Global cycling of methyl bromide and methyl chloride... and some thoughts on their natural variability

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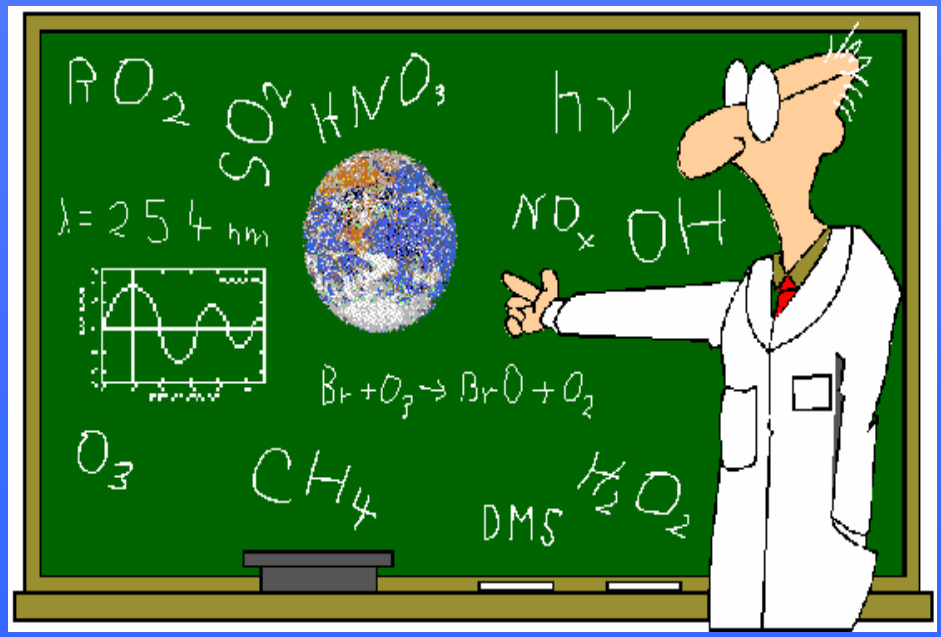


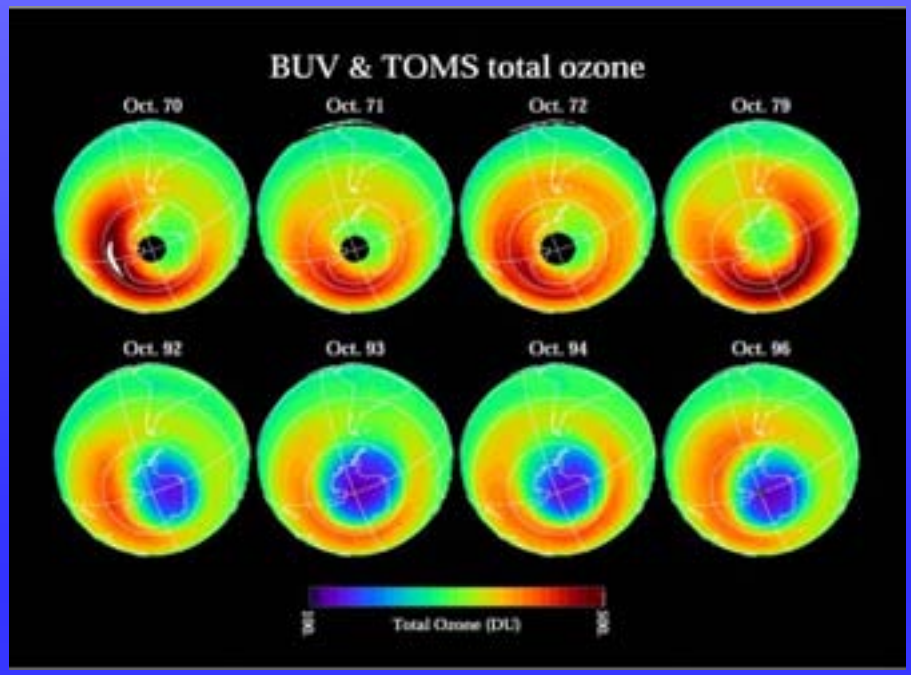
...and many, many others!!!

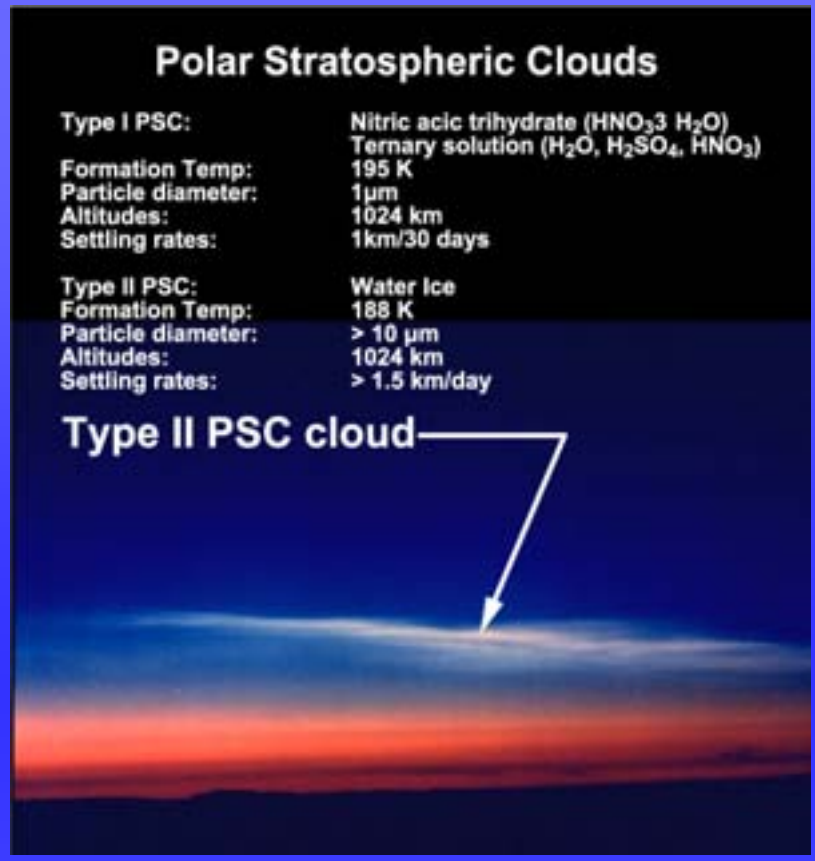
A quick synopsis for the temporarily impaired....

1. bottom up budgets for methyl halides are very difficult, but they must be done

2. ice cores can provide some answers, and some new questions....but is the past the key to the future?

Stratospheric ozone loss….





stratospheric halogen sources…

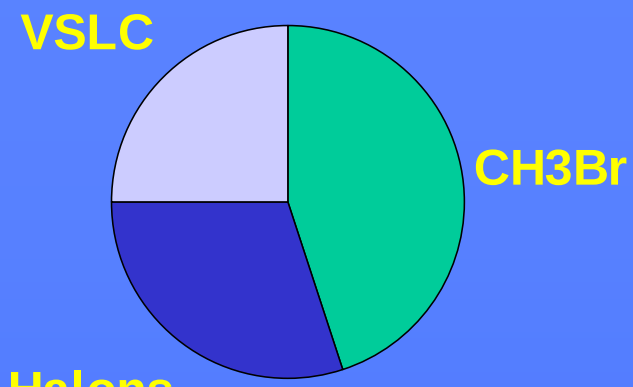
anthropogenic - *CFC's, halons,…*

and natural - *CH_3Cl, CH_3Br, CH_3I, CH_2Br_2, $CHBr_3$, ...*

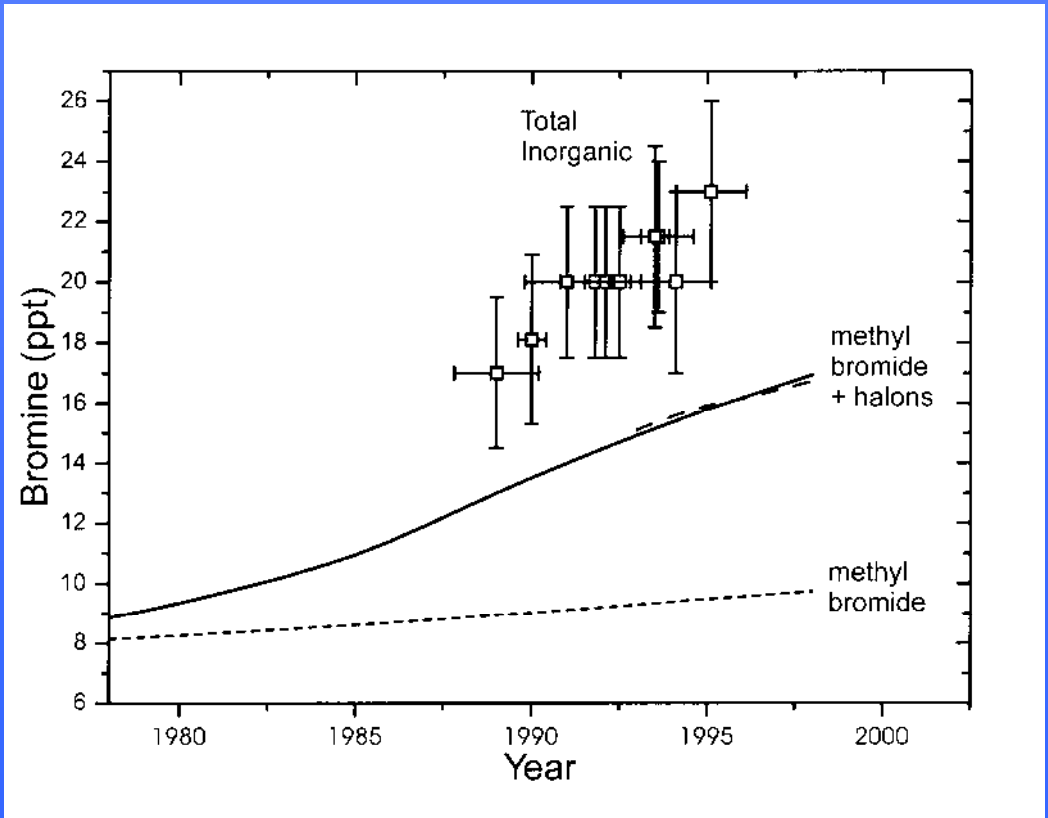
Catalytic ozone destruction
Br is ~50x more effective than Cl!

$$Br + O_3 \rightarrow BrO + O_2$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$BrO + ClO \rightarrow Br + Cl + O_2$$
$$net: 2O_3 \rightarrow 3O_2$$

Methyl bromide and stratospheric bromine ...

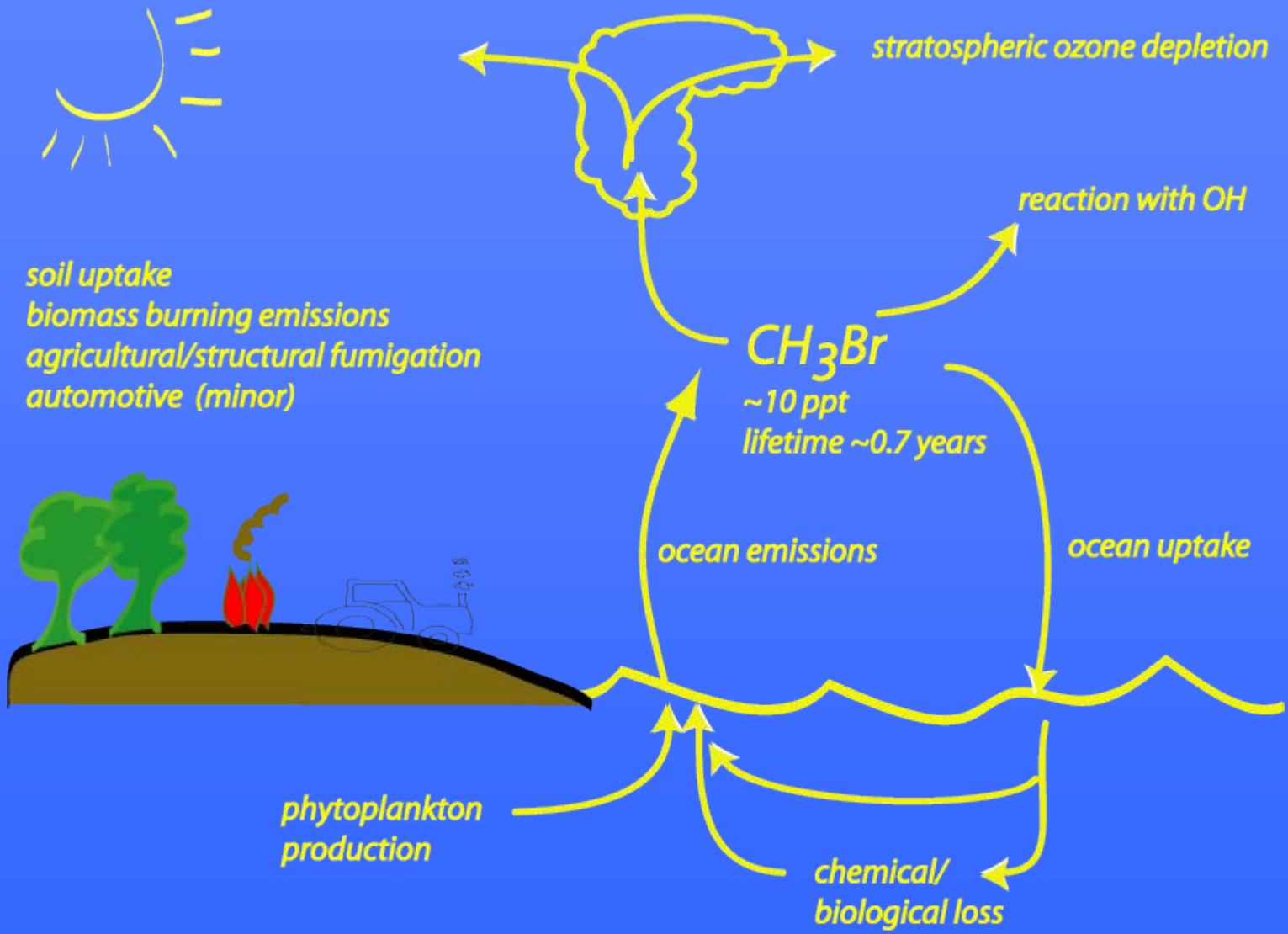


$C_xF_yCl_?Br_z$



Montzka and Fraser, WMO 2002

Global CH_3Br cycle



Question #1:

How will the atmosphere respond to phase-out of agricultural use of CH_3Br under the Montreal Protocol?

<u>need to know:</u>

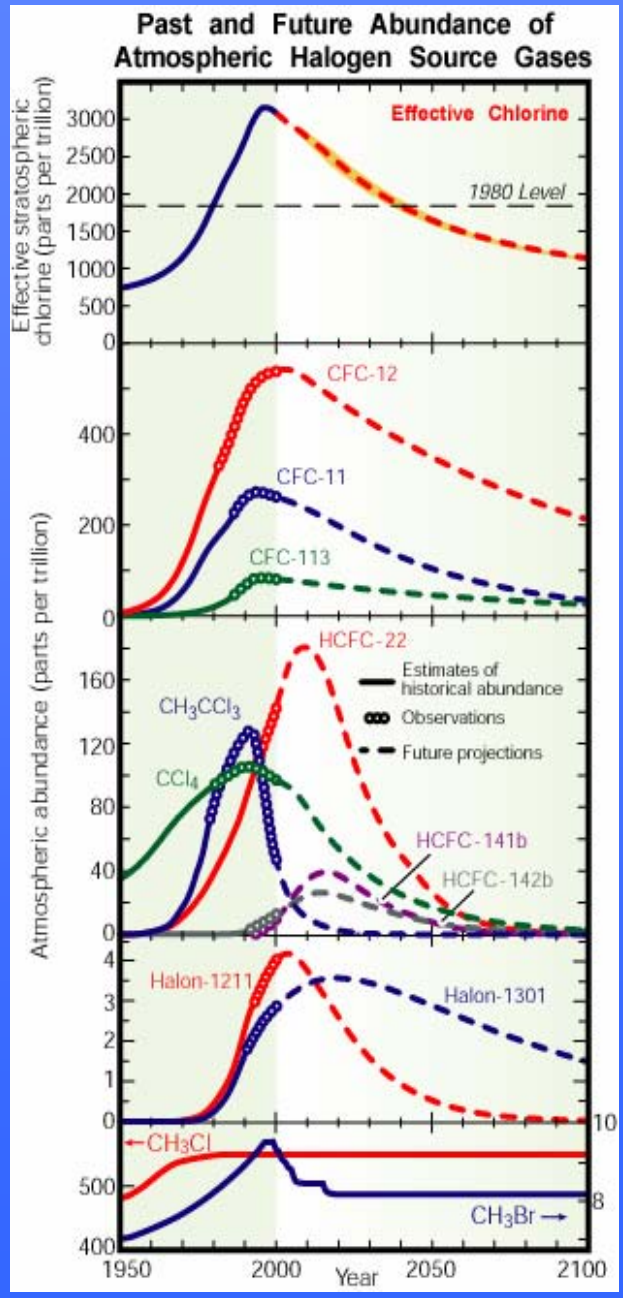
- *the total budget (i.e. all sources/sinks)* √
- *fraction of anthropogenic sources* **X**
- *response of the ocean ("buffering capacity")* ~√
- *atmospheric lifetime (0.7 years via OH, soils)* √

Question #2: Global climate change

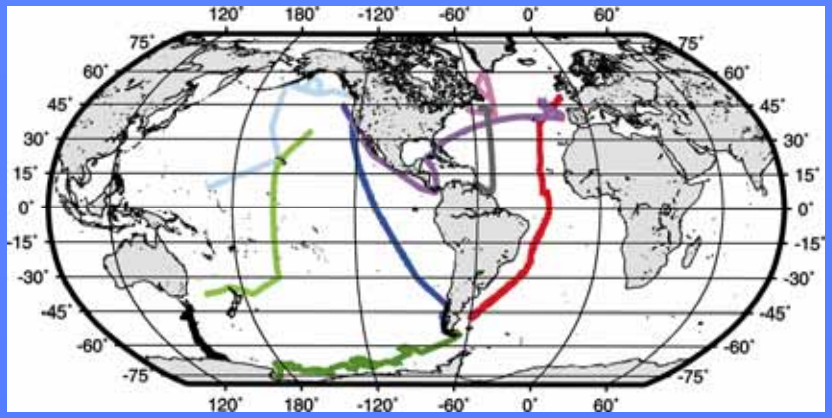
How will atmospheric CH_3Br respond to future changes in global climate?

- *changing climatic conditions means changes in both physical and biological systems*
- *predicting the response of atmospheric methyl halides even to simple physical forcing requires understanding the dynamics of the system, not just the current net fluxes.*

<u>need to know:</u> ...basically everything!



WMO 2002



CH_3Br saturation anomaly vs SST

$$\Delta_g = \text{Saturation Anomaly} = \frac{(C_W / H - p_a)}{p_a} \times 100$$

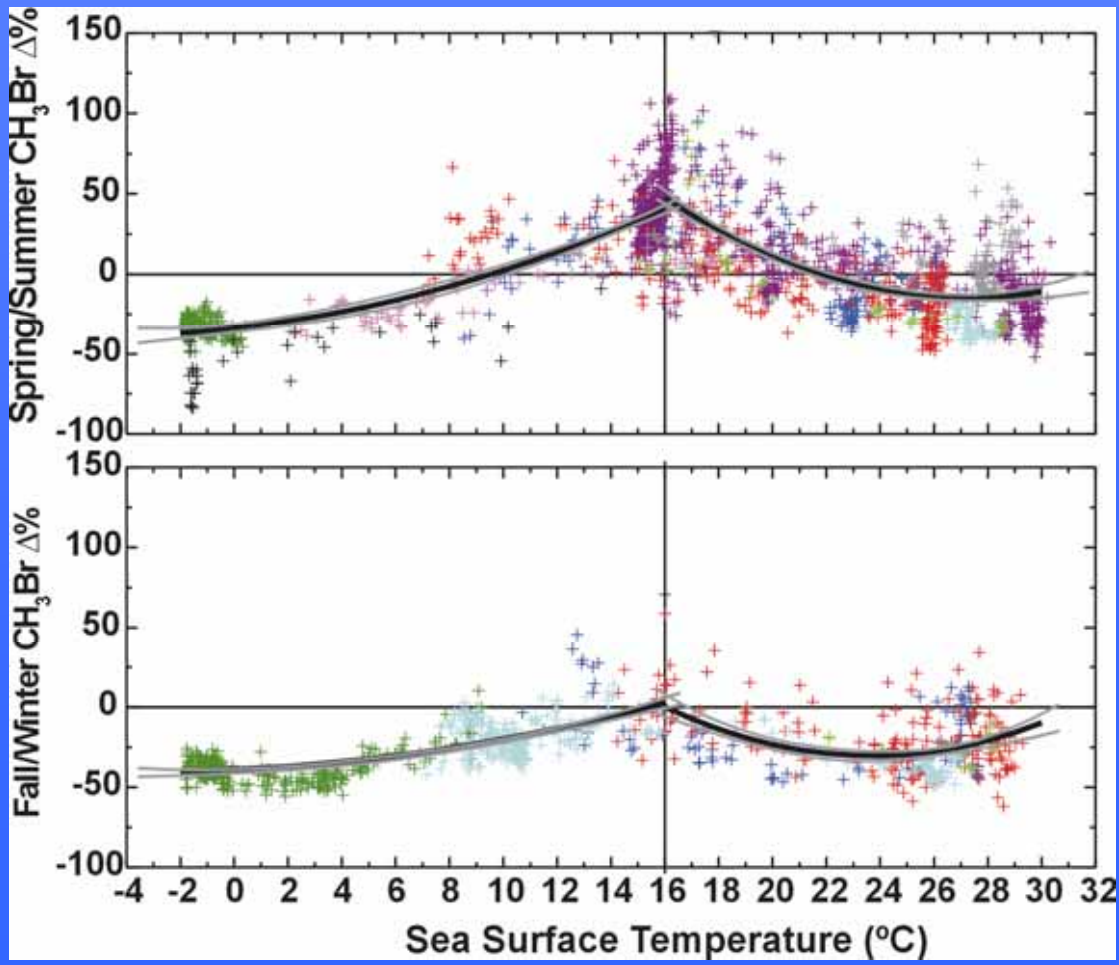
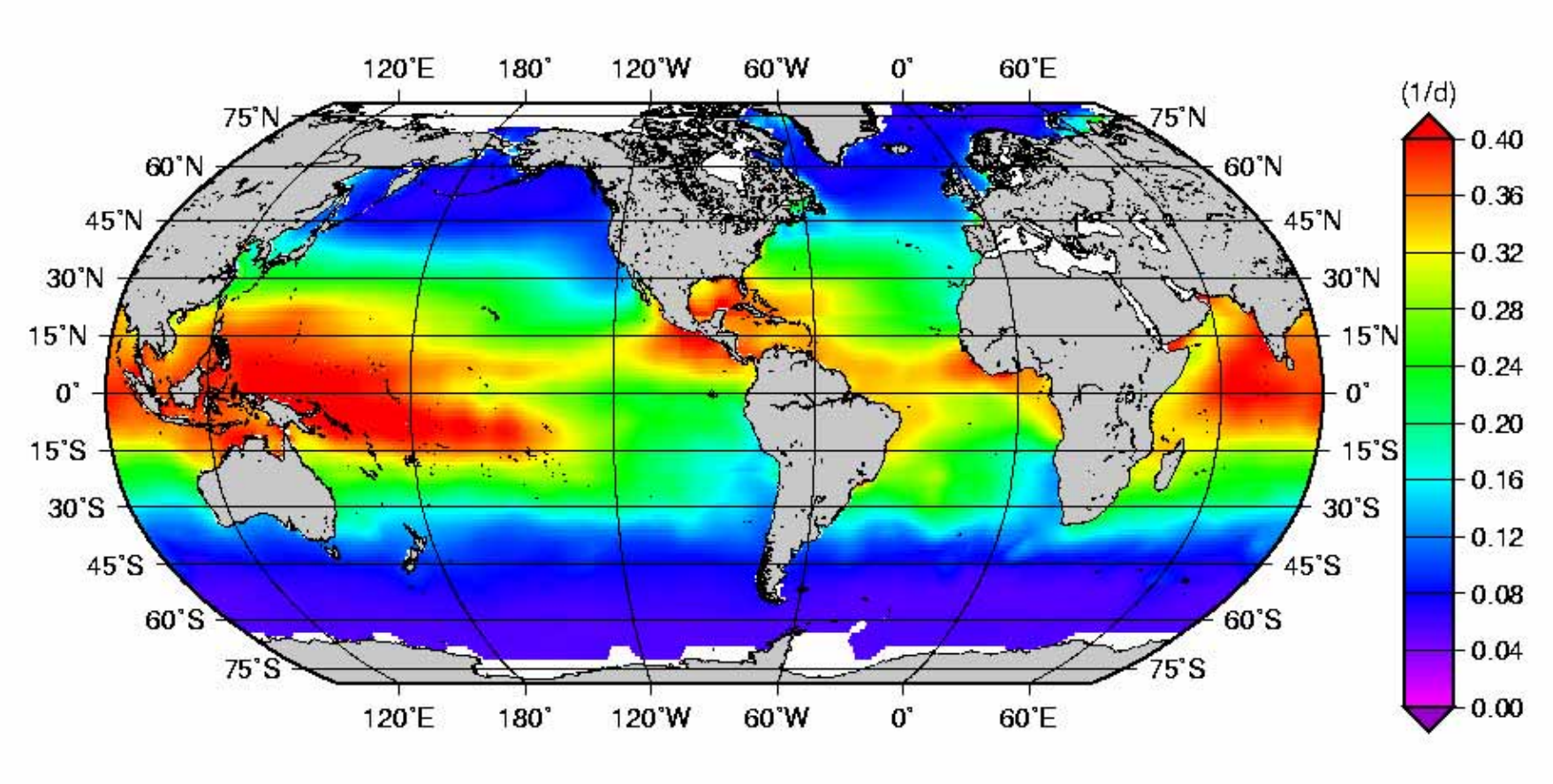


Figure 1. Nine cruises of CH_3Br Δ_g data with a map showing cruise tracks where Δ_g data was collected: BLAST I, BLAST II, BLAST III, GasEx98, RB-99-06, CLIVAR SR3, GM98A, GM98P, and G99 (a), CH_3Br saturation Δ_g data from the nine cruises plotted against SST and separated by season with spring/summer (b) and fall winter (c). Quadratic fits (—) are used to describe the data. Figure and data from *King et al.* [2002] and references therein.

CH_3Br loss rate constant

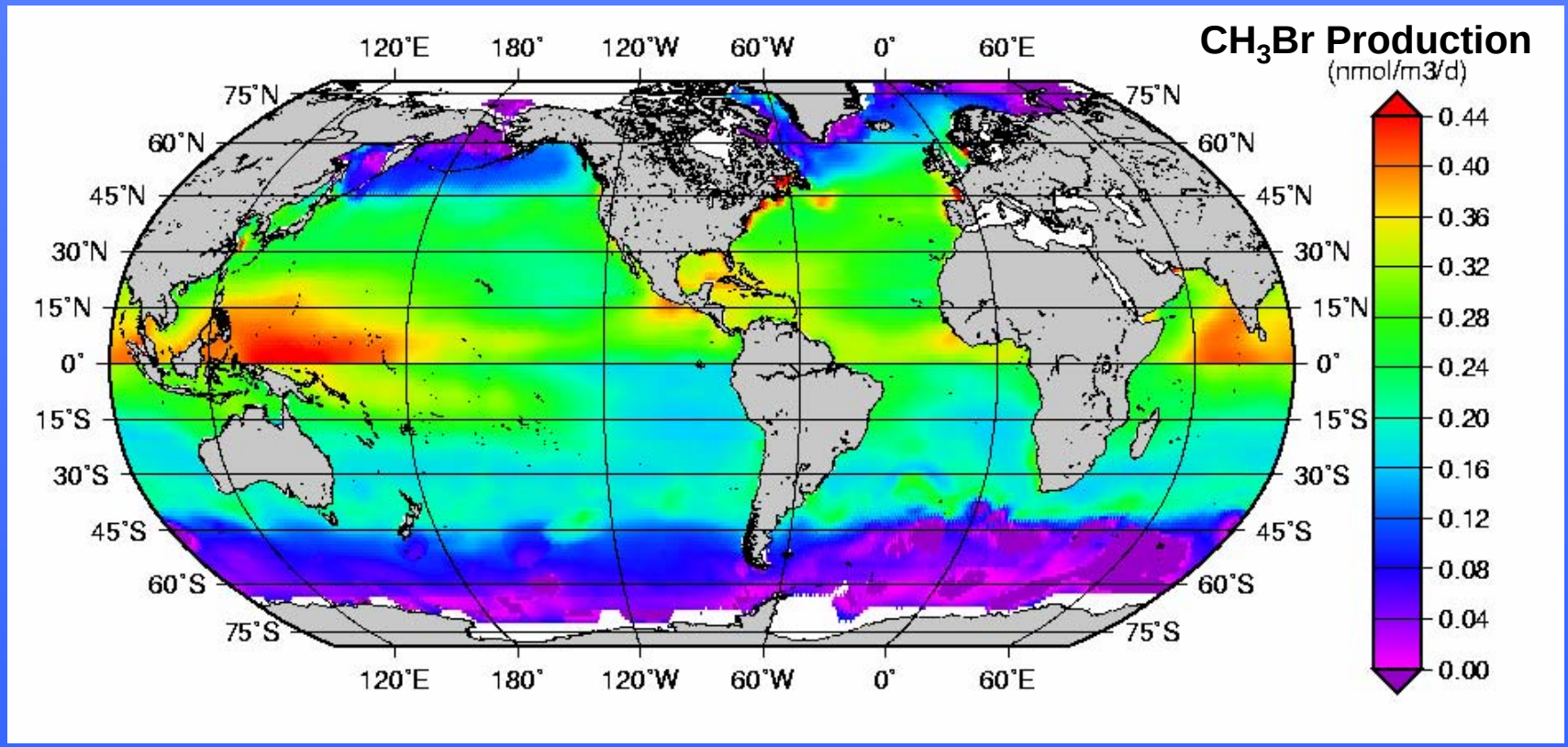


chloride substitution/hydrolysis

biological (bacterial?) uptake

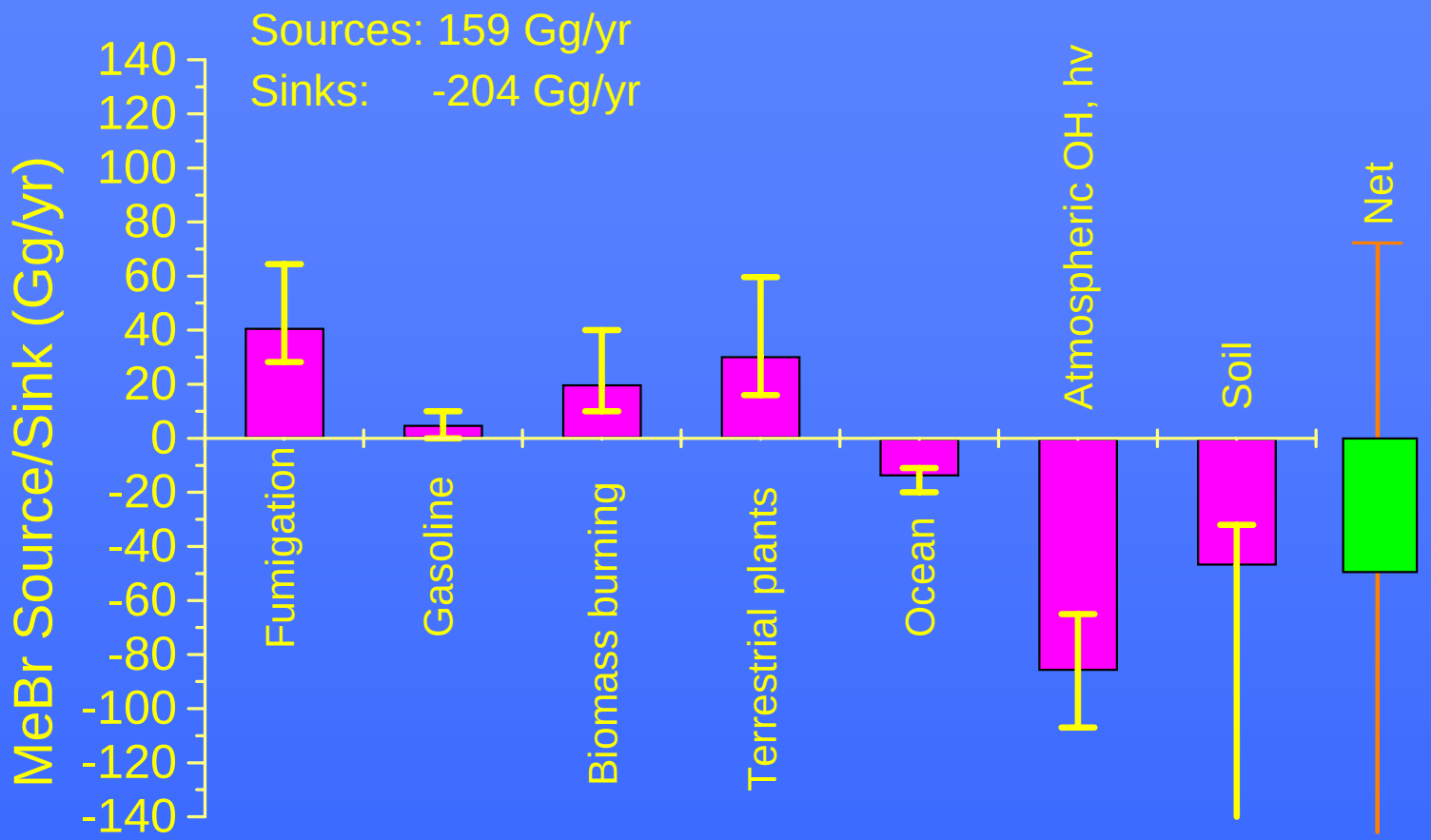
Inferred distribution of annually averaged CH_3Br oceanic production rates (nmol m^{-3} d^{-1})

$$\text{Production} = \frac{K_W}{z}\left(\frac{\Delta_g - \Delta_{f11}}{100}\right)\frac{p_a}{H} + (k_{chem} + k_{biol})C_W - \frac{D_z}{z}\frac{\Delta C}{\Delta z}$$



organisms responsible?
biochemical pathways?

Atmospheric CH_3Br budget

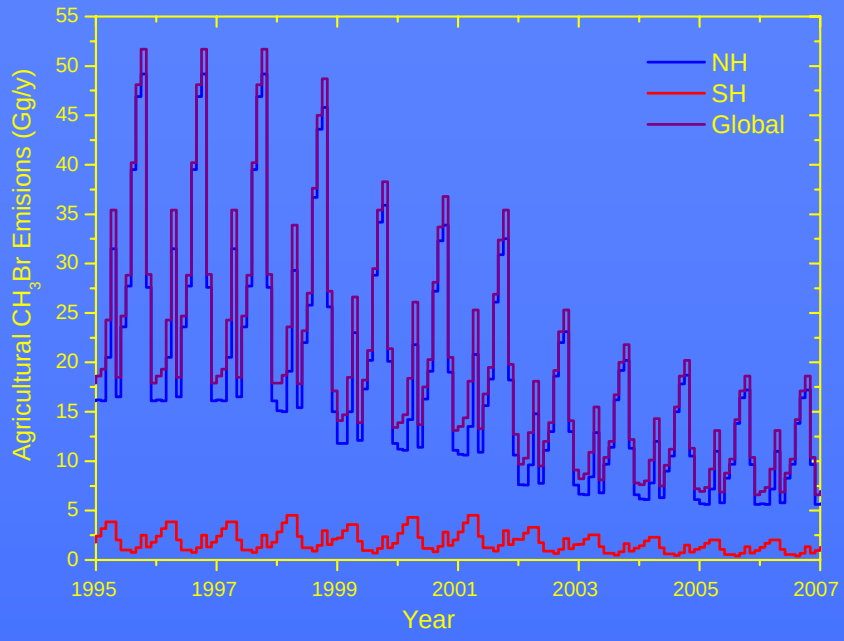


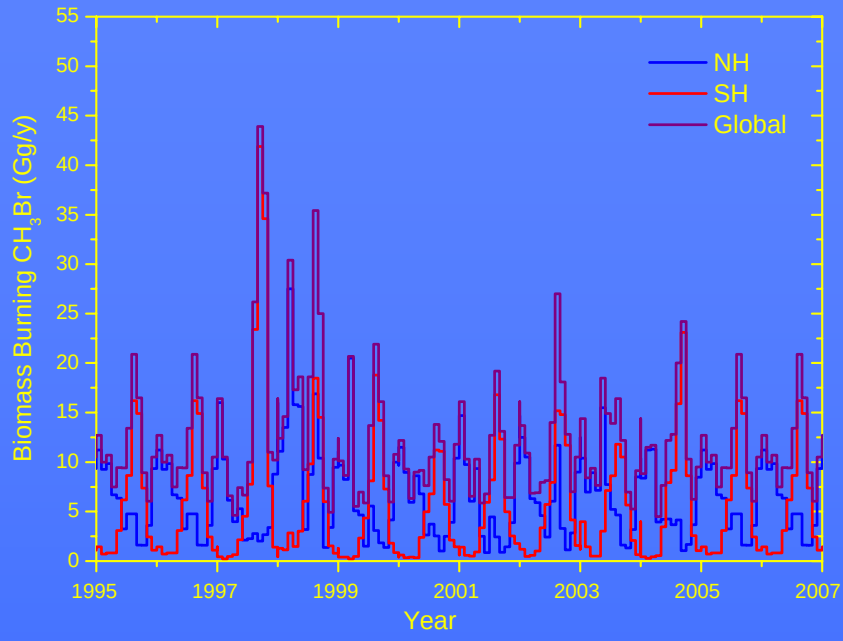
Note: The oceanic contribution to atmospheric CH3Br is the net effect of a large oceanic source (56 Gg/yr) and a large oceanic sink (77 Gg/yr) !

So what?

Source: WMO 2002

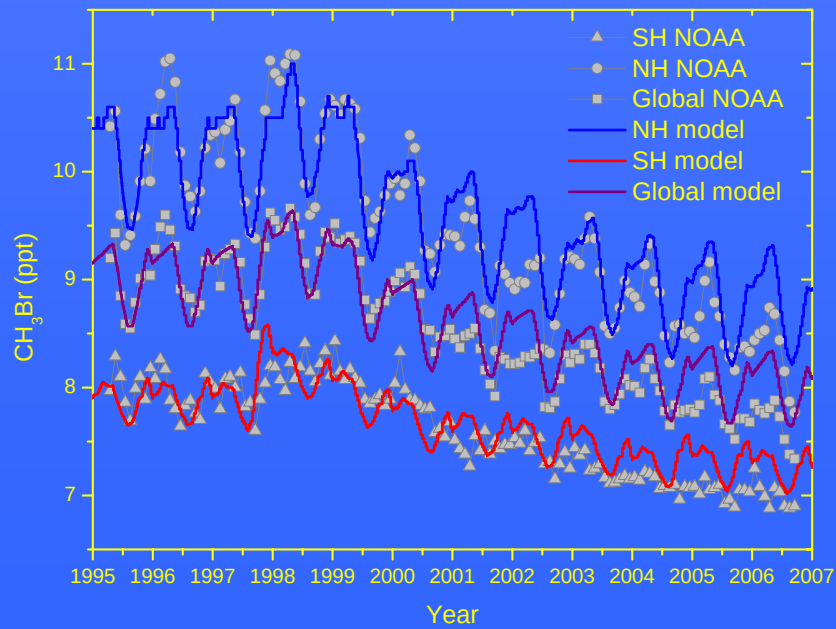
CH_3Br – recent trends (1995-2006)



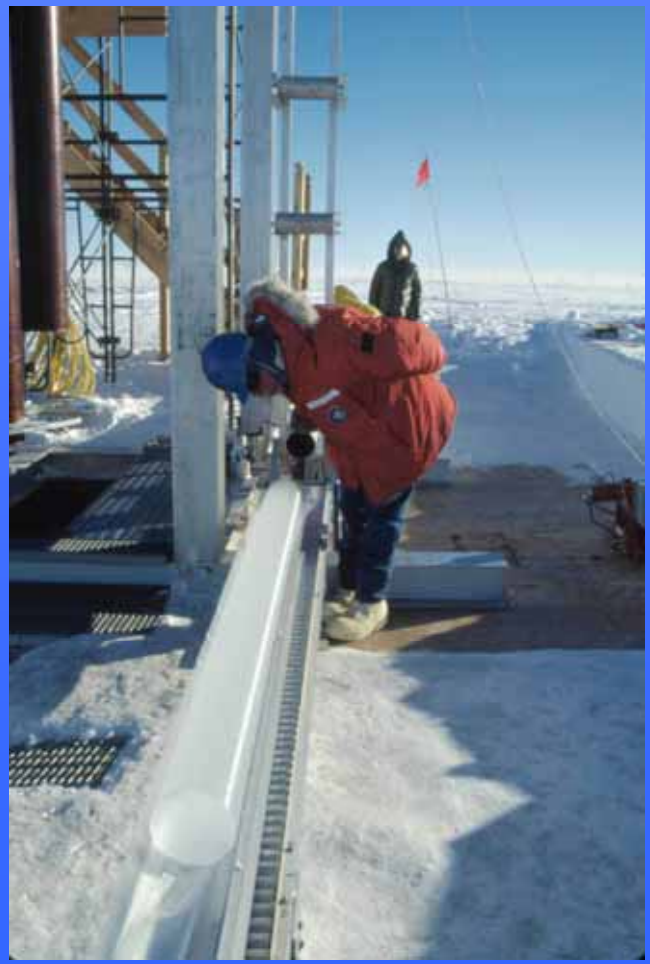


- Agricultural emissions
- Biomass burning

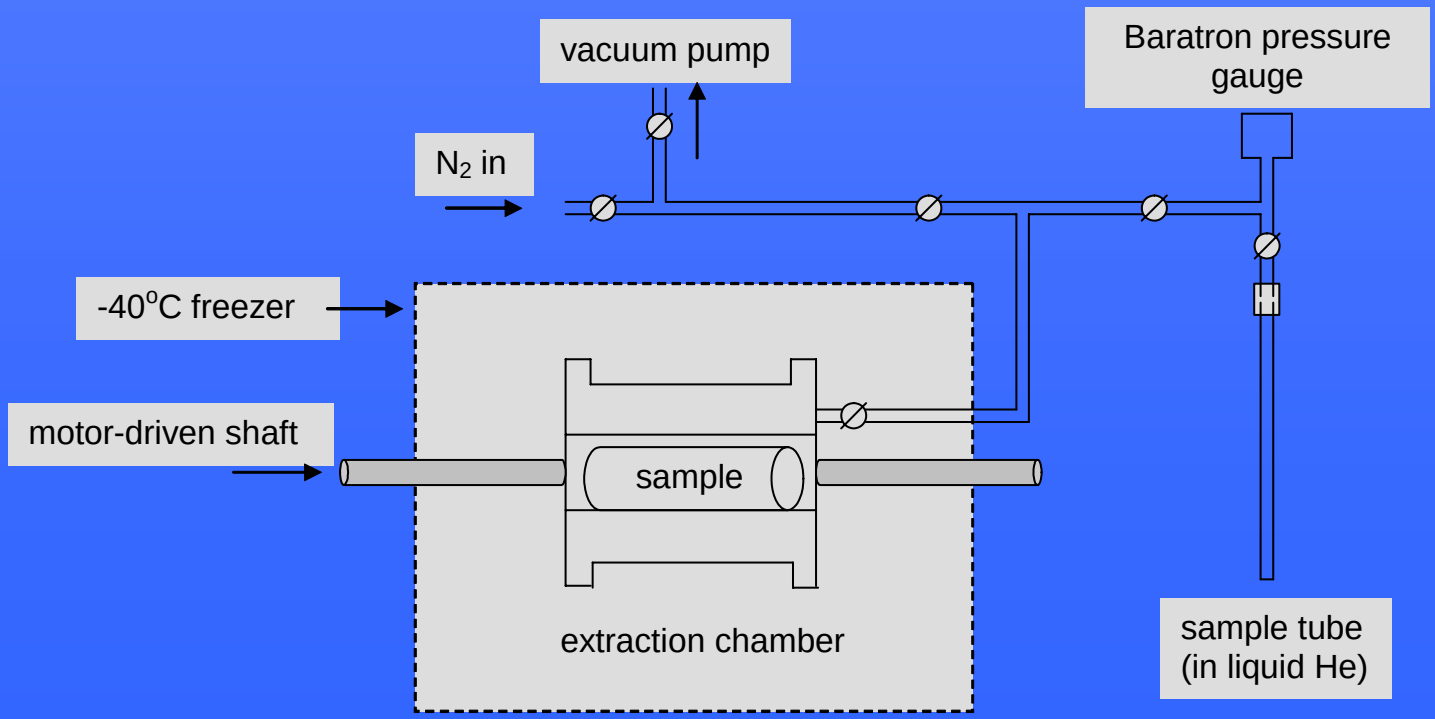
Model vs observations… →



... to the ice core record!



Dry extraction of trace gases from ice cores...

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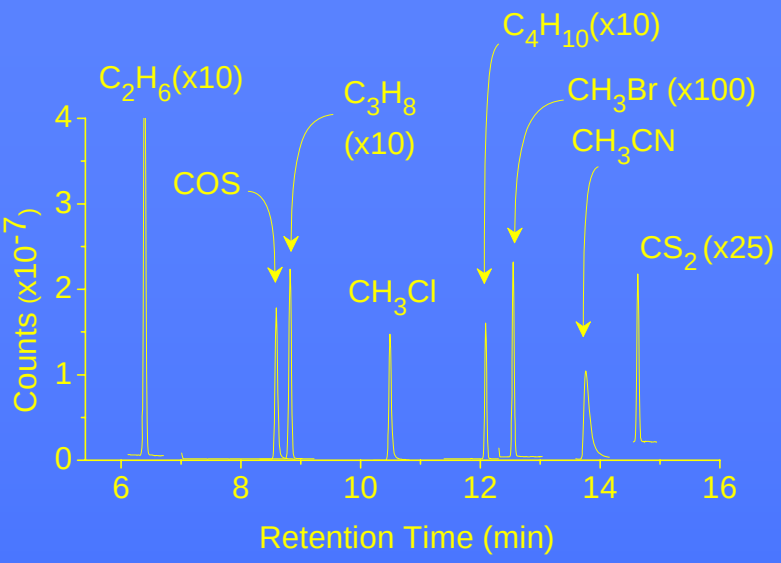
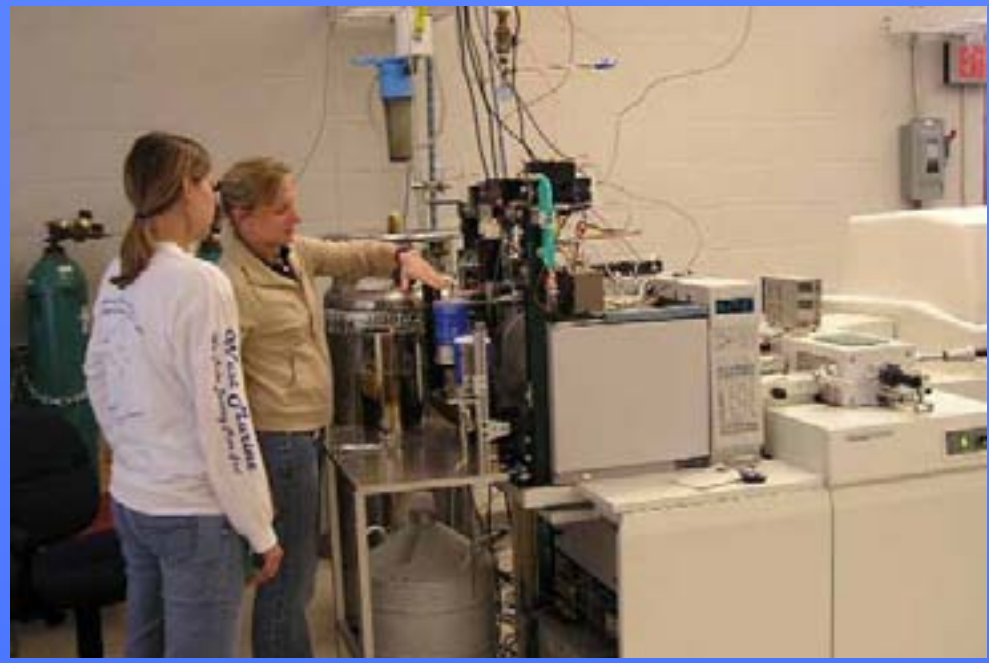
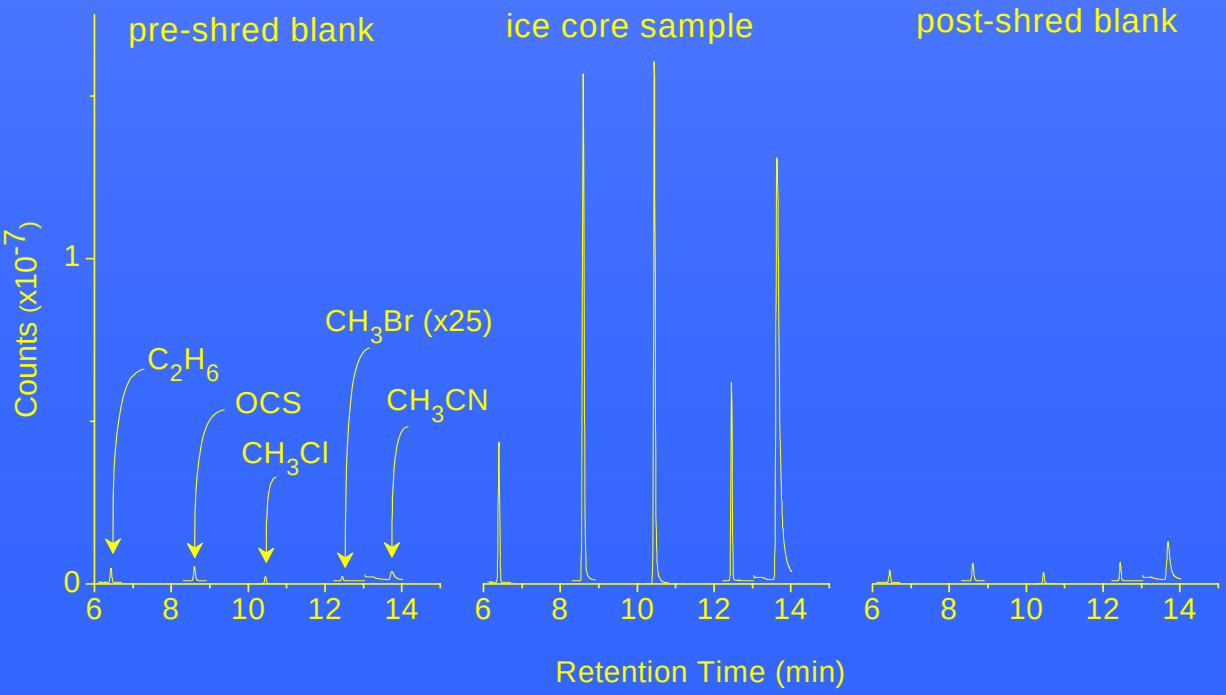
Cut for: Dr. Eric Saltzman
Core: SDMA
Section: 74
Tube: 74
TD: 65.416
BD: 65.616
Cut: MCA.02
Length: .2m.
Cut by: Todd Wojcik
1/27/2003

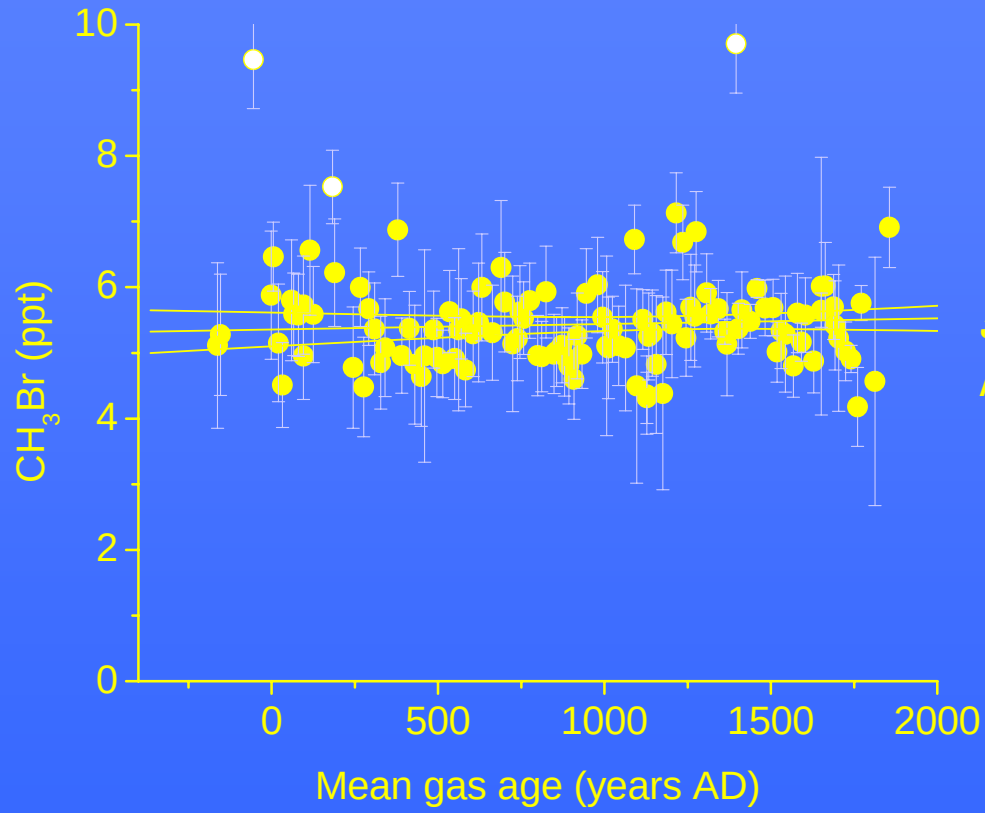
Ice core trace gas analysis...







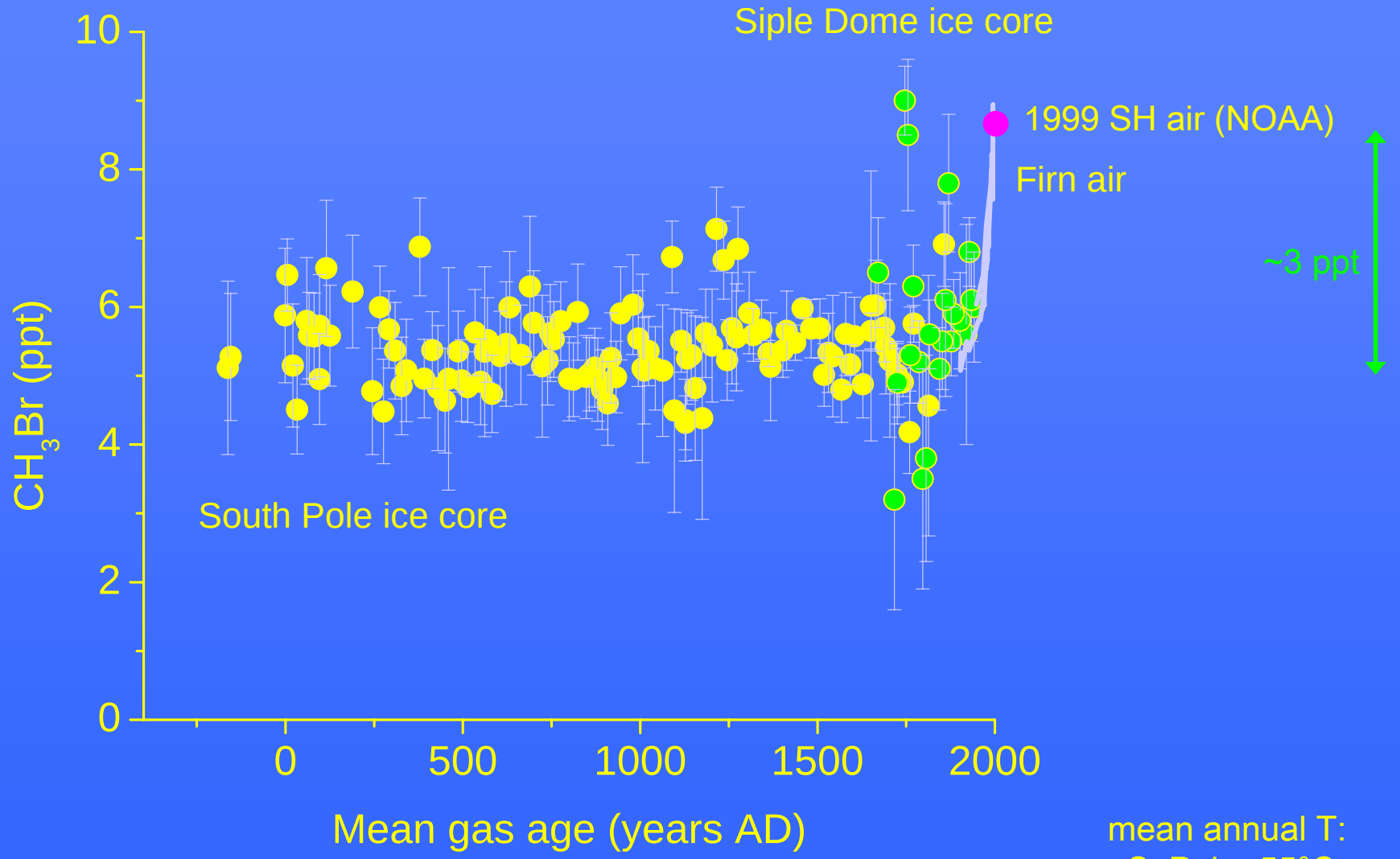
2,000 year record of atmospheric CH_3Br from a South Pole ice core



5.39 ± .06 ppt (1s.e, n=109)
no trend

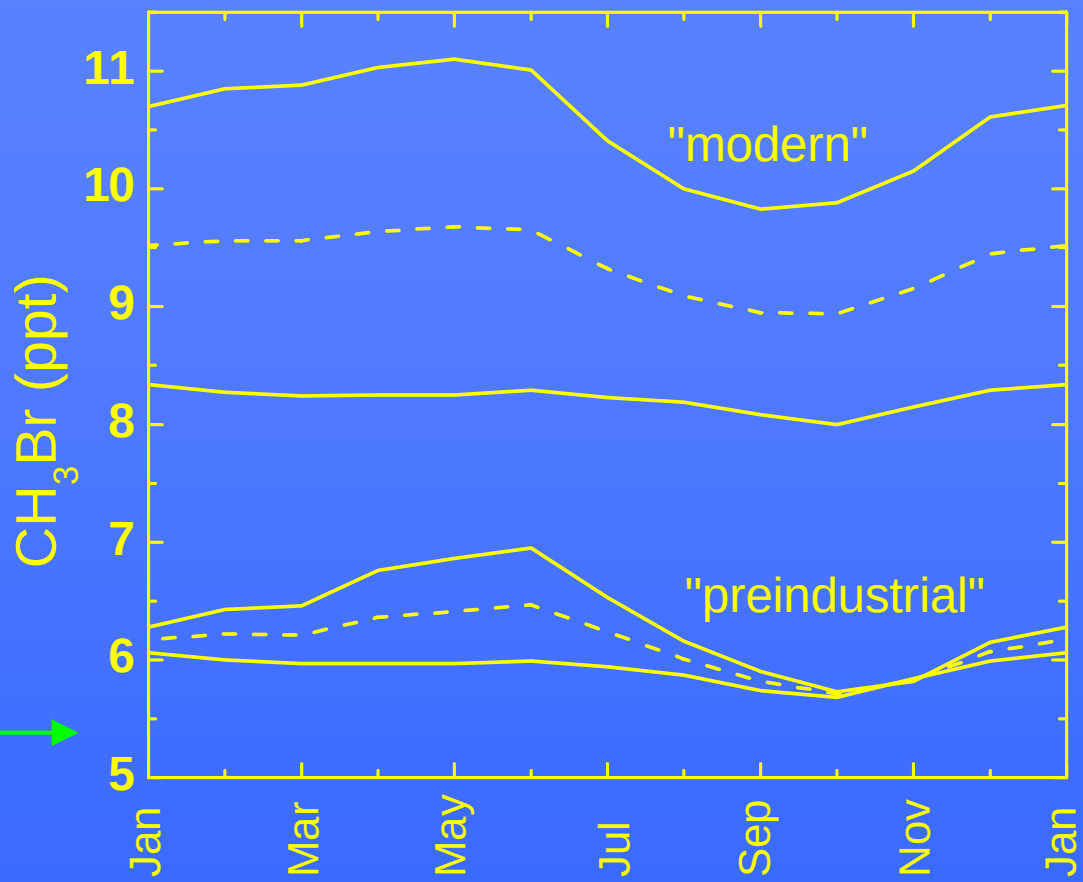
(note to paleoceanographers: time marches to the right...)

Man's impact on the CH_3Br cycle…



mean annual T:
S. Pole -55°C
Siple Dome -25°C

Model simulations...

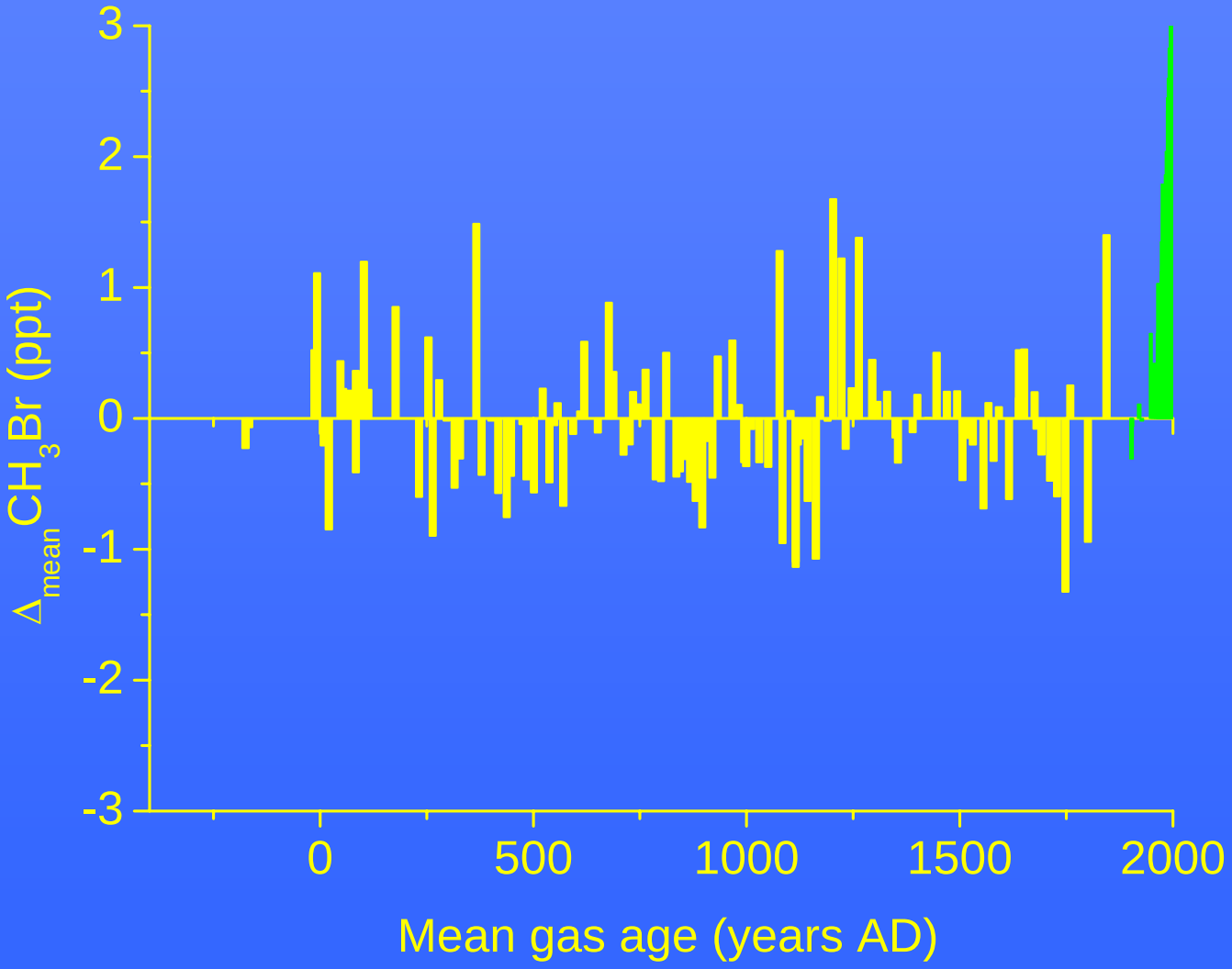


ice core →

reasonable, *assuming SH missing source is natural and nothing else changed...*

Saltzman et al., 2004

Evidence of centennial-scale variability... or noise?



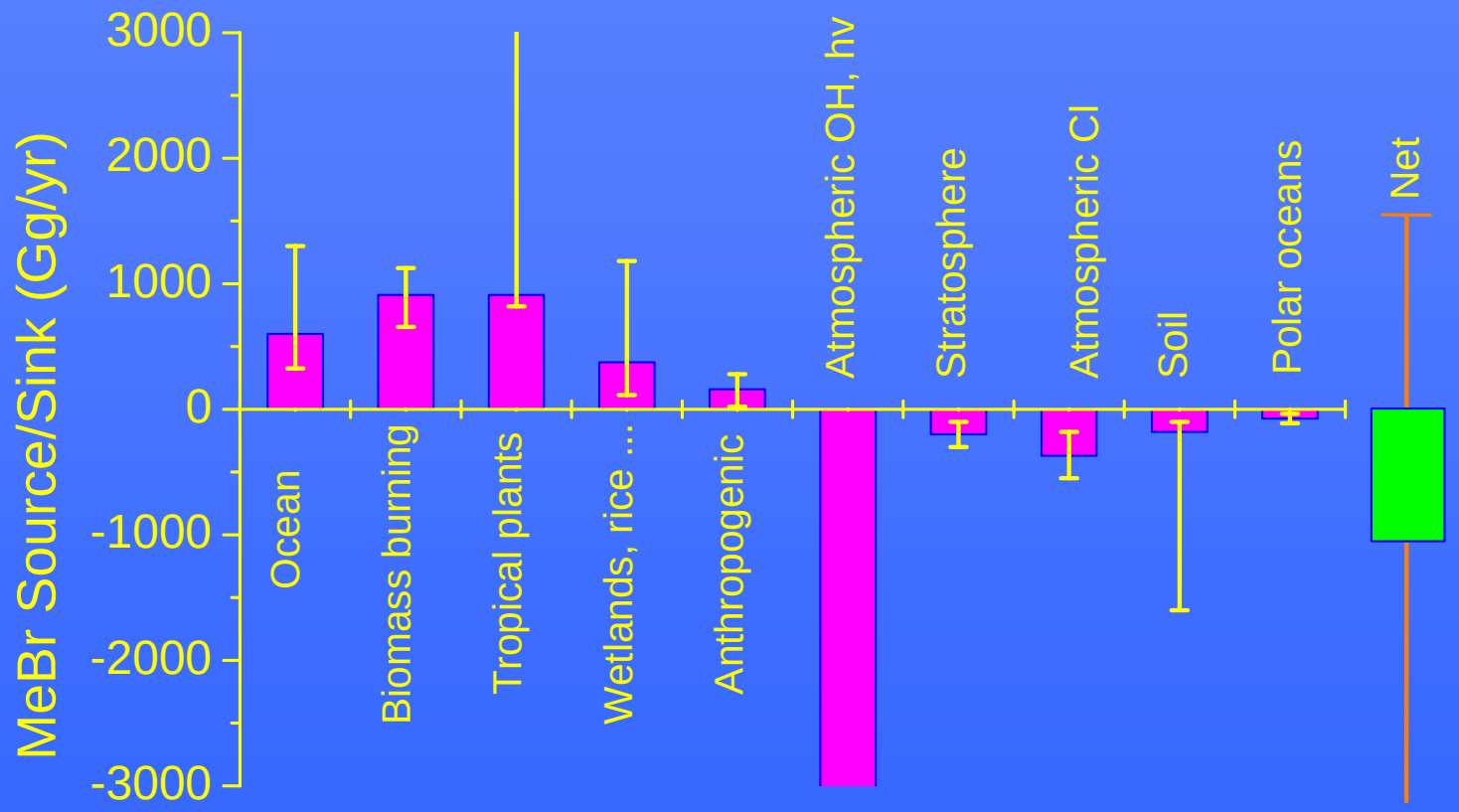
Some points to consider:

- *CH_3Br seems to be stable in polar ice!*
- *Southern hemisphere CH_3Br levels ~30% lower for past 2ky prior to industrialization*
- *Natural variability might be significant, but …*
  - *it's awfully close to experimental uncertainty*
  - *Late Holocene climate change was modest*
- *The phase-out of CH_3Br will probably result in a 3 ppt SH decrease (4.5 ppt global; 225 ppt Cl equivalent). That's a good thing.*

CH_3Cl global budget

mixing ratio 550 ppt
atm lifetime ~1 year

Sources: 2,956 Gg/yr
Sinks: -1,049 Gg/yr

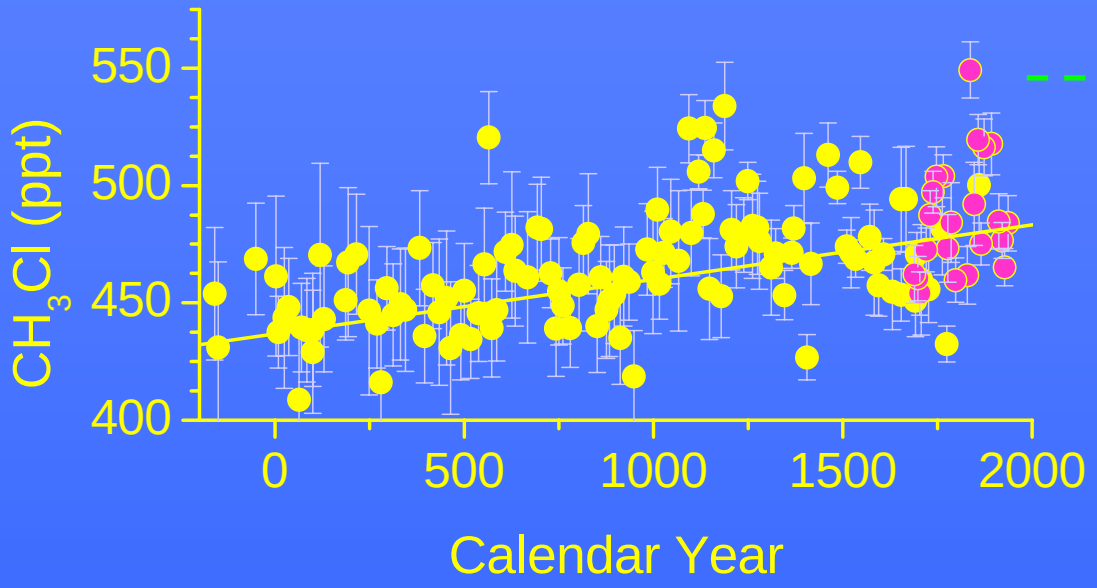


Source: WMO 2002

ice core methyl chloride...

South Pole ice core ●

Siple Dome ice core ●



trend: 3 ppt/100 years

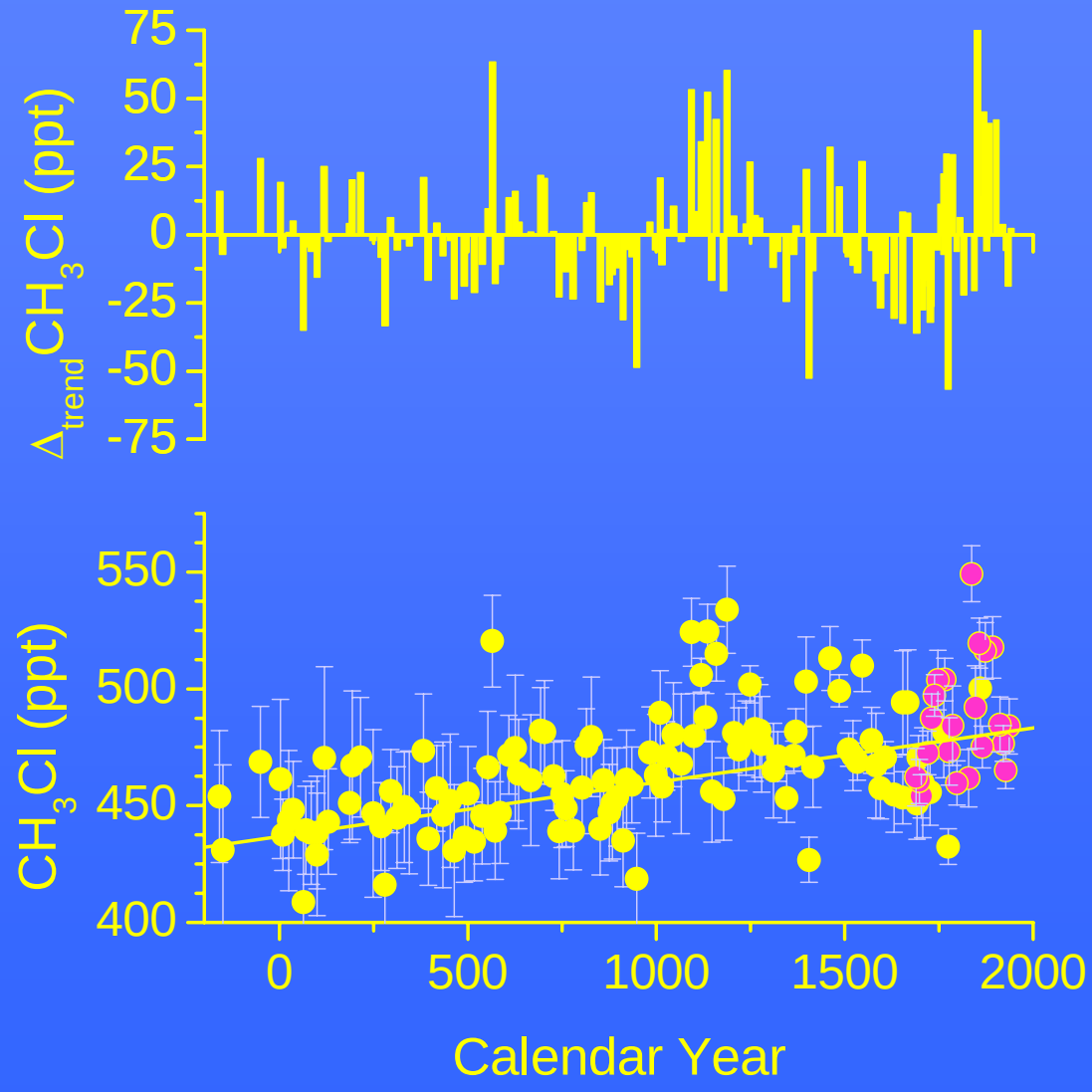
Long-term variability or downcore loss?

Williams et al., in press

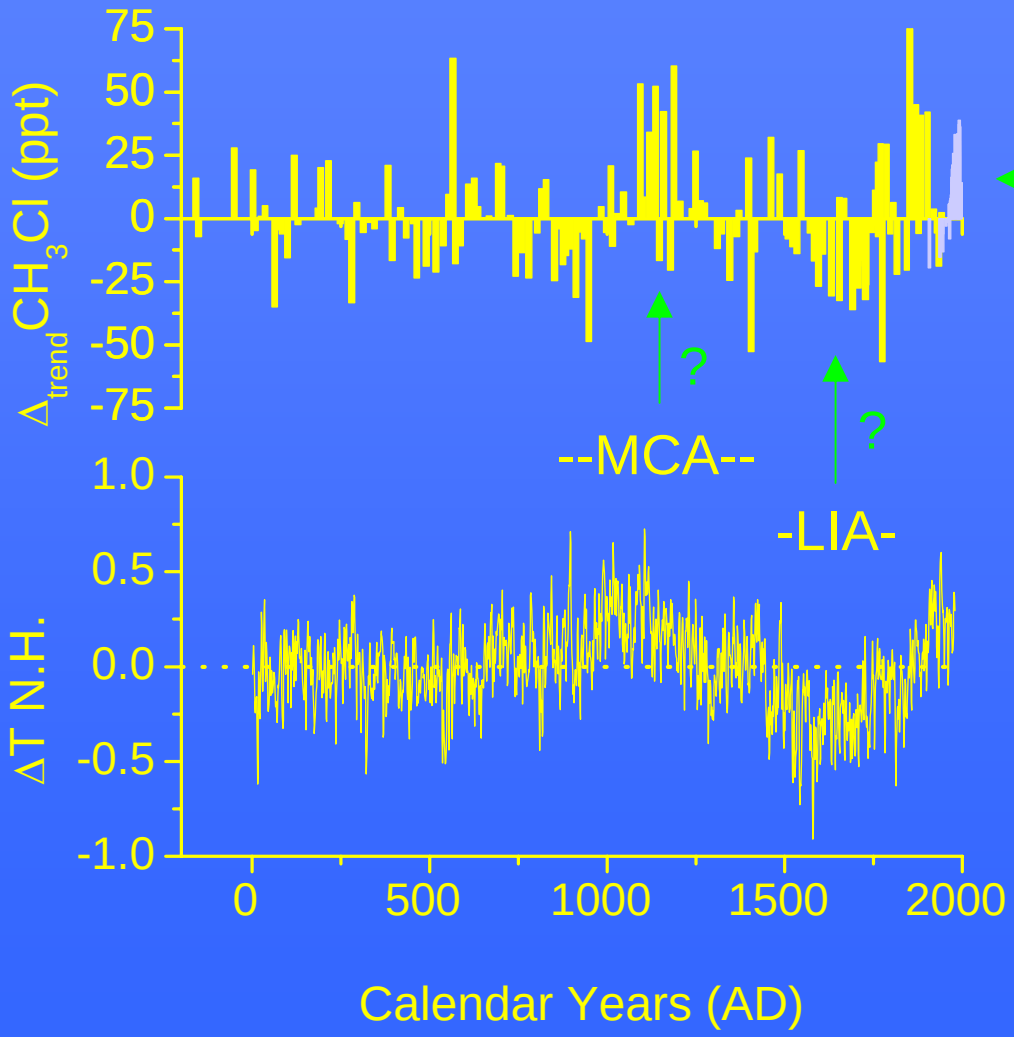
ice core methyl chloride...

South Pole ice core

Siple Dome ice core



ice core methyl chloride... climate-controlled variability?



Moberg et al., 2005

multi-proxy reconstruction

Take home messages...

- CH_3Cl appears climate-sensitive, and CH_3Br might be. Is this an ocean signal, a terrestrial signal, or both?
- Global warming may increase CH_3Cl and CH_3Br levels by >100 ppt Cl_{eq}. *That's probably not a good thing.*
- caveat...in the future, tropical land use changes might trump climate-signals
- In a warmer world, will atmospheric halogens (and stratospheric ozone) return to their preindustrial state? *Probably not.*