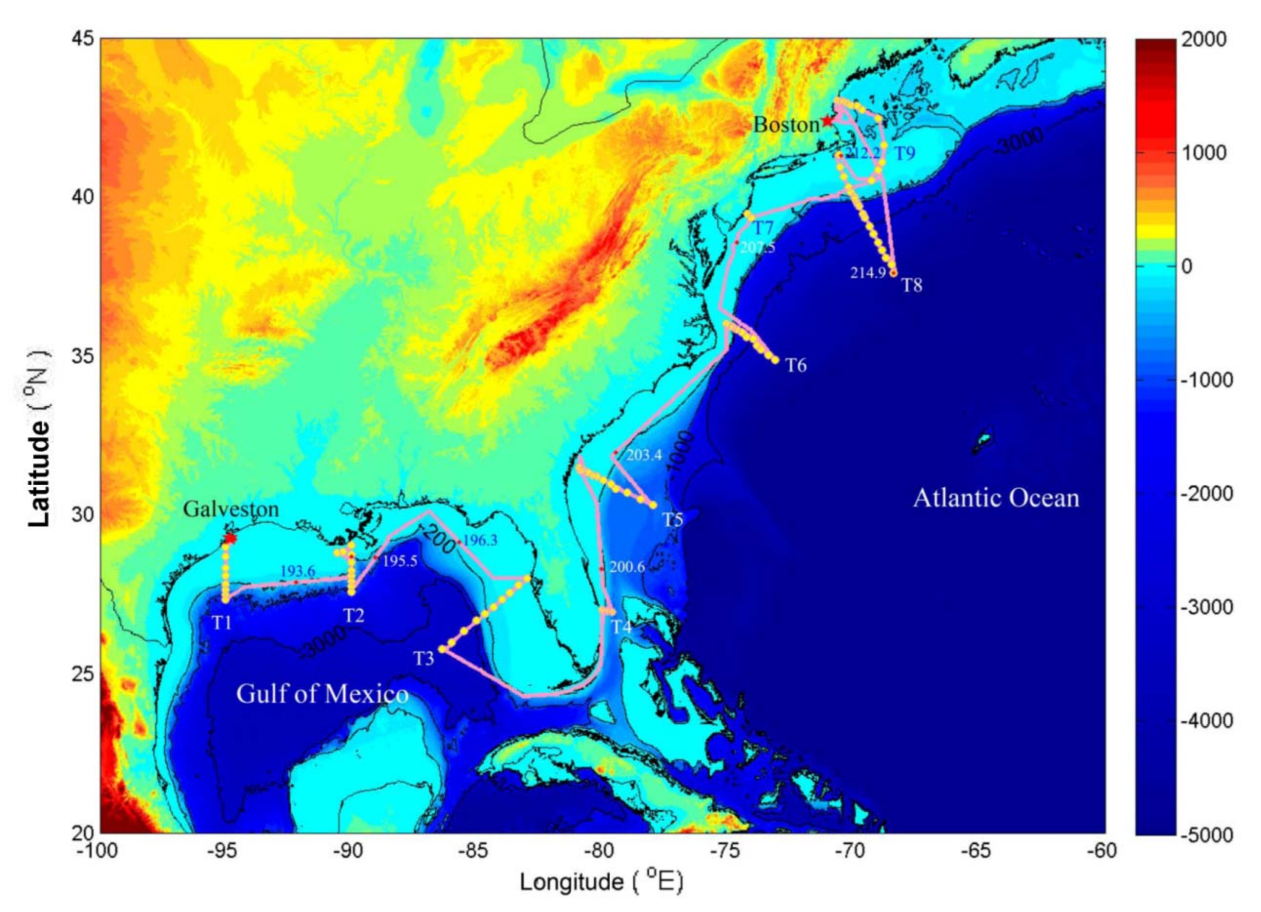
Summary and Conclusions

- Atmospheric methyl bromide concentrations measured during the recent cruises are consistent with the NOAA flask network data.
- The degradation rate constants measured in 2010 are consistent with previous measurements.
- The observed global mean saturation anomaly increased to ~3.4%
- The oceans became a small net source of CH_3Br to the atmosphere with a global mean flux of ~3 Gg/y

Differences Between Coastal-Oceanic Areas and Open-Oceanic Areas



Cruise Track of GOMECC (Hu, et al., 2010, GBC)

- **Production Rates:**

Mean production rate in coastal areas of HalocAST and GOMECC: 0.62 nmol m^{-3} d^{-1}.

Global open-ocean production rate: 0.15 nmol m^{-3} d^{-1} (Yvon-Lewis et al., 2004)

- **Biological degradation rate constant**

Coastal ocean (King et al., 1997): 0.09 d^{-1}

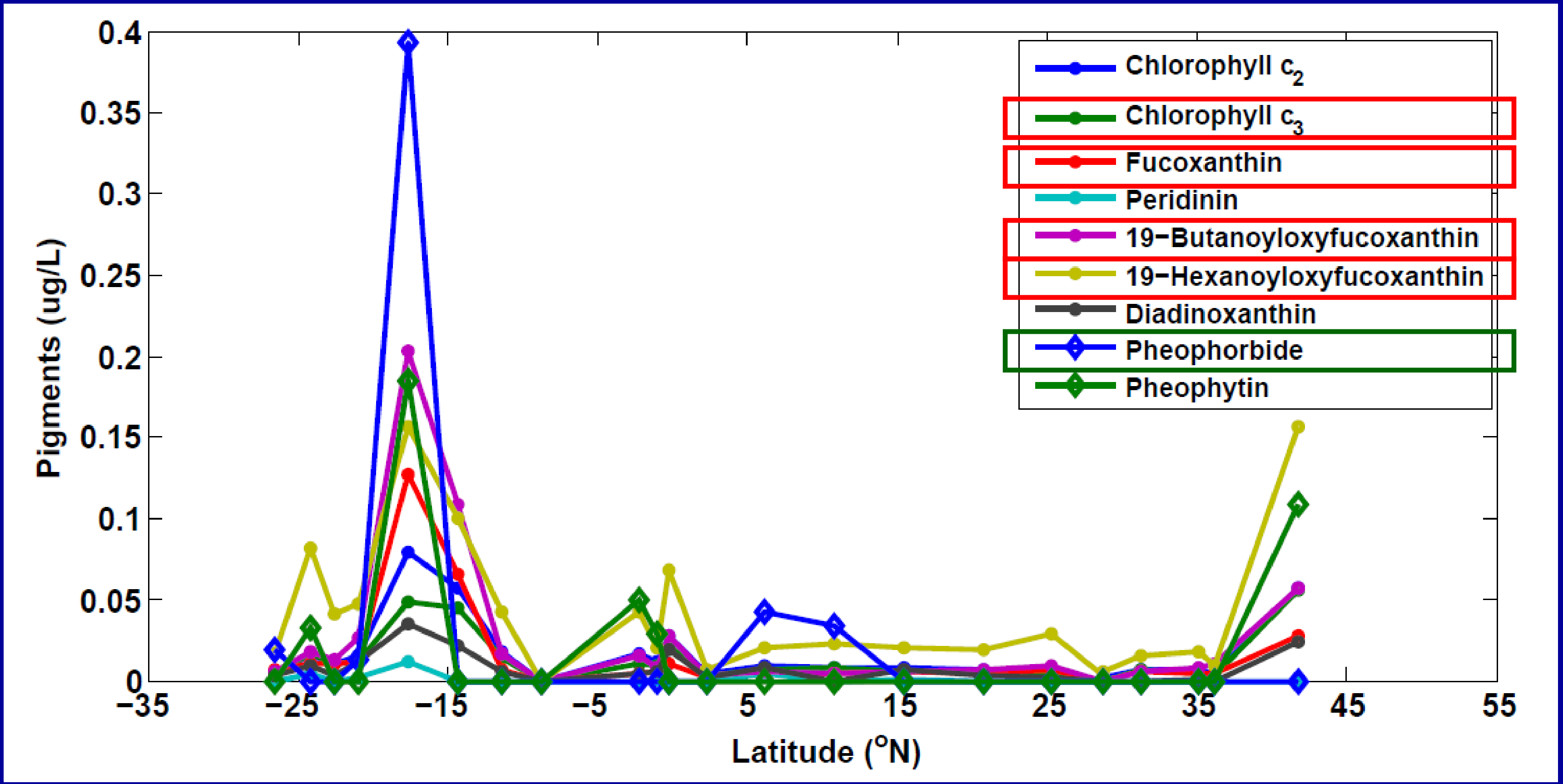
Global open ocean mean: 0.05 d^{-1}

Atmospheric Methyl Bromide Budget (Gg yr^{-1})

	1996 - 1998	Range	2008	Range
SOURCES				
Fumigation - dispersive (soils)	41.5	28.1 to 55.6	6.5	4.6 to 9.0
Fumigation - quarantine/pre-shipment	7.9	7.4 to 8.5	7.6	7.1 to 8.1
Ocean	**42**	**34 to 49**	**42**	**34 to 49**
Biomass Burning	29	10 to 40	29	10 to 40
Leaded Gasoline	5.7	4.0 to 7.4	<5.7	
Temperature peatlands	0.6	-0.1 to 1.3	0.6	-0.1 to 1.3
Rice Paddies	0.7	0.1 to 1.7	0.7	0.1 to 1.7
Coastal Salt Marshes	7	0.6 to 14	7	0.6 to 14
Mangroves	1.3	1.2 - 1.3	1.3	1.2 - 1.3
Shrublands	0.2	0 to 1	0.2	0 to 1
Rapeseed	4.9	3.8 to 5.8	5.1	4.0 to 6.1
Fungus (Litter Decay)	1.7	0.5 to 5.2	1.7	0.5 to 5.2
Fungus (Leaf-cutter Ants)	0.5		0.5	
Subtotal (Sources)	**143**		**111.5**	
SINKS				
Ocean	**56**	**49 to 64**	**49**	**45 to 52**
OH and Photolysis	77		63.6	
Soils	40	23 to 56	32	19 to 44
Subtotal (Sinks)	**177**		**147.6**	
Total (SOURCES - SINKS)	**-34**		**-36.1**	

Montzka and Reimann et al., 2011

Pigments that correlated with seawater CH_3Br during 13 to 25 °S



- Elevated CH_3Br was associated with two main algal groups, prymnesiophytes and dinoflagellates.
- *Emiliania huxleyi* and *Phaeocystis sp*. can produce CH_3Br at a significant rate.
- It is likely that elevated CH_3Br was at least partly associated with *phaeocystis sp*., which were grazed by zooplankton, or at the senescent stage or underwent autolysis.

Hu, Yvon-Lewis, Liu and Bianchi, Submitted, GBC