SOLAS Halocarbon Intercalibration Workshop

Overview

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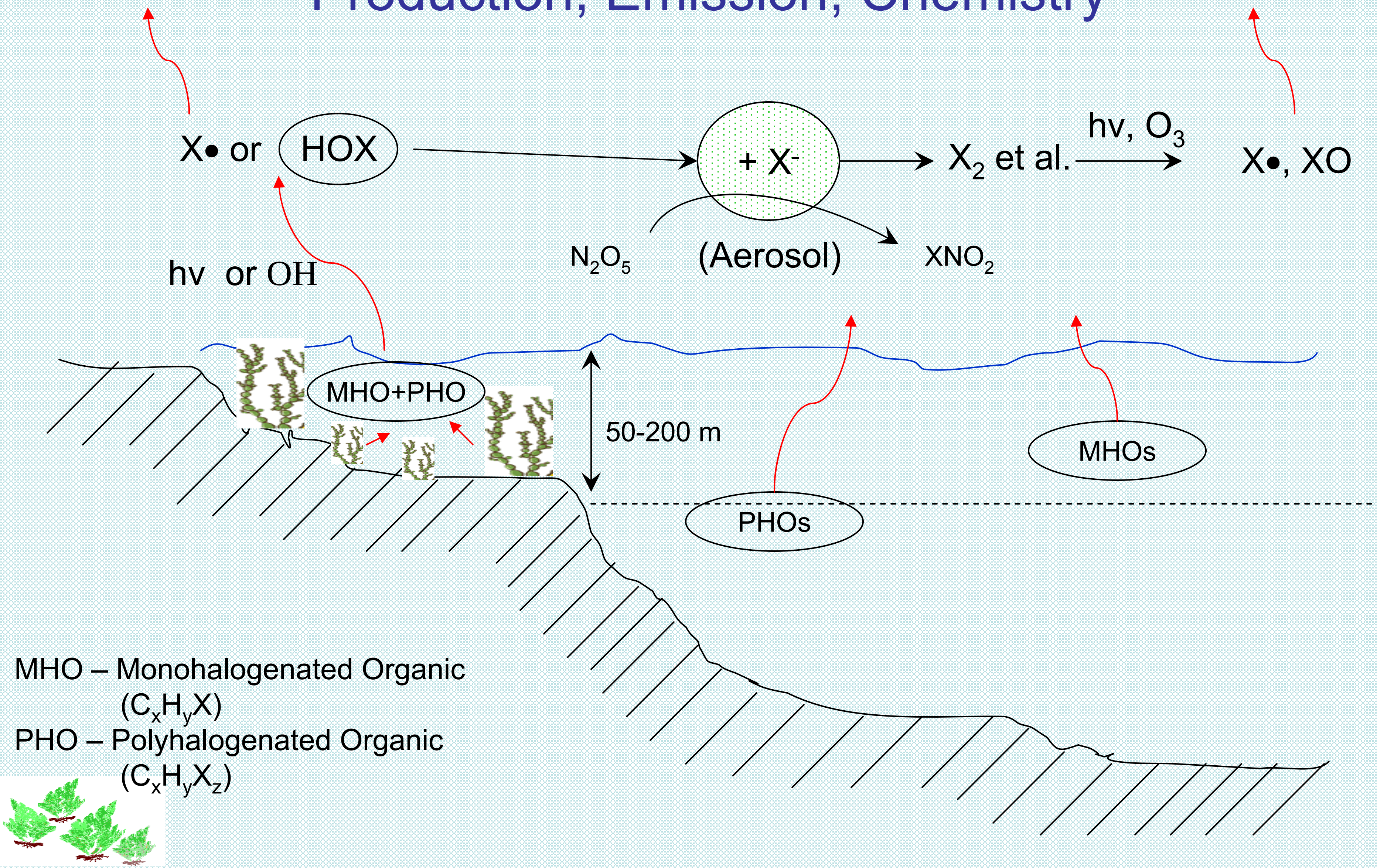
Definition of Very Short-lived Substances (Ozone Assesment)

- Very short-lived substances (VSLS) are defined as trace gases whose local tropospheric lifetimes are comparable to, or shorter than, tropospheric transport time scales, such that their . . . distributions are non-uniform. In practice, VSLS are considered to have atmospheric lifetimes of less than 6 months.

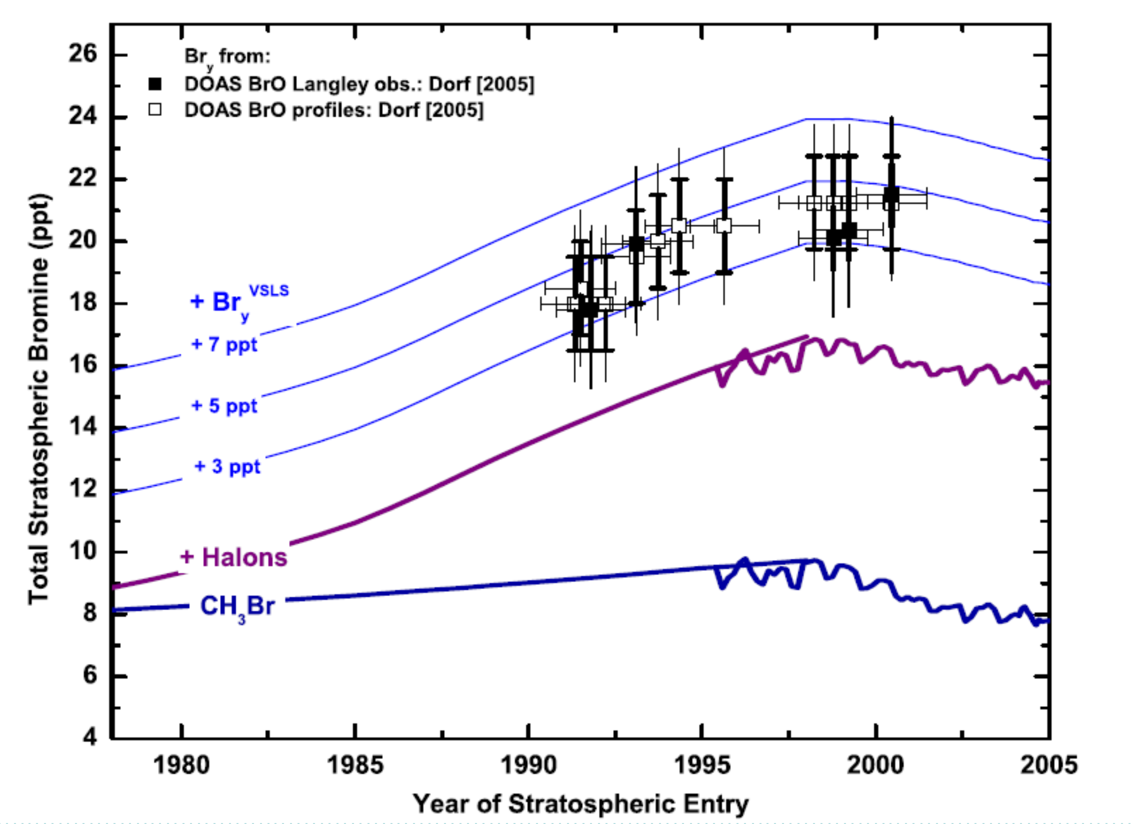
Production, Emission, Chemistry



MHO – Monohalogenated Organic (C_xH_yX)

PHO – Polyhalogenated Organic ($C_xH_yX_z$)

Apparent Imbalance of Br in the Stratosphere



- Inorganic, stratospheric Br is 3-8 ppt (15-45%) higher than anticipated
- Can shorter-lived gases be making up the difference?
- Given the slow decline in long-lived gases, could global change affect this contribution?

Concluding statements from the 2006 Assessment

- . . . Brominated VSLS (are) believed to make a significant contribution to total stratospheric bromine and its effect on stratospheric ozone.
- Various lines of evidence show that brominated VSLS contribute about 5 ppt (with estimates ranging from 3 to 8 ppt) to total stratospheric inorganic bromine

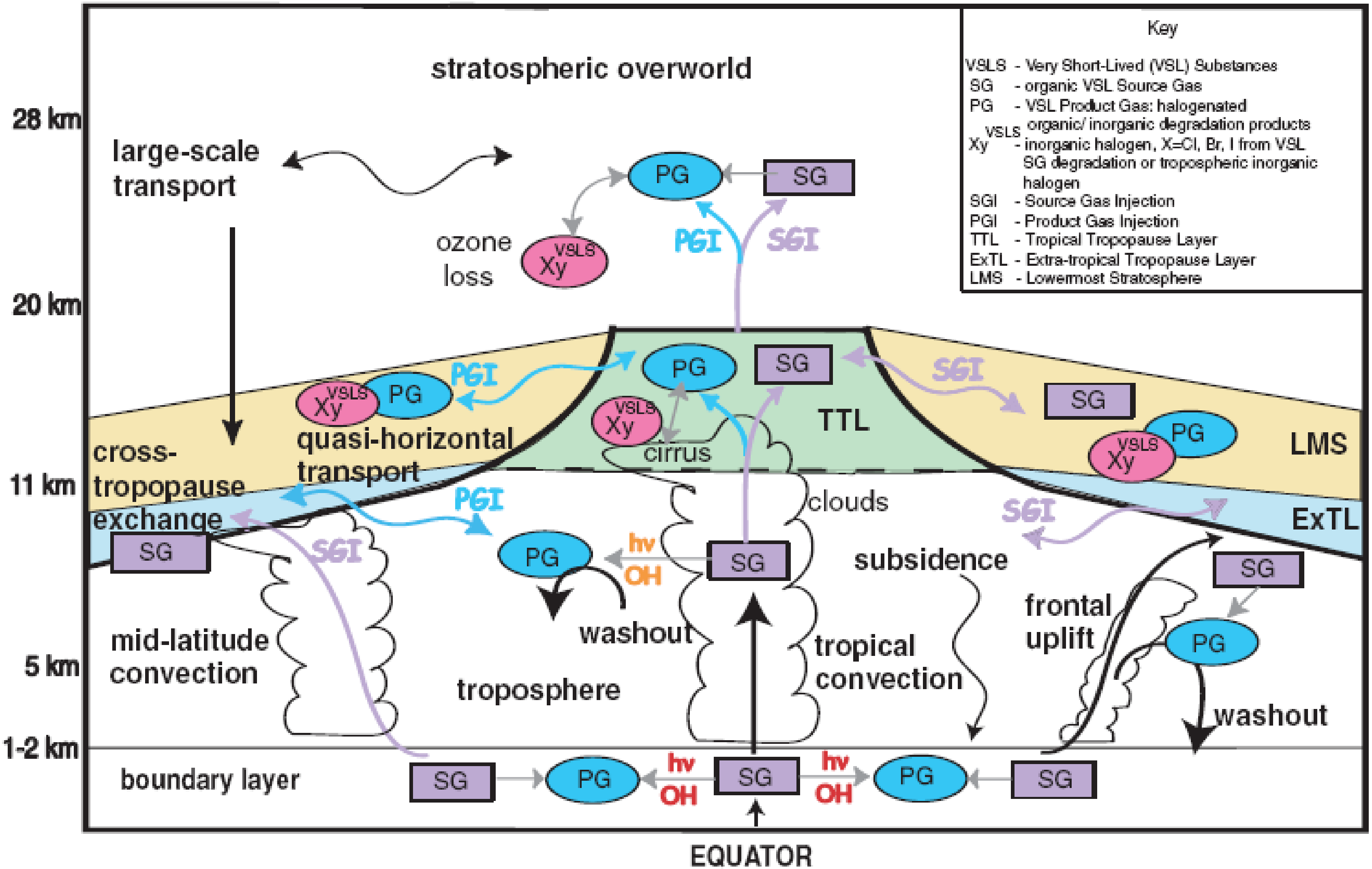
More Concluding Statements . . .

- The majority of known brominated VSL source gases are of natural origin.
- Most brominated VSL source gases are emitted from the ocean, with higher emissions in tropical coastal regions.
  - Sea surface supersaturations (are) . . . elevated in the tropical open ocean
  - High concentrations in air have been observed near coasts over tropical and temperate waters.
- There is no evidence for a trend in the sum of brominated VSL source gases during the latter half of the 20th century.
- The inclusion of additional stratospheric Bry from VSLS in models leads to larger ozone destruction at midlatitudes and polar regions

. . . And More . . .

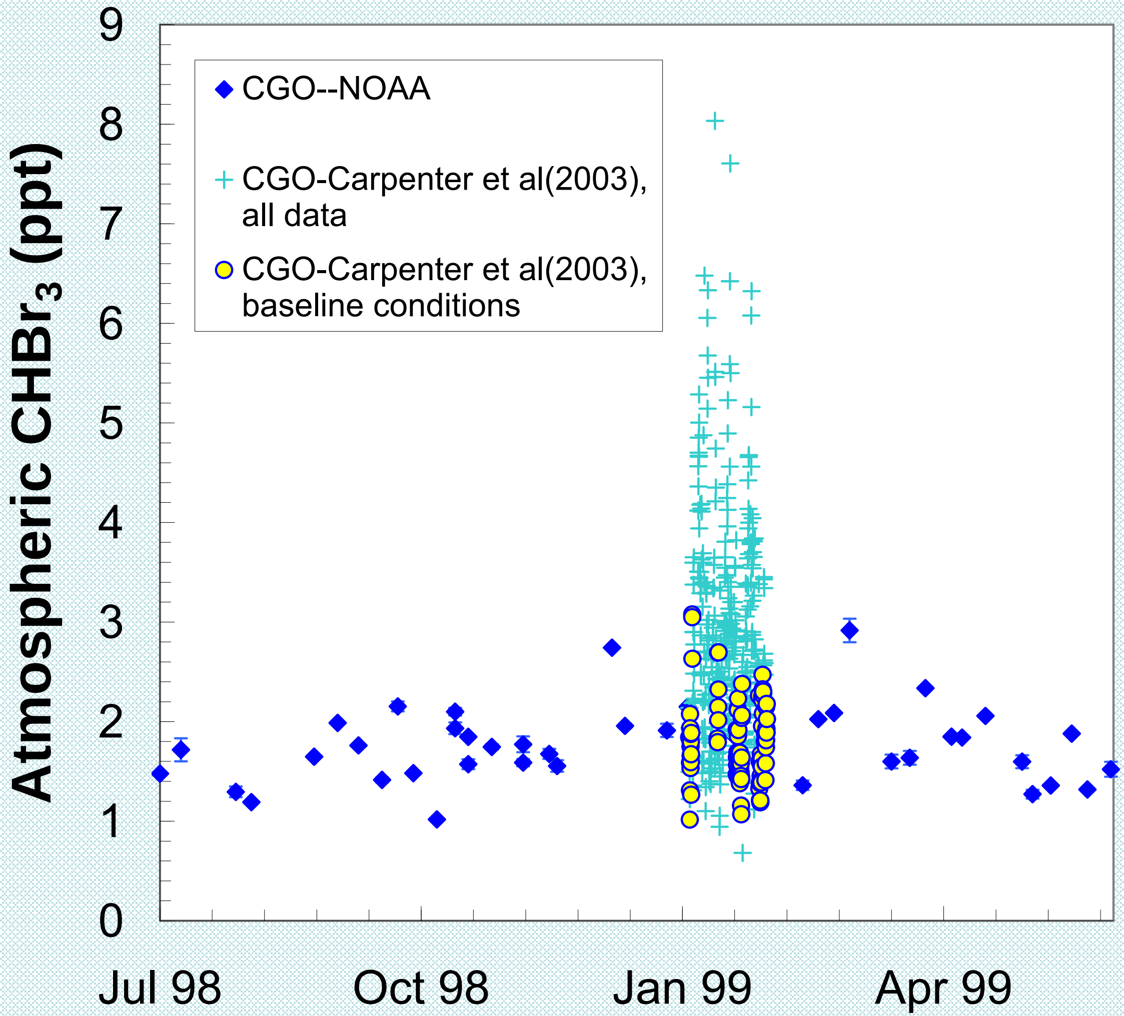
- The predominant pathways for VSLS transport into the upper troposphere are likely to be in tropical convection regions, co-located with high emissions of VSLS over tropical oceans.
- The amount of VSL product gases entering the stratosphere depends on the locations of their tropospheric production and loss processes.
- Natural VSLS emissions may respond to future changes in climate processes.

Chemical and Dynamical Processes Affecting VSLS



Field Comparisons

Intercomparison without Intercalibration



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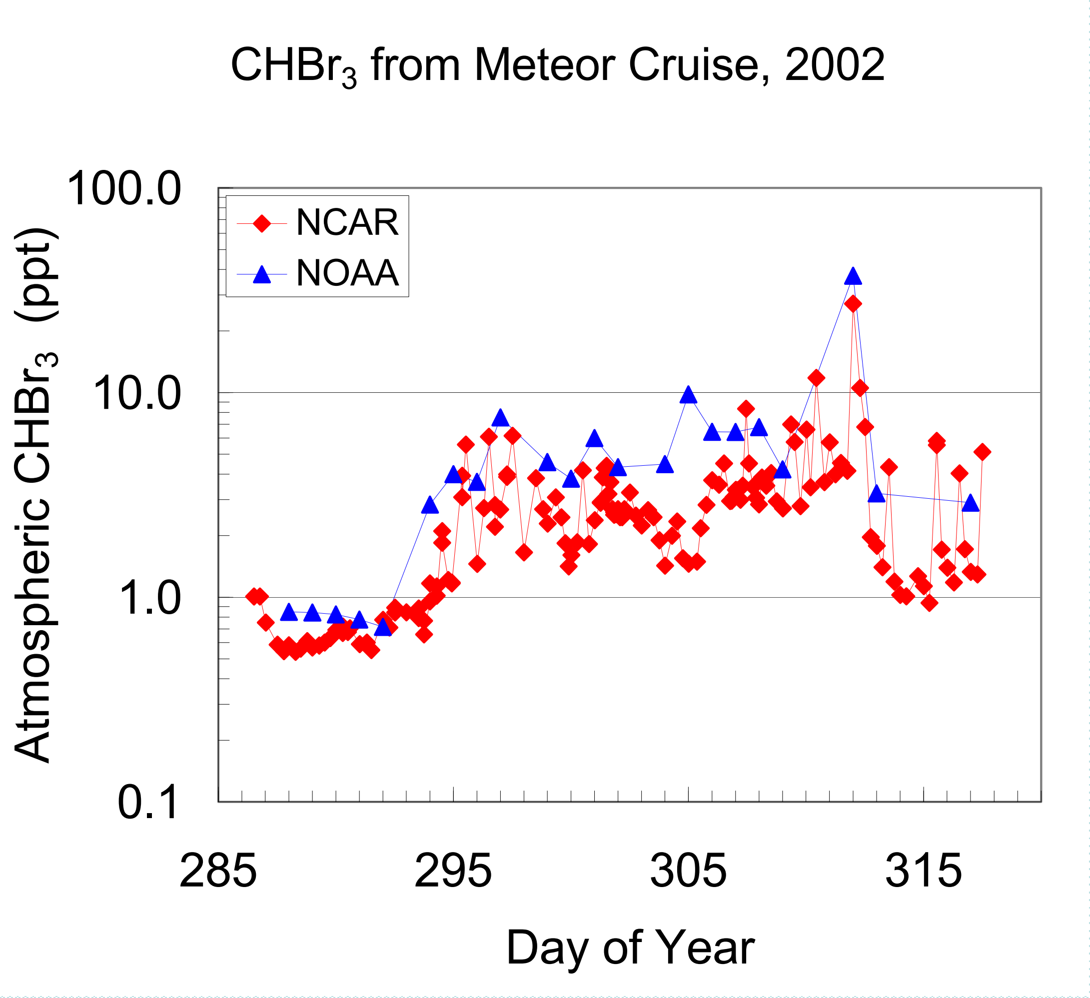
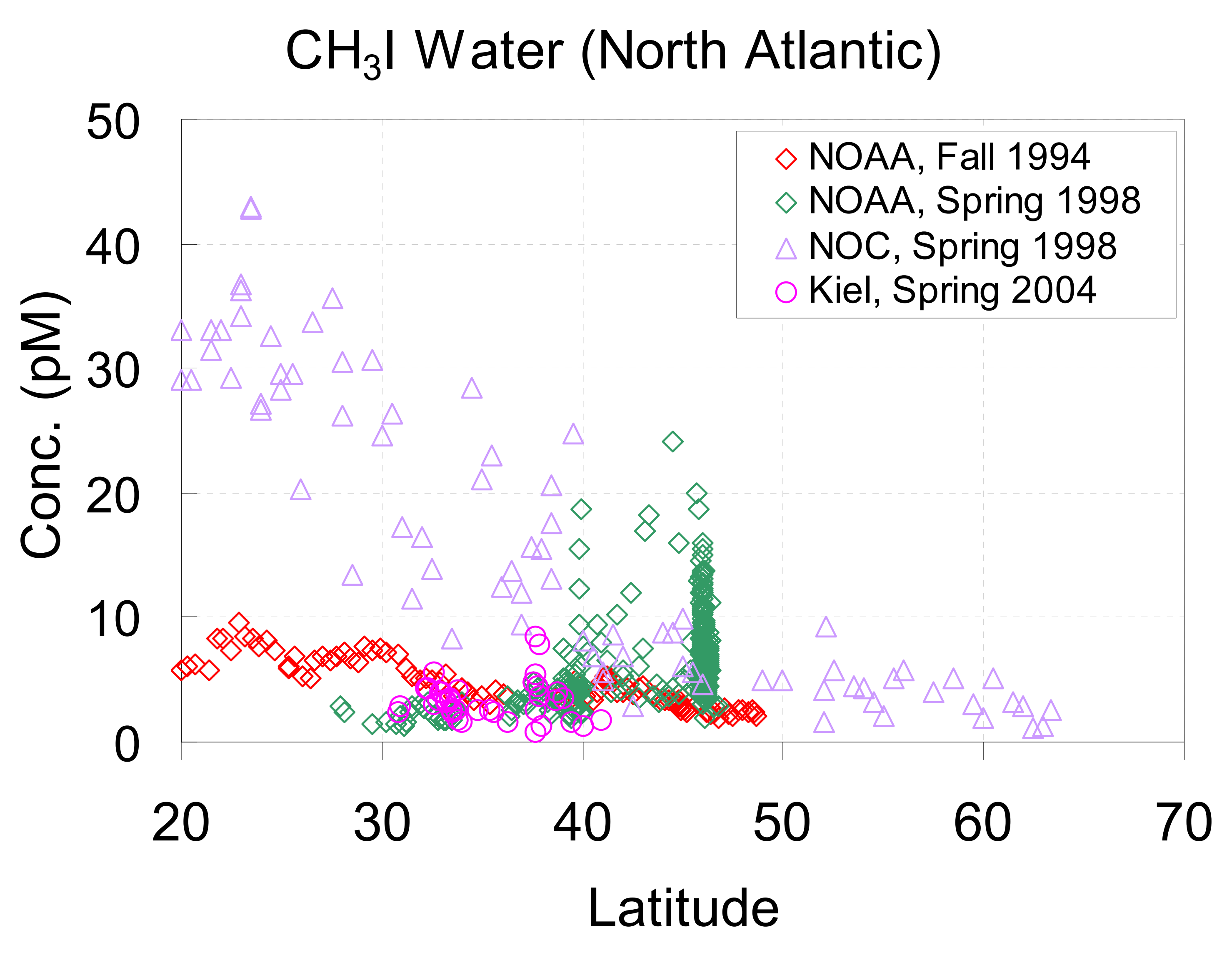
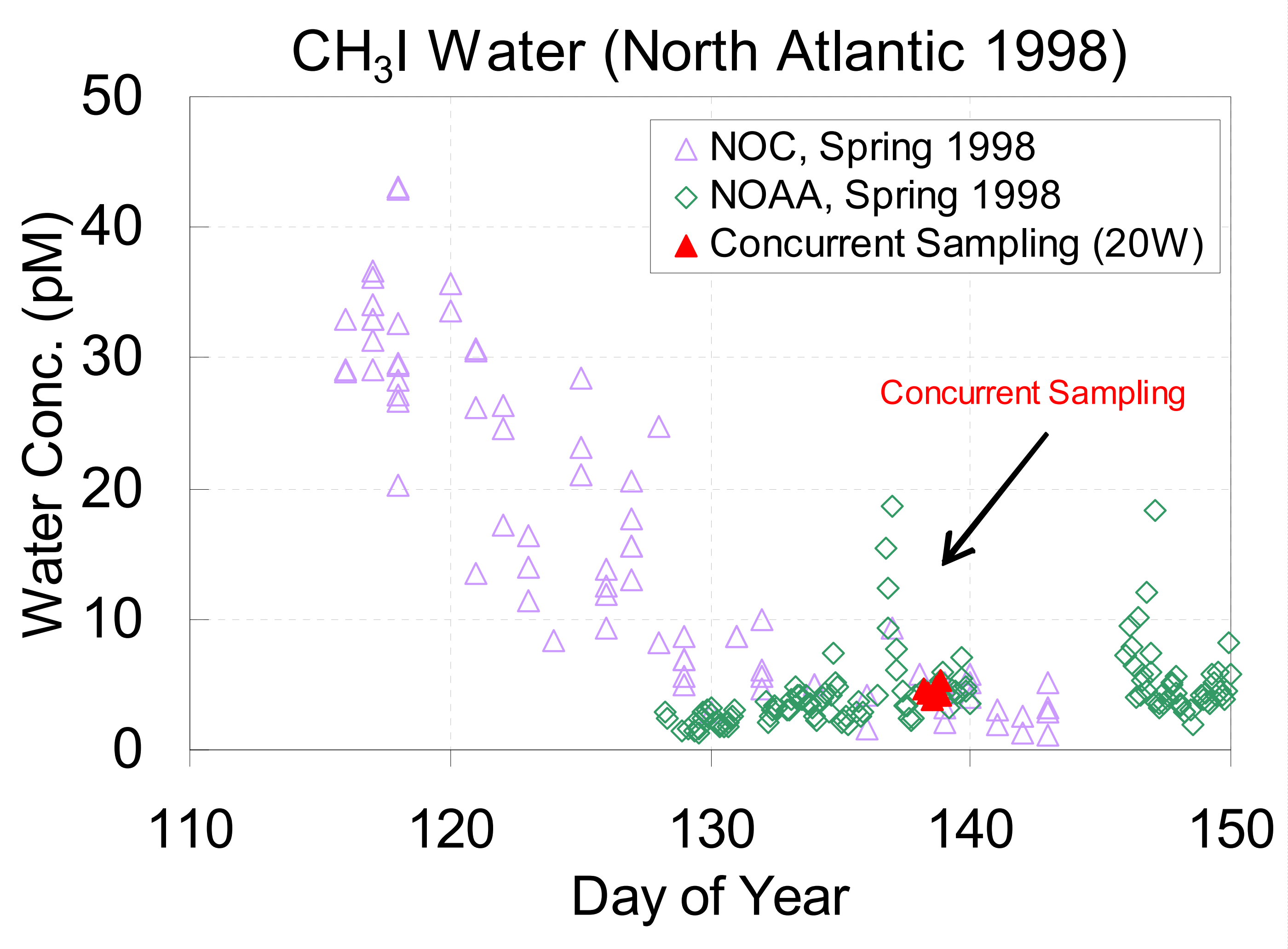
Intercomparison without Intercalibration -- again



No intercomparison



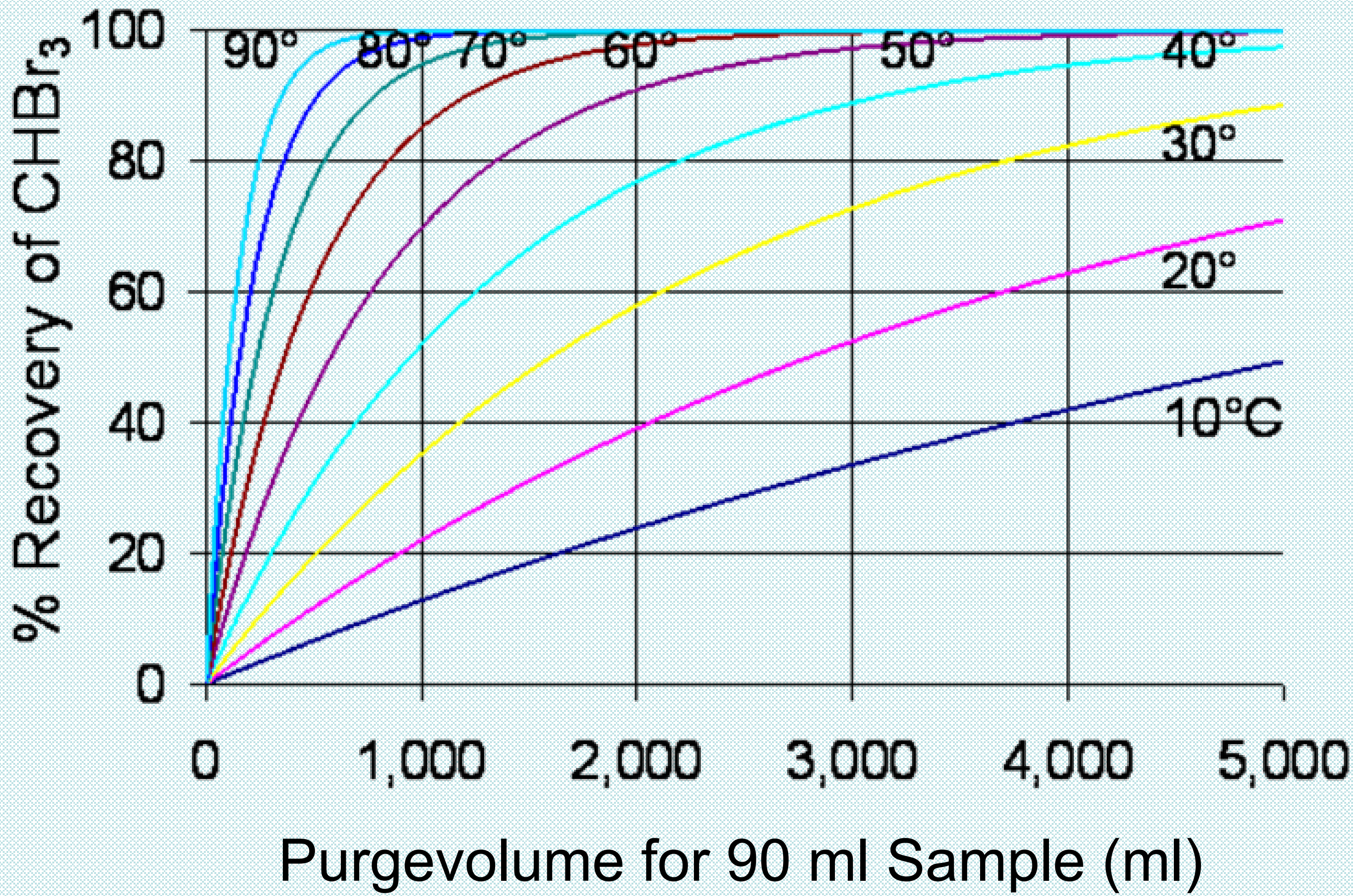
No intercomparison



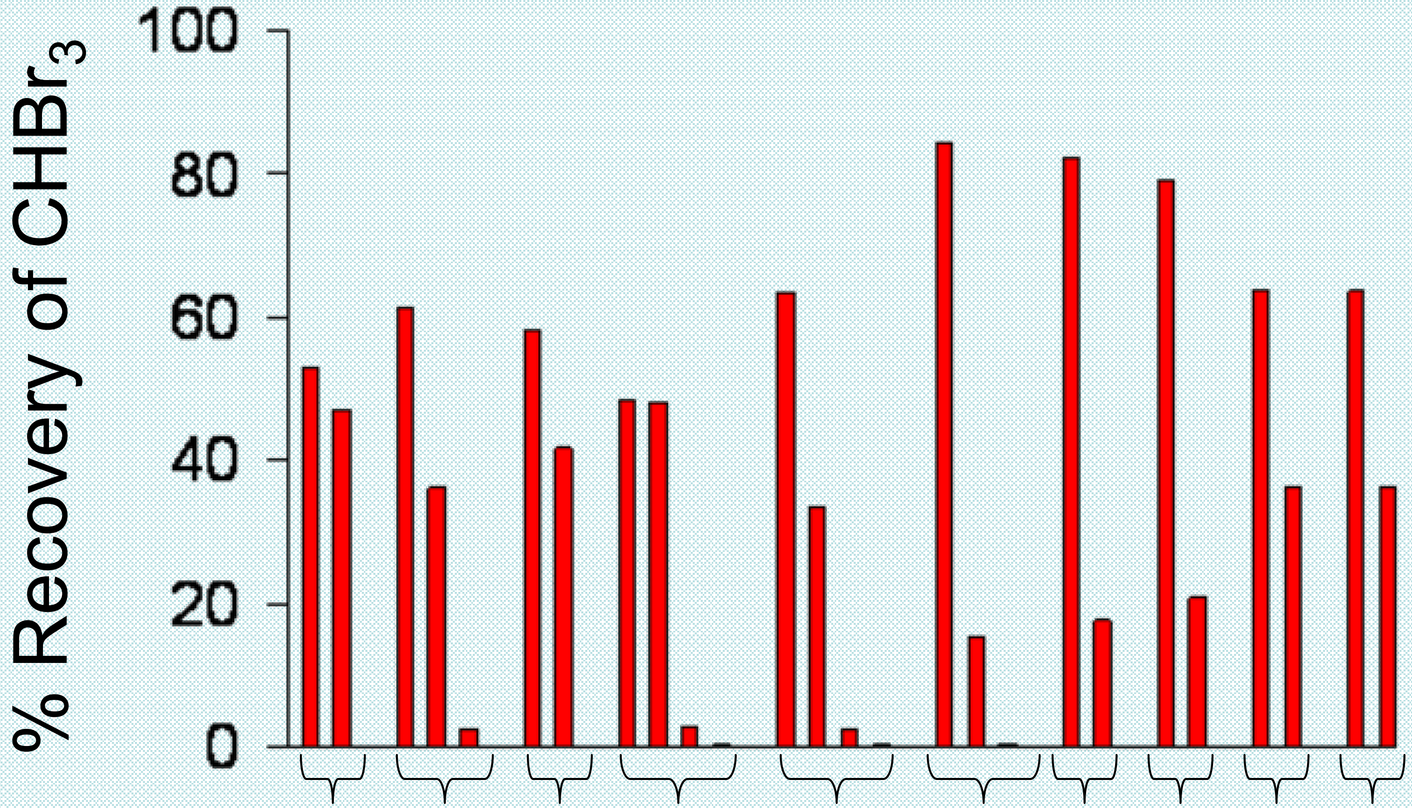
Need: Systematic Intercomparisons of measurements

Analytical Approaches

Theoretical Yields



Results in the Field

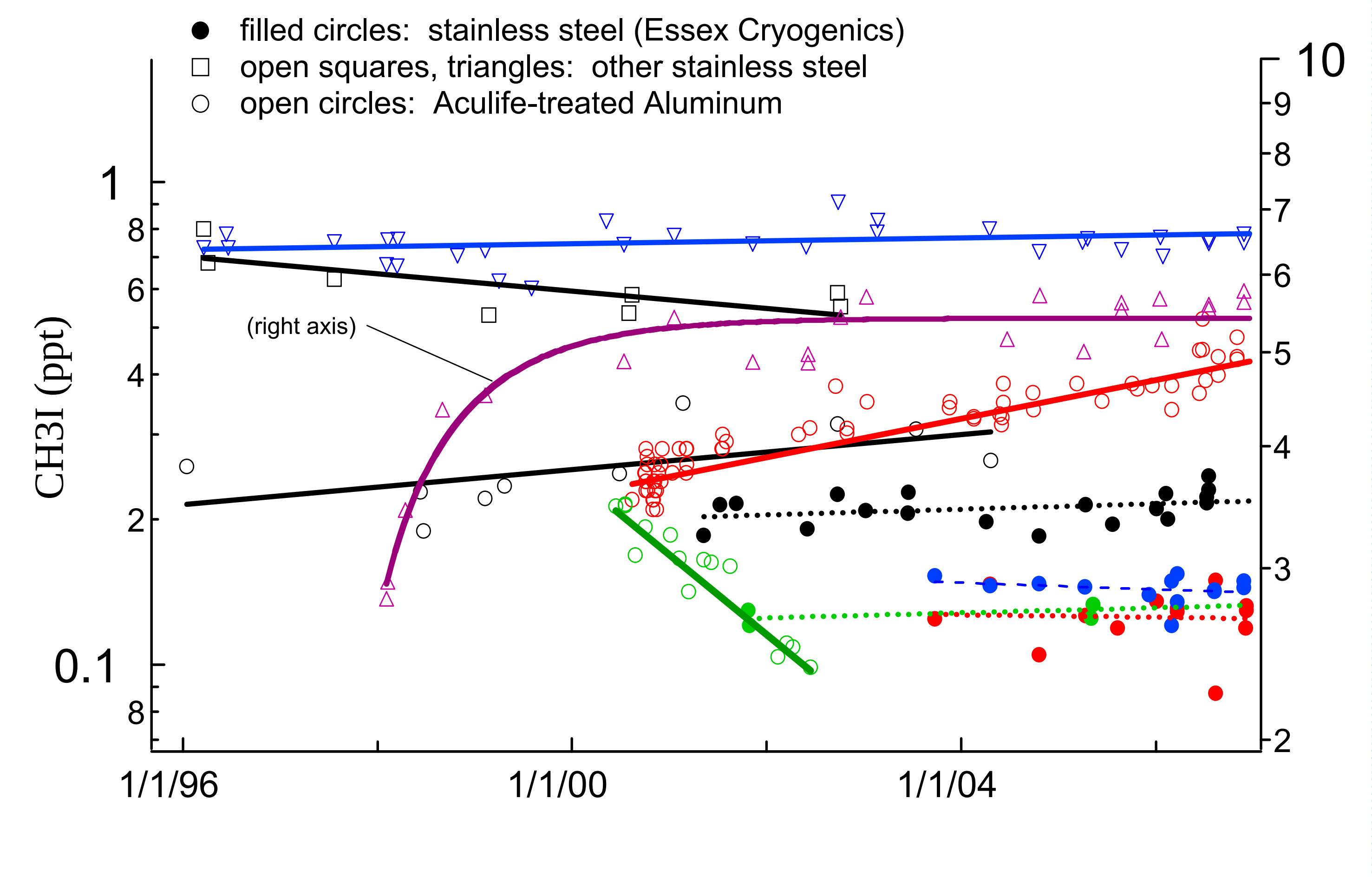


2 to 4 repeated purges (1000ml He at 70°C each) of different oceanic samples. Sum is 100%.

Need: Agreed-upon measurement guidelines for each gas

Calibration Approaches

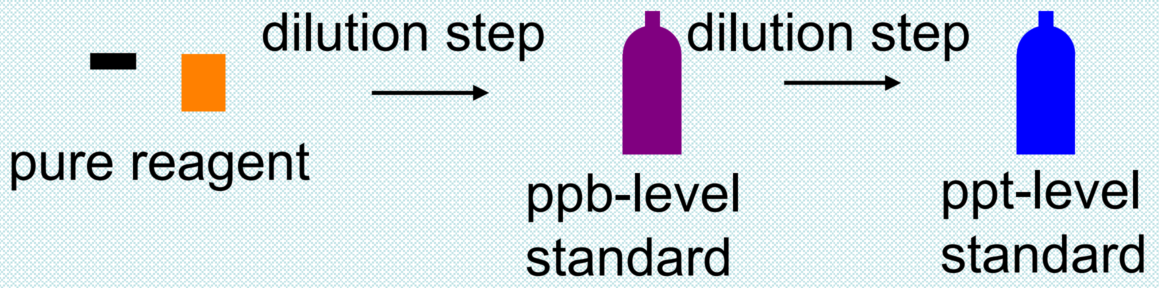
Stability of CH_3I in various types of gas cylinders



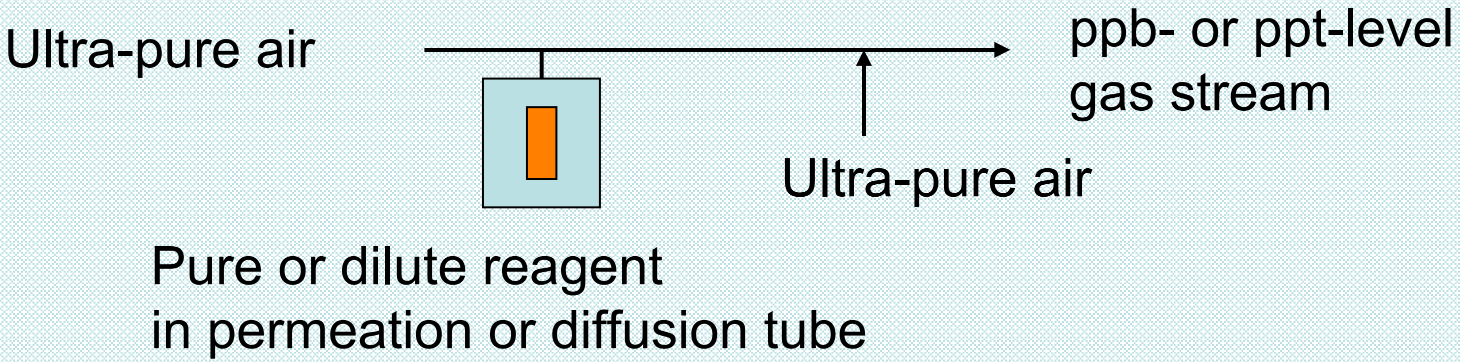
Long-term stability of short-lived gases depends upon container type as well as the individual container.

Calibration Methods

1) Static Dilution (Compressed Gas Standards)



2) Dynamic Dilution (Calibrated Gas Stream)



Need: An intercalibration program with standards and procedures appropriate to each gas

Proposal

- *Seek to establish a coordinated, international calibration program and measurement guidelines for short-lived halocarbons*.

Approaches or options to consider

- Expand on or incorporate existing bilateral arrangements such as that between NOAA and NASA's AGAGE program for atmospheric halocarbons to include these gases in ranges observed in both the atmosphere and ocean.
- Expand intercalibration programs such as IHALACE to include the ocean community and to encompass ranges of concentrations that capture the ranges encountered in marine measurements.
- Build a working group through WMO to establish measurement guidelines and to oversee intercalibration efforts and other quality-control activities.

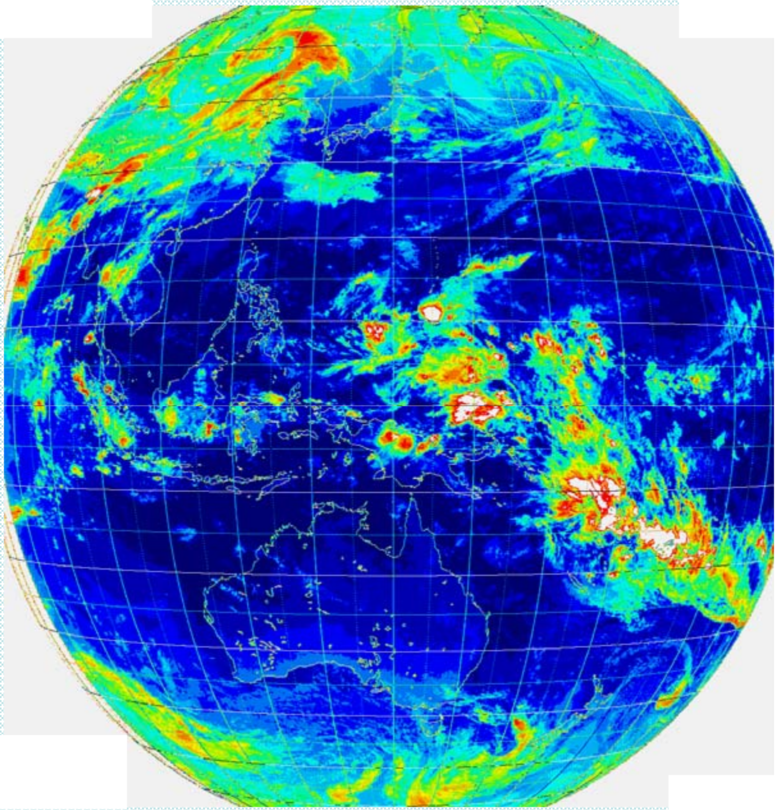
Workshop Outline

- Welcome & Overview (Hare, Bell, Butler)
- Guided Discussions
  - Scientific Need (von Glasow)
  - Measurement Uncertainty (Carpenter)
  - Existing Standardization Techniques (Hall)
  - Current Intercomparisons (Quack)
- Discussion of Path Forward (Butler)

Desired Outcome

- Identify gases that need intercalibration
- Identify options for conducting intercalibrations
- Identify approaches for intercomparison activities
- Identify the next steps forward

Transport and Delivery . . .



How much halogen can deep convection deliver?

Backups

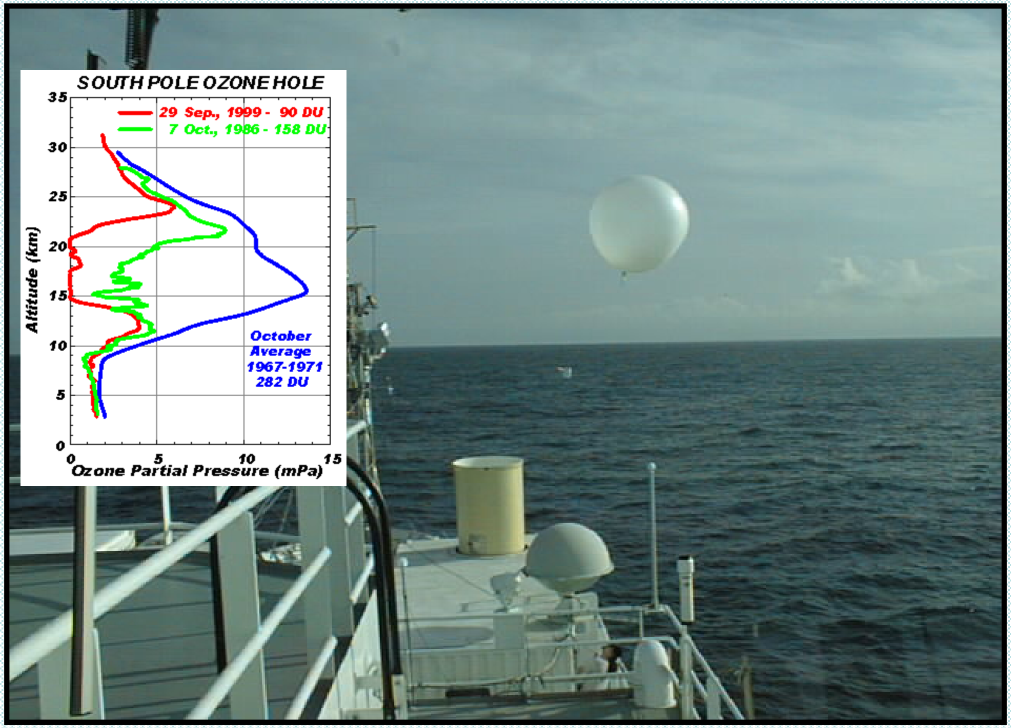
Halogenated Very Short-Lived Substances (2006)

- **Lead Authors:** K.S. Law ,W.T. Sturges
- **Coauthors:** D.R. Blake, N.J. Blake, J.B. Burkholder, J.H. Butler, R.A. Cox, P.H. Haynes, M.K.W. Ko, K. Kreher, C. Mari, K. Pfeilsticker, J.M.C. Plane, R.J. Salawitch, C. Schiller, B.-M. Sinnhuber, R. von Glasow, N.J. Warwick, D.J. Wuebbles, S.A. Yvon-Lewis
- **Contributors:** A. Butz, D.B. Considine, M. Dorf, L. Froidevaux, L.J. Kovalenko, N.J. Livesey, R. Nassar, C.E. Sioris, D.K. Weisenstein

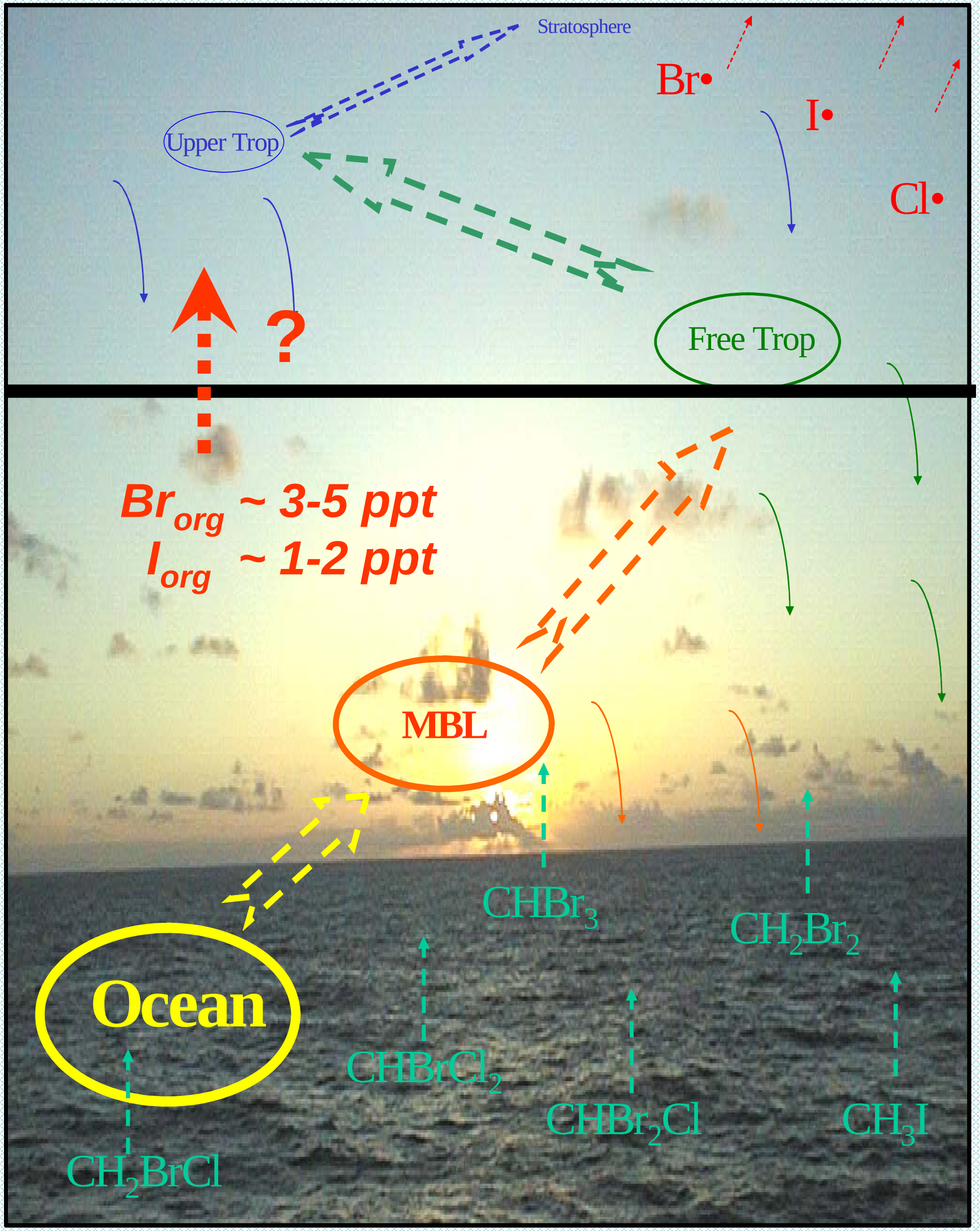
Very Short-Lived Halogen and Sulfur Substances (2002)

- **Lead Authors:** M.K.W. Ko, G. Poulet
- **Coauthors:** D.R. Blake, O. Boucher, J.H. Burkholder, M. Chin, R.A. Cox, C. George, H.-F. Graf, J.R. Holton, D.J. Jacob, K.S. Law, M.G. Lawrence, P.M. Midgley, P.W. Seakins, D.E. Shallcross, S.E. Strahan, D.J. Wuebbles, Y. Yokouchi,
- **Contributors:,** N.J. Blake, J.H. Butler, A.R. Douglass, V.L. Dvortsov, I. Folkins, P.H. Haynes, A. Mellouki, M.J. Prather, J.M. Rodríguez, S.M. Schauffler, T.G., Shepherd, C. Textor, C. Timmreck, D.K. Weisenstein

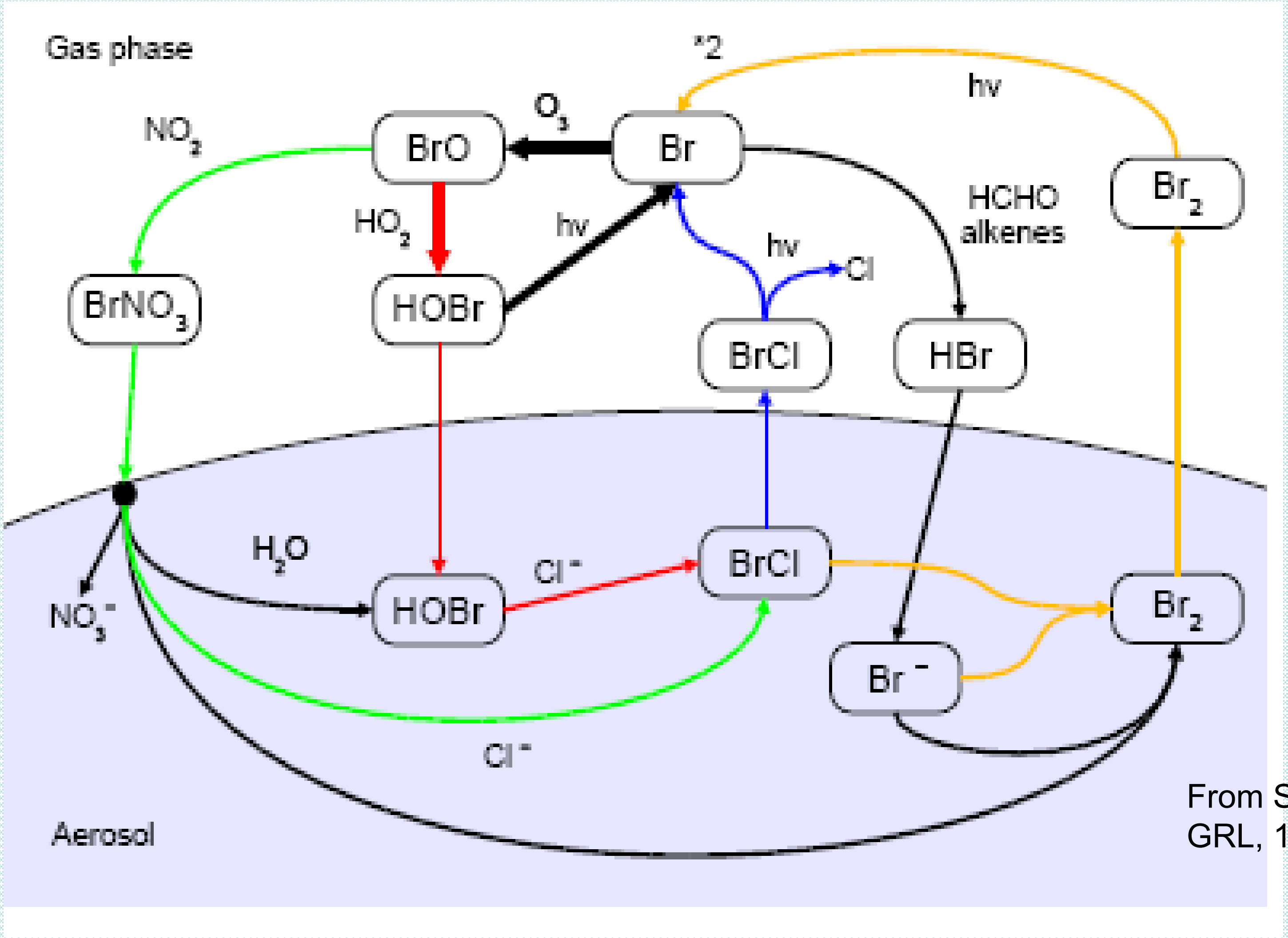
Stratospheric Ozone Depletion



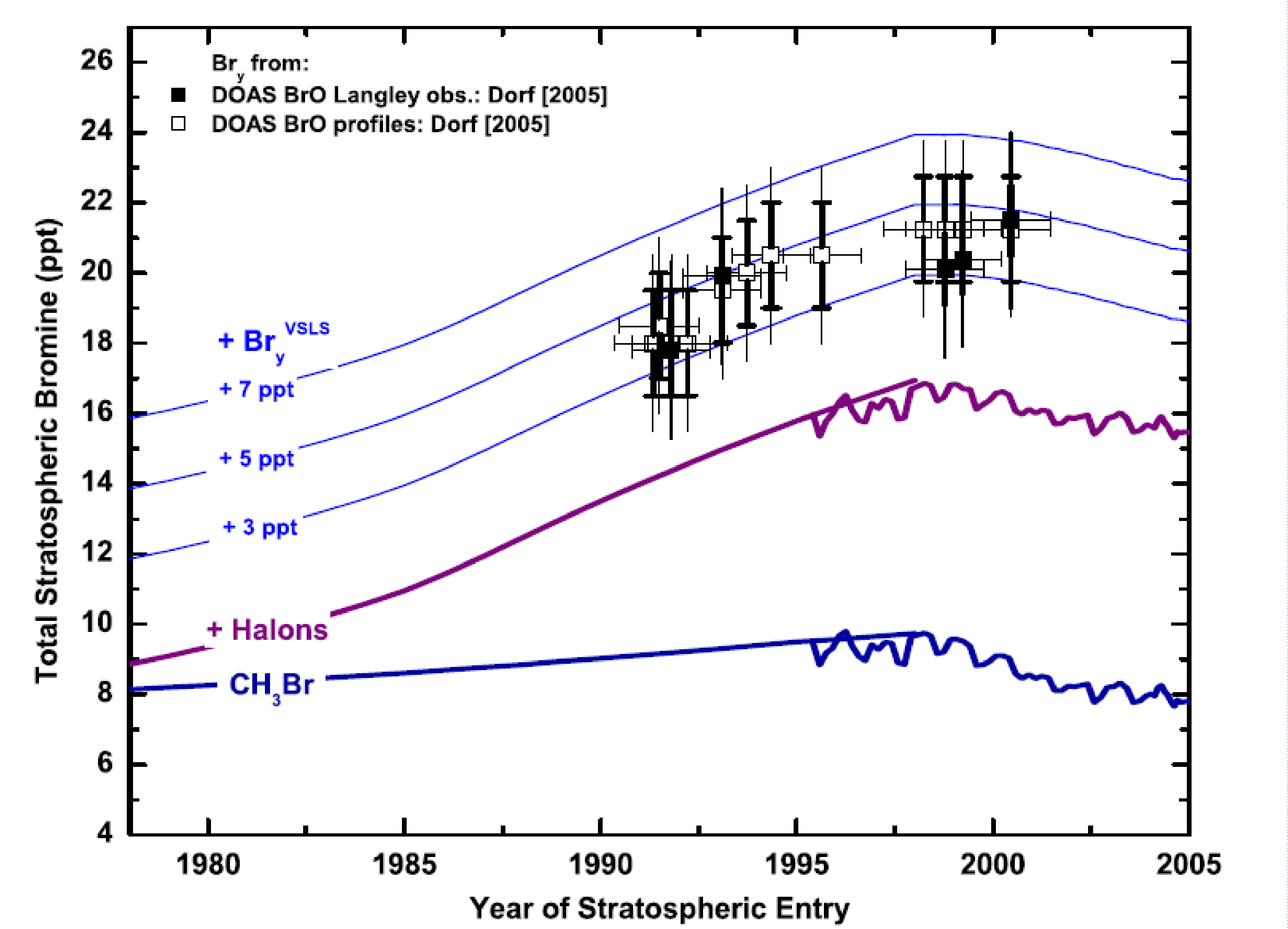
- A concern since the 1970s
- Mainly caused by man-made gases containing Cl and Br
- Major ozone-depleting gases decreasing in the atmosphere today
- Pre-ozone hole conditions projected at ~2050
- Is there something we're missing?


Stratosphere
Br•
I•
Cl•
Upper Trop
?
Free Trop
Br_{org} ~ 3-5 ppt
I_{org} ~ 1-2 ppt
MBL
$CHBr_3$
CH_2Br_2
Ocean
$CHBrCl_2$
$CHBr_2Cl$
CH_3I
CH_2BrCl

Example of Heterogeneous Halogen Chemistry



From Sander *et al.*, GRL, 1999



Br$_y$ from:
DOAS BrO Langley obs.: Dorf [2005]
DOAS BrO profiles: Dorf [2005]
+ Br$_y^{VSLS}$
+ 7 ppt
+ 5 ppt
+ 3 ppt
+ Halons
CH_3Br
Total Stratospheric Bromine (ppt)
Year of Stratospheric Entry
26
24
22
20
18
16
14
12
10
8
6
4
1980
1985
1990
1995
2000
2005