Current intercomparison issues

statistics,
field studies,
standard comparsions,
analytical considerations

Birgit Quack
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IFM-GEOMAR

IFM-GEOMAR
Leibniz-Institut für Meereswissenschaften an der Universität Kiel

Halocarbon interalibration meeting London 4 February 2008

	First name	Surname	Location
6	Katarina	Abrahamson	Sweden
1	Elliot	Atlas	Miami, USA
	Georgia	Bayliss-Brown	SOLAS IPO, UEA, UK
	Tom	Bell	Project Integrator, UEA, UK
2	Don	Blake	Irvine California, USA
4	Jim	Butler	NOAA, USA
3	Lucy	Carpenter	York, UK
4	Brad	Hall	NOAA, USA
5	Claire	Hughes	UEA, UK
6	Anders	Karlsson	Sweden
	Charlotte	Jones	York, UK
8	Michela	Maione	Italy
9	Manuela	Martino	UEA, UK
	Martin	Milton	National Physical Laboratory, UK
10	Bob	Moore	Dalhousie, Canada
15	Pascal	Morin	Roscoff, France
11	Phil	Nightingale	Plymouth Marine Lab, UK
	Simon	O'Doherty	Bristol, UK
13	Dave	Oram	UEA, UK
14	Birgit	Quack	IFM-GEOMAR, Germany
15	Stefan	Raimund	Roscoff, France
16	Heinfried	Scholer	Heidelberg, Germany
22	Detlef	Schulz-Bull	Germany
17	Barkley	Sive	New Hampshire, USA
18	Denise	Smythe-Wright	Southampton Oceanography Centre, UK
	Roland	von Glasow	UEA, UK
	Nicola	Warwick	Cambridge, UK
19	Ray	Weiss	San Diego, USA
20	Jonathan	Williams	Mainz, Germany
21	Yoko	Yokouchi	Japan

Halocarbon Intercalibration Meeting

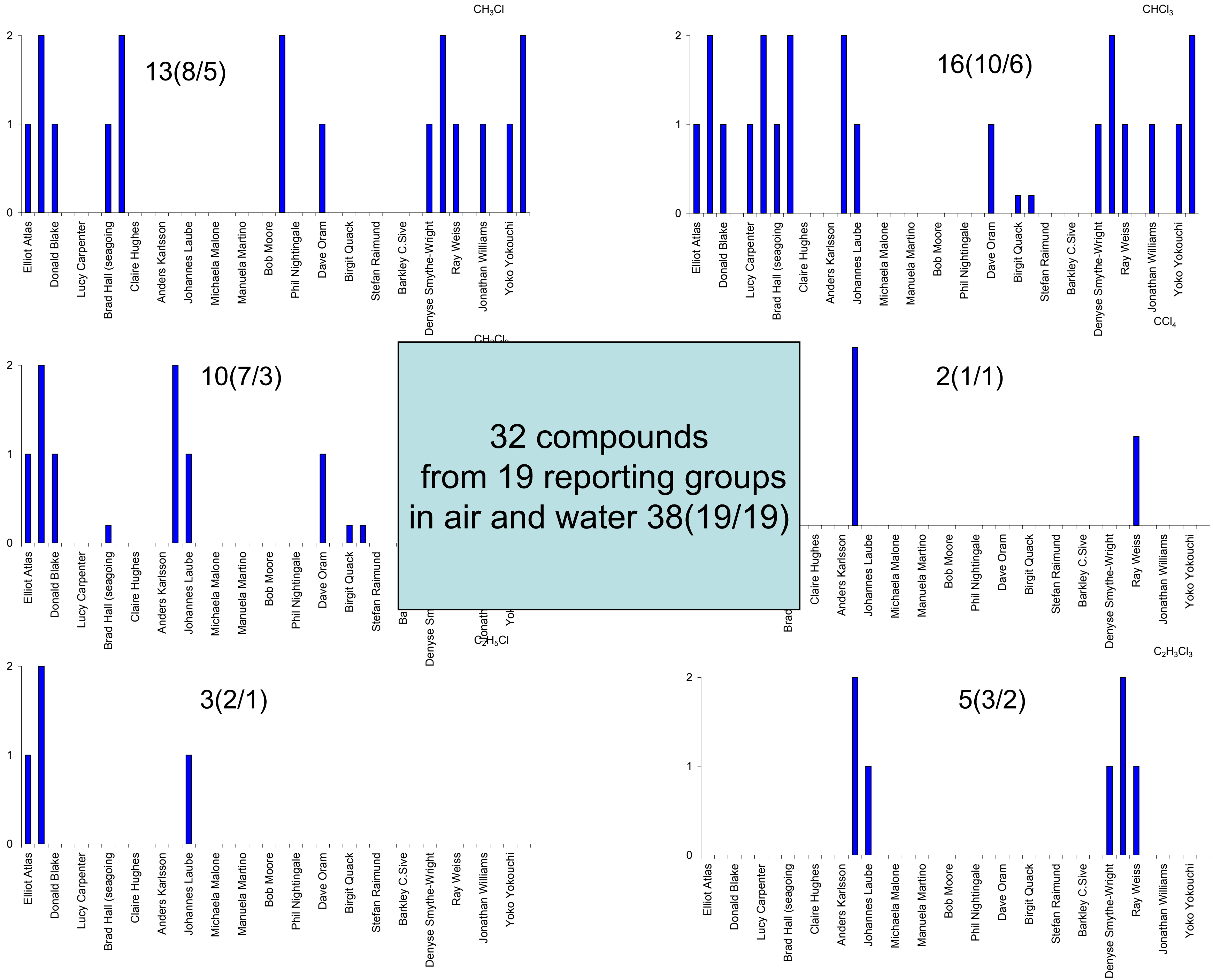
11 countries
21 institutions

Medium analyzed by different groups (standards used)

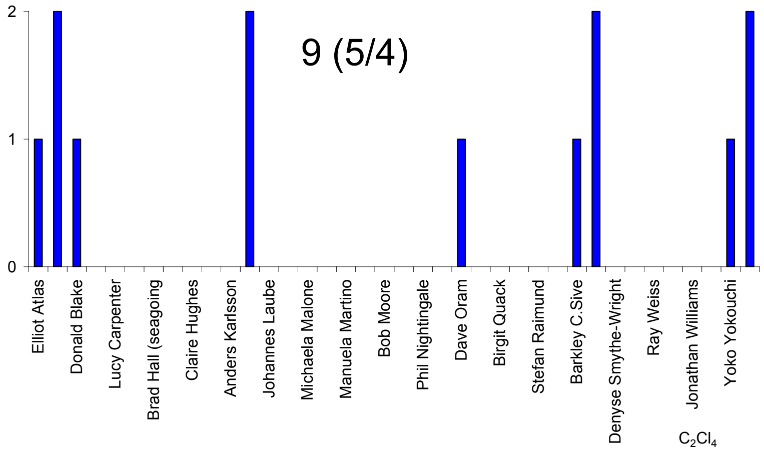
	Air+Water	Air (g)	Water (l)
	1 (g+l)	2	5
	3 (g)	7	6
	4 (g)	8	9
	14 (g + l)	13	10
	15 (l)	17	11
	18(g)	19	
	21 (g+l)	20	
total:	7	7	5

Cryofocussing of air, purge or equilibrator gas, subsequent analytical method

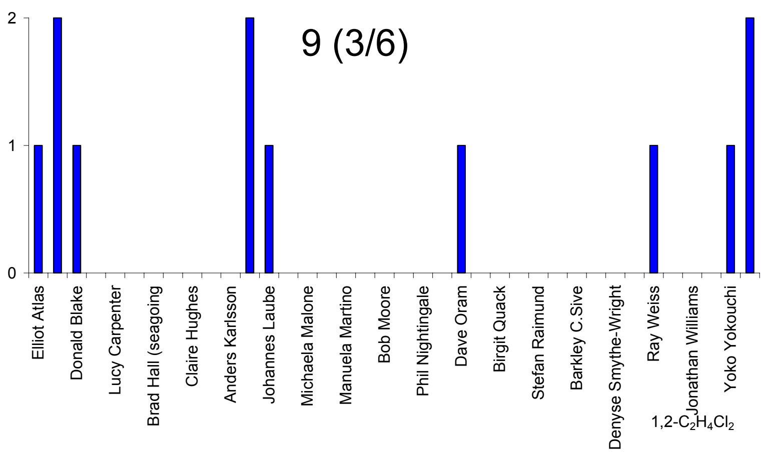
	GC/MS+GC/ECD	GC/MS	GC/ECD
	2	1 (+NCI)	15
	6	3	
	7 (+NCI)	4	
	11	5	
	17	8	
	18	9	
	19	10	
		13 (+NCI)	
		14	
		20	
		21	
total:	7	11	1


CH3Cl
13(8/5)
CHCl3
16(10/6)
CH2Cl2
10(7/3)
CCl4
2(1/1)
32 compounds
from 19 reporting groups
in air and water 38(19/19)
C2H5Cl
3(2/1)
C2H3Cl3
5(3/2)
Elliot Atlas
Donald Blake
Lucy Carpenter
Brad Hall (seagoing
Claire Hughes
Anders Karlsson
Johannes Laube
Michaela Malone
Manuela Martino
Bob Moore
Phil Nightingale
Dave Oram
Birgit Quack
Stefan Raimund
Barkley C.Sive
Denyse Smythe-Wright
Ray Weiss
Jonathan Williams
Yoko Yokouchi

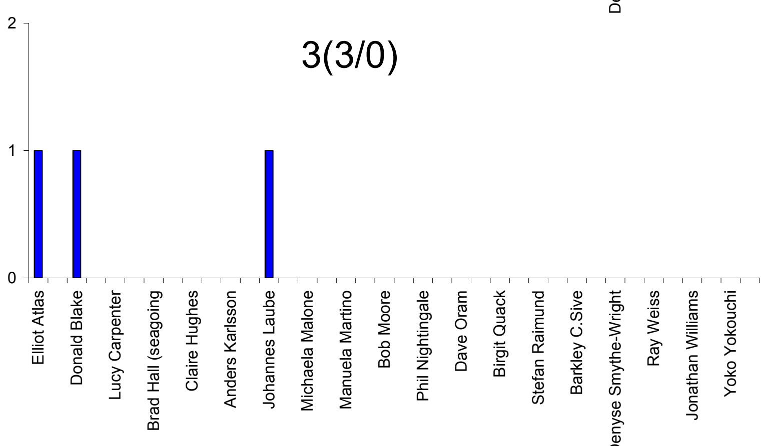
C_2HCl_3



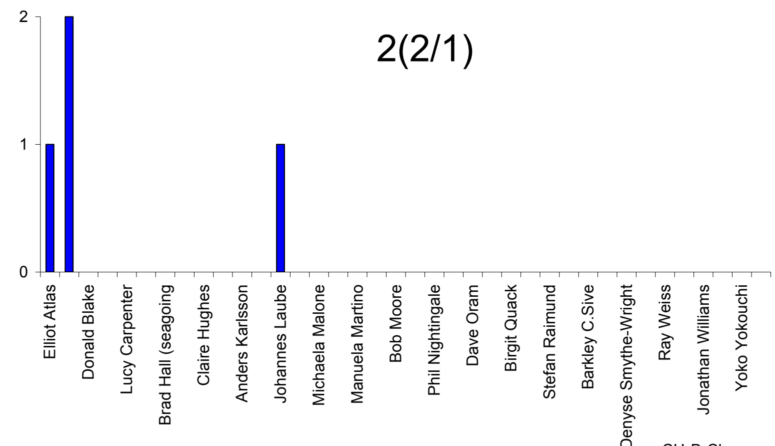
C_2Cl_4



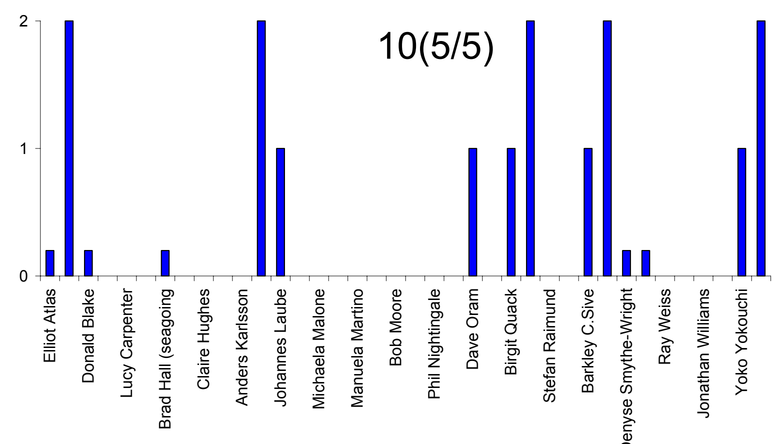
1,2-$C_2H_4Cl_2$

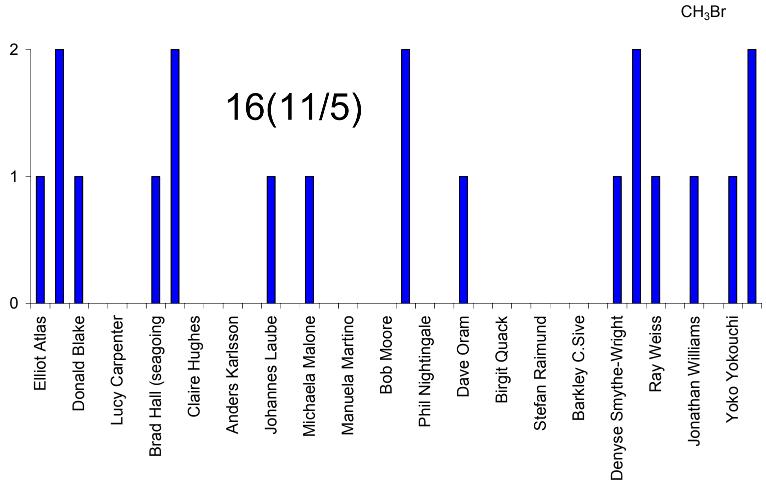


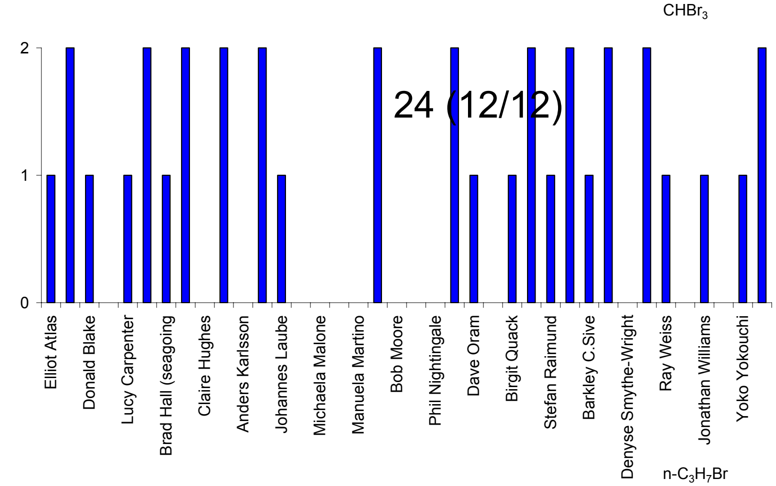
C_2H_5Br

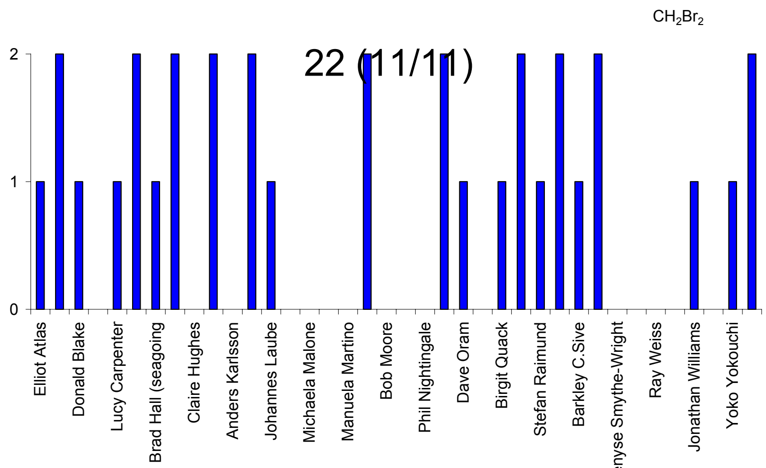


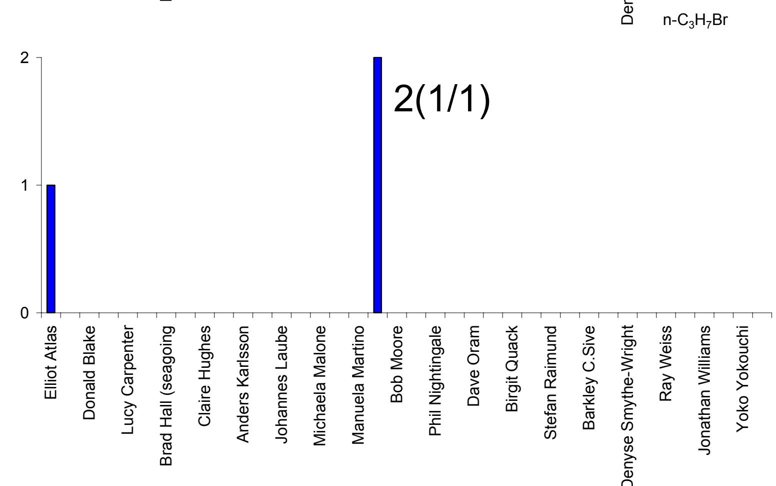
CH_2BrCl

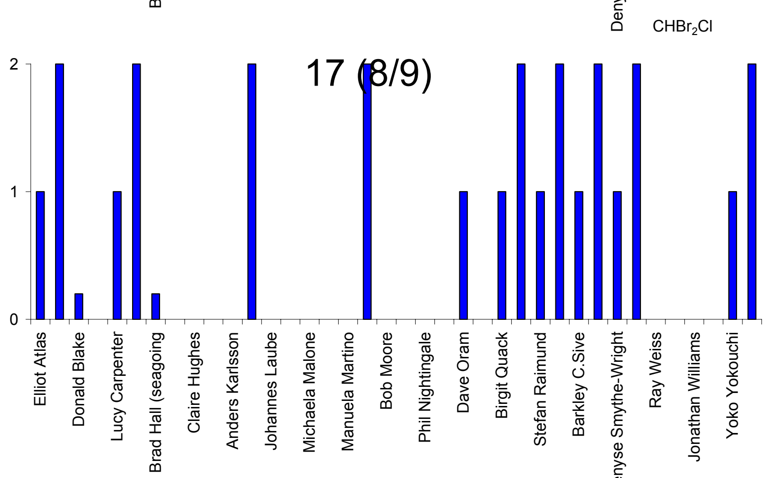


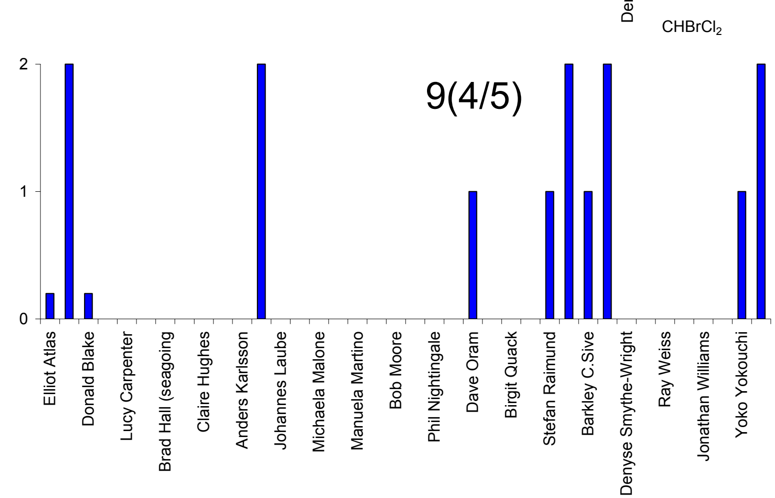

CH_3Br
16(11/5)
2
1
0
Elliot Atlas
Donald Blake
Lucy Carpenter
Brad Hall (seagoing
Claire Hughes
Anders Karlsson
Johannes Laube
Michaela Malone
Manuela Martino
Bob Moore
Phil Nightingale
Dave Oram
Birgit Quack
Stefan Raimund
Barkley C.Sive
Denyse Smythe-Wright
Ray Weiss
Jonathan Williams
Yoko Yokouchi

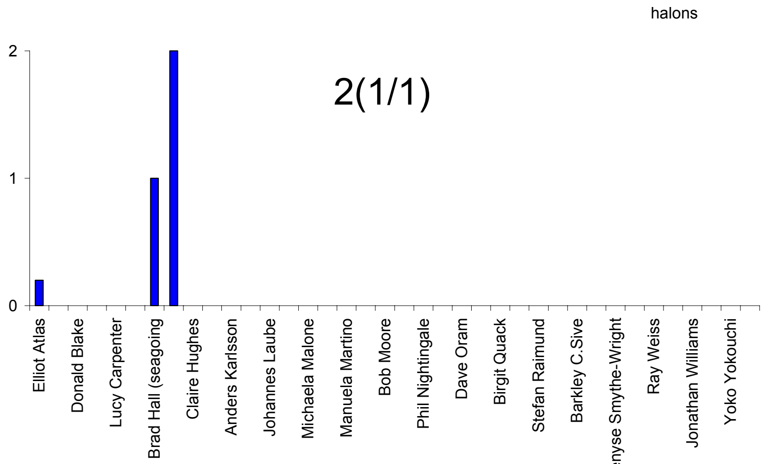

$CHBr_3$
24 (12/12)
2
1
0
Elliot Atlas
Donald Blake
Lucy Carpenter
Brad Hall (seagoing
Claire Hughes
Anders Karlsson
Johannes Laube
Michaela Malone
Manuela Martino
Bob Moore
Phil Nightingale
Dave Oram
Birgit Quack
Stefan Raimund
Barkley C.Sive
Denyse Smythe-Wright
Ray Weiss
Jonathan Williams
Yoko Yokouchi

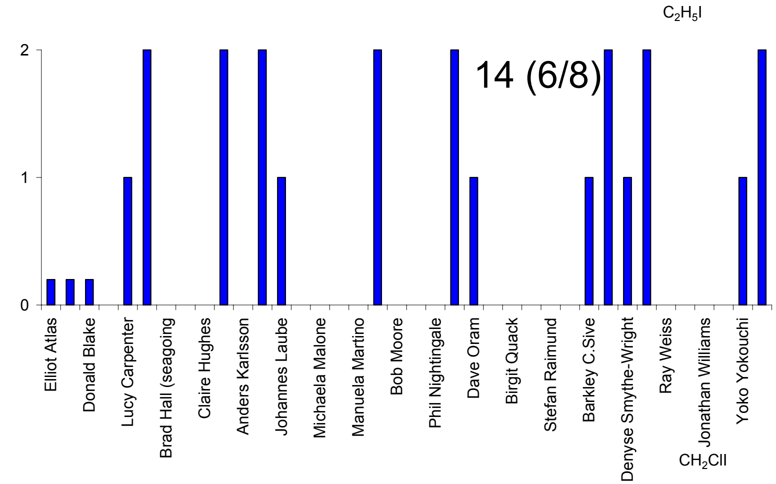

CH_2Br_2
22 (11/11)
2
1
0
Elliot Atlas
Donald Blake
Lucy Carpenter
Brad Hall (seagoing
Claire Hughes
Anders Karlsson
Johannes Laube
Michaela Malone
Manuela Martino
Bob Moore
Phil Nightingale
Dave Oram
Birgit Quack
Stefan Raimund
Barkley C.Sive
Denyse Smythe-Wright
Ray Weiss
Jonathan Williams
Yoko Yokouchi

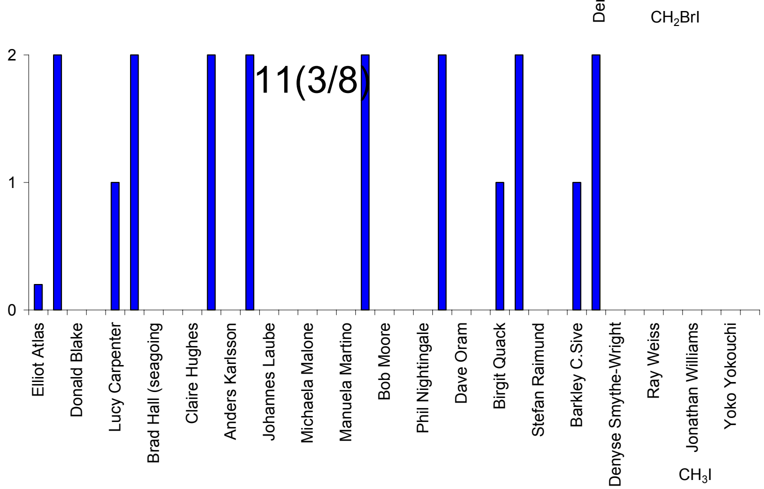

$n\text{-}C_3H_7Br$
2(1/1)
2
1
0
Elliot Atlas
Donald Blake
Lucy Carpenter
Brad Hall (seagoing
Claire Hughes
Anders Karlsson
Johannes Laube
Michaela Malone
Manuela Martino
Bob Moore
Phil Nightingale
Dave Oram
Birgit Quack
Stefan Raimund
Barkley C.Sive
Denyse Smythe-Wright
Ray Weiss
Jonathan Williams
Yoko Yokouchi

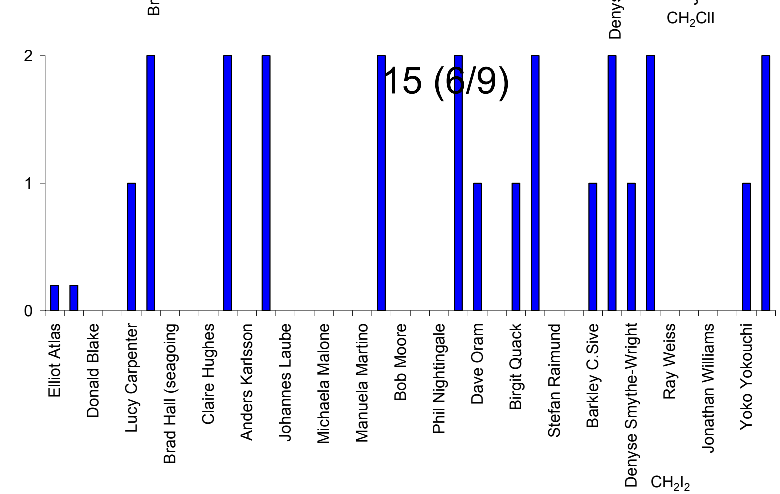

$CHBr_2Cl$
17 (8/9)
2
1
0
Elliot Atlas
Donald Blake
Lucy Carpenter
Brad Hall (seagoing
Claire Hughes
Anders Karlsson
Johannes Laube
Michaela Malone
Manuela Martino
Bob Moore
Phil Nightingale
Dave Oram
Birgit Quack
Stefan Raimund
Barkley C.Sive
enyse Smythe-Wright
Ray Weiss
Jonathan Williams
Yoko Yokouchi


$CHBrCl_2$
9(4/5)
2
1
0
Elliot Atlas
Donald Blake
Lucy Carpenter
Brad Hall (seagoing
Claire Hughes
Anders Karlsson
Johannes Laube
Michaela Malone
Manuela Martino
Bob Moore
Phil Nightingale
Dave Oram
Birgit Quack
Stefan Raimund
Barkley C.Sive
Denyse Smythe-Wright
Ray Weiss
Jonathan Williams
Yoko Yokouchi


halons
2(1/1)
0
1
2
Elliot Atlas
Donald Blake
Lucy Carpenter
Brad Hall (seagoing
Claire Hughes
Anders Karlsson
Johannes Laube
Michaela Malone
Manuela Martino
Bob Moore
Phil Nightingale
Dave Oram
Birgit Quack
Stefan Raimund
Barkley C.Sive
Denyse Smythe-Wright
Ray Weiss
Jonathan Williams
Yoko Yokouchi


C_2H_5I
14 (6/8)
0
1
2
Elliot Atlas
Donald Blake
Lucy Carpenter
Brad Hall (seagoing
Claire Hughes
Anders Karlsson
Johannes Laube
Michaela Malone
Manuela Martino
Bob Moore
Phil Nightingale
Dave Oram
Birgit Quack
Stefan Raimund
Barkley C.Sive
Denyse Smythe-Wright
Ray Weiss
Jonathan Williams
Yoko Yokouchi


CH_2BrI
11(3/8)
0
1
2
Elliot Atlas
Donald Blake
Lucy Carpenter
Brad Hall (seagoing
Claire Hughes
Anders Karlsson
Johannes Laube
Michaela Malone
Manuela Martino
Bob Moore
Phil Nightingale
Dave Oram
Birgit Quack
Stefan Raimund
Barkley C.Sive
Denyse Smythe-Wright
Ray Weiss
Jonathan Williams
Yoko Yokouchi


CH_2ClI
15 (6/9)
0
1
2
Elliot Atlas
Donald Blake
Lucy Carpenter
Brad Hall (seagoing
Claire Hughes
Anders Karlsson
Johannes Laube
Michaela Malone
Manuela Martino
Bob Moore
Phil Nightingale
Dave Oram
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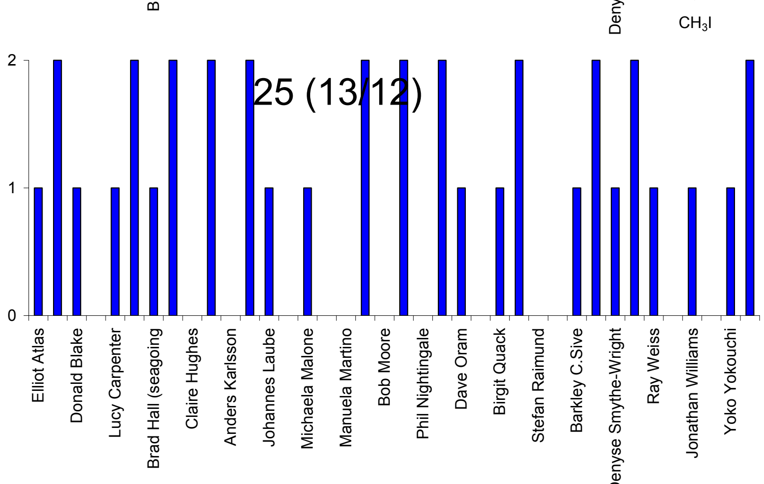
Ray Weiss
Jonathan Williams
Yoko Yokouchi


CH_3I
25 (13/12)
0
1
2
Elliot Atlas
Donald Blake
Lucy Carpenter
Brad Hall (seagoing
Claire Hughes
Anders Karlsson
Johannes Laube
Michaela Malone
Manuela Martino
Bob Moore
Phil Nightingale
Dave Oram
Birgit Quack
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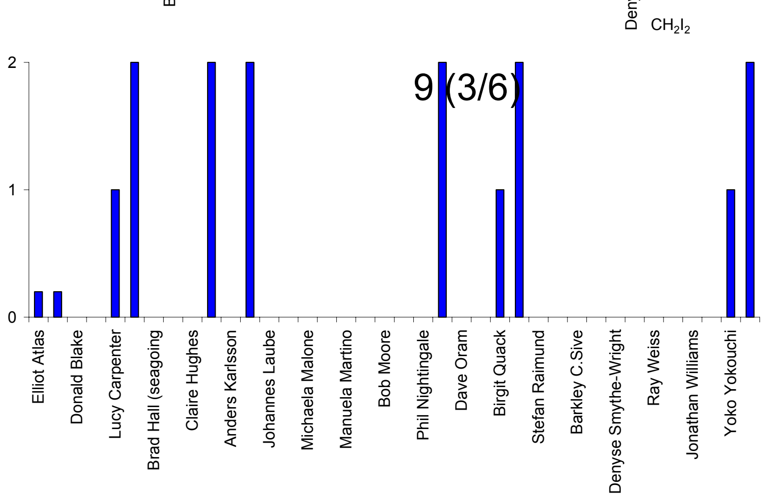
Barkley C.Sive
Denyse Smythe-Wright
Ray Weiss
Jonathan Williams
Yoko Yokouchi


CH_2I_2
9 (3/6)
0
1
2
Elliot Atlas
Donald Blake
Lucy Carpenter
Brad Hall (seagoing
Claire Hughes
Anders Karlsson
Johannes Laube
Michaela Malone
Manuela Martino
Bob Moore
Phil Nightingale
Dave Oram
Birgit Quack
Stefan Raimund
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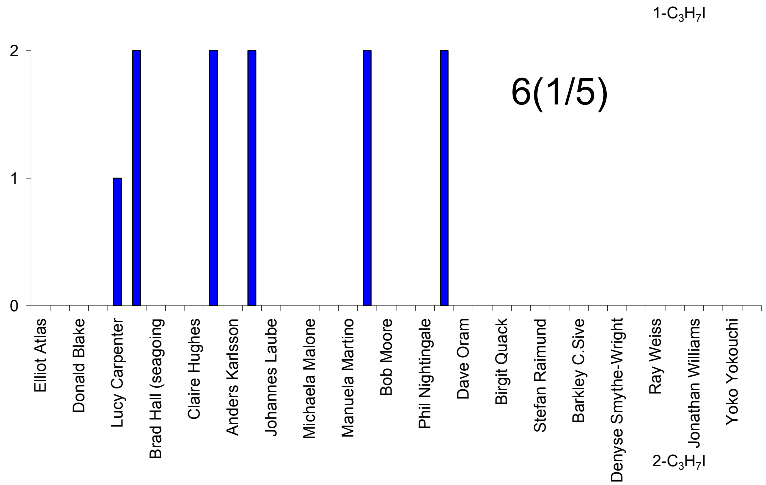
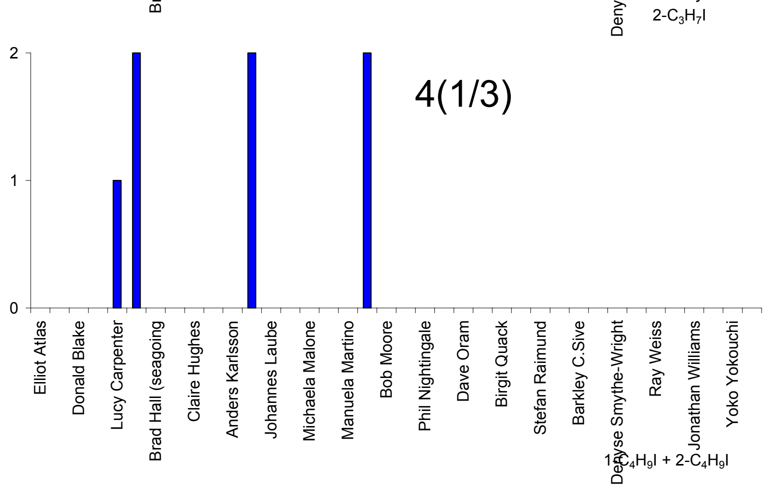
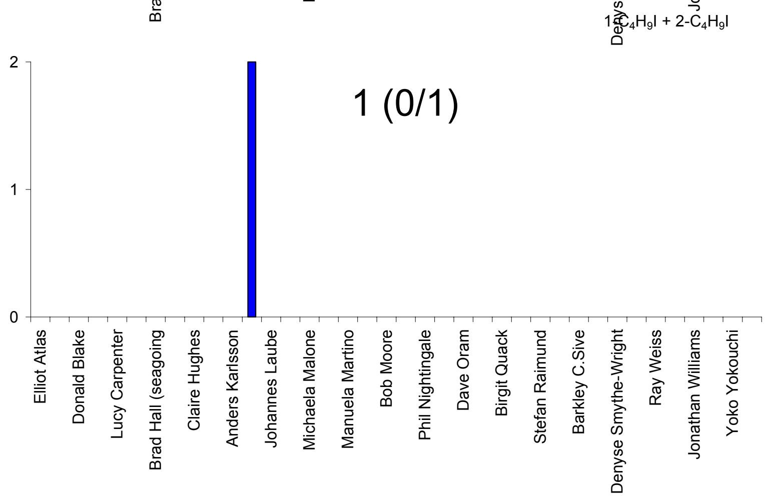
Denyse Smythe-Wright
Ray Weiss
Jonathan Williams
Yoko Yokouchi



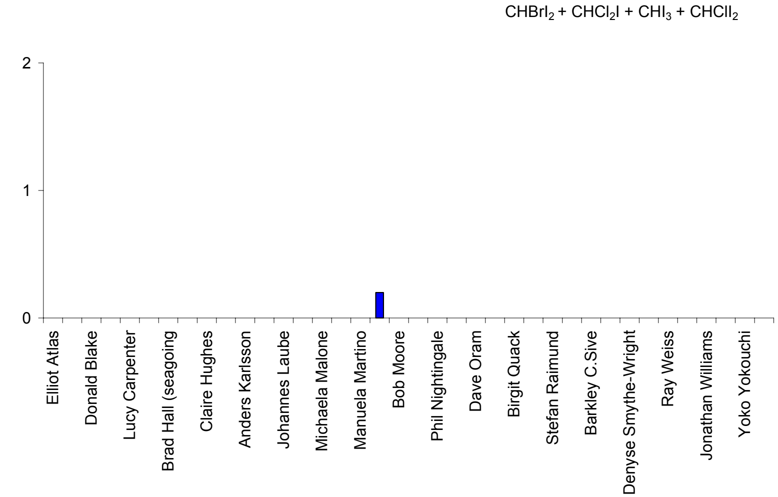
$1\text{-}C_3H_7I$
6(1/5)
2
1
0
Elliot Atlas
Donald Blake
Lucy Carpenter
Brad Hall (seagoing
Claire Hughes
Anders Karlsson
Johannes Laube
Michaela Malone
Manuela Martino
Bob Moore
Phil Nightingale
Dave Oram
Birgit Quack
Stefan Raimund
Barkley C.Sive
Denyse Smythe-Wright
Ray Weiss
Jonathan Williams
Yoko Yokouchi



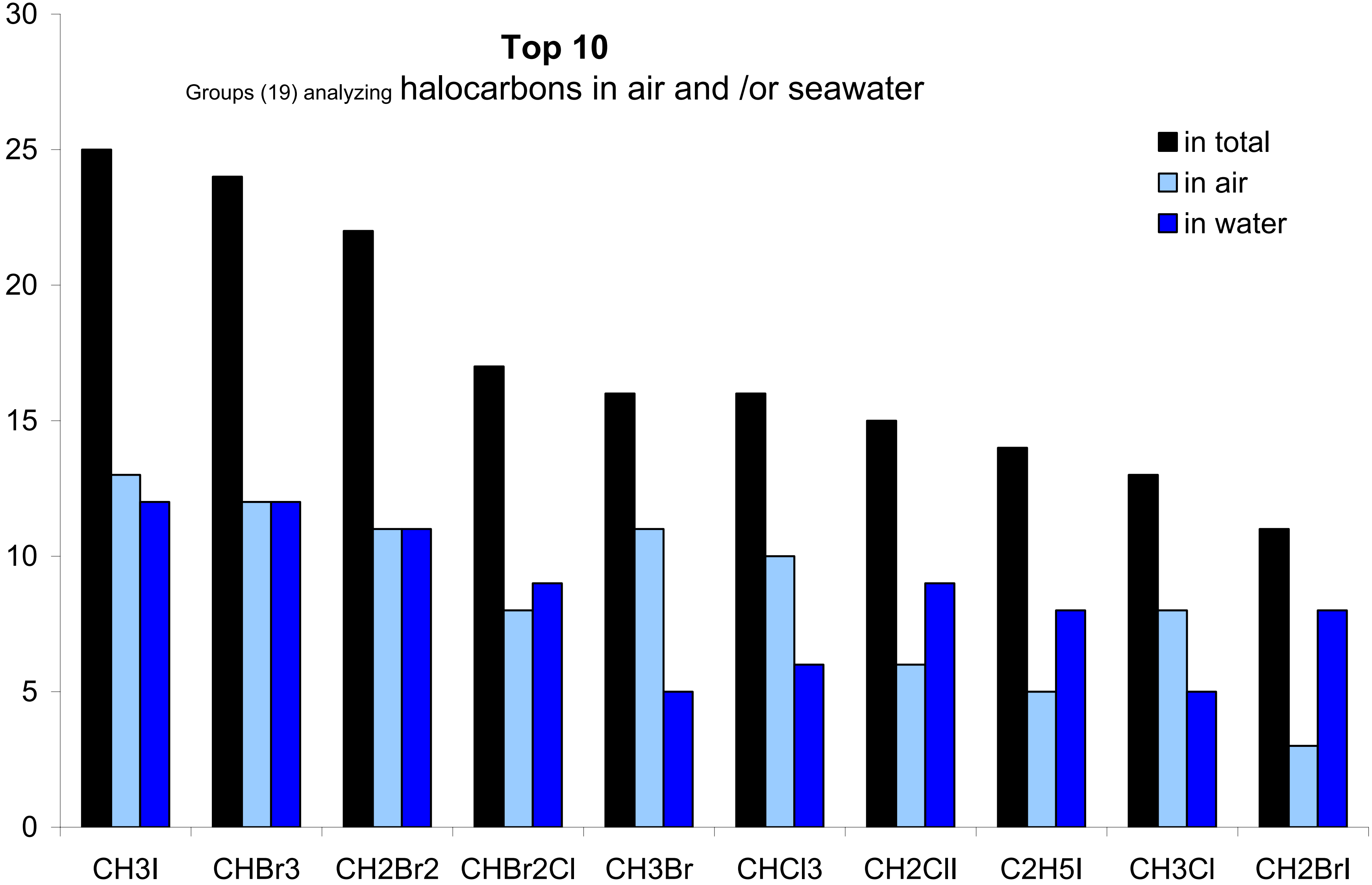
$2\text{-}C_3H_7I$
4(1/3)
2
1
0
Elliot Atlas
Donald Blake
Lucy Carpenter
Brad Hall (seagoing
Claire Hughes
Anders Karlsson
Johannes Laube
Michaela Malone
Manuela Martino
Bob Moore
Phil Nightingale
Dave Oram
Birgit Quack
Stefan Raimund
Barkley C.Sive
Denyse Smythe-Wright
Ray Weiss
Jonathan Williams
Yoko Yokouchi



$1\text{-}C_4H_9I + 2\text{-}C_4H_9I$
1 (0/1)
2
1
0
Elliot Atlas
Donald Blake
Lucy Carpenter
Brad Hall (seagoing
Claire Hughes
Anders Karlsson
Johannes Laube
Michaela Malone
Manuela Martino
Bob Moore
Phil Nightingale
Dave Oram
Birgit Quack
Stefan Raimund
Barkley C.Sive
Denyse Smythe-Wright
Ray Weiss
Jonathan Williams
Yoko Yokouchi



$CHBrI_2 + CHCl_2I + CHI_3 + CHClI_2$
2
1
0
Elliot Atlas
Donald Blake
Lucy Carpenter
Brad Hall (seagoing
Claire Hughes
Anders Karlsson
Johannes Laube
Michaela Malone
Manuela Martino
Bob Moore
Phil Nightingale
Dave Oram
Birgit Quack
Stefan Raimund
Barkley C.Sive
Denyse Smythe-Wright
Ray Weiss
Jonathan Williams
Yoko Yokouchi



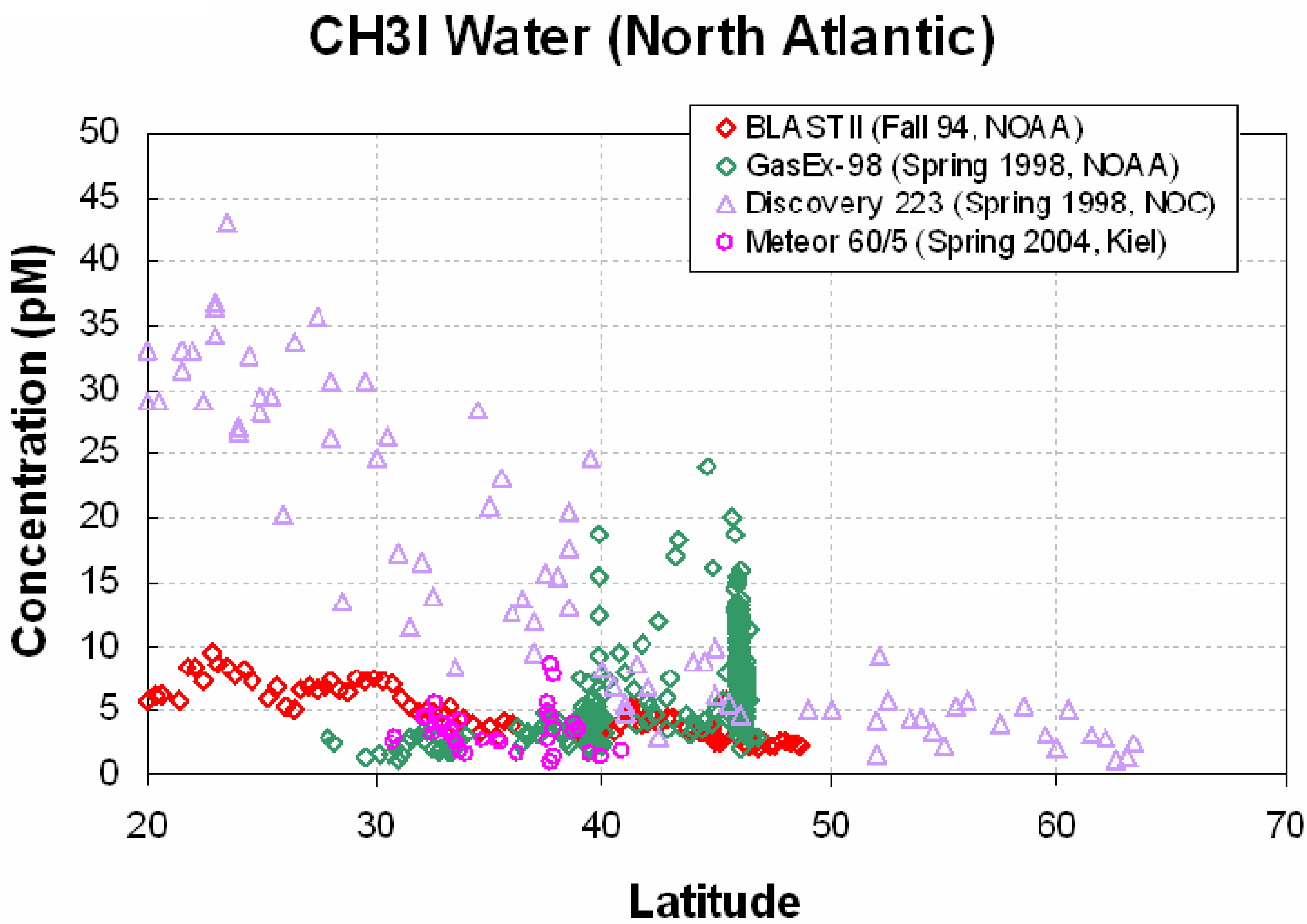
Top 10
Groups (19) analyzing halocarbons in air and /or seawater
in total
in air
in water
30
25
20
15
10
5
0
CH3I
CHBr3
CH2Br2
CHBr2Cl
CH3Br
CHCl3
CH2ClI
C2H5I
CH3Cl
CH2BrI

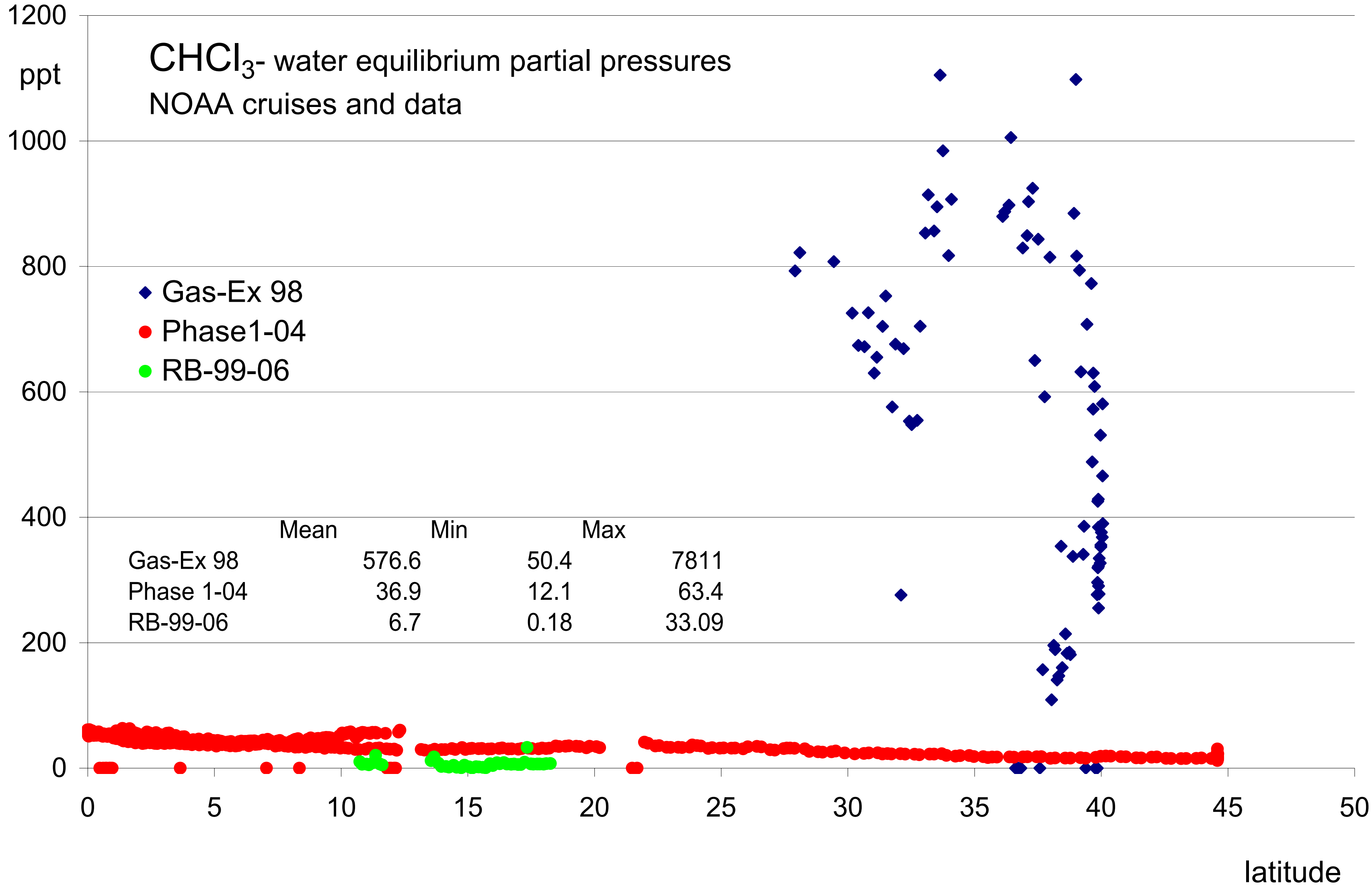
Primary Standards in use: number refers to institution (slide 2)

Scott-Marin calibrated with AED against Nist-Hydrocarbon: NCAR-scale	: 1, 2, 17, 20
(Apel- Riemer Environmental)	: 17, 20
NOAA (inhouse gravimetrical): NOAA-scale	: 4, 7, 13,14,18
SIO (inhouse gravimetrical): AGAGE scale	: 8,18, 19 — for CH_3I: NOAA, NCAR ,NIES; for C_2Cl_4, $CHBr_3$: NOAA
Happell (gravimetrcial, 13 years old in Aculife)	: 10 (14 CH_3I)
Taiyo Nippon Sanso corporation: NIES-scale	: 21
(standard gas from liquid standard)	: 3
perm tubes: homemade	: 3
perm tubes: certified Kintec	: 11, 18
gravimetrically prepared liquid standard in MetOH	: 1, 5, 6, 9,11
gravimetrically prepared liquid standard in pentane	: 14, 22 (other hydrocarbon)
Commercial in MetoH Ultra scientific (100 µg ml^{-1})	: 15,16

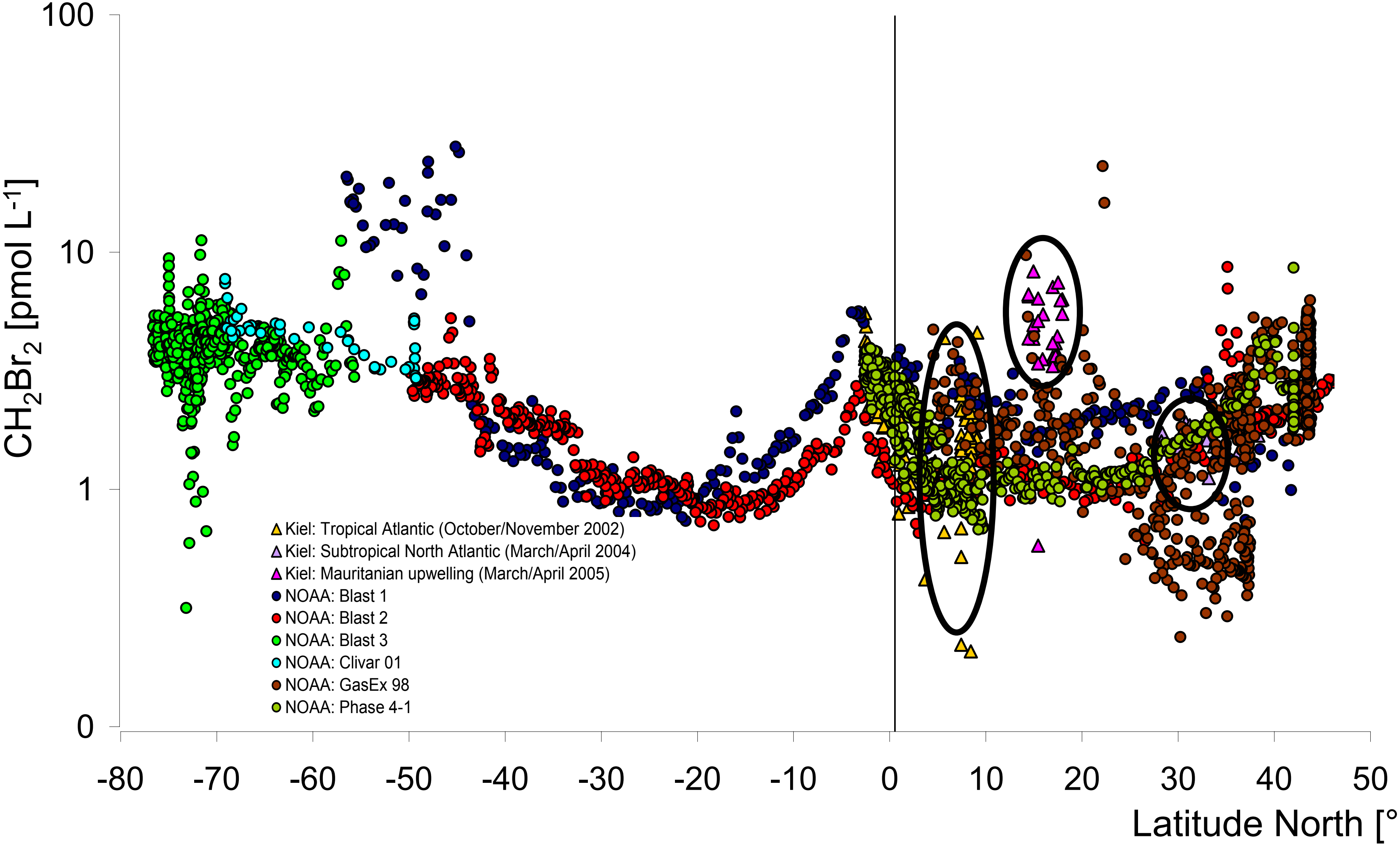
Past comparisons

- High points
- Low points
- Successes
- Failures


CH3I Water (North Atlantic)
BLAST II (Fall 94, NOAA)
GasEx-98 (Spring 1998, NOAA)
Discovery 223 (Spring 1998, NOC)
Meteor 60/5 (Spring 2004, Kiel)
Concentration (pM)
Latitude
0
5
10
15
20
25
30
35
40
45
50
20
30
40
50
60
70

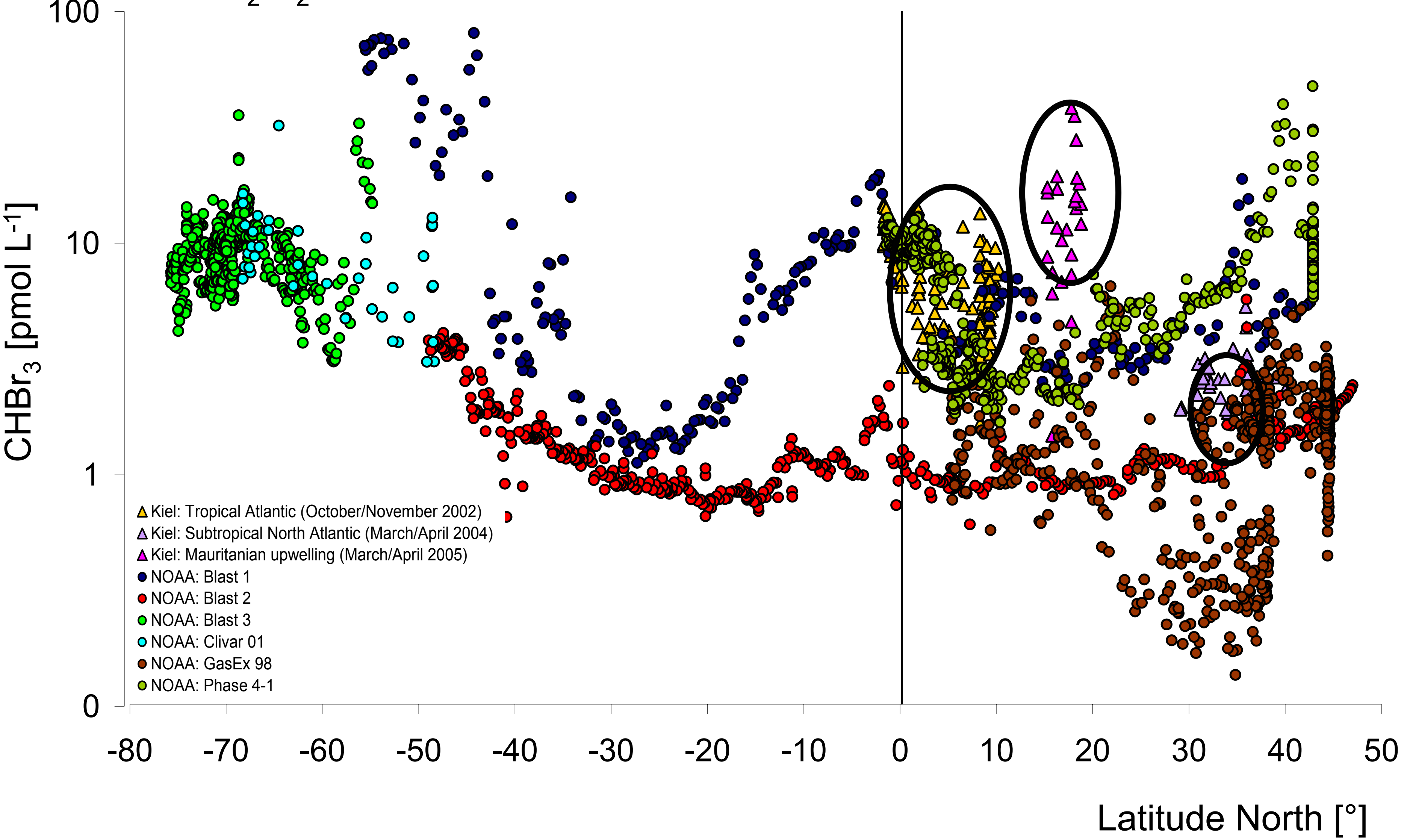


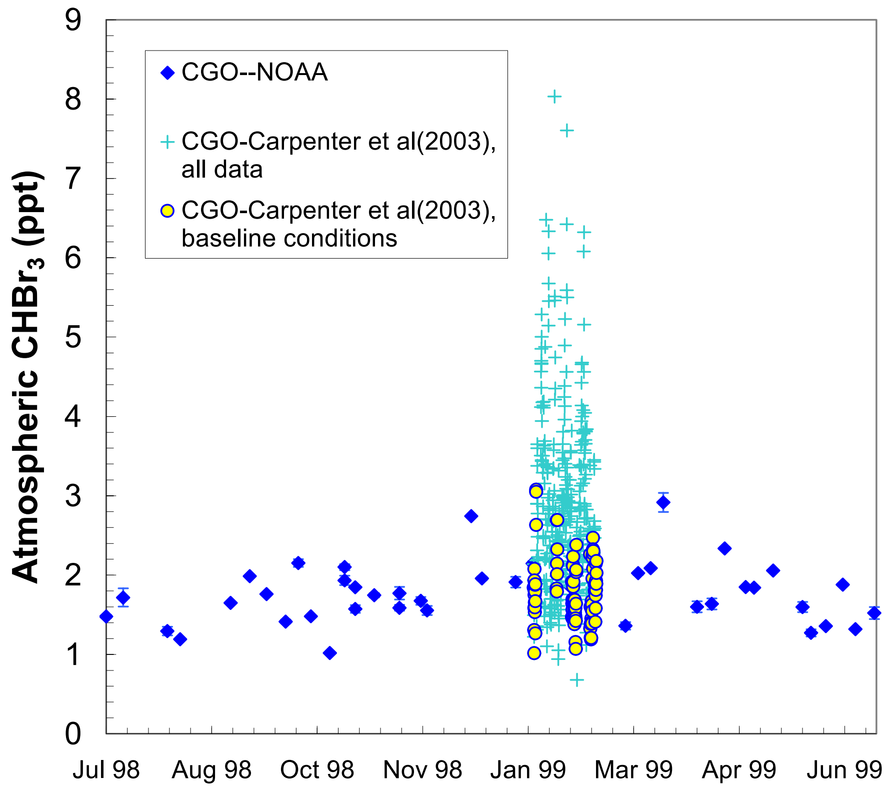
CHCl3- water equilibrium partial pressures
NOAA cruises and data
ppt
1200
1000
800
600
400
200
0
Gas-Ex 98
Phase1-04
RB-99-06
Mean Min Max
Gas-Ex 98 576.6 50.4 7811
Phase 1-04 36.9 12.1 63.4
RB-99-06 6.7 0.18 33.09
0
5
10
15
20
25
30
35
40
45
50
latitude

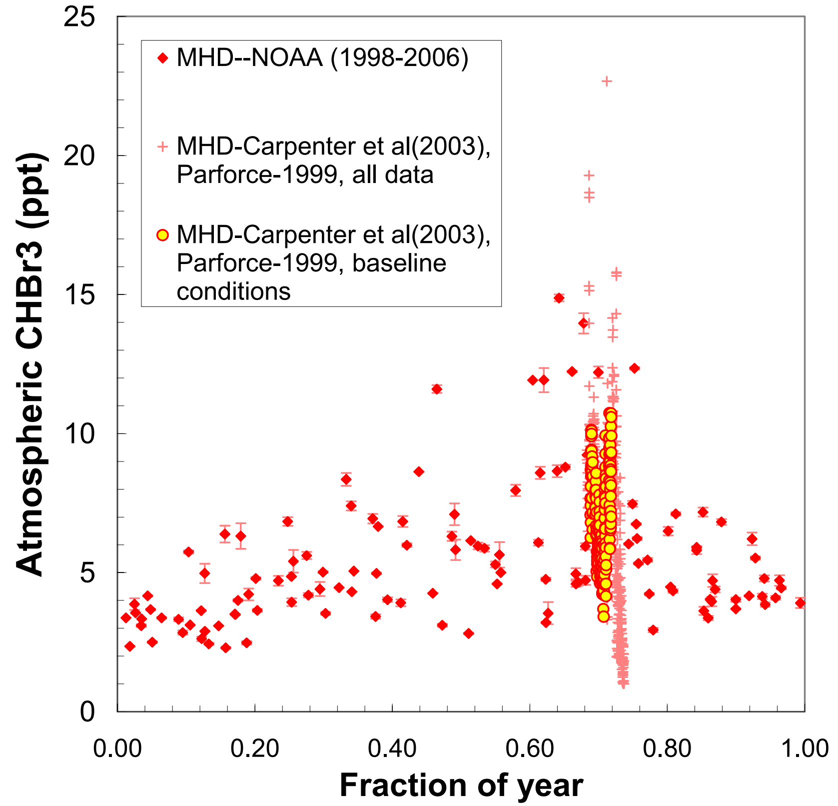


100
10
1
0
CH2Br2 [pmol L-1]
-80
-70
-60
-50
-40
-30
-20
-10
0
10
20
30
40
50
Latitude North [°]
Kiel: Tropical Atlantic (October/November 2002)
Kiel: Subtropical North Atlantic (March/April 2004)
Kiel: Mauritanian upwelling (March/April 2005)
NOAA: Blast 1
NOAA: Blast 2
NOAA: Blast 3
NOAA: Clivar 01
NOAA: GasEx 98
NOAA: Phase 4-1

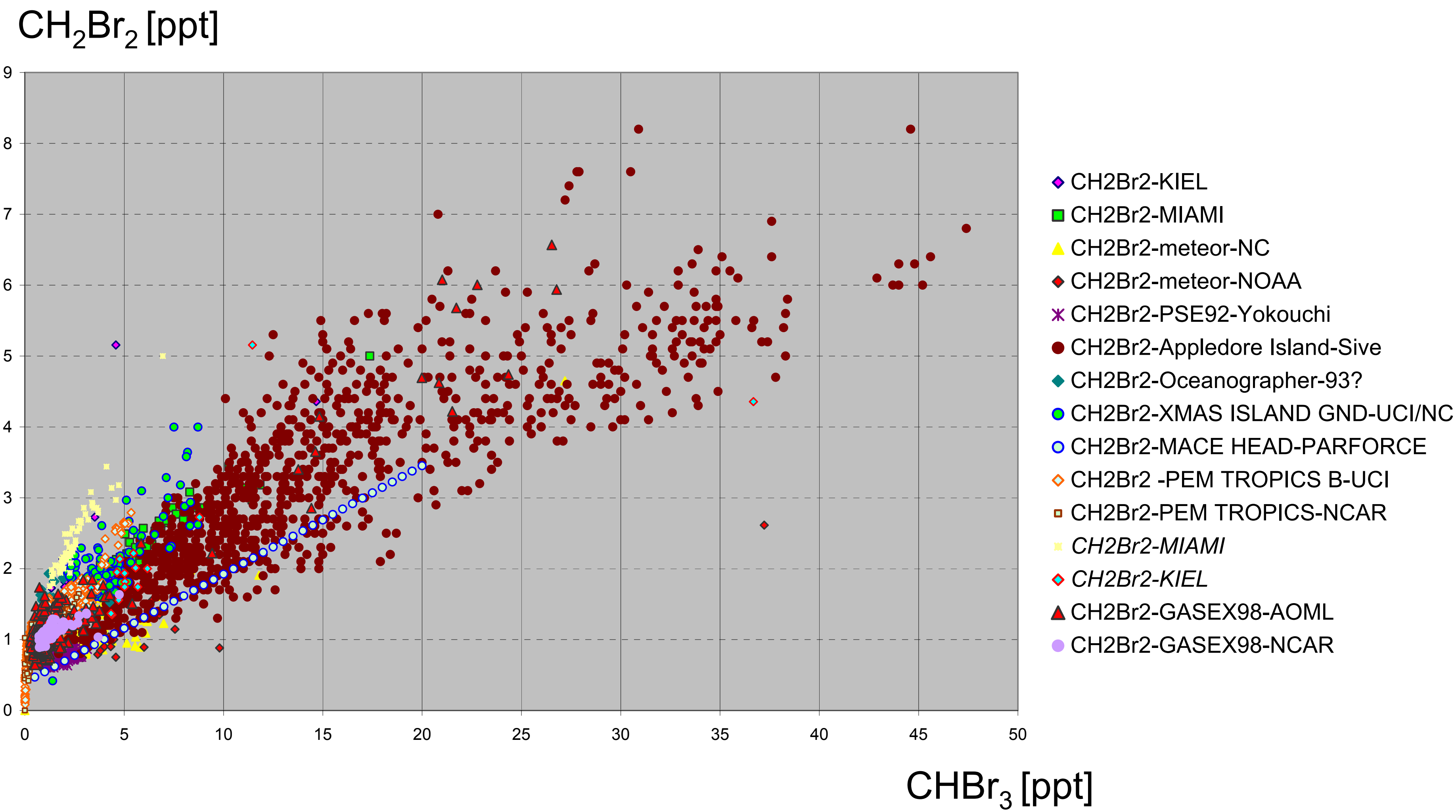
CHBr$_3$ between NOAA and Kiel Atlantic looks ok!?
CH$_2$Br$_2$ data are more consistent





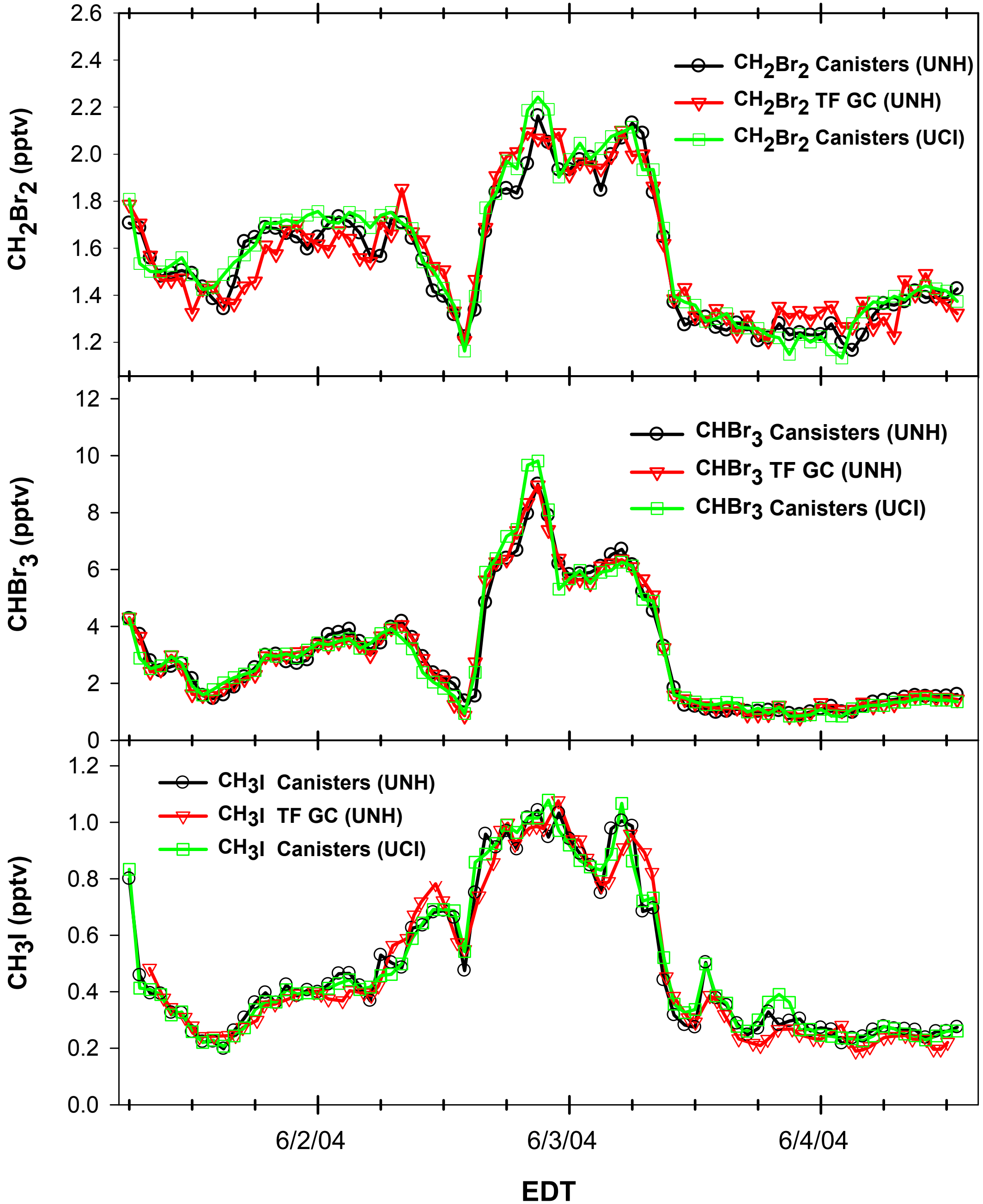


We did compare in our poster Lucy's data at Mace Head and Cape Grim with some from NOAA and they seemed OK, but there was no intercalibration. Is that an issue or is it a possible solution to the problem?



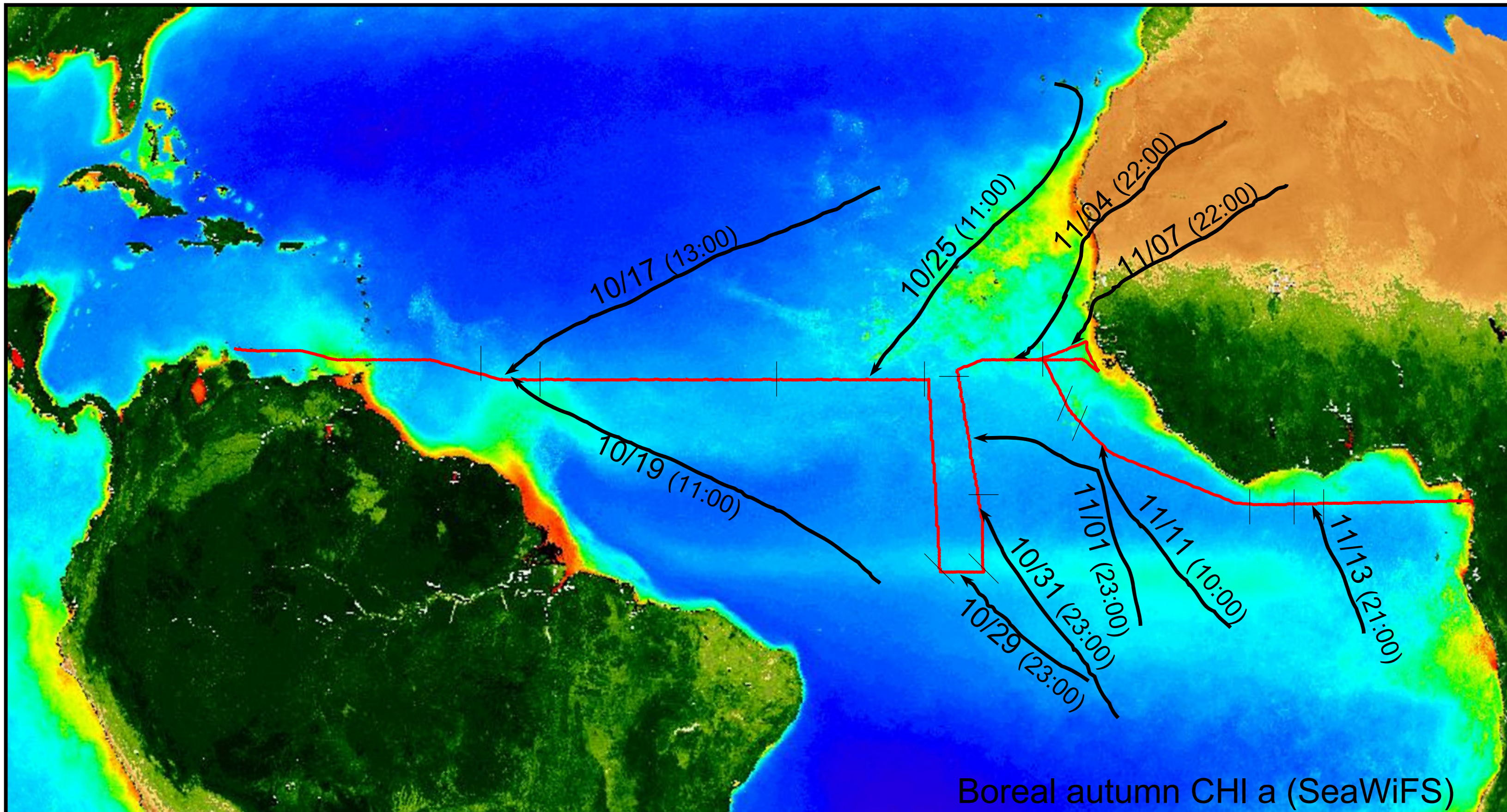
Compilation of Elliot Atlas

pre-ICARTT Intercomparison AIRMAP Observing Station at Thompson Farm Durham, NH

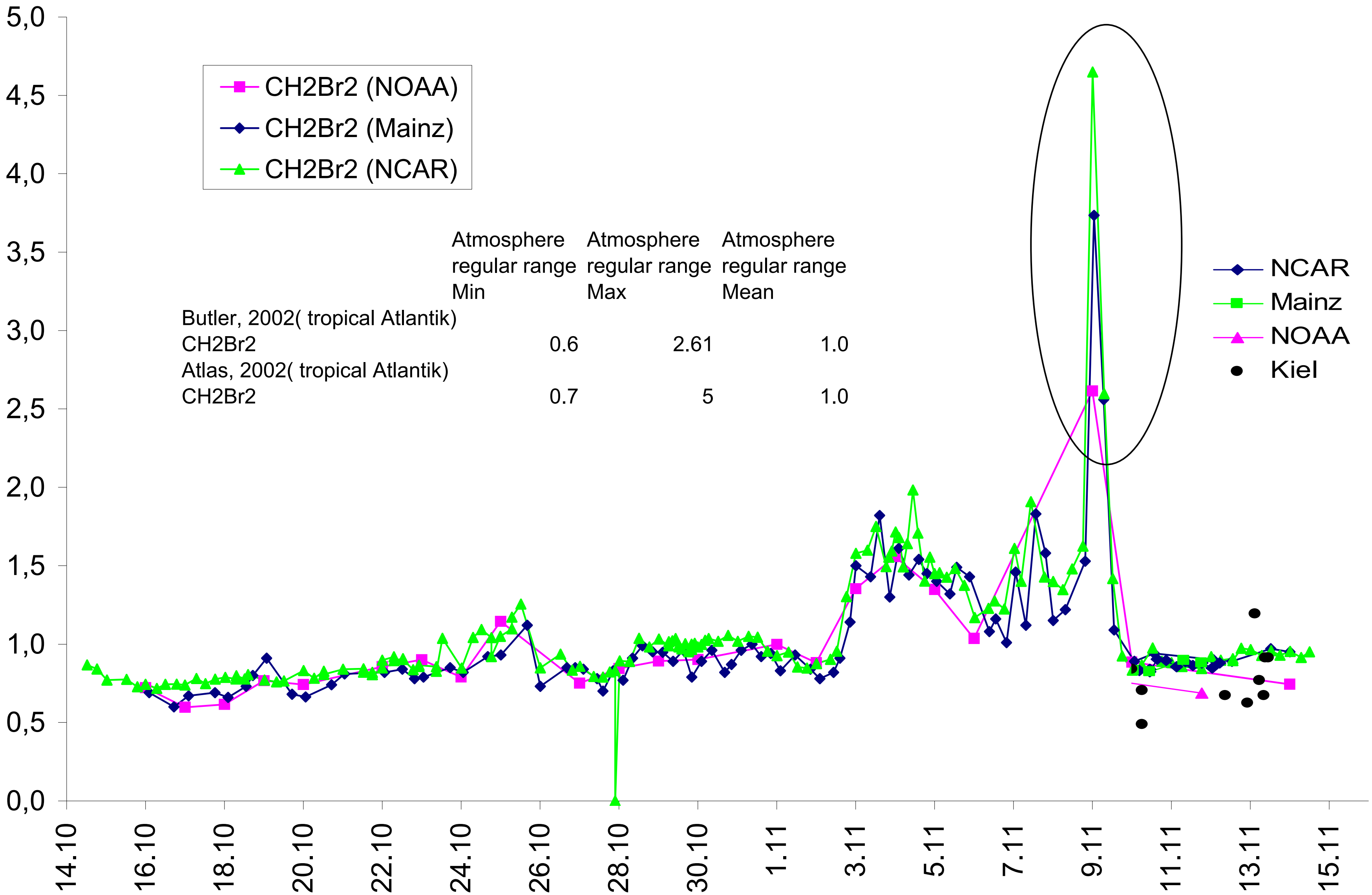


Past direct comparisons high points, low points, successes, failures

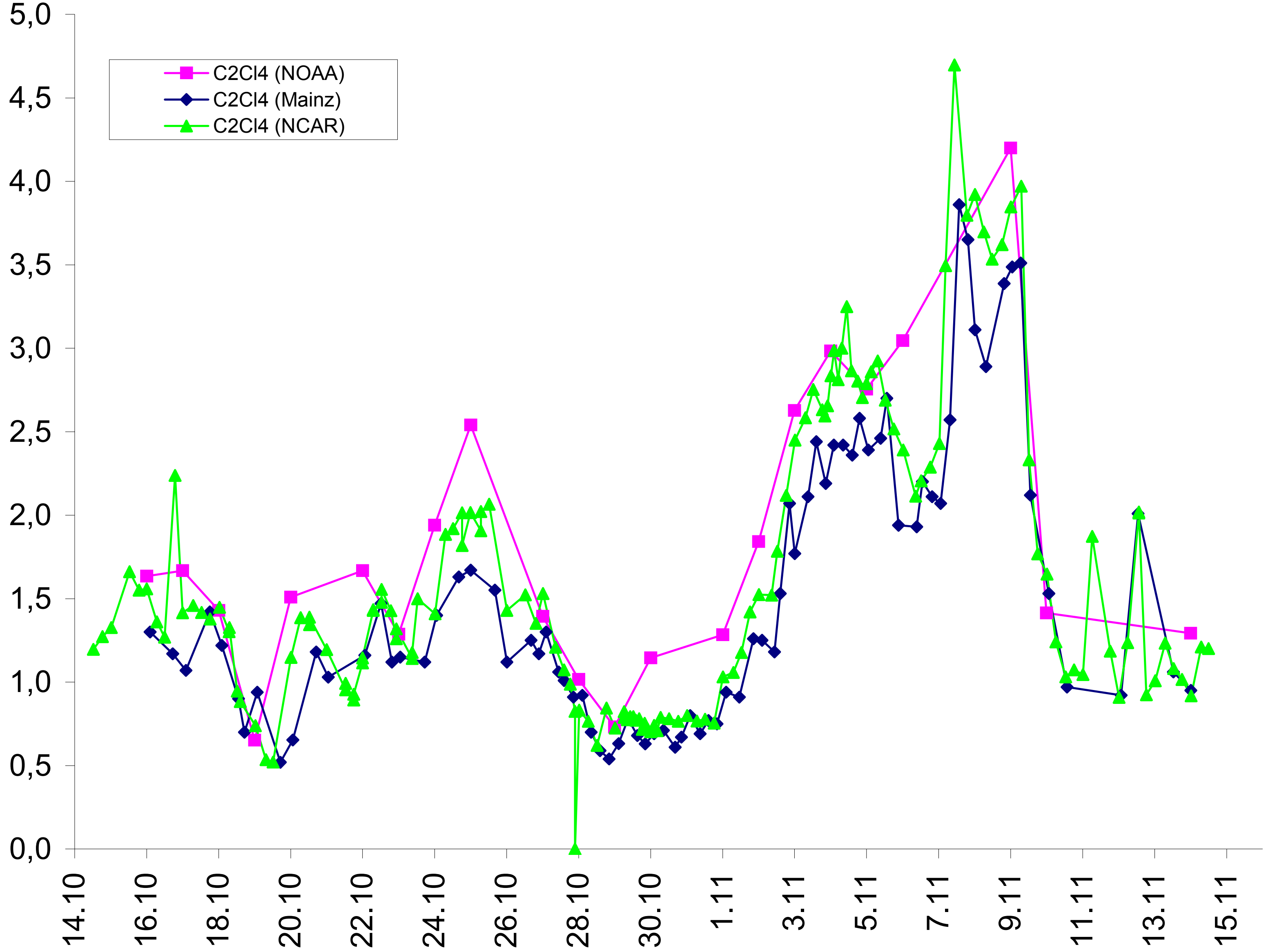
Cruise M55 October 12 - November 17. 2002 (Curacao-Douala)
with air mass 120hr-backward trajectories



Steve Montzka, Elliot Atlas, Jonathan Williams tropical Atlantic October 2002, Meteor 55

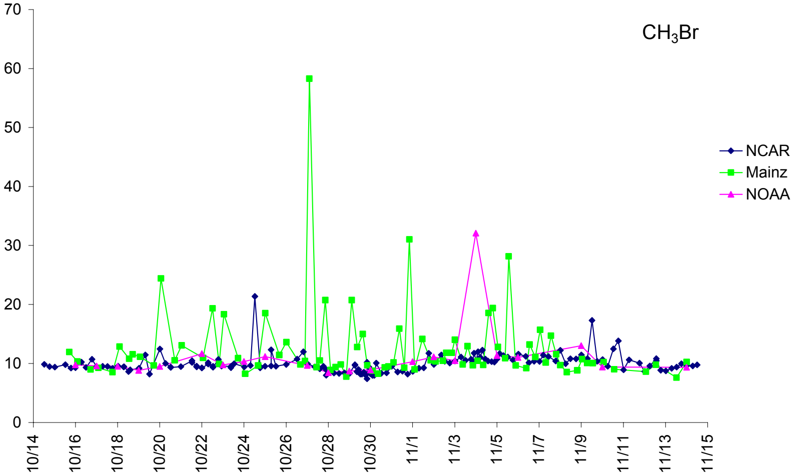


Looks good for CH2Br2 .



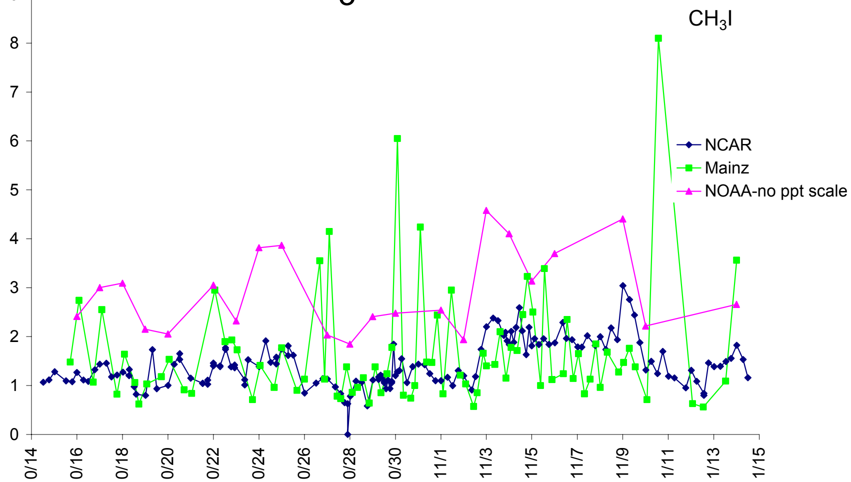
Systematic small offset for C_2Cl_4, also between Mainz and NCAR , although they use the same scale.

CH_3Br

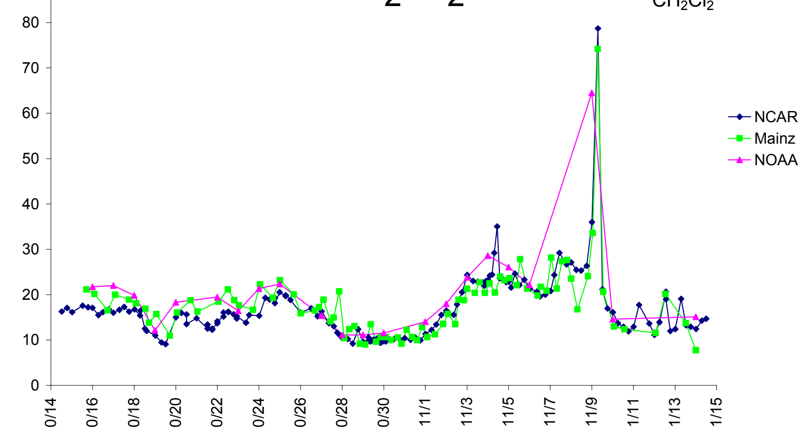


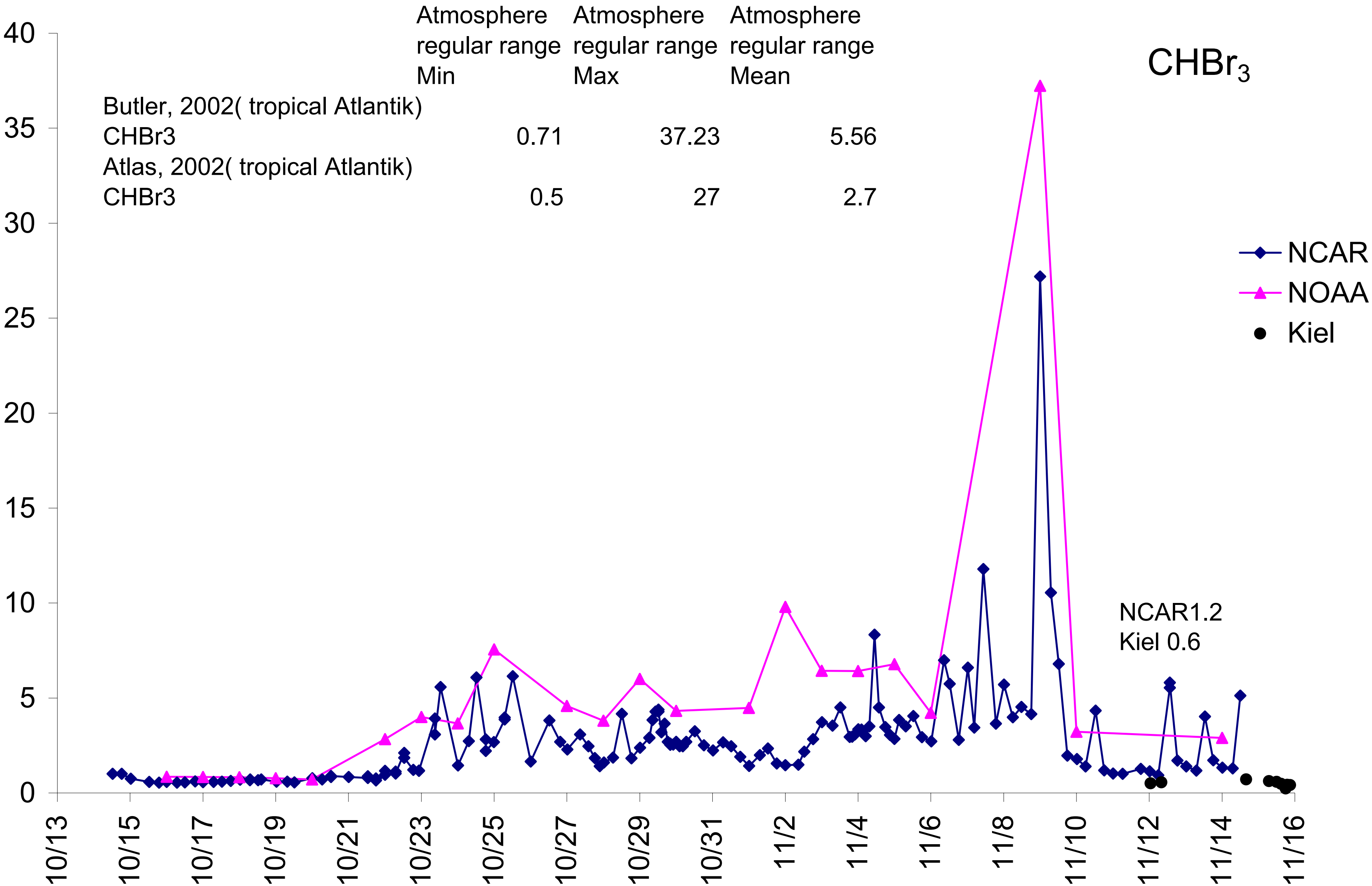
$CHCl_3$

CH_3I



CH_2Cl_2

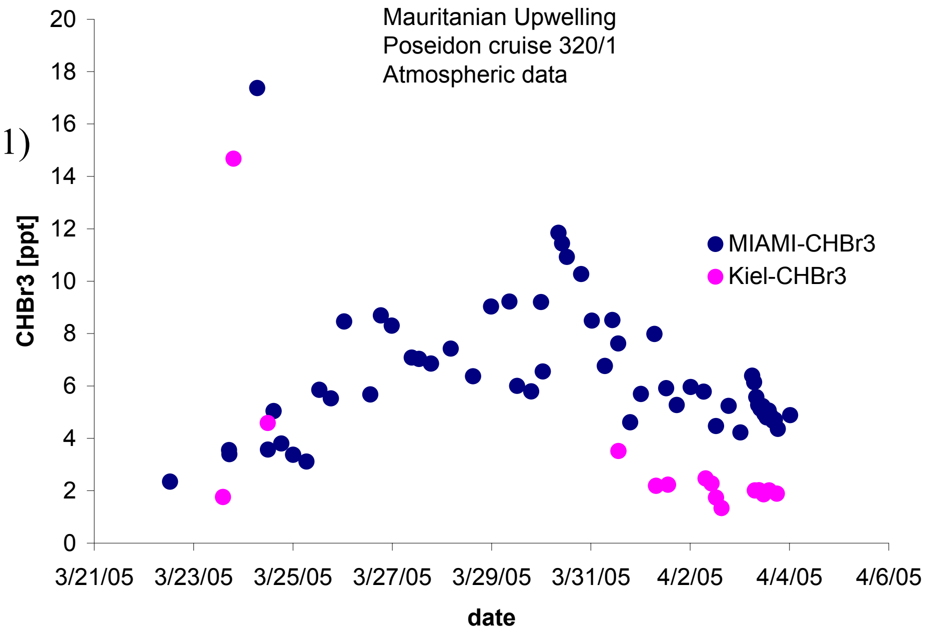




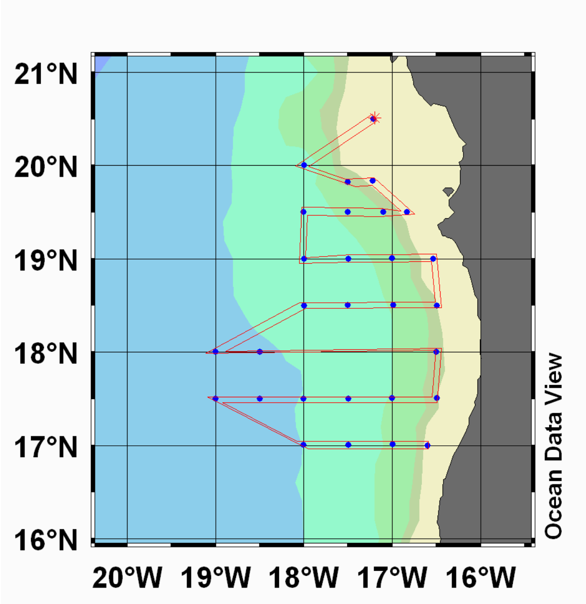
Factor of two difference for $CHBr_3$

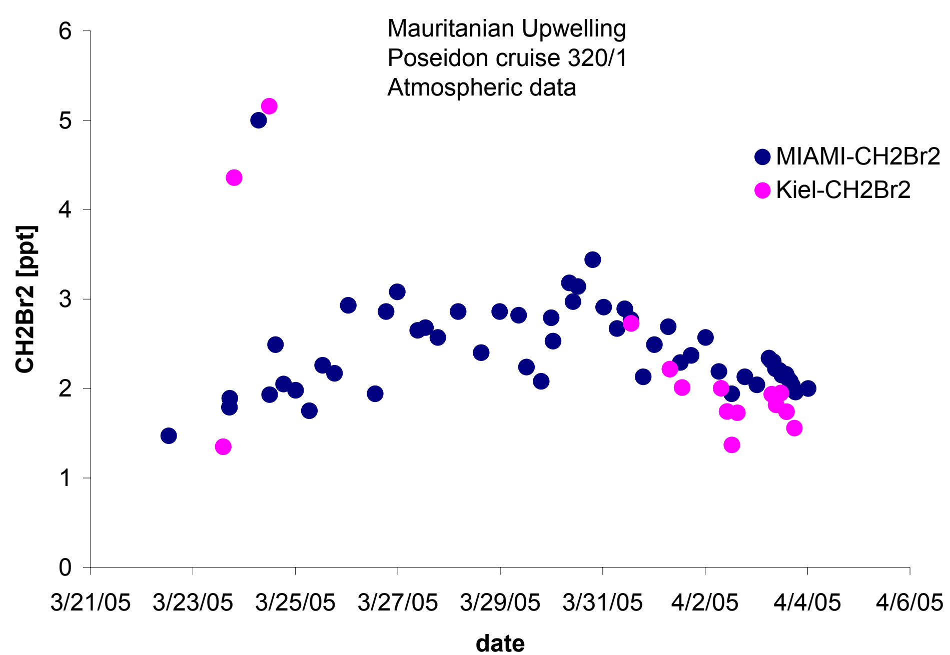
The systematic calibration offset caused a flux difference:
mean CHBr3 flux (Miami-calibration): 1.050 pmol m2 hr-1)
mean CHBr3 flux (Kiel-calibration): 2600 pmol m2 hr-1)
Quack et al., 2007, in press

Again a factor of two calibration offset for $CHBr_3$ between Kiel and Miami, now treated as systematic...

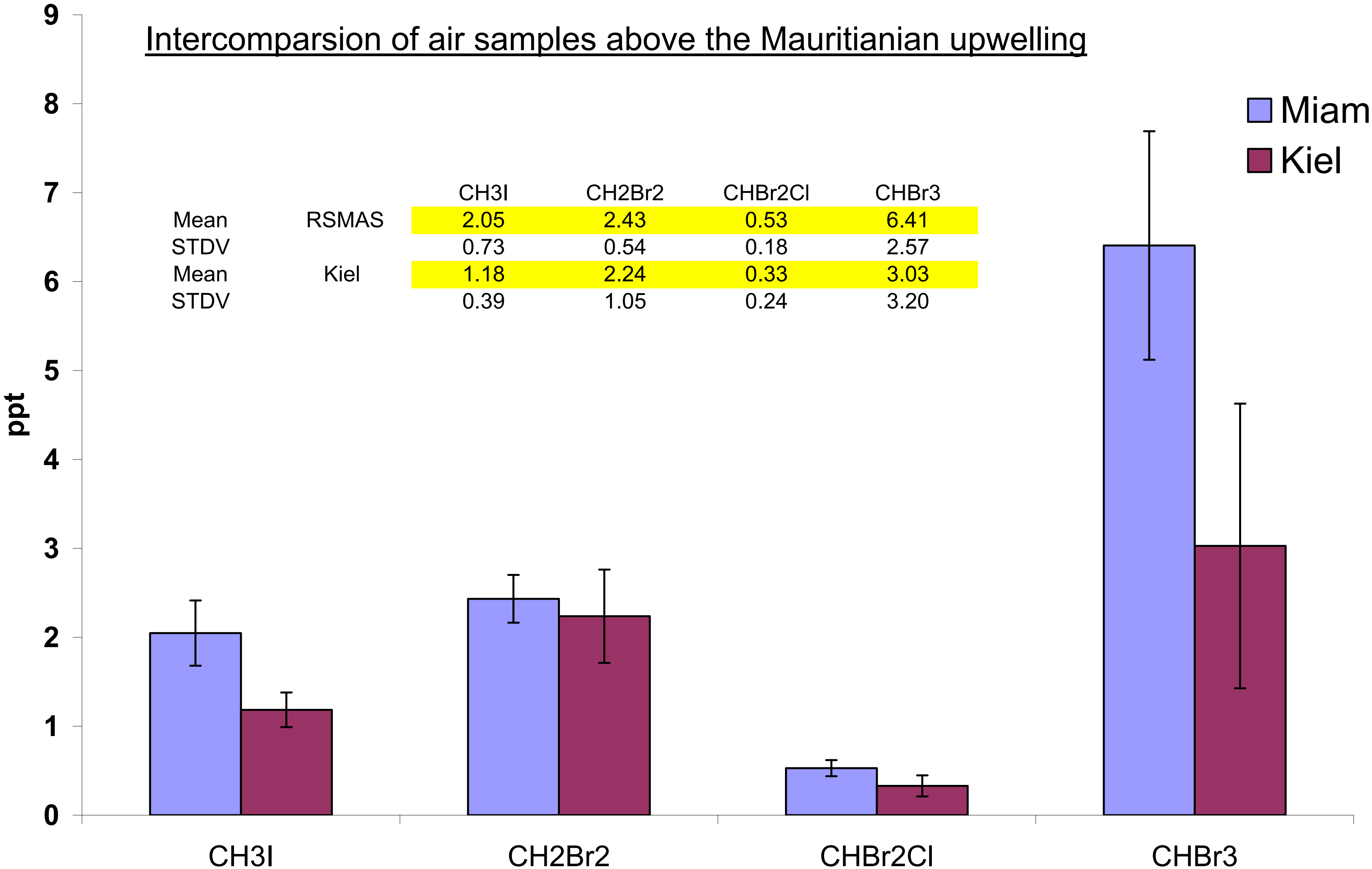


Poseidon 320/1 (March /April 2005) cruise track



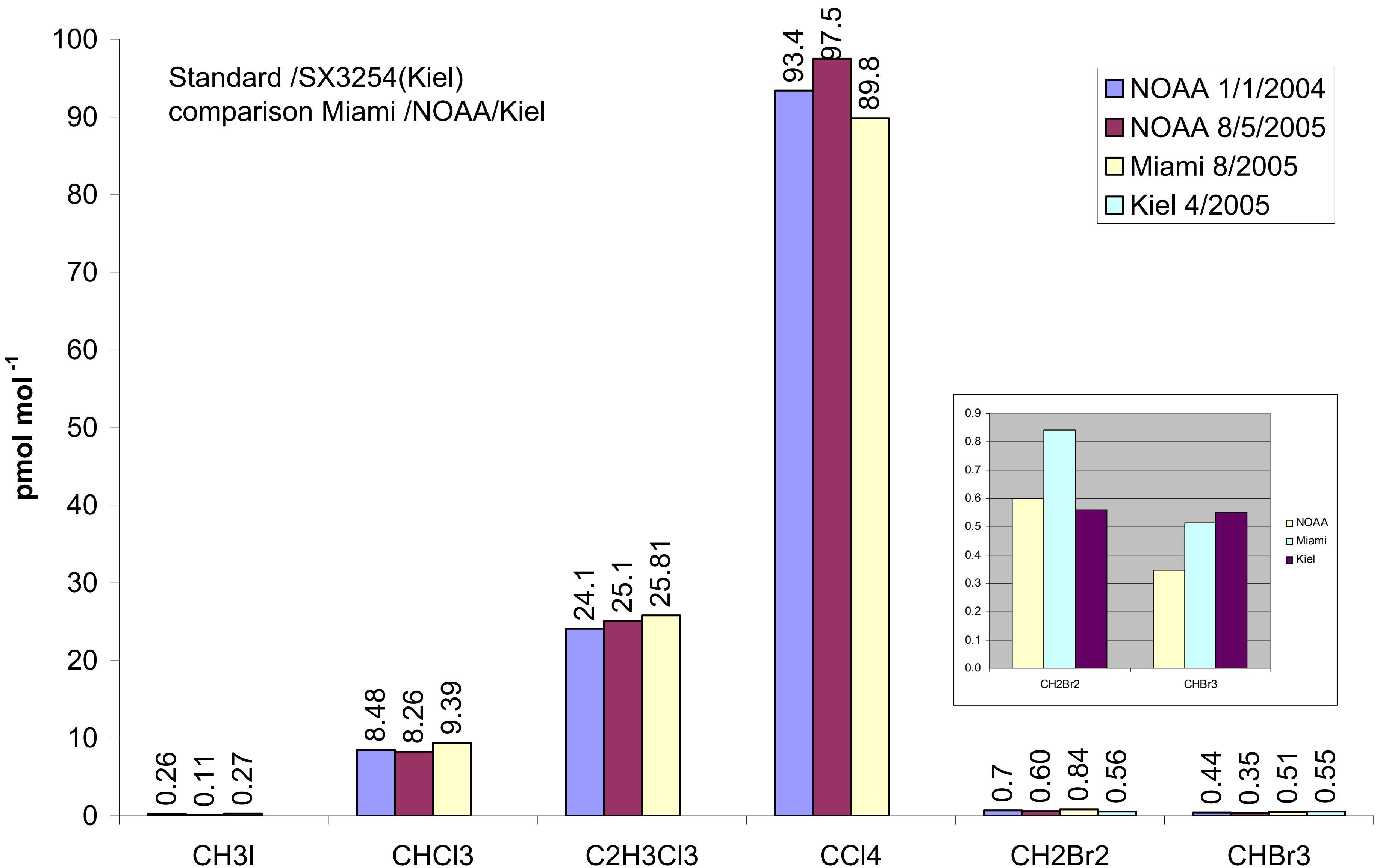


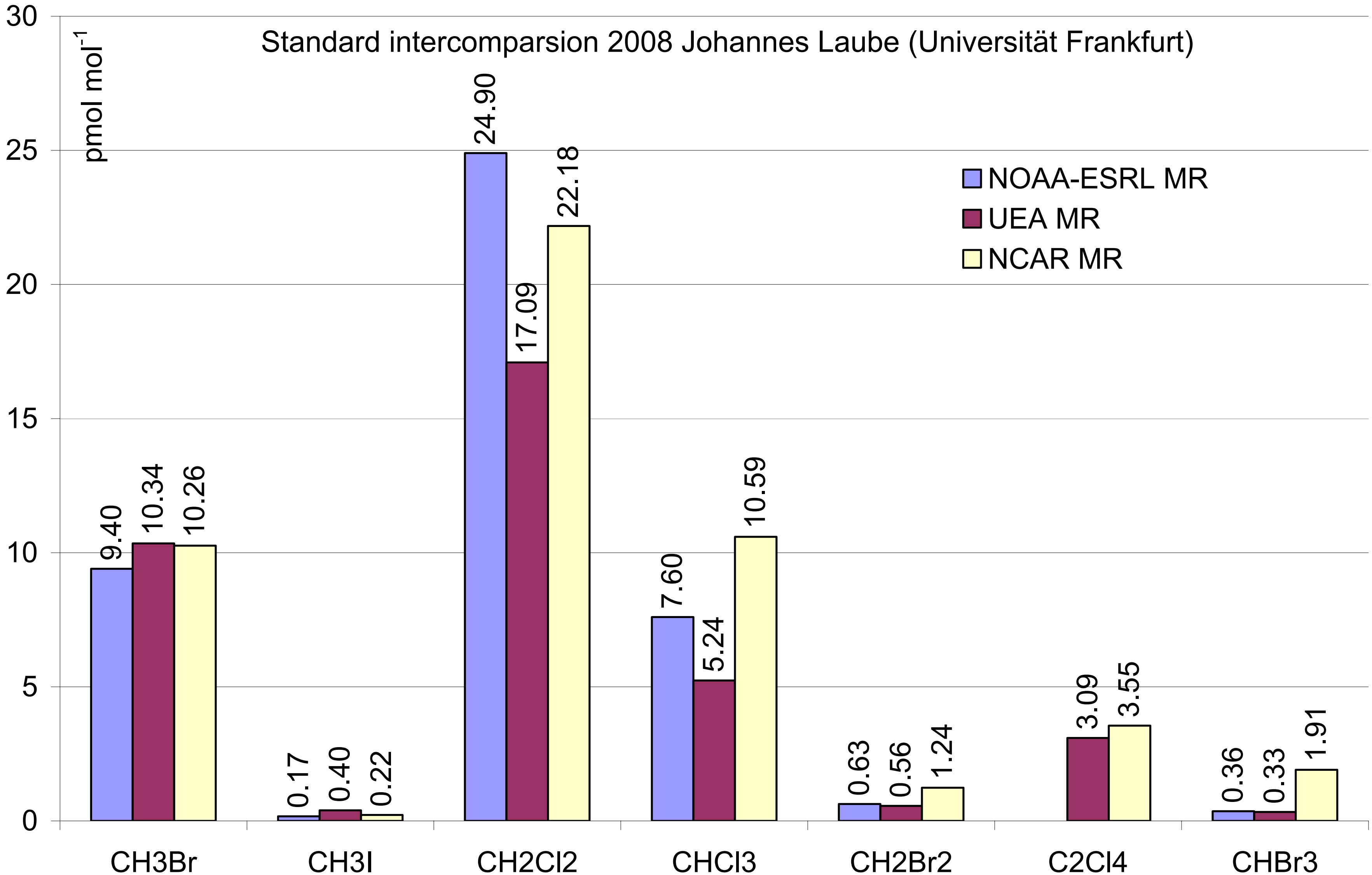
Quack, Atlas et al., 2007



		CH3I	CH2Br2	CHBr2Cl	CHBr3
Mean	RSMAS	2.05	2.43	0.53	6.41
STDV		0.73	0.54	0.18	2.57
Mean	Kiel	1.18	2.24	0.33	3.03
STDV		0.39	1.05	0.24	3.20

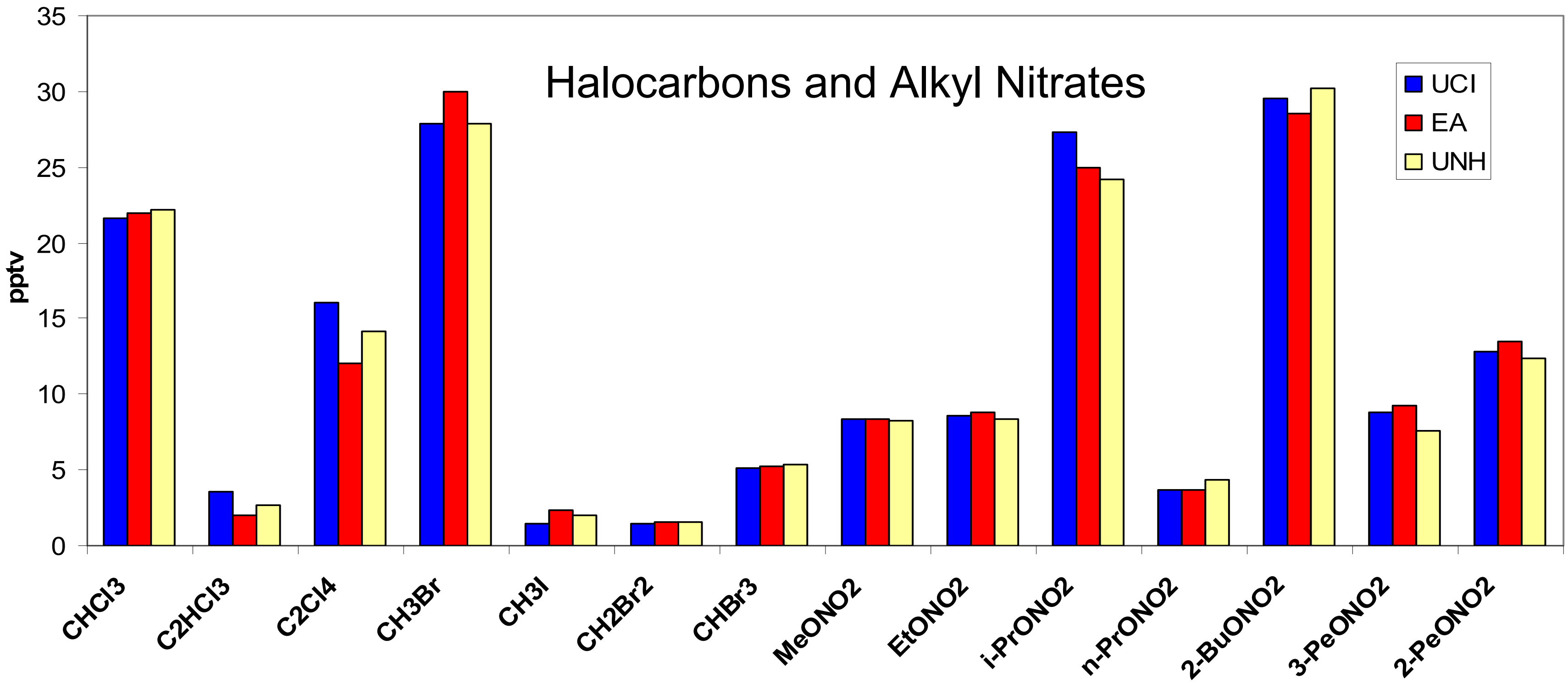
The systematic calibration offset for $CHBr_3$ caused a flux difference:
mean CHBr3 flux (Miami-calibration): 1.050 pmol m2 hr-1)
mean CHBr3 flux (Kiel-calibration): 2600 pmol m2 hr-1)
Quack, Atlas et al., 2007,


Standard /SX3254(Kiel)
comparison Miami /NOAA/Kiel
pmol mol⁻¹
NOAA 1/1/2004
NOAA 8/5/2005
Miami 8/2005
Kiel 4/2005
0.26
0.11
0.27
8.48
8.26
9.39
24.1
25.1
25.81
93.4
97.5
89.8
0.7
0.60
0.84
0.56
0.44
0.35
0.51
0.55
CH3I
CHCl3
C2H3Cl3
CCl4
CH2Br2
CHBr3
NOAA
Miami
Kiel



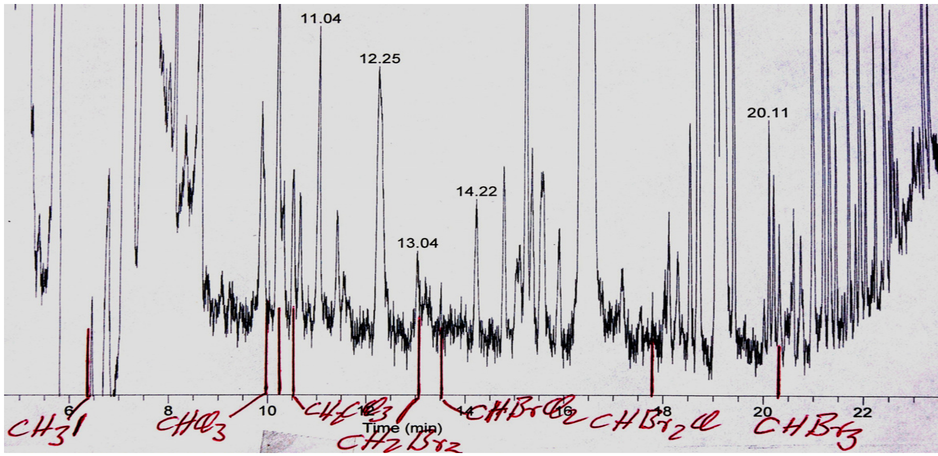
other intercomparisons should be available: Weiss, Oram, Sive ?

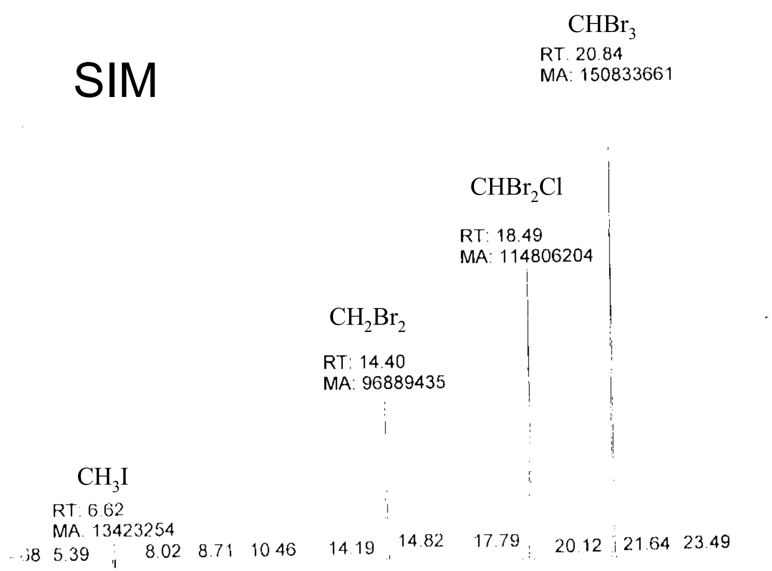
ICARTT Informal VOC Intercomparison (Subset of 51 gases)
Don Blake - UCI



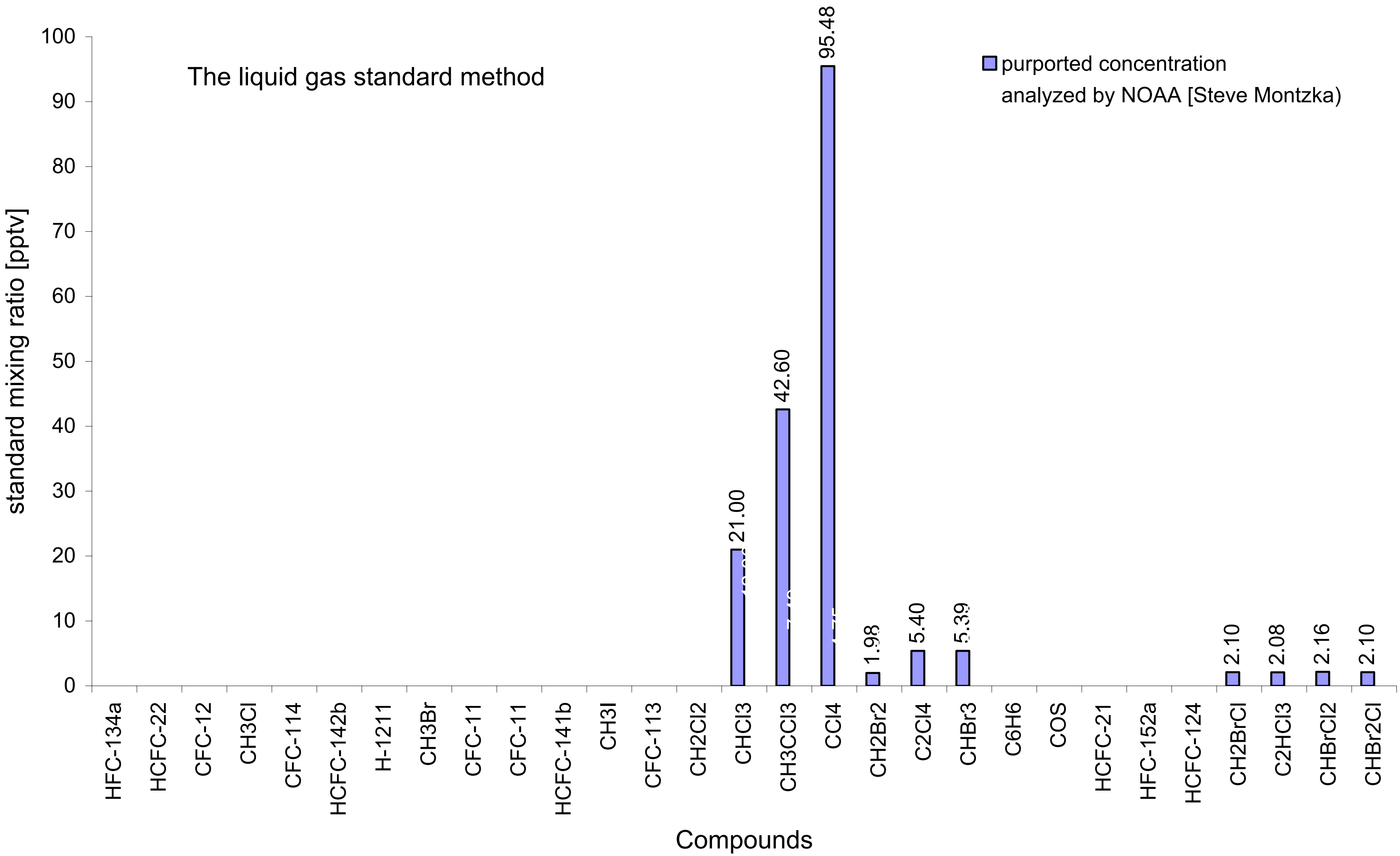
	MW	RT	Ion	RT-Window
Acetaldehyde	44	**5,42**	43/42/26/29/15	**5.0-6.0**
Metanol	32	**5,5**	31/29/30/15	
Iod methan	142	**7,08**	127/141/142/139	**6.0-7.5**
Acetone	58	**7,72**	43/58/59/15	**7.5-8.1**
dichlor methan	88	**7,72**	84/86/49/47/51	
Acetonitril	61	**8,45**	39/40/41/26	**8.1-8.6**
Brom propan	122	**8,77**	122/124/43/41/39	**8.6-9.1**
1,1 dichlor ethan	102	**8,88**	63/65/83/85	
Iod ethan	156	**9,53**	156/127/27/29	**9.1-9.7**
dichlor propan	116	**9,82**	77/79/97/99	
Bromchlor methan	129	**9,96**	130/128/93/95/49/51	**9.7-10.2**
trichlor methan	121	**10,04**	83/85/47/48	
tetrachlor methan	157	**10,3**	117/119/121/82/74	**10.2-10.9**
trichlor ethan	135	**10,4**	97/99/61/63/60	
Formic acid	46	**10,66**	45/46/29/44/30	
2- Iod propan	170	**11,45**	127/170/155/141	**10.9-11.6**
trichlor ethen	133	**11,86**	95/97/130/132/60/62	**11.6-12.2**
Acetic acid	60	**11,96**	43/60/61/28	
dibrom methan	174	**12,54**	93/95/79/81/91	**12.2-13.0**
Bromdichlor methan	164	**12,78**	83/85/47/48/129	
1-Iod propan	160	**12,8**	127/170/129/155/141	
Formaldehyde	30	**13,1**	31/29/28/30/15	**13.0-13.6**
Chlor iod methan	177	**13,28**	178/176/127/141	
2-Iod Butan	184	**14,8**	184/127/155	
tetrachlor ethen	166	**15,02**	94/96/129/131/166/164	**13.6-15.3**
1,1 dichlor propan	114	**15,58**	76/78/41/39	
dibromchlor methan	208	**15,68**	127/129/79/81/131/91/93	**15.3-15.9**
Iod butan	184	**16,04**	127/184/141/155	**15.9-16-3**
dibrom ethan	188	**16,15**	107/109/27/26	
1,1,1,2 tetrachlor ethan	168	**17,3**	131/133/95/60/61/97	**16.3-17.5**
tribrom methan	250	**18,59**	173/171/175/79/81/91/93/94	**17.5-18.8**
di Iod methan	268	**19,45**	127/141/268	**18.8-19.7**
1,1,2,2 tetrachlor ethan	168	**20,13**	83/85/60/61/95/96	**19.7-20.3**
1,2,3-trichlor propan	149	**20,43**	75/77/110/112/61	**20.3-20.7**
di Iod ethan	282	**22,83**	155/127/27	**20.7-23.3**

Total ion chromatogramm of sea water

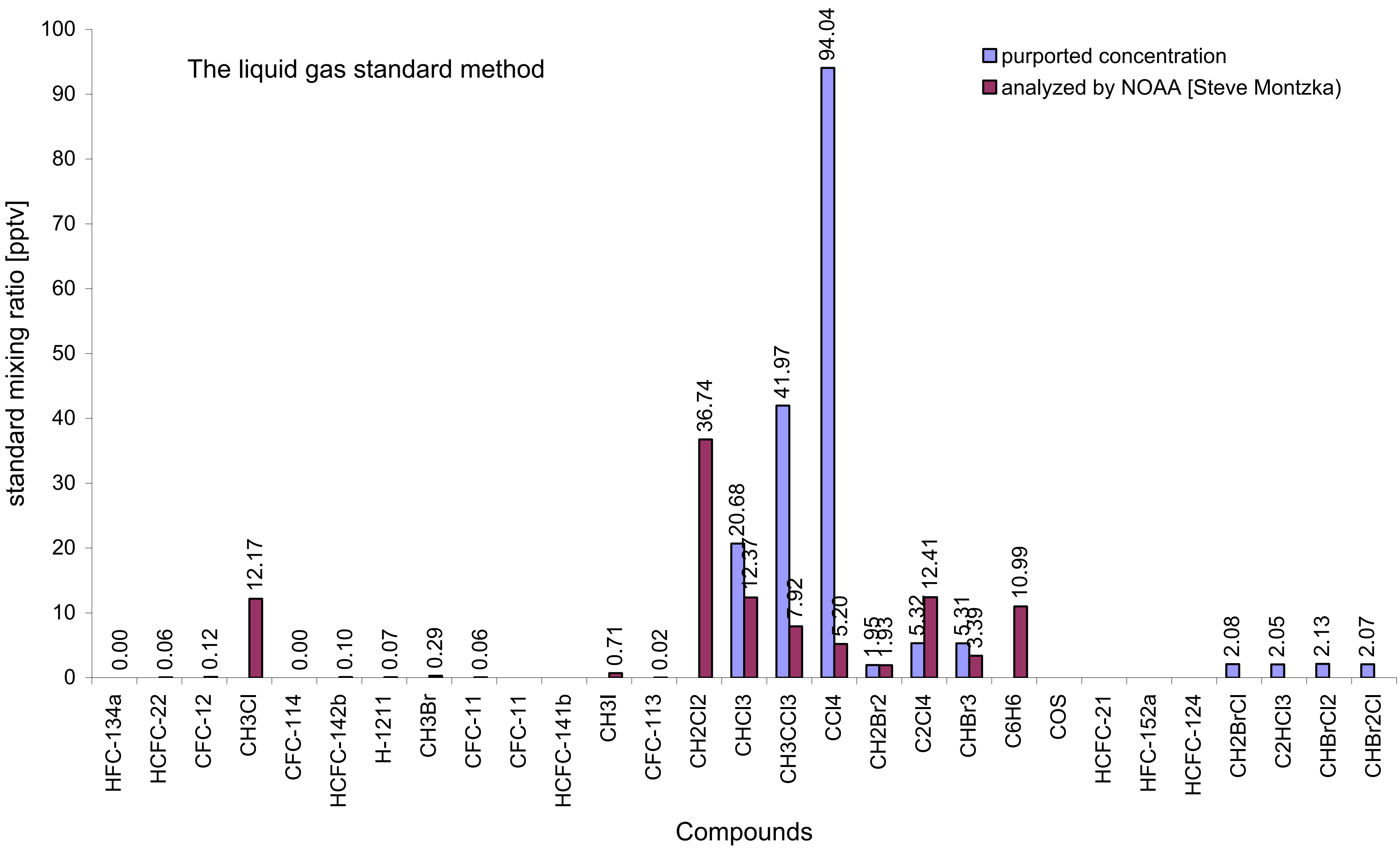




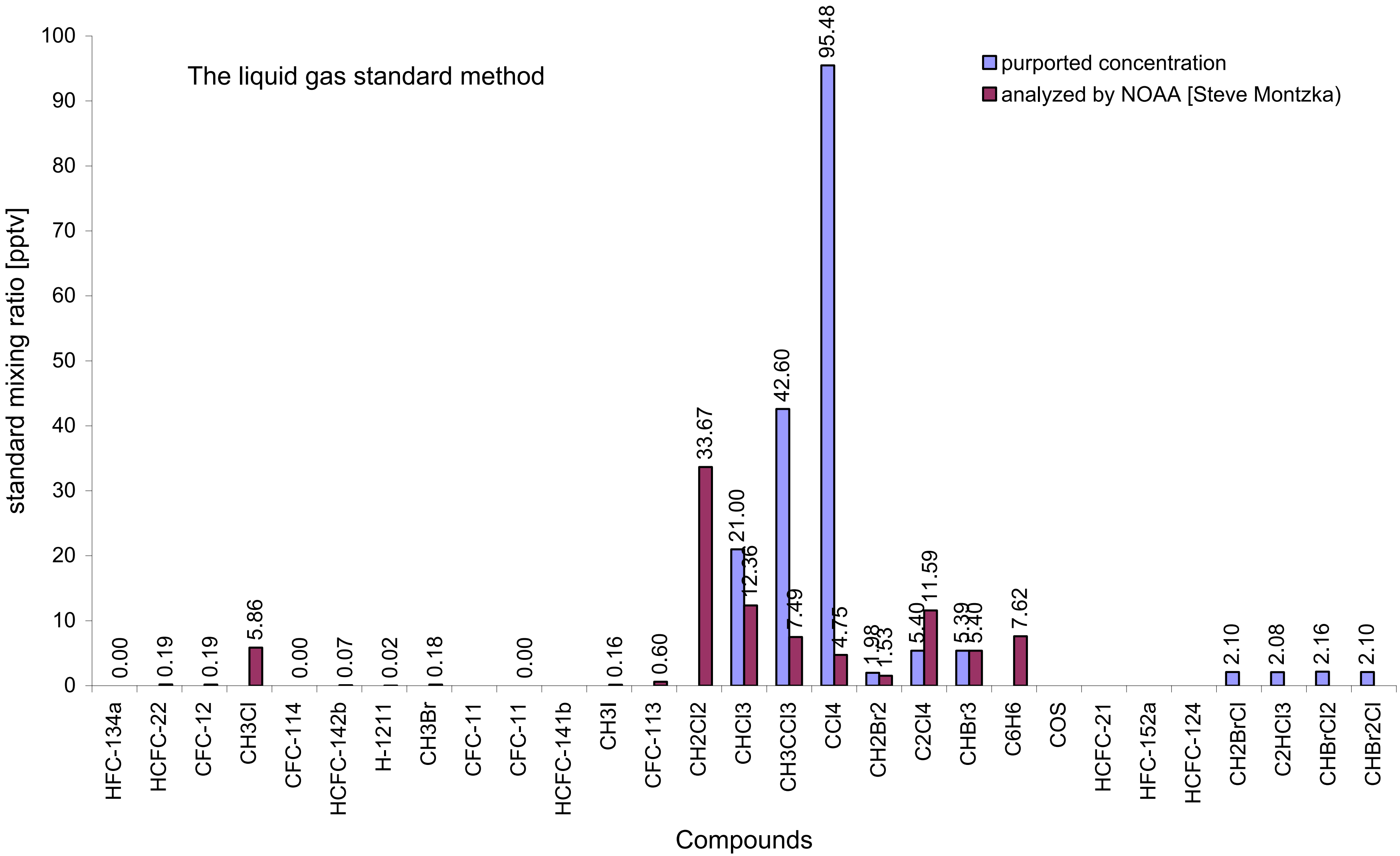
Halocarbons are in pmol, while hydrocarbons coelute in n-µmol, often yielding the same fragments (M, M+1 and M-1 at high concentrations): 43(42,44).. +14...85...127,141,.



The compounds have been diluted in water in advance, injected in a steel tank via a sixport-valve-loop and then pressurized with Nitrogen.



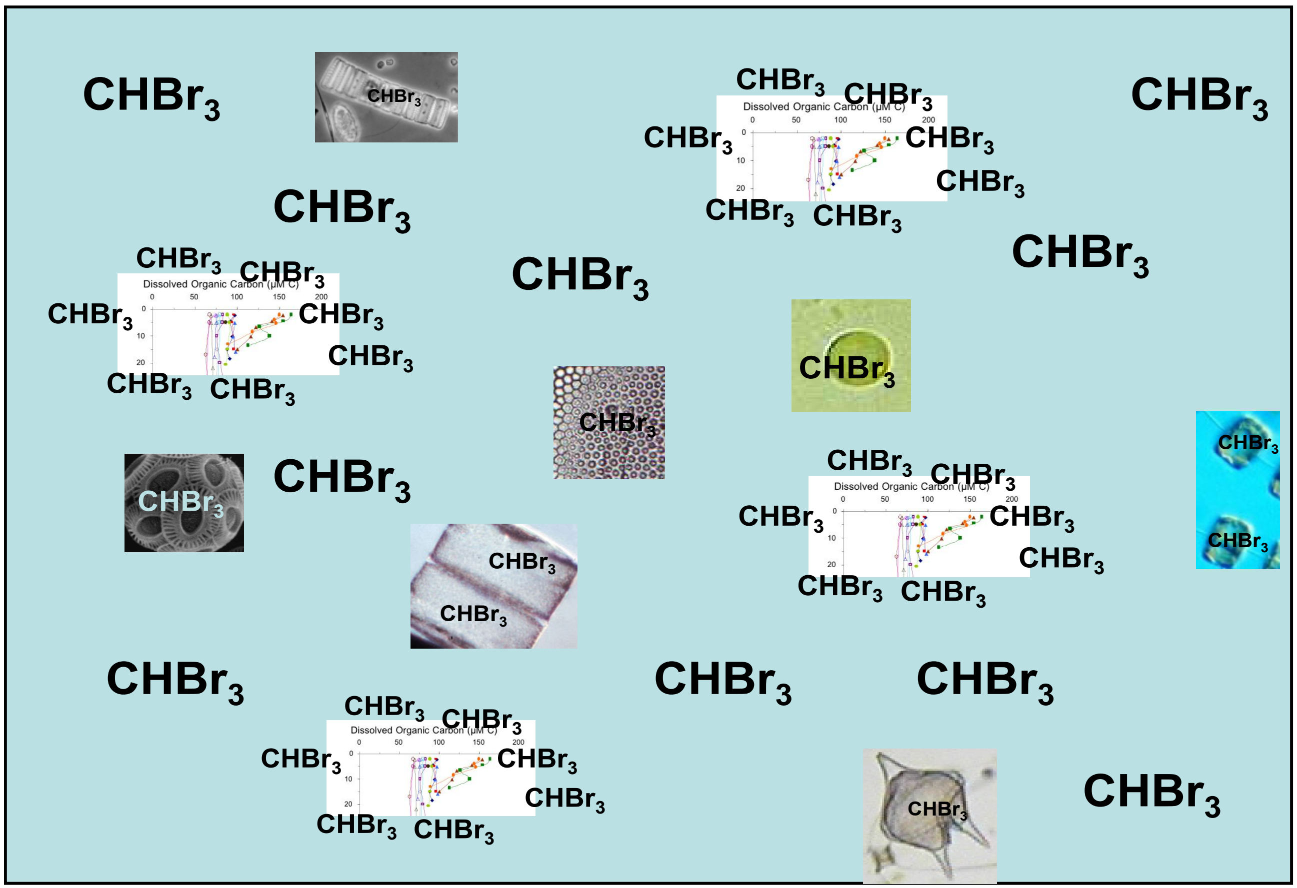
Purported and actual measured compounds and concentrations vary extremst in flask 1.



Purported and actual measured compounds and concentrations also show the same differences in flask 2. (Dilution of compounds had been aided in an ultrasonic bath which possibly has destroyed the compounds)

Sample issues

Distribution of e.g. $CHBr_3$ (CH_3I) and others in a water sample

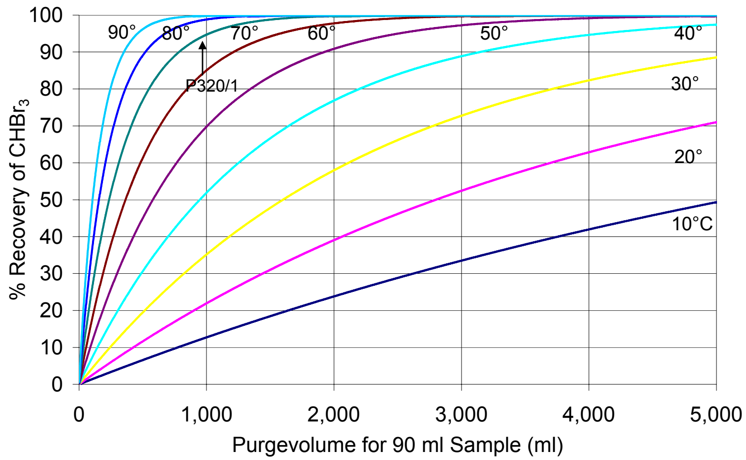


Storage is not possible without conservation (anybody tried?)
After three days in the refrigerator there were >30% differences

Analytical Concerns

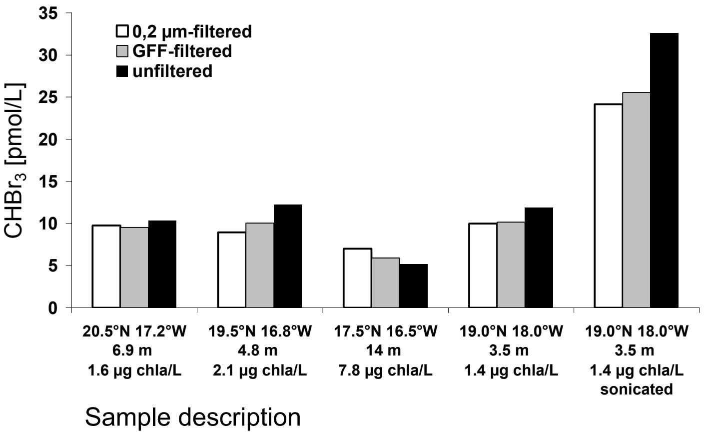
$CHBr_3$ Example

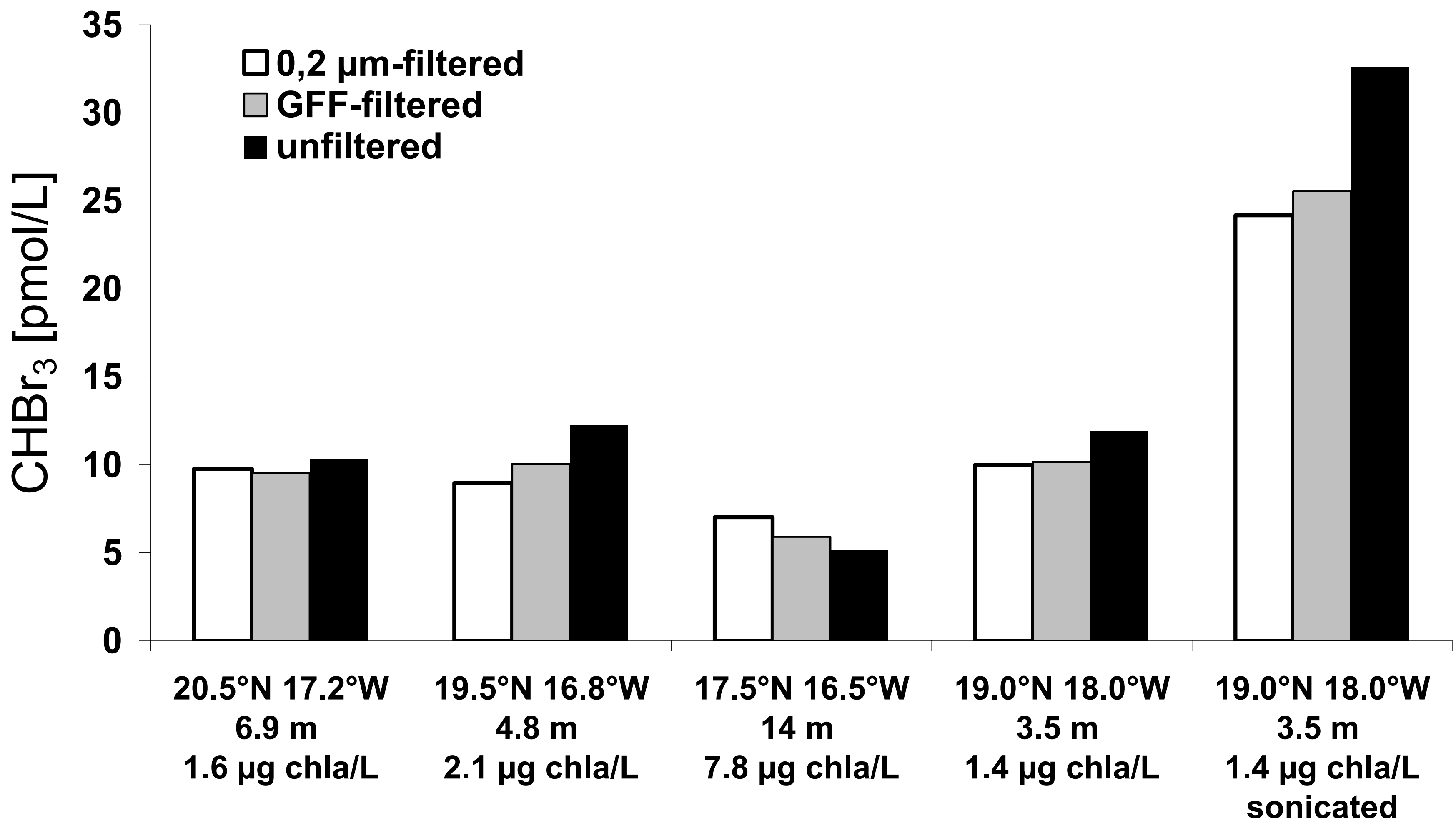
Bromoform is a difficult gas to recover from water samples. Recoveries are influenced by temperature and dessicant used, but also by the composition of the oceanic sample. Optimizing and standardizing techniques would improve comparison of independent data sets.



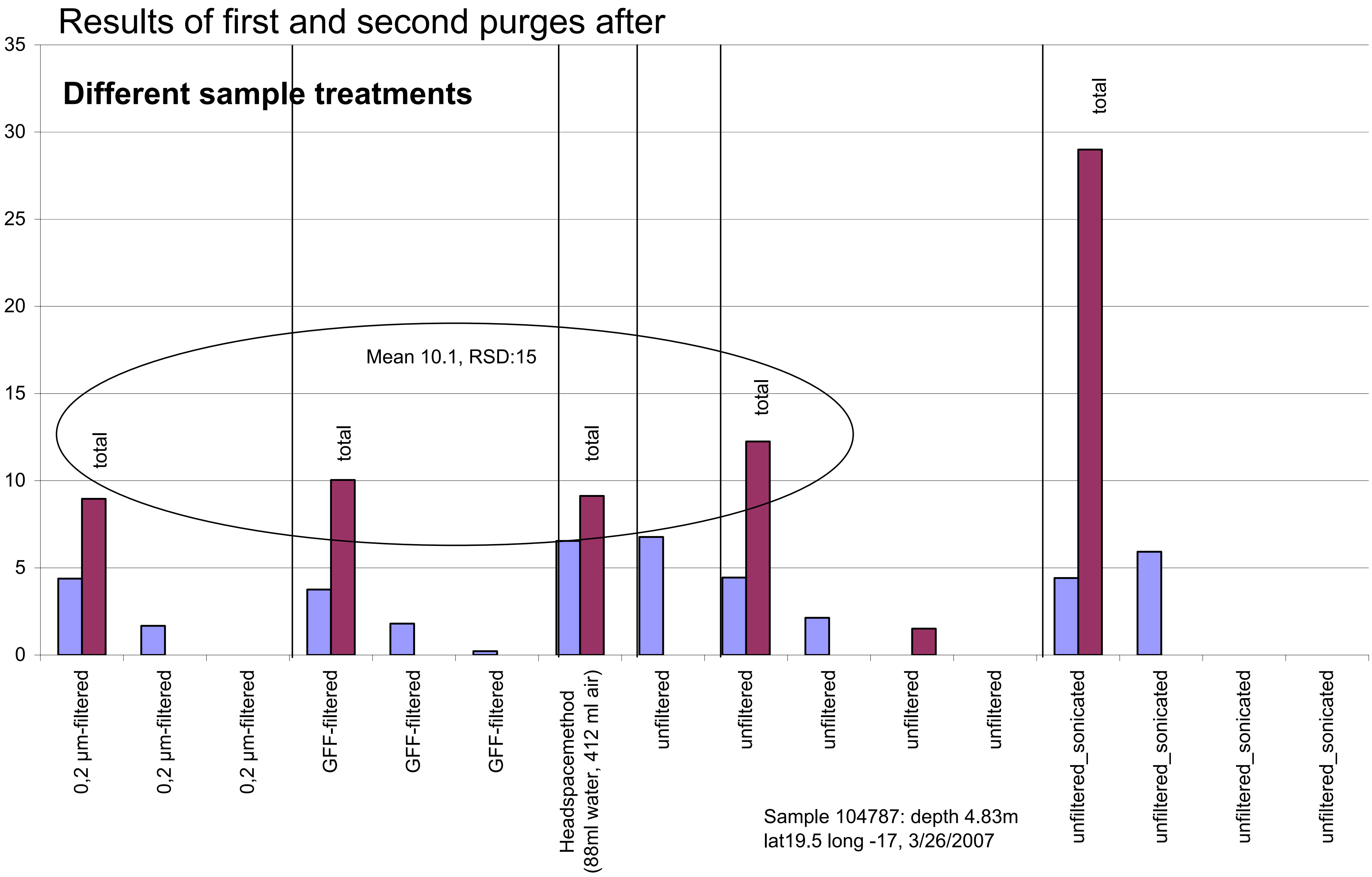
Theoretical recovery rates based on Moore et al. (1995)

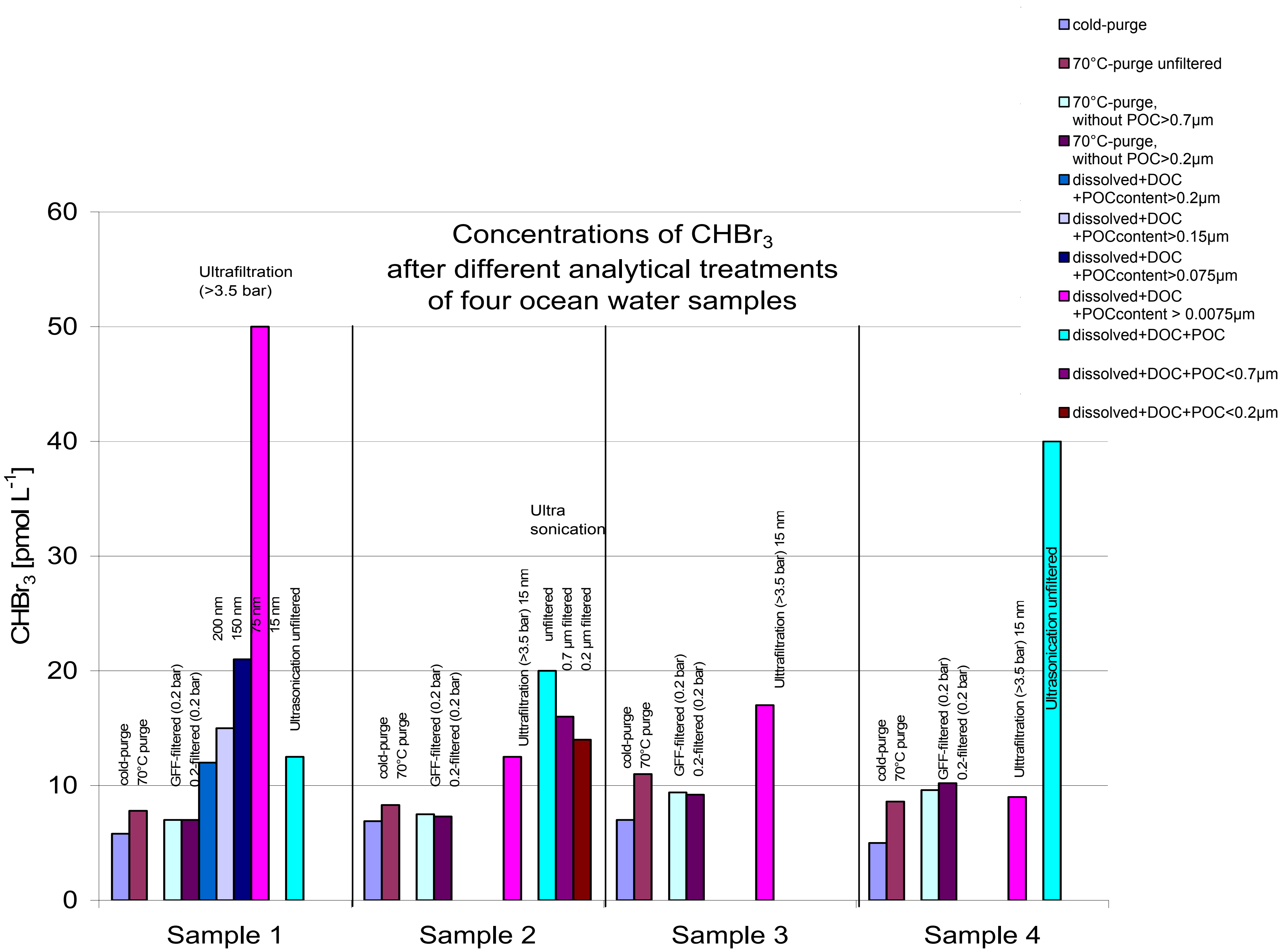
Total $CHBr_3$ in a water sample appears distributed among dissolved, adsorbed, and particulate phases.





The influence of filtration on $CHBr_3$ concentrations in waters samples of various chl a content.


Results of first and second purges after
Different sample treatments
Mean 10.1, RSD:15
total
total
total
total
total
0,2 µm-filtered
0,2 µm-filtered
0,2 µm-filtered
GFF-filtered
GFF-filtered
GFF-filtered
Headspacemethod (88ml water, 412 ml air)
unfiltered
unfiltered
unfiltered
unfiltered
unfiltered
unfiltered_sonicated
unfiltered_sonicated
unfiltered_sonicated
unfiltered_sonicated
Sample 104787: depth 4.83m
lat19.5 long -17, 3/26/2007
35
30
25
20
15
10
5
0



Concentrations of $CHBr_3$
after different analytical treatments
of four ocean water samples
$CHBr_3$ [pmol L^{-1}]
0
10
20
30
40
50
60
Sample 1
Sample 2
Sample 3
Sample 4
Ultrafiltration
(>3.5 bar)
Ultra
sonication
cold-purge
70°C purge
GFF-filtered (0.2 bar)
0.2-filtered (0.2 bar)
200 nm
150 nm
75 nm
15 nm
Ultrasonication unfiltered
Ultrafiltration (>3.5 bar) 15 nm
unfiltered
0.7 µm filtered
0.2 µm filtered
Ultrasonication unfiltered
cold-purge
70°C-purge unfiltered
70°C-purge,
without POC>0.7µm
70°C-purge,
without POC>0.2µm
dissolved+DOC
+POCcontent>0.2µm
dissolved+DOC
+POCcontent>0.15µm
dissolved+DOC
+POCcontent>0.075µm
dissolved+DOC
+POCcontent > 0.0075µm
dissolved+DOC+POC
dissolved+DOC+POC<0.7µm
dissolved+DOC+POC<0.2µm

Practical considerations (some issues from Jim Butler).

What is the most reliable standard?
Are perm tubes reliable? (Issues involved, e.g.)
Are liquids reliable? (e.g.: degradation, longterm stabitlity)
What is the repeatability?
Are cylinders reliable? (e.g.: degradation, longterm stabitlity)

Is the analytics firm? (e.g.: coelutions)

Can the data of different analytical methods be compared? (e.g.:equilibrator, purge and trap)

How does one make a comparison between someone who is using liquid standards and someone who uses cylinders?

How to best intercalibrate between atmospheric and ocean analysis?

Also, how to deal with super-short-lived compounds?

How to deal with compounds that are analyzed differently?

Intercomparison is the short-term answer. Intercalibration, combined with intercomparison is a long-term answer, but in the end, how do we make this happen?