Flask measurements at CGBAPS by the HATS group of NOAA/ESRL/GMD
(for Baseline 2009-2010)
S.A. Montzka, C. Siso, D. Mondeel, B. Miller, B. Hall, J.W. Elkins, J.H. Butler

NOAA halocarbon flasks have been collected at the CGBAPS since the early 1990s. A suite of halocarbons, hydrocarbons, and sulfur-containing gases have been measured in these flasks at NOAA/ESRL/GMD Boulder Laboratories (see Table 1). Results from Cape Grim provide a critical record for understanding how the atmospheric concentrations of trace gases are changing in the remote SH atmosphere (Figure 1). Samples are collected only under background conditions so this data record is predominantly free of local influences, which for some gases emitted from coastal or oceanic environments can be quite substantial at the CGBAPS. Results from this site are among the most consistent records obtained from any site where NOAA flask measurements of halocarbons are made owing to a number of factors: the highly capable observatory staff, the conditional sampling restrictions on collecting flasks employed at the site, and the nature of the site (low mixing ratio variability owing to the site being far removed from the largest sources of most anthropogenically-emitted gases).

Data from the CGAPS have been essential for allowing robust conclusions regarding the atmospheric distributions and global abundances and their time-dependent changes for a range of trace gases that influence climate, stratospheric ozone, and air quality. Because the CGBAPS station provides the cornerstone for SH changes in atmospheric composition, NOAA publications have included these data in all their estimates of global atmospheric changes for these trace gases. As such, the NOAA flask data from CGAPBS represent a critical addition to data used in many of our past publications (Table 2).

Data from this program are regularly updated on the NOAA web data server (http://www.esrl.noaa.gov/gmd/dv/data/ or http://www.esrl.noaa.gov/gmd/dv/ftpdata.html), and they are also archived at the WDCGG.

Station personnel strive to sample paired NOAA flasks once per week. The sampling frequency has historically been lower than 52 pair/yr, however, owing to conditions often being non-background (Figure 2).

Flasks sampled at the CGBAPS are analyzed on multiple instruments once they arrive at the NOAA/ESRL/GMD Boulder laboratories. Though each instrument provides results for a wider range of gases than those indicated in Table 1, the instrument associated with each compound in this Table is the one that provides the most consistent and accurate measurements over the entire record. Results shown (Figure 1) from ECD instrumentation are from a single instrument over the entire record (Otto). For GCMS results, the original Agilent 5971 GCMS instrument was retired in mid-2009 (after 18 years of use) and replaced with an Agilent 5973 instrument. Analysis precision improved for many compounds with the newer 5973 instrument (Figure 3), even for CH_3CCl_3 despite the ongoing exponential decline in the mixing ratio of this gas. The delay

between sampling and analysis on the GCMS instrument is, on average, about three weeks.

NOAA flask samples have been historically collected in paired stainless-steel flasks. Since 2001, however, we have asked CGBAPS personnel to periodically collect nearly concurrent samples in paired glass flasks for the purpose of assessing the influence of flask type on trace gas results. The results demonstrate no substantial biases associated with sample flask type for many different gases, including three methyl halides, carbonyl sulfide, and bromoform ($CHBr_3$) (Figure 4).

Acknowledgements: Station personnel at the CGBAPS who painstakingly and carefully collect samples for us. To Paul Fraser for his oversight of this program, and to Paul Krummel for the useful periodic comparisons between results from NOAA flasks and in-situ instrumentation at the CGBAPS.

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Table 1. Chemicals measured by the NOAA HATS group in flask air samples collected at the CGBAPS.

Chemical	beginning in year	instrument
Hydrochlorofluorocarbons		
-22	1991	GCMS
-141b	1993	GCMS
-142b	1992	GCMS
Chlorofluorocarbons		
-11	1991	GC-ECD
-12	1991	GC-ECD
-113	1991	GCMS and GC-ECD
-115	2007	GCMS-b
Halons		
-1211	1991	GCMS (GC-ECD initially)
-1301	1992	GCMS (GC-ECD initially)
-2402	1995	GCMS (discontinuous)
Hydrofluorocarbons		
-134a	1994	GCMS
-152a	2000	GCMS
-125	2007	GCMS-b
-143a	2007	GCMS-b
-32	2009	GCMS-b
-227ea	2007	GCMS-b
-365mfc	2007	GCMS-b
Brominated gases		
CH_3Br	1994	GCMS
CH_2Br_2	1998	GCMS
$CHBr_3$	1997	GCMS
Solvents		
CH_3CCl_3	1991	GCMS
CCl_4	1991	GCMS
CH_3Cl	1994	GCMS
CH_2Cl_2	1995	GCMS
$CHCl_3$	1994	GCMS
C_2Cl_4	1993	GCMS
Others:		
Nitrous Oxide		GC-ECD
SF_6		GC-ECD

COS	2000	GCMS
CH_3I	1995	GCMS
acetylene	2007	GCMS-b
benzene	1999	GCMS
propane	2007	GCMS-b
n-butane	2007	GCMS-b

Notes: Instrument acronyms are gas chromatography with mass spectrometry detection (GCMS), and gas chromatography with electron capture detection (GC-ECD). GCMS-b is a second GCMS instrument having a different separation column compared to the primary GCMS; this second GCMS allows measurements of additional trace gases but only in a subset of flasks sampled at the CGBAPS (frequency of ~2/month).

Table 2. List of peer-reviewed publications during 2009-2010 in which data from NOAA measurements of flasks collected at the CGBAPS were used (*Paul: articles published in 2011 and 2012 are not included, which I presume you don't want*):

1. Arndt, D.S., M.O. Baringer, and M.R. Johnson, Eds., State of the Climate in 2009. *Bull. Amer. Meteor. Soc*., *91* (7), S1-S224, 2010.
2. Xiao, X., R.G. Prinn, P.J. Fraser, P.G. Simmonds, R.F. Weiss, S. O'Doherty, B.R. Miller, P.K. Salameh, C.M. Harth, P.B. Krummel, L.W. Porter, J. Mühle, B.R. Greally, D. Cunnold, R. Wang, S.A. Montzka, J.W. Elkins, G.S. Dutton, T.M. Thompson, J.H. Butler, B.D. Hall, S. Reimann, M. K. Vollmer, F. Stordal, C. Lunder, M. Maione, J. Arduini, and Y. Yokouchi, Optimal estimation of the surface fluxes of methyl chloride using a 3-D global chemical transport model, *Atmos. Chem. Phys*., *10*, 5515-5533, 2010.
3. Dlugokencky, E. J., L. Bruhwiler, J.W.C. White, L.K. Emmons, P.C. Novelli, S.A. Montzka, K.A. Masarie, P.M. Lang, A.M. Crotwell, J.B. Miller, and L.V. Gatti., Observational constraints on recent increases in the atmospheric CH_4 burden, *Geophys. Res. Lett., 36*, L18803, doi:10.1029/2009GL039780, 2009.
4. Hofmann, D.J., and S.A. Montzka, Recovery of the Ozone Layer: The Ozone Depleting Gas Index, *EOS Trans., 90*, 1, 2009.
5. Montzka, S.A., B.D. Hall, J.W. Elkins, Accelerated increases observed for hydrochlorofluorocarbons since 2004 in the global atmosphere, *Geophys. Res. Lett*., *36*, L03804, doi:10.1029/2008GL036475, 2009.
6. Peterson, T.C., and M.O. Baringer, Eds., State of the Climate in 2008. *Bull. Amer. Meteor. Soc*., *90*, S1–S196, 2009.
7. Yvon-Lewis, S.A., E.S. Saltzman, S.A. Montzka, Recent trends in atmospheric methyl bromide: analysis of post-Montreal Protocol variability, *Atmos. Chem. Phys., 9*, 5963, 2009.

From previous years *(Paul S: I don't know if you want these included!)*:

8. Montzka, S.A., J.S. Daniel, J. Cohen, and K. Vick, Current Trends, Mixing Ratios, and Emissions of Ozone-Depleting Substances and Their Substitutes. In: *Trends in Emissions of Ozone-Depleting Substances, Ozone Layer Recovery, and Implications for Ultraviolet Radiation Exposure*. A Report by the U.S. Climate Change Science Program and the Subcommittee on Global Change Research. [Ravishankara, A.R., M.J. Kurylo, and C.A. Ennis (eds.)]. Department of Commerce, NOAA's National Climatic Data Center, Asheville, NC, pp. 29–78, 2008.
9. Suntharalingam, P., A.J. Kettle, S.A. Montzka, D.J. Jacob, Global 3-D model analysis of the seasonal cycle of atmospheric carbonyl sulfide: Implications for terrestrial vegetation uptake, *Geophys. Res. Lett.*, 35, L19801, doi:10.1029/2008GL034332, 2008.
10. Clerbaux, C., and D. Cunnold (Lead Authors), J. Anderson, P. Bernath, A. Engel, P.J. Fraser, E. Mahieu, A. Manning, J. Miller, S.A. Montzka, R. Prinn, S. Reimann, C.P. Rinsland, P. Simmonds, D. Verdonik, D. Wuebbles, and Y. Yokouchi, Long-lived compounds, Chapter 2 in *Scientific Assessment of Ozone Depletion: 2006*, Global Ozone Research and Monitoring Project—Report No. 50, 571 pp., World Meteorological Organization, Geneva, Switzerland, 2007.

11. Daniel, J.S., G.J.M. Velders, S. Solomon, M. McFarland, and S.A. Montzka, Present and future sources and emissions of halocarbons: Towards new constraints, *J. Geophys. Res.*, 112, D02301, doi:10.1029/2006JD007275, 2007.
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16. Hofmann, D.J., J.H. Butler, E.J. Dlugokencky, J.W. Elkins, K. Masarie, S.A. Montzka, and P. Tans, The role of carbon dioxide in climate forcing from 1979 – 2004, *Tellus, 58B*, p. 614-619, 2006.
17. Kuijpers, L., P. Ashford, S.A. Montzka (co-chairs), N. Campbell, D. Clodic, J.S. Daniel, P. Midgley, I.D. Rae, G. Velders, D. Verdonik, *Task Force on Emissions Discrepancies Report*, UNEP, October, 2006.
18. Lelieveld, J., C.A.M. Brenninkmeijer, P. Joeckel, I.S.A. Isaksen, M.C. Krol, J.E. Mak, E. Dlugokencky, S.A. Montzka, P.C. Novelli, W. Peters, and P.P. Tans, New Directions: Watching over tropospheric hydroxyl, *Atmospheric Environment, 40*, 5741-5743, 2006.
19. Newman, P.A., E.R. Nash, S.R. Kawa, S.A. Montzka, and S.M. Schauffler, When will the Antarctic ozone hole recover? *Geophys. Res. Lett., 33*, L12814, doi:10.1029/2005GL025232, 2006.
20. Notholt, J., H. Bingemer, H Berresheim, J. Holton, A. Kettle, E. Mahieu, and S. Montzka, Precursor gas measurements, Chapter 2 of *SPARC Assessment of Stratospheric Aerosol Properties*, L. Thomson and Th. Peter, eds., Toronto, 2006.
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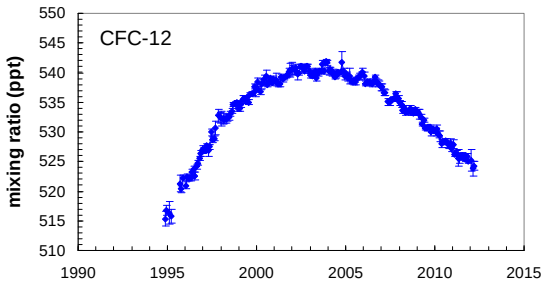
Figure Captions:
Paul: should data be shown only through 2010 for this version of Baseline?

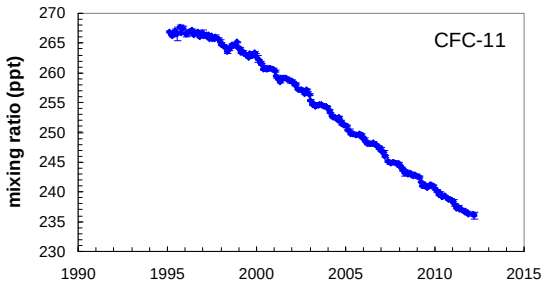
Figure 1. Monthly mean mixing ratios for a subset of trace gases measured by NOAA/ESRL/GMD in flasks collected at CGBAPS. Points represent monthly means, uncertainties (±1 s.d.) are shown but are often smaller than the symbols. Results for CFC-12, CFC-11, and CCl_4 are from analysis by GC-ECD instrumentation; for all other compounds the analysis is performed by GC-MS.

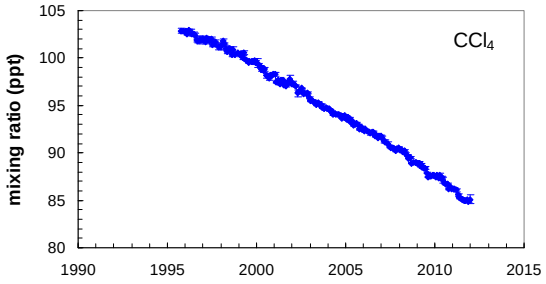
Figure 2. Flask sampling frequency (per year) of NOAA flasks at CGBAPS. Although weekly sampling is desired, the frequency is often reduced because of non-background conditions. Glass flasks are sampled on the same day and close in time to the stainless-steel flasks (see also Figure 4).

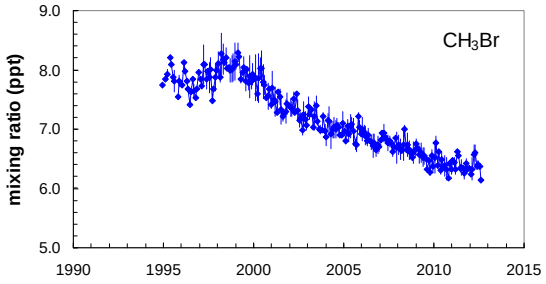
Figure 3. Replicate injection precision for the two ions used for quantification of CH_3CCl_3 by the HATS GCMS instrument over the entire measurement record. The lines represent the running median standard deviation of two replicate injections from 30 flask analyses. A worsening of measurement precision is evident in 2008 owing to problems with the original GCMS, which was replaced in 2009. The worsening of the precision at the end of the record results from the mixing ratio of CH_3CCl_3 becoming very low (7 ppt by the end of 2010, see Figure 1).

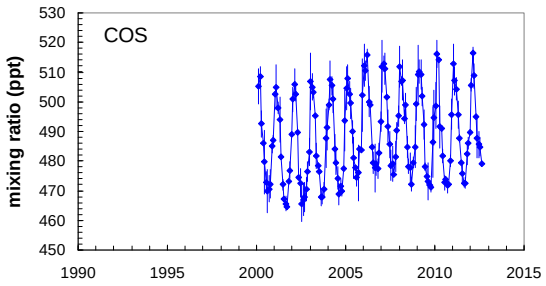
Figure 4. A comparison of measurement results from different flask types: glass and stainless steel. Each point represents the ratio of GCMS results from a pair of glass flasks relative to a pair of stainless steel flasks sampled on the same day. The time delay between the collection of the two different pairs is, on average, 90 min (this delay ranges from 7 min to 240 min). Only results where the flask pair difference was insignificant relative to analysis precision are included here. Note that the bottom two panels have a different y-scale.

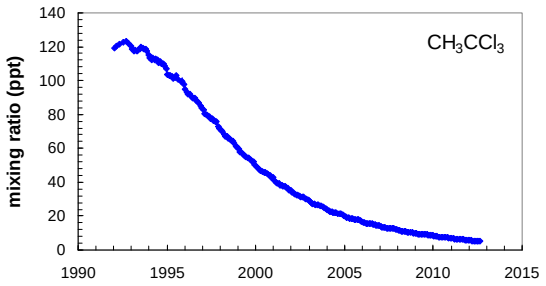

CFC-12
mixing ratio (ppt)
550
545
540
535
530
525
520
515
510
1990
1995
2000
2005
2010
2015

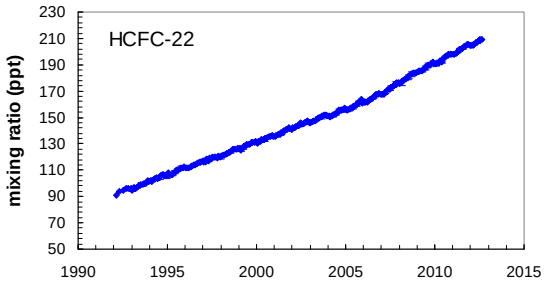

CFC-11
mixing ratio (ppt)
270
265
260
255
250
245
240
235
230
1990
1995
2000
2005
2010
2015

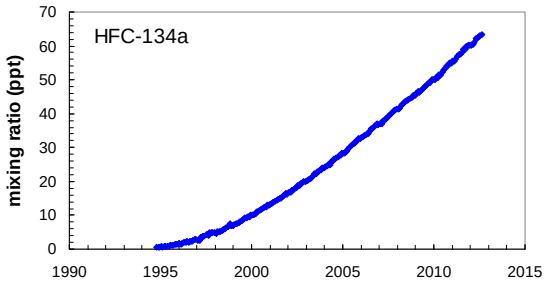

CCl4
mixing ratio (ppt)
105
100
95
90
85
80
1990
1995
2000
2005
2010
2015

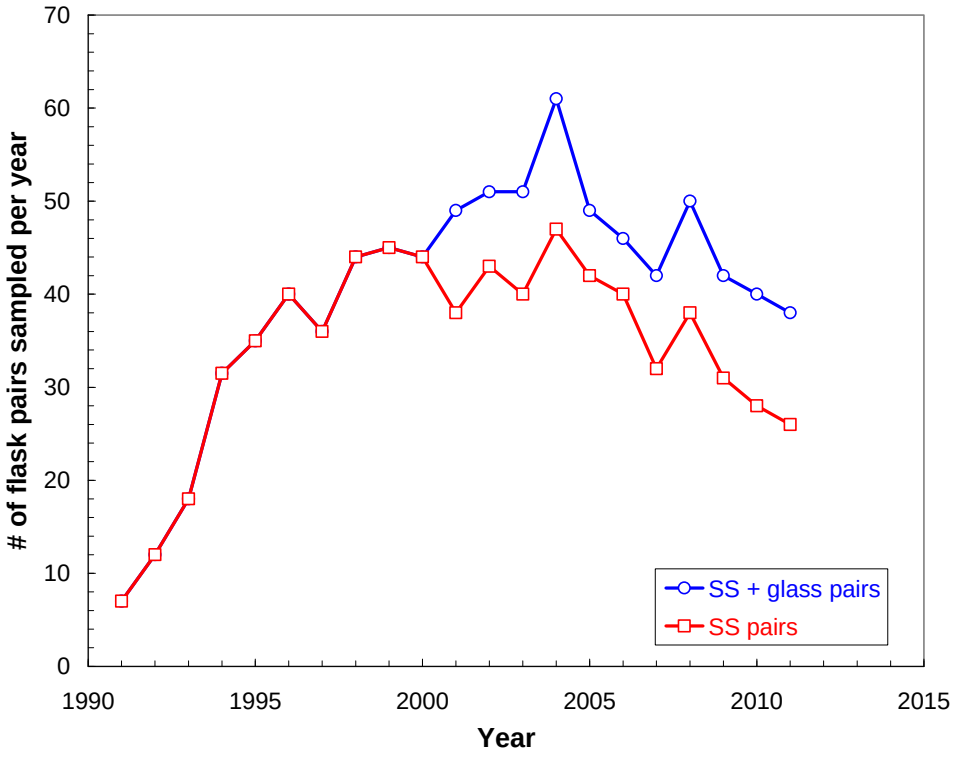

CH3Br
mixing ratio (ppt)
9.0
8.0
7.0
6.0
5.0
1990
1995
2000
2005
2010
2015

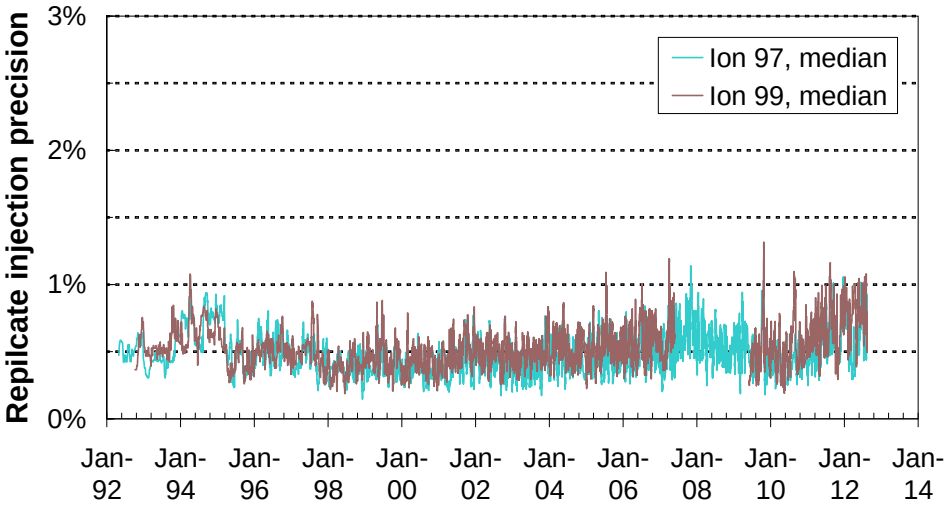

COS
mixing ratio (ppt)
530
520
510
500
490
480
470
460
450
1990
1995
2000
2005
2010
2015

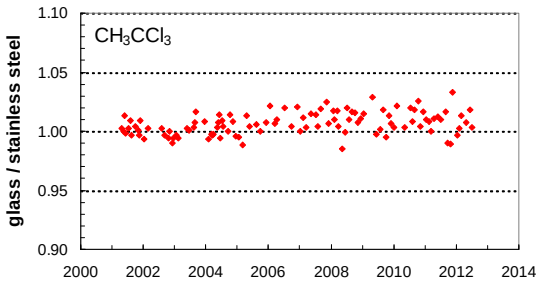

CH3CCl3
mixing ratio (ppt)
140
120
100
80
60
40
20
0
1990
1995
2000
2005
2010
2015

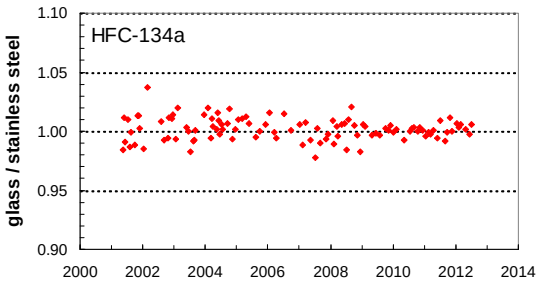

HCFC-22
mixing ratio (ppt)
230
210
190
170
150
130
110
90
70
50
1990
1995
2000
2005
2010
2015

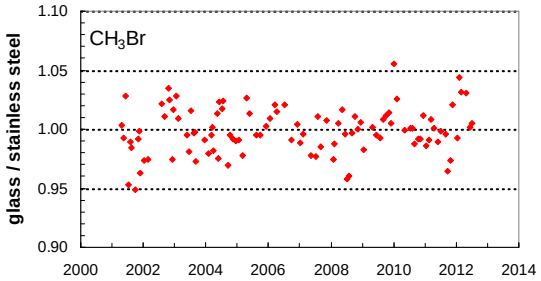

HFC-134a
mixing ratio (ppt)
70
60
50
40
30
20
10
0
1990
1995
2000
2005
2010
2015

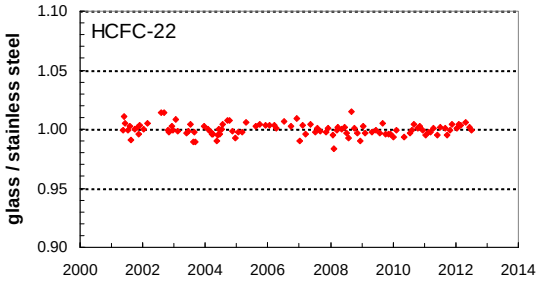

70
60
50
40
30
20
10
0
# of flask pairs sampled per year
1990
1995
2000
2005
2010
2015
Year
SS + glass pairs
SS pairs

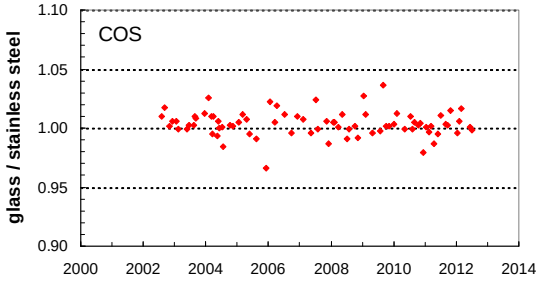

Repilcate injection precision
3%
2%
1%
0%
Ion 97, median
Ion 99, median
Jan-92
Jan-94
Jan-96
Jan-98
Jan-00
Jan-02
Jan-04
Jan-06
Jan-08
Jan-10
Jan-12
Jan-14

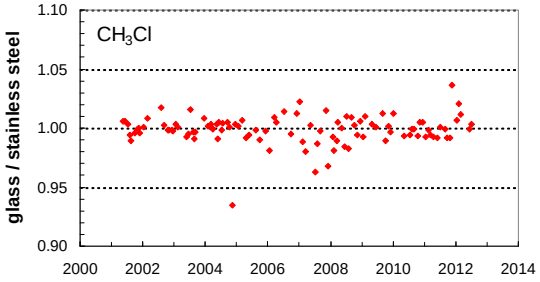

CH3CCl3
glass / stainless steel
1.10
1.05
1.00
0.95
0.90
2000
2002
2004
2006
2008
2010
2012
2014

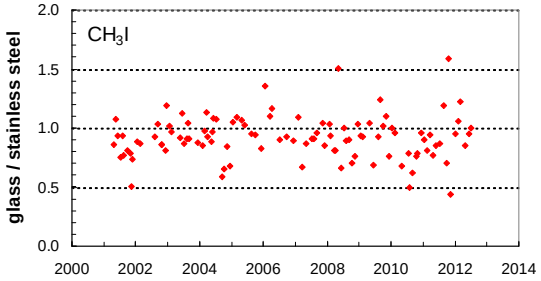

HFC-134a
glass / stainless steel
1.10
1.05
1.00
0.95
0.90
2000
2002
2004
2006
2008
2010
2012
2014

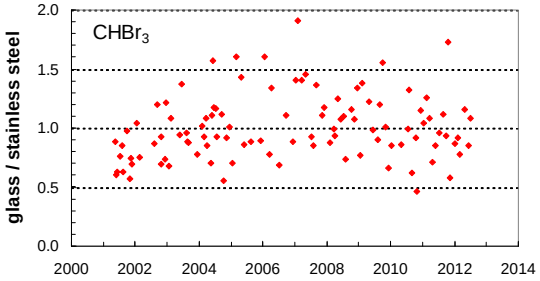

CH3Br
glass / stainless steel
1.10
1.05
1.00
0.95
0.90
2000
2002
2004
2006
2008
2010
2012
2014


HCFC-22
glass / stainless steel
1.10
1.05
1.00
0.95
0.90
2000
2002
2004
2006
2008
2010
2012
2014


COS
glass / stainless steel
1.10
1.05
1.00
0.95
0.90
2000
2002
2004
2006
2008
2010
2012
2014


CH3Cl
glass / stainless steel
1.10
1.05
1.00
0.95
0.90
2000
2002
2004
2006
2008
2010
2012
2014


CH3I
glass / stainless steel
2.0
1.5
1.0
0.5
0.0
2000
2002
2004
2006
2008
2010
2012
2014


CHBr3
glass / stainless steel
2.0
1.5
1.0
0.5
0.0
2000
2002
2004
2006
2008
2010
2012
2014