Challenges in Evaluating the Influence of the Ocean on Atmospheric Composition

Air-Sea Gas Flux Workshop
6-9 September
Brest, France

GasEx-98, North Atlantic Ocean

James Butler,
NOAA ESRL Global Monitoring Division
Boulder, Colorado, USA

Outline

RB-99 (Phase), North Pacific Ocean

- Fundamentals
- Tools and Toys
- Early Examples
  - N_2O
  - CFCs
  - CH_3CCl_3
- CH_3Br
- CCl_4
- Possibilities . . .

Behavior of a Gas in the Atmosphere

$$\frac{dG}{dt} = Emission\ Rate\ - Loss\ Rate$$

$$\frac{dG}{dt} = E - kG$$

$$k\ = \frac{1}{\tau} = \frac{1}{\tau_{strat}} + \frac{1}{\tau_{trop}} + \frac{1}{\tau_{ocean}} + \frac{1}{\tau_{soils}} + \cdots\ ,$$

Air sea exchange formula

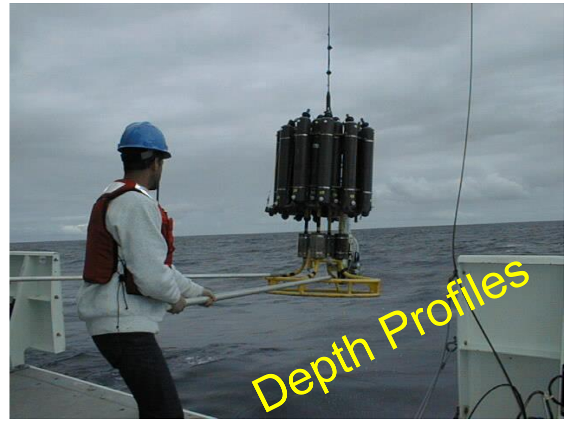
Kinetics

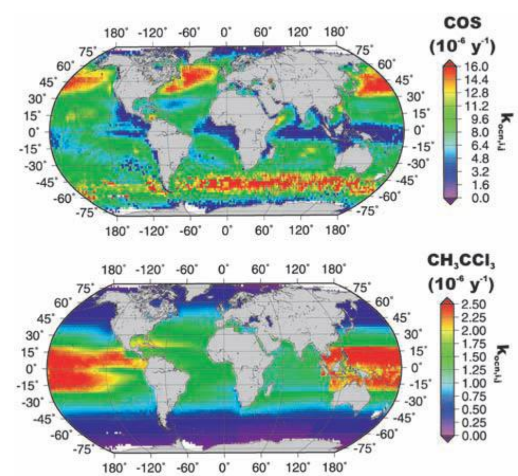
$$Flux = \frac{K_w A}{H}(p_w - p_a)$$

Thermodynamics

Ultimate Drivers: Partial pressure difference
Wind speed
temperature
salinity

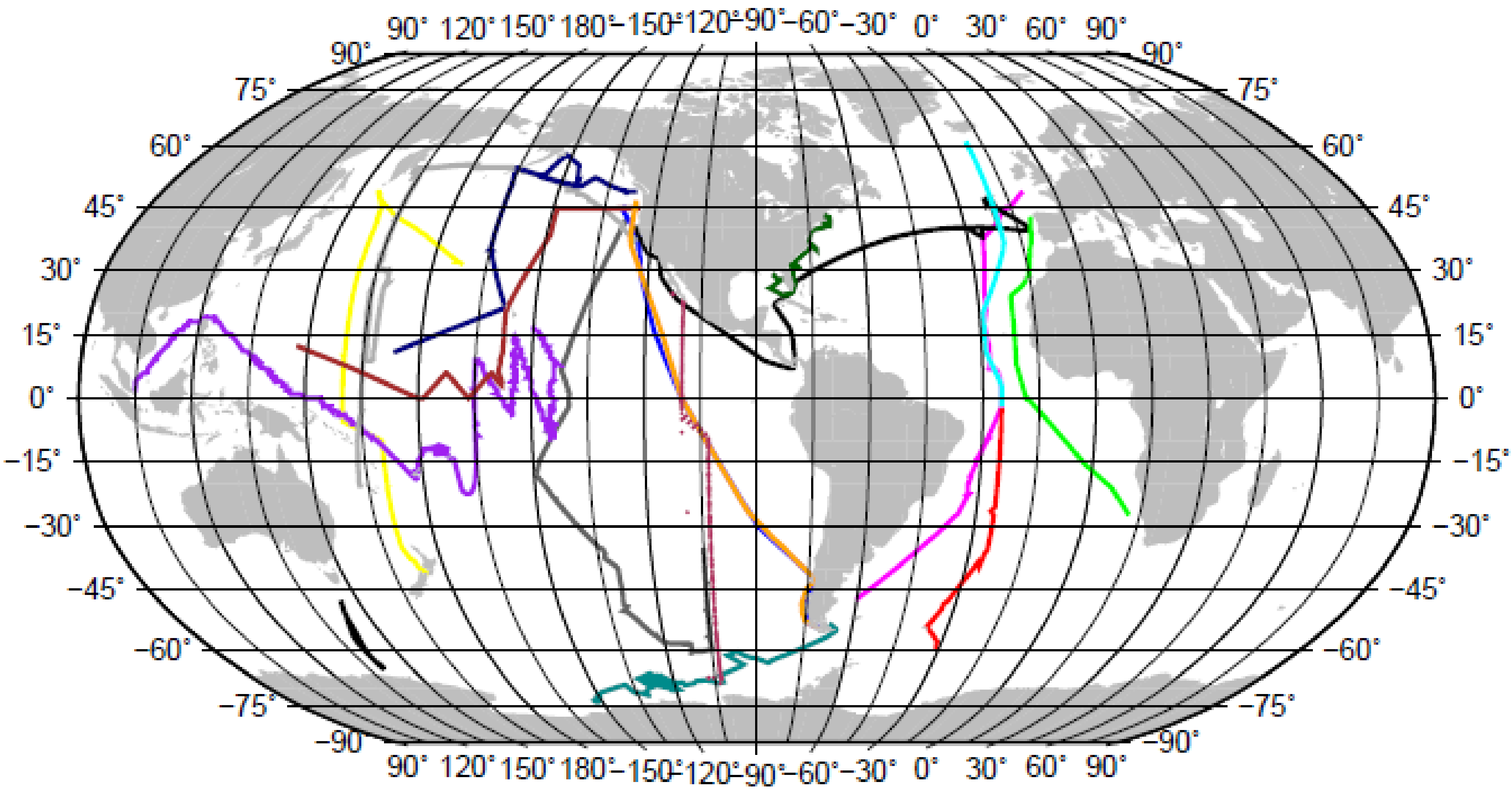
Tools





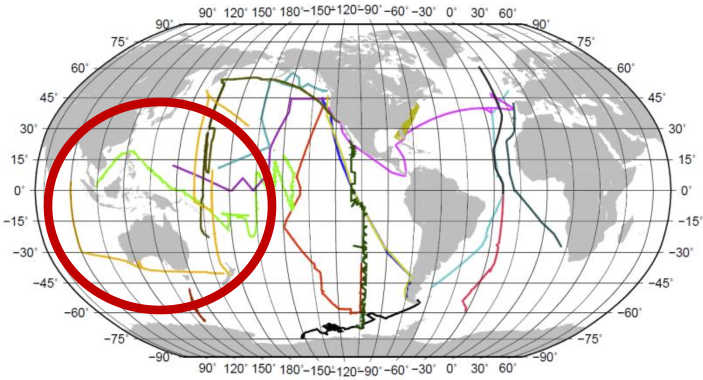
$$\frac{dM_a}{dt} = S_A + F_I - \frac{K_w A}{H}(p_w - p_a) - k_{OH} p_a M - k_s p_a M$$

Research Cruises 1987-2010

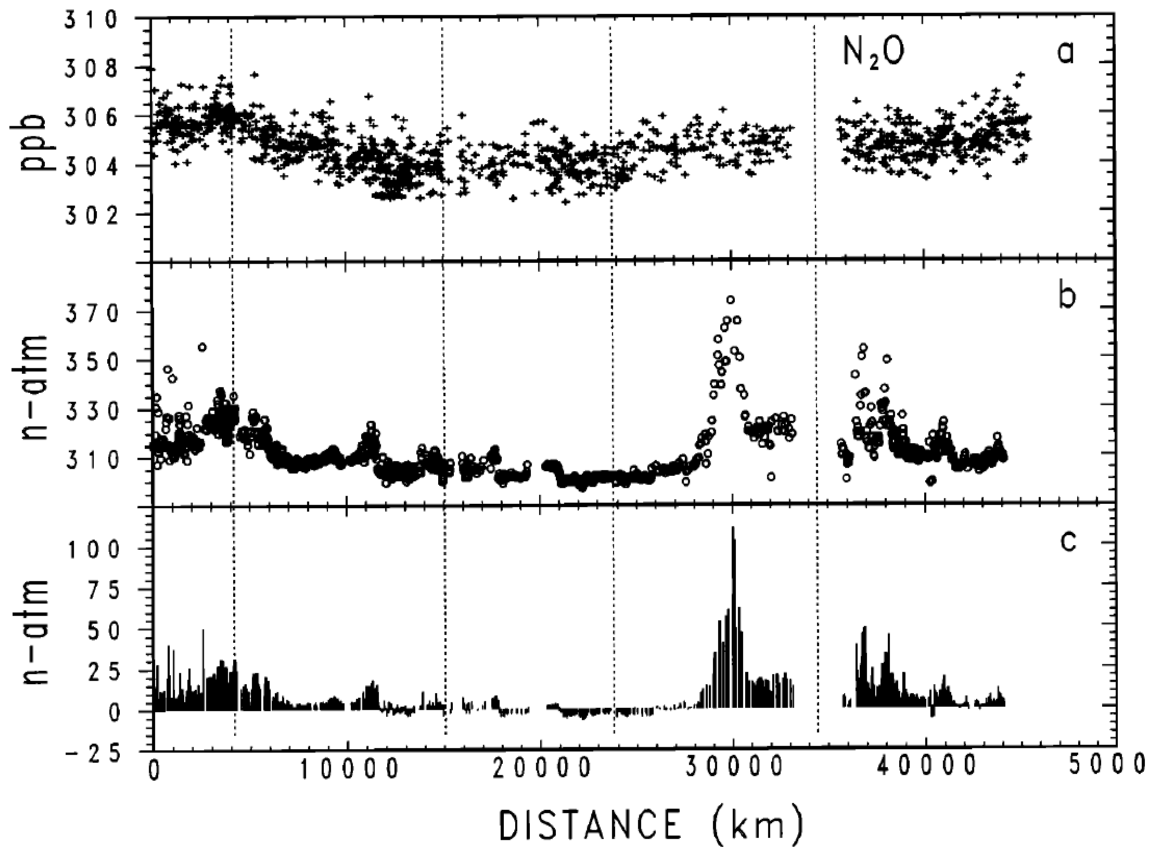


SAGA2 (1987), RITS89 (1989; also P18), SAGA3 (1990), OAXTC (1990; also P13), BLAST1 (1994), BLAST2 (1994), BLAST3 (1996), GasEx98 (1998), RB9906 (1999), CLIVAR01 SR3 (2001), A16N (2003), A16S (2005), PHASE (2004), P18 (2008), HalocAST A (2009), GOMECC (2010), HalocAST-P (2010)

N_2O Emissions (1987)



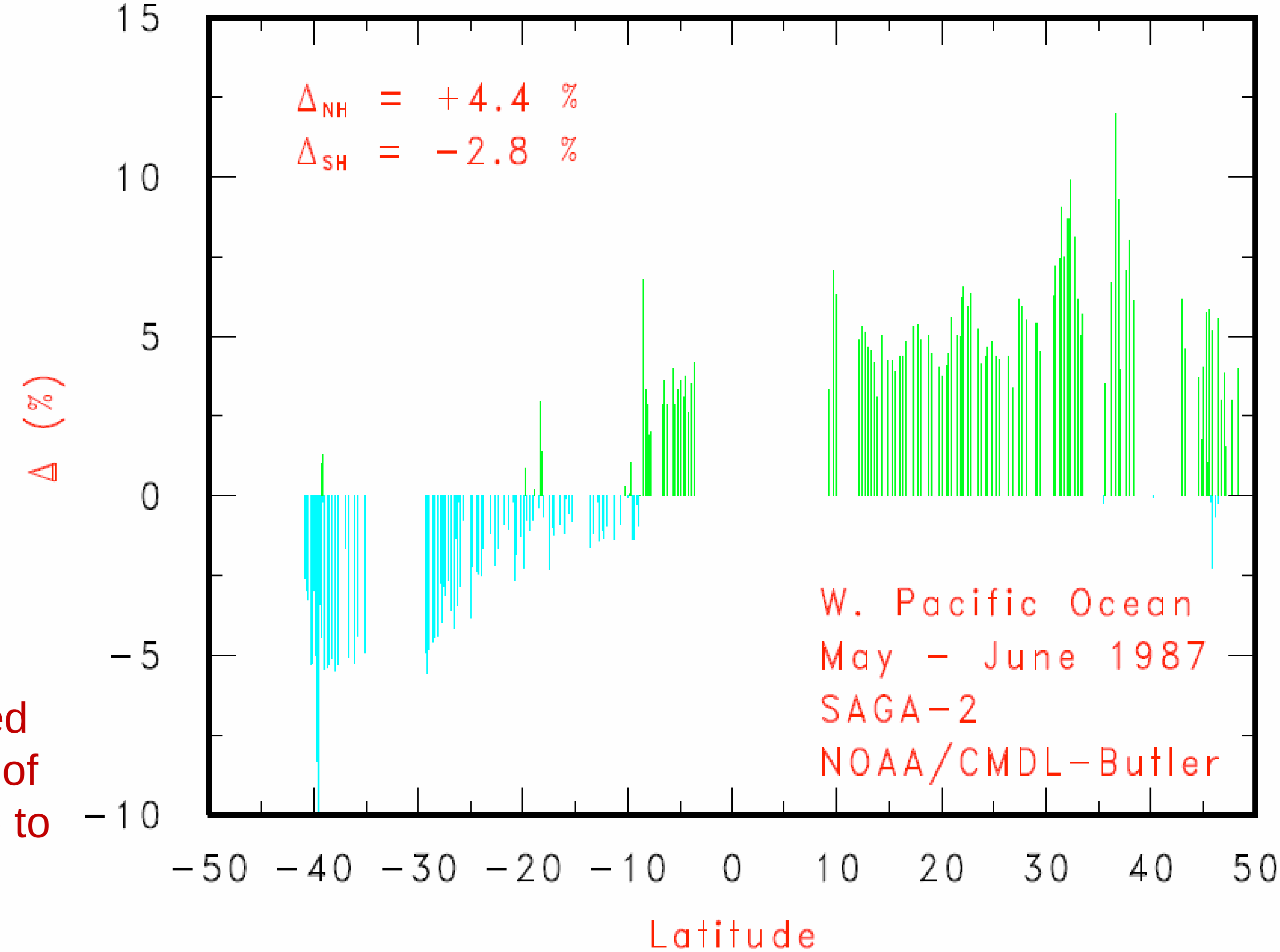
- West Pacific and East Indian Oceans
- Emissions associated with upwelling
- N_2O produced at mid-depth



10-20% of atmospheric N_2O comes from the ocean

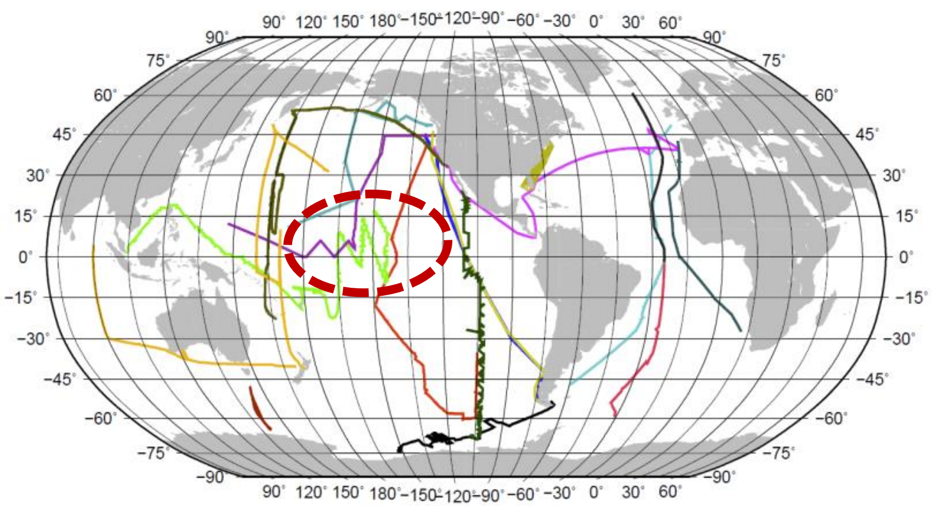
Physical Effects – "Inert" CFC-11 (1987)

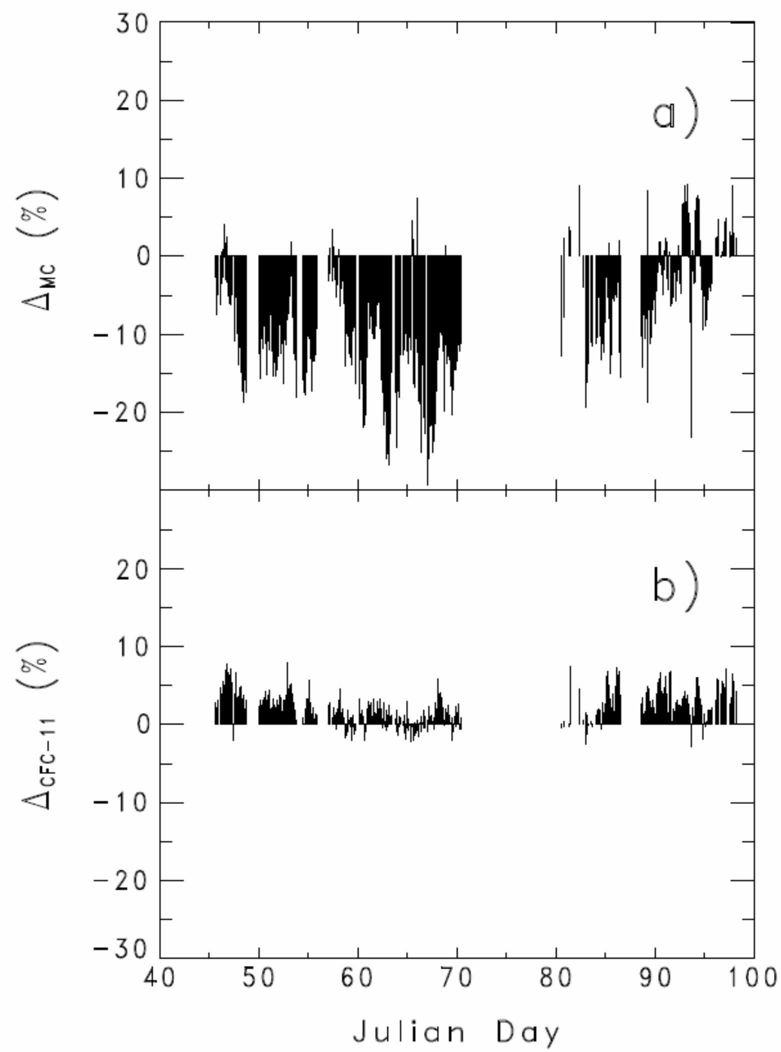
- Warming & Cooling
- Transport
- Mixing
- Air Injection



Much of an observed saturation anomaly of any gas can be due to physical effects.

Chemical Consumption – CH_3CCl_3 (1990)





- 5-11% of atmospheric CH_3CCl_3 is consumed by hydrolysis in surface seawater
- This finding reduced the atmospheric lifetime of CH_3CCl_3
- And, it increased the estimated lifetime of all other gases consumed by tropospheric OH
- And it changed its ozone-depletion potential

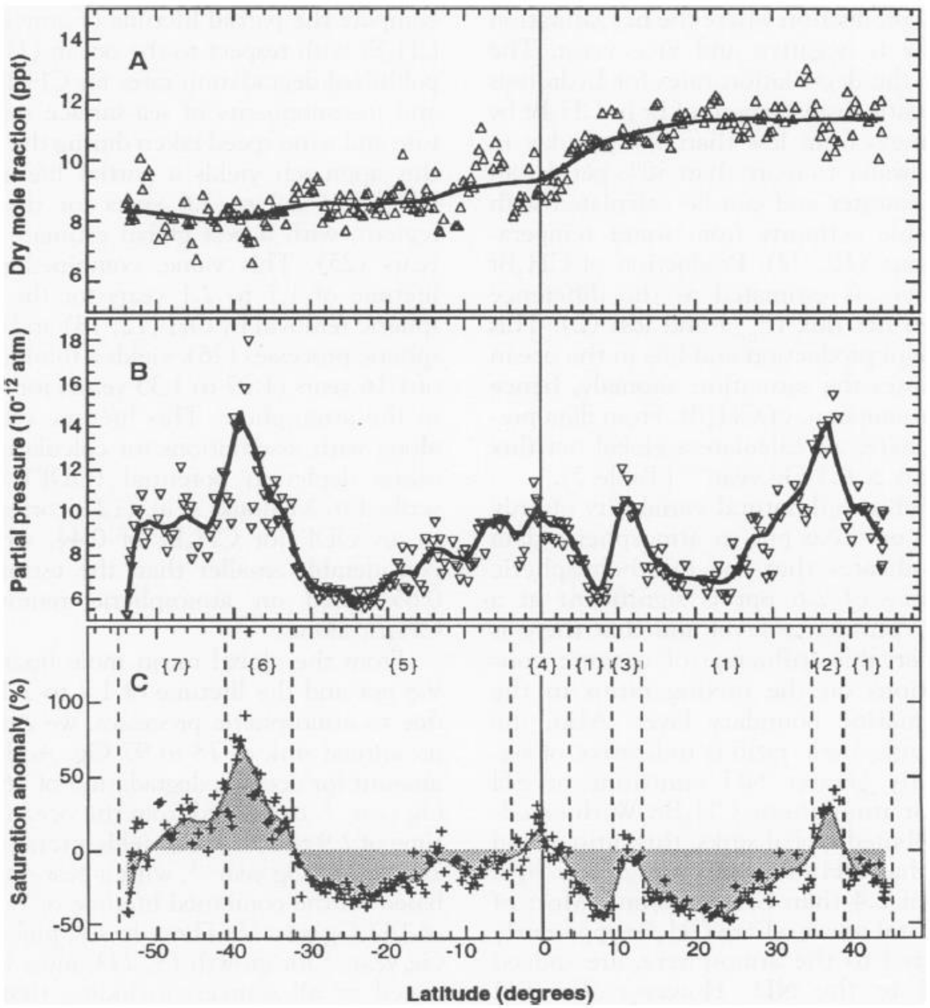
And then came CH_3Br . . .

Where we really learned something . . .

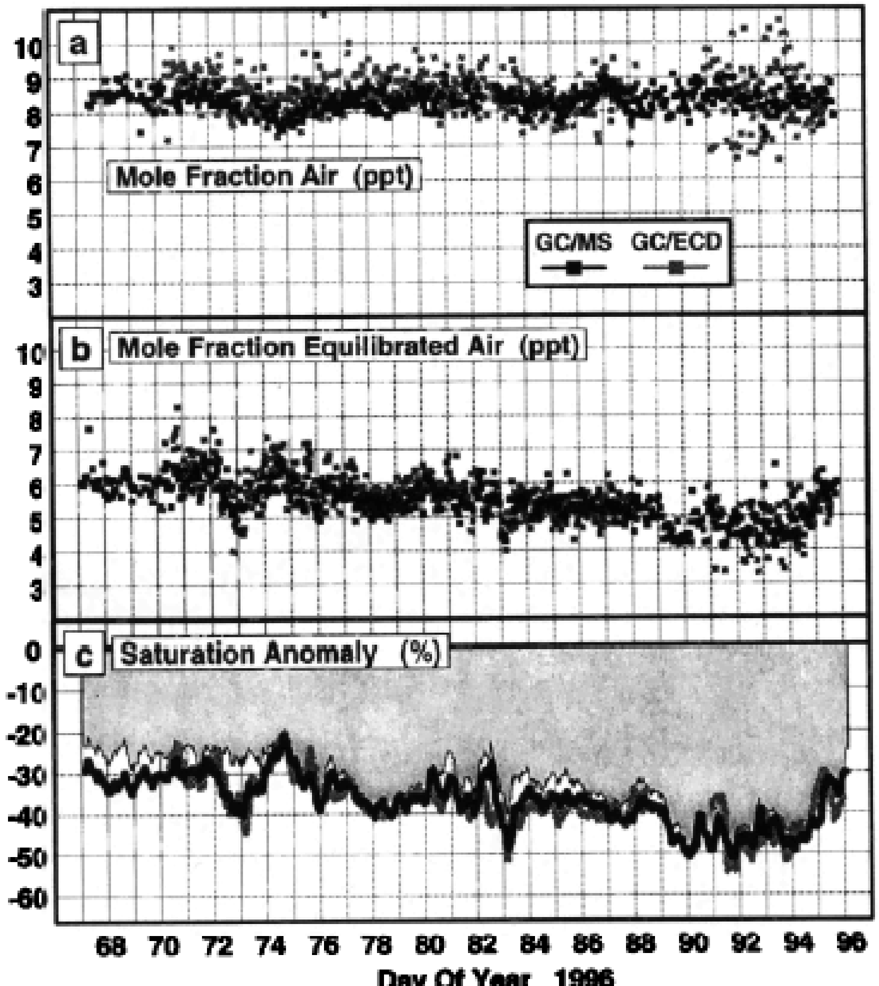
Properties of and issues with CH_3Br

- Consumed in the surface ocean by nucleophilic displacement of Br by Cl^- (10-15%/d)
- Produced in surface seawater by microorganisms at similar rates (Ocean once believed to be hugely supersaturated.)
- Consumed in surface seawater by microorganisms at similar rates
- Surface fluxes reflect the sum of all of these
- How to separate them and get reliable estimates?
- Other questions:
  - Early issues with sampling and analysis reliability
  - Human emissions are significant for ozone depletion, but…
  - Only about 1/3 of the CH_3Br in the atmosphere is (was) anthropogenic

Observations

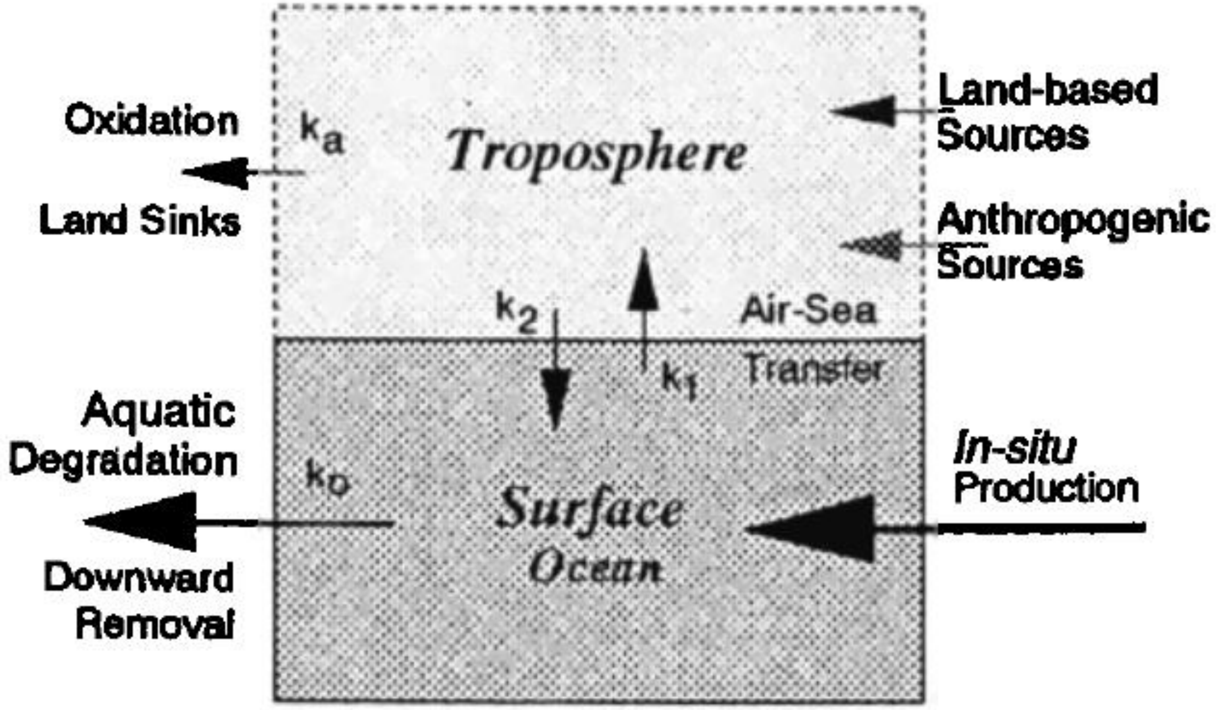


East Pacific Ocean - 1994



Southern Ocean - 1996

Simple Model



$$\frac{dM_a}{dt} = S_A + F_l + k_1 M_o - k_2 M_a - k_a M_a$$

$$\frac{dM_o}{dt} = P - k_1 M_o + k_2 M_a - k_o M_o$$

Simple lifetime equation

$$\frac{dM_a}{dt} = S_A + F_l + \frac{K_w A}{H}(p_w - p_a) - k_{OH} p_a M - k_s p_a M$$

$$\frac{dM_o}{dt} = P_o + \frac{K_w A}{H}(p_w - p_a) - k_d M_o - \frac{K_{ed}}{z} M_o$$

$$k_1 = \frac{K_w}{z}$$

$$k_2 = \frac{K_w A}{HM}$$

$$k_o = k_d + \frac{K_{ed}}{z}$$

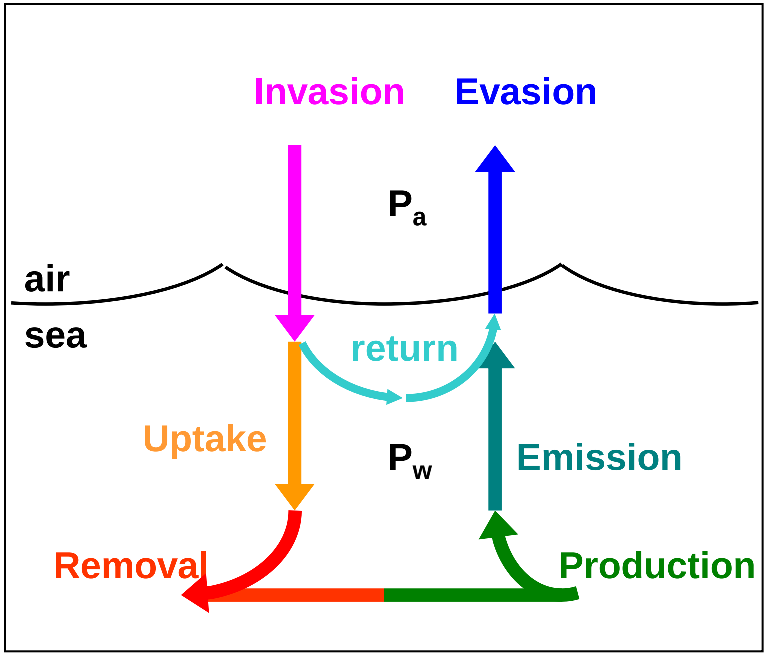
$$R = \frac{k_o}{(k_1 + k_o)}$$

In situ degradation (k_o)

Return to atmosphere (k_1)

$$\frac{1}{\tau_o} = k_2 R$$

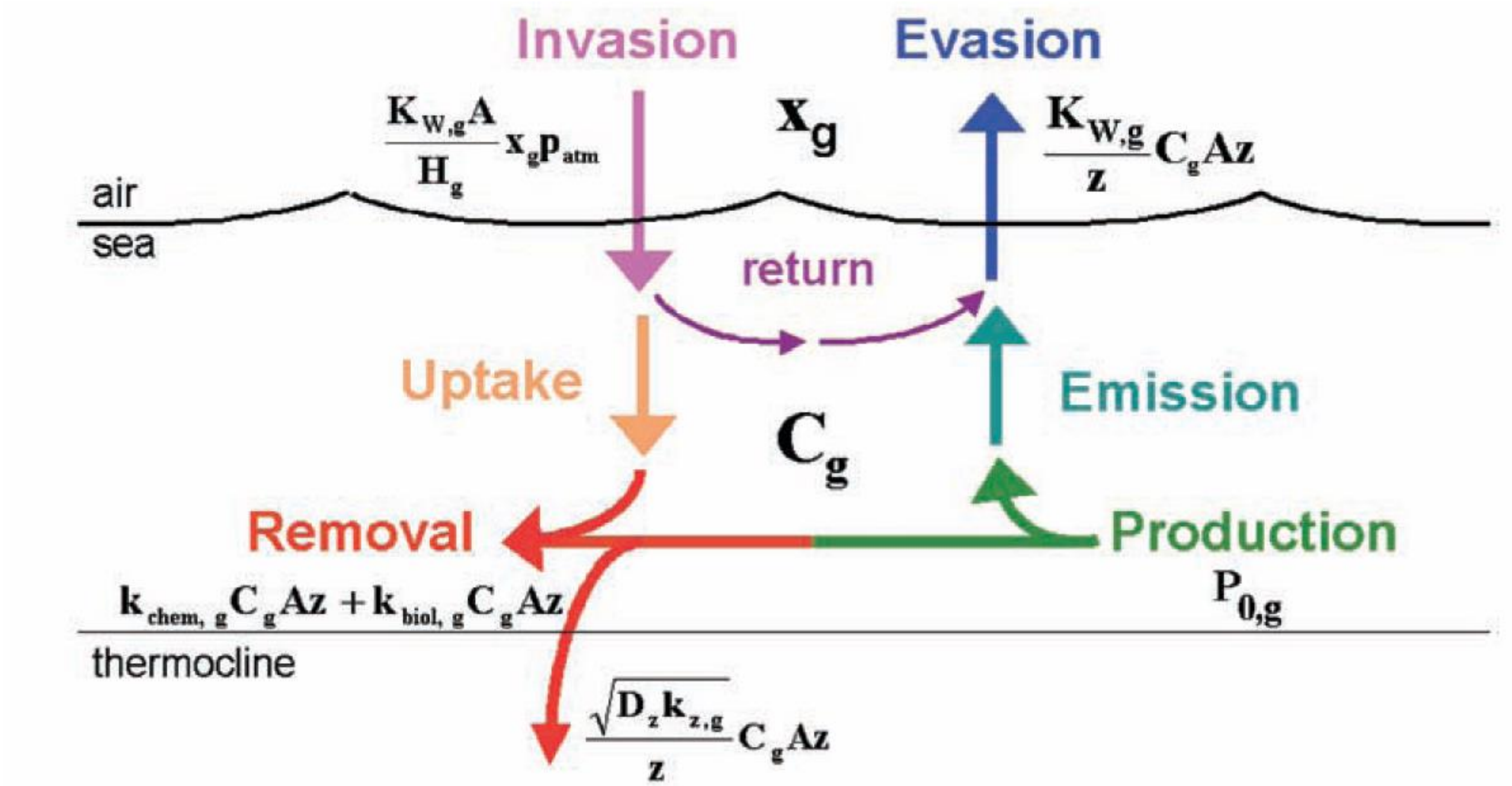
Partial atmospheric lifetime with respect to the ocean (τ_o)

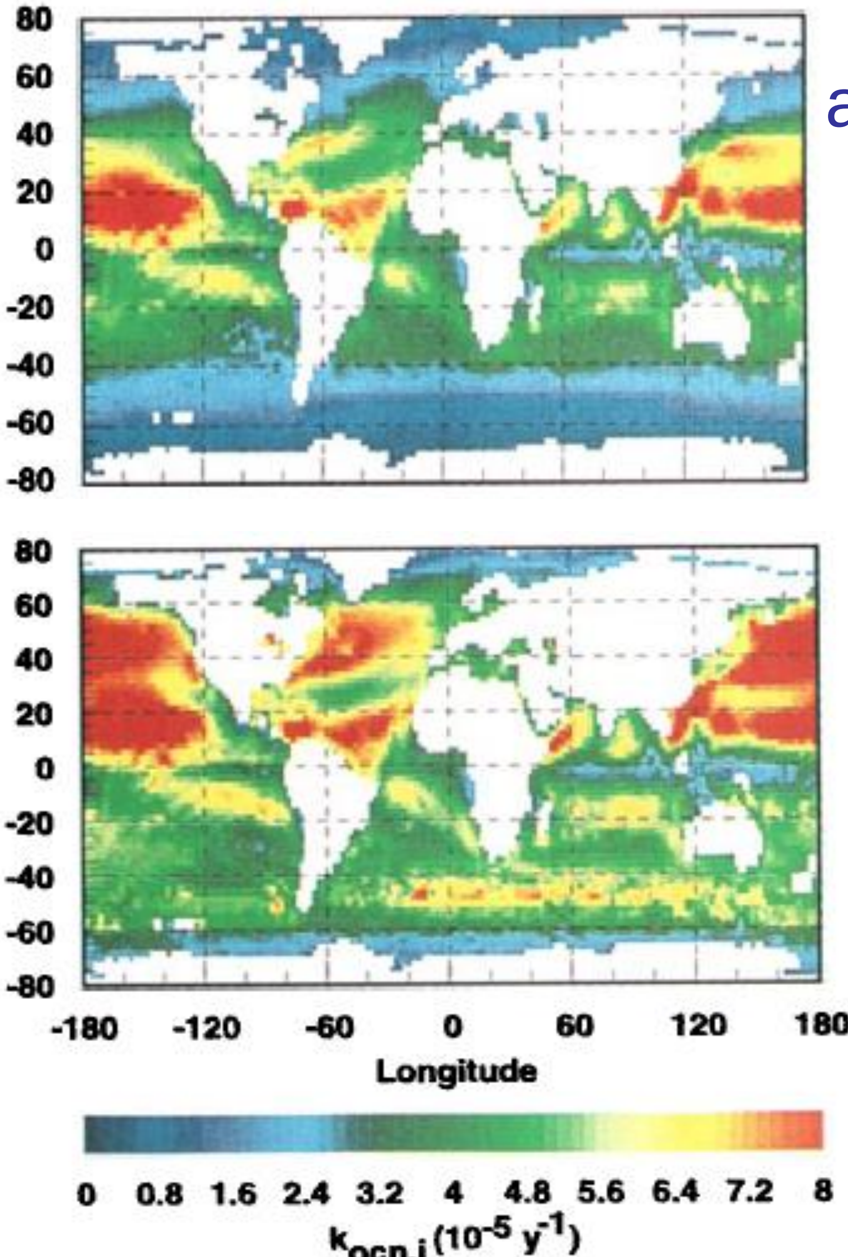


Terms for Calculations

Term	Formula	Equivalent
Invasion	$\frac{K_w A p_{ga}}{H_g}$	Uptake + Return
Evasion	$\frac{K_w A p_{gw}}{H_g}$	Emission + Return
Return Flux	$(1\text{-}R)\frac{K_w A p_{ga}}{H_g}$	Invasion - Uptake
Uptake	$\frac{n_{tr} p_{ga}}{.95\tau_o}$	Evasion - Emission Invasion - Return
Production	P	
Removal	$\frac{k_d A z p_{gw}}{H_g}$	Prod - Emis + Upt
Emission	$(1-R)P$	Evasion - Return Net Flux - Uptake
Net Flux	$\frac{K_w A(pgw - pga)}{H_g}$	Prod. - Removal Evasion - Invasion Emission - Uptake

- Measure
  - Partial Pressure difference
  - SST
  - Salinity
  - Windspeed
- Calculate
  - Solubility
  - Diffusivity
  - Viscosity
  - Air-sea exchange coefficient

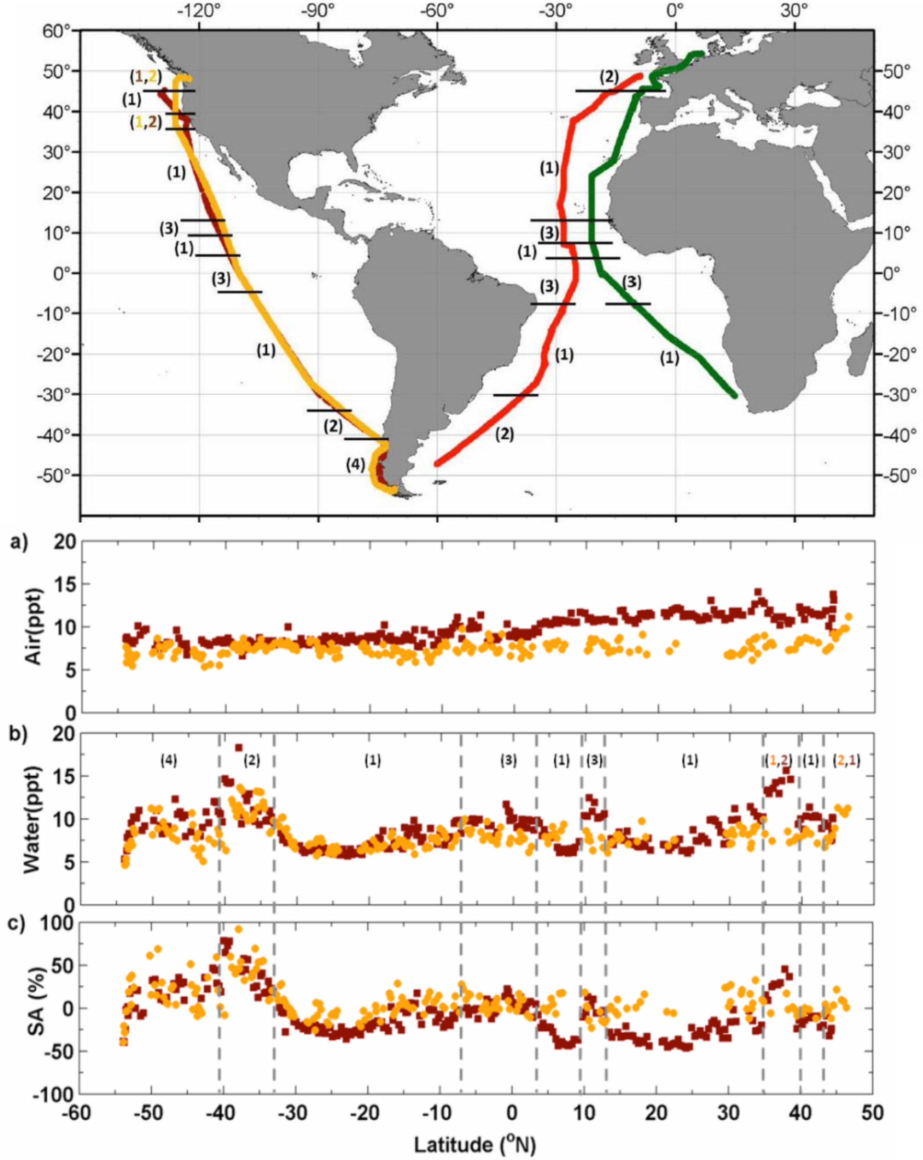




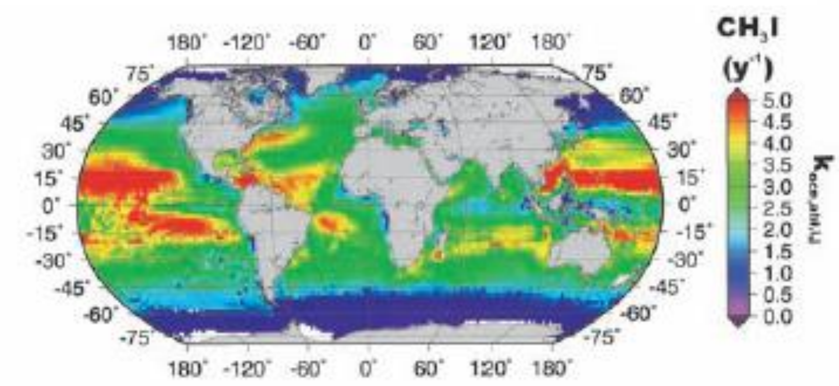
Influence of changes on atmospheric lifetime of CH_3Br

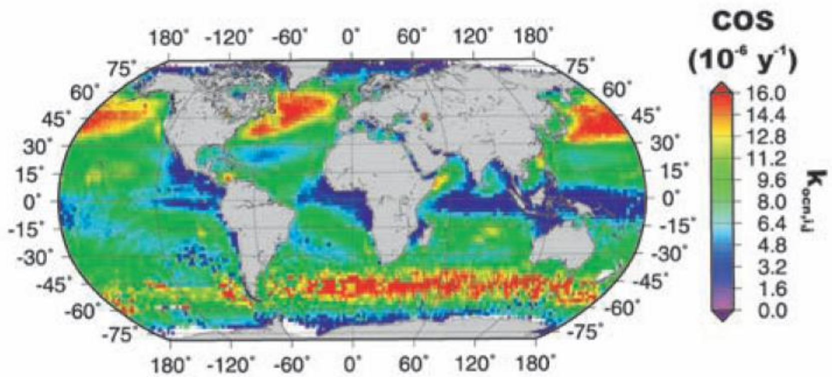
- No Ocean (and no soils)
  - Tau(atm) 2.2 y
- Two-box model
  - Tau(atm) 1.2 y
  - Range 0.7-1.8 y
- 1º x 1º model (chem only)
  - Tau(atm) 0.8 y
  - Range 0.6-1.4 y
- 1º x 1º model (chem+ bio)
  - Tau(atm) 0.7 y
  - Range 0.6-0.9
- 2014 Ozone Assessment
  - Tau(atm) 0.80 y
- 2014 with $W_{(2014)}$ K_w
  - Tau(atm) 0.84 y

Footnote for CH_3Br

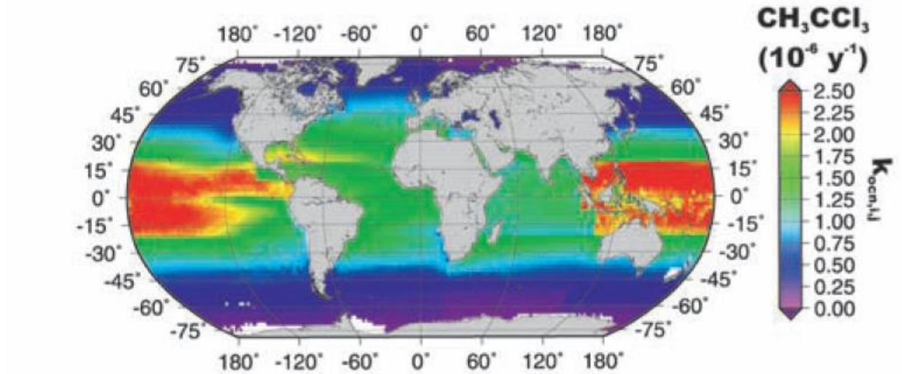


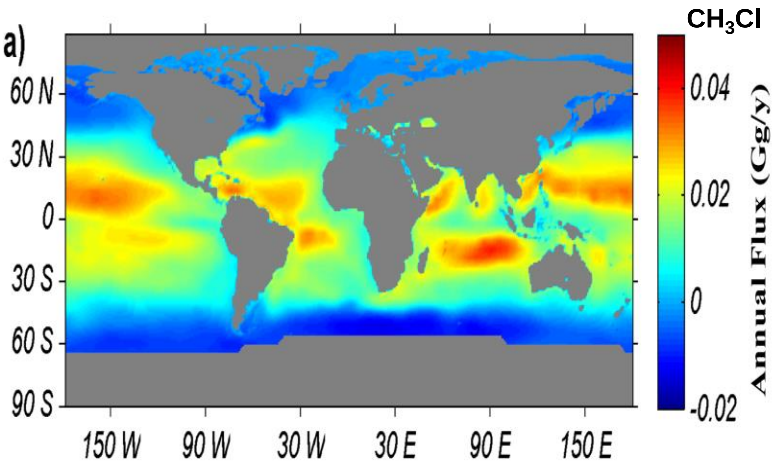
- Lei Hu et al., 2012, Oceanic Saturation State of CH_3Br, *Global Biogeochemical Cycles*
- Human Emissions reduced
- Atmospheric amount has dropped from ~11 to 7.5 ppt since 1999.
- Net flux is now positive
  - 0 to 3Gg/y
  - Previously ~ -14Gg/y !! (2002 Scientific Assessment)
- Atm. Lifetime still 0.8 (0.6-0.9) y

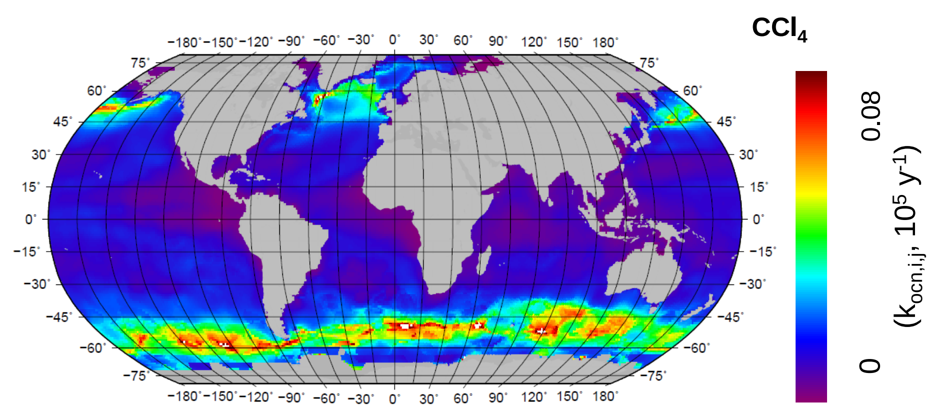




. . . .can do this for any gas!

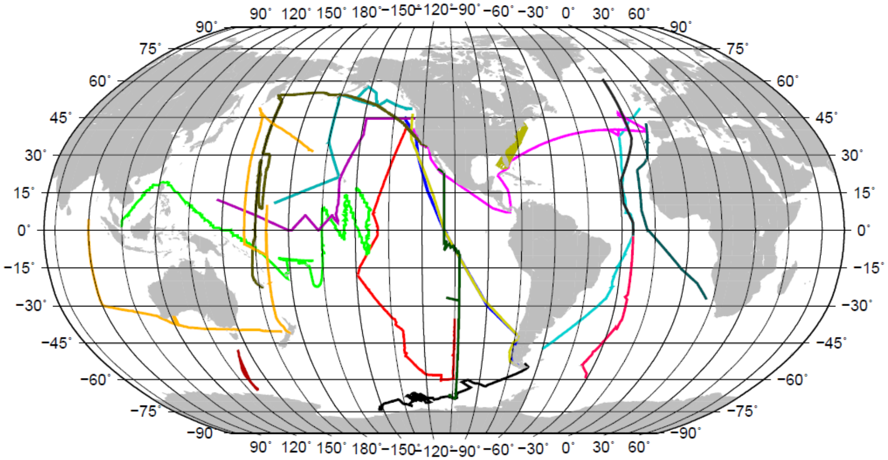






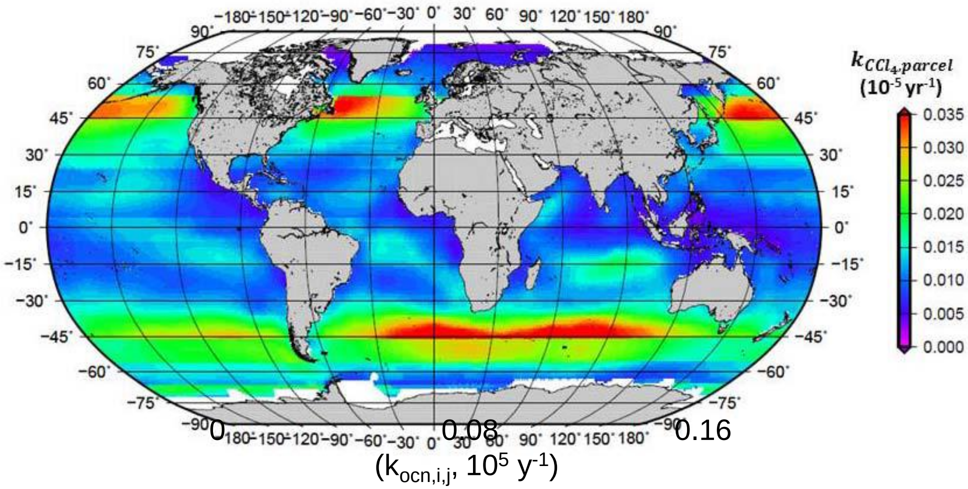
Our Latest Effort – CCl_4

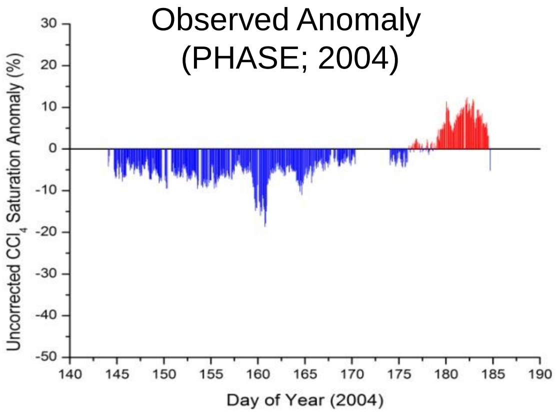
Research cruises

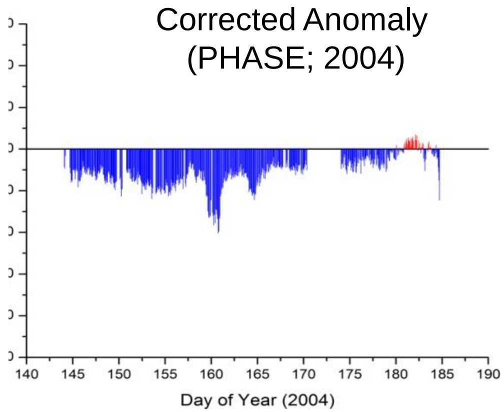


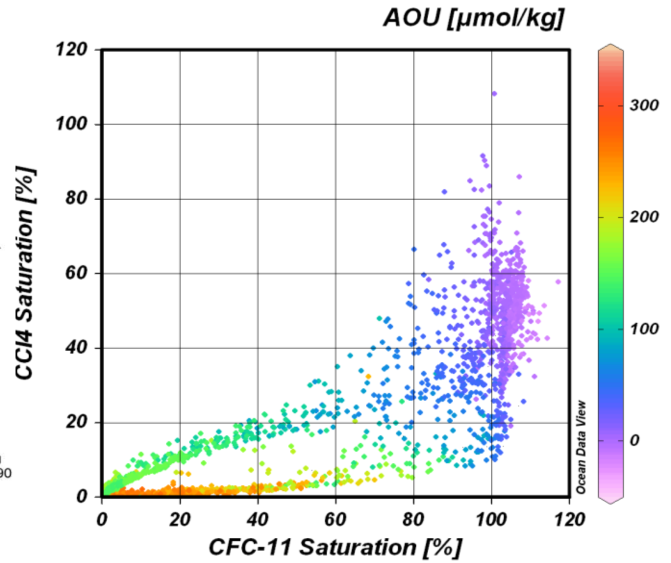
SAGA-2, RITS89, SAGA-3, OAXTC, BLAST1, BLAST2, BLAST3, GasEx98, RB9906, CLIVAR01, A16N, A16S, PHASE, P18, GOMECC, HalocAST-P, HalocAST-A

Oceanic Uptake Rate Constant



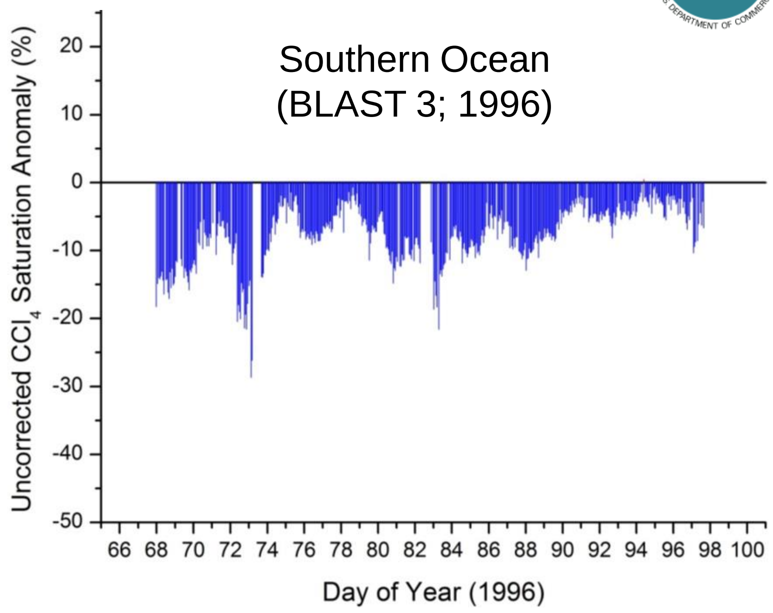


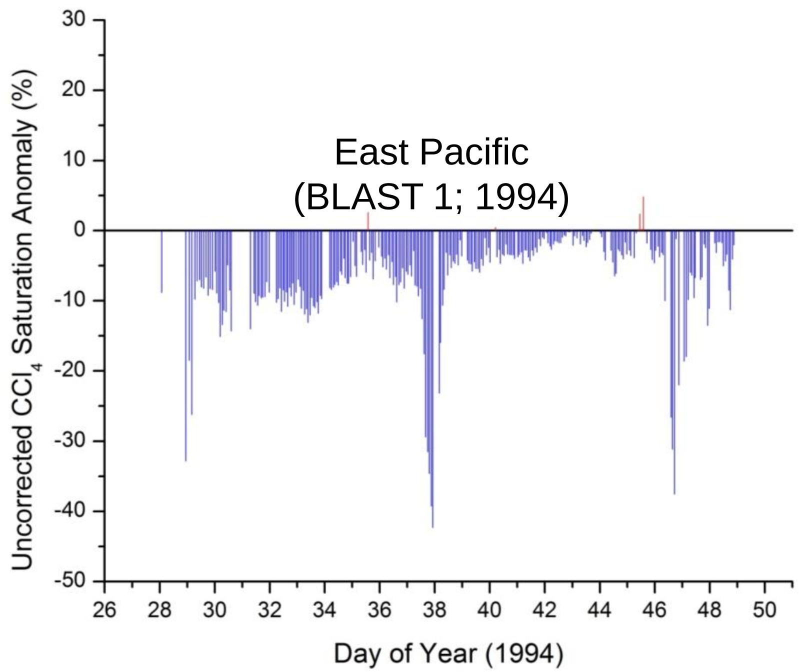




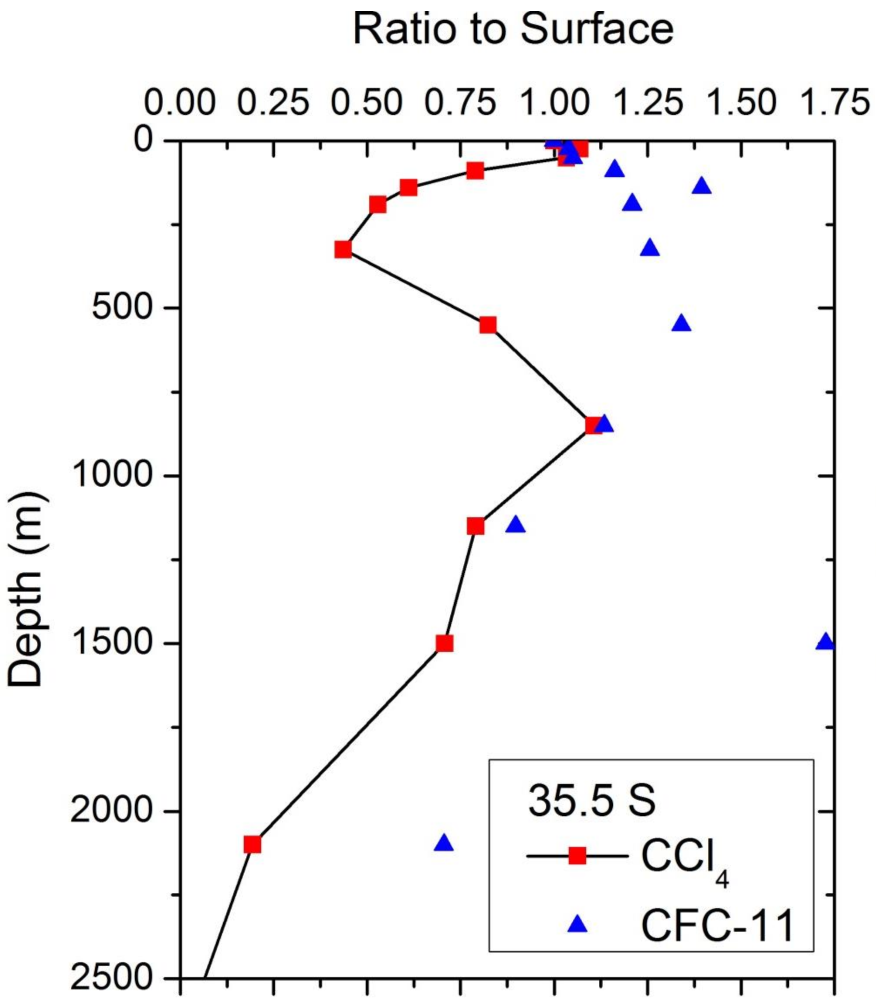
Biological (?) Consumption of CCl_4 (1987-2011)

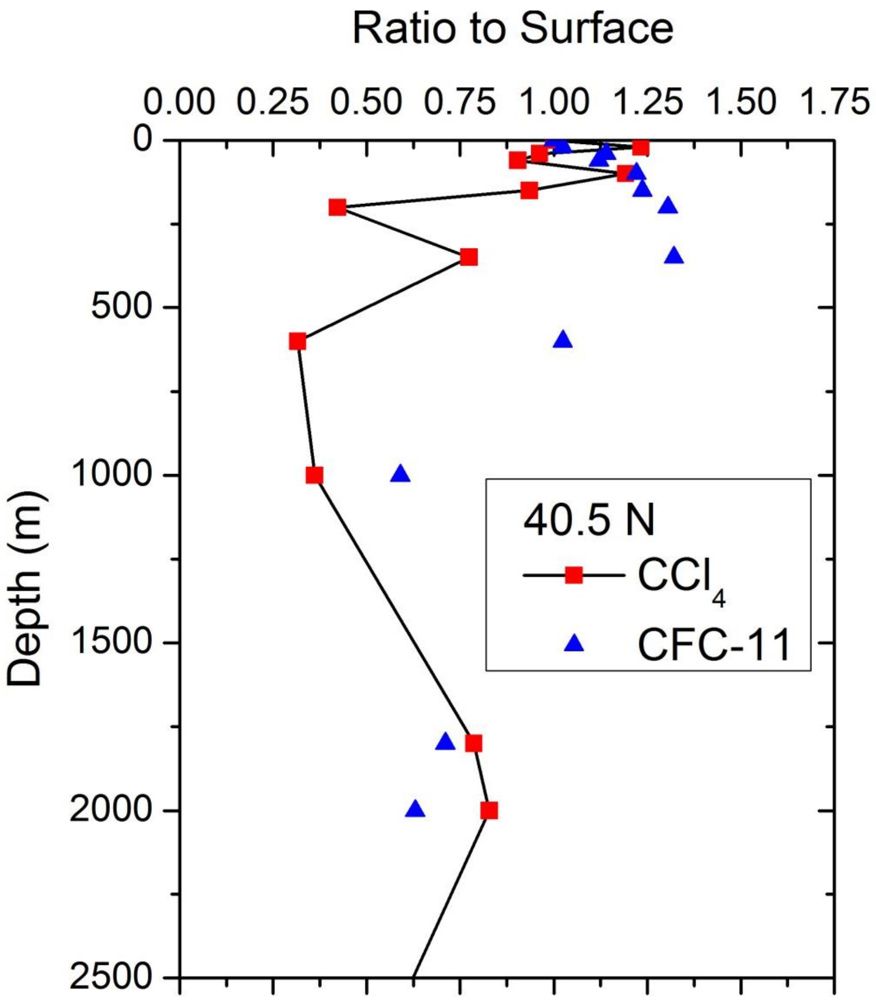
- CCl_4 is under-saturated everywhere, all the time
  - No relationship to temperature
  - No significant chemical sink
- But CCl_4 is consumed at mid-depth (O_2 minimum)
  - CCl_4 is deficit carried to the surface by mixing and transport
  - But not enough to explain deficit
- Exchange with the atmosphere leads to 18% of atmospheric CCl_4 being removed irreversibly by the ocean
  - Lowers atmospheric lifetime
  - Lowered ozone-depletion potential
  - Policy-relevant





CCl_4 at Depth





How much does K_w change things for CCl_4?

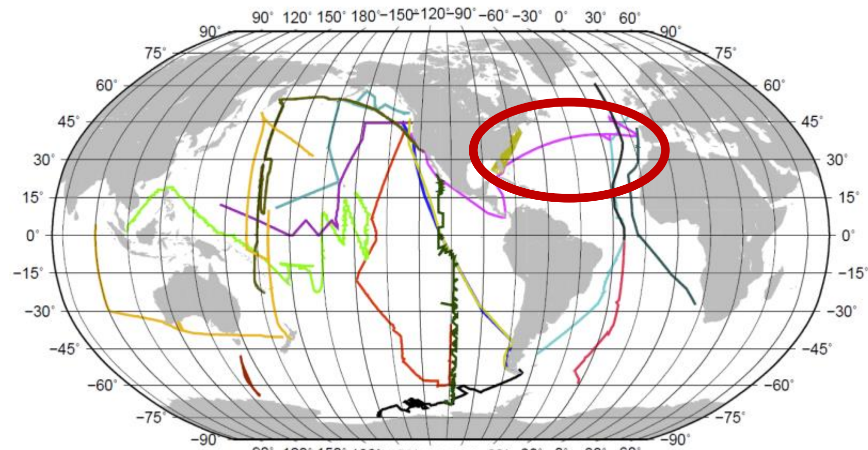
	$W_{(1992)}$	$W_{(2014)}$	% change
τ_{ocn} (y)	139	180	30%
τ_{strat} (y)	44	44	–
τ_{soil} (y)	375	375	–
τ_{total} (y)	30.6	32.3	6%

Do these gases have utility for evaluating K_w ?

CFC-11		Kw		sd	cv%
		4.9	m/d	0.8	16%
		20.4	cm/h	3.2	
Property	**Mean**	**sd**	**n**	**se**	**cv(se)**
hz (m)	50				5.0%
dt (d)	46.26	1.92	116	0.18	0.4%
Kappa (%/deg)	4.48			0.07	1.6%
dT (deg)	3.93	0.96	114	0.09	2.3%
Del(g) end (%)	3.81	2.36	39	0.38	9.9%
Del(g) avg (%)	3.04	1.98	37	0.32	10.7%

CFC-12		Kw		sd	cv%
		6.3	m/d	1.4	23%
		26.2	cm/h	6.0	
Property	**Mean**	**sd**	**n**	**se**	**cv(se)**
hz (m)	50				5.0%
dt (d)	46.26	1.92	116	0.18	0.4%
Kappa (%/deg)	3.95			0.06	1.6%
dT (deg)	3.93	0.96	114	0.09	2.3%
Del(g) end (%)	2.83	2.35	33	0.41	14.5%
Del(g) avg (%)	2.18	2.11	33	0.37	16.9%

CH3CCl3		Kw		sd	cv%
Thermal Diseq alone		13.7	m/d	7.0	51.3%
		57.1	cm/h	29.3	
with Hydrolysis		4.4	m/d		
		18.2	cm/h		
Property	**Mean**	**sd**	**n**	**se**	**cv(se)**
hz (m)	50				5.0%
dt (d)	46.26	1.92	116	0.18	0.4%
Kappa (%/deg)	4.04			0.06	1.6%
dT (deg)	3.93	0.96	114	0.09	2.3%
Del(g) end (%)	3.03	3.12	38	0.51	16.7%
Del(g) avg (%)	1.01	2.93	36	0.49	48.2%



Variability = ±19%

[Wanninkhof (2014) uncert = ±20%]


Questions?