UEA update on halocarbon observations: 'new' and old gases, plus isotopes

INGOS meeting

Florence

15/10/2014

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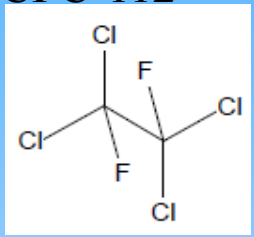
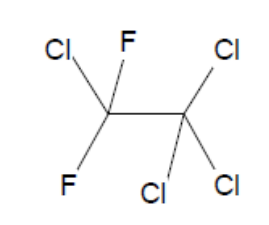
Update on 'new' CFCs & HCFC

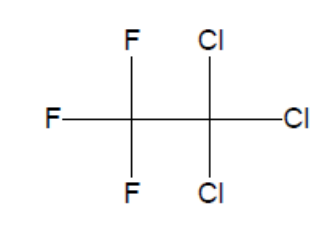
CFC-112



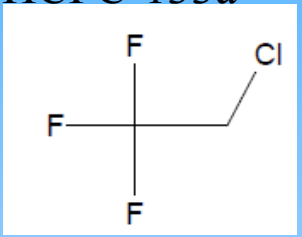
CFC-112a

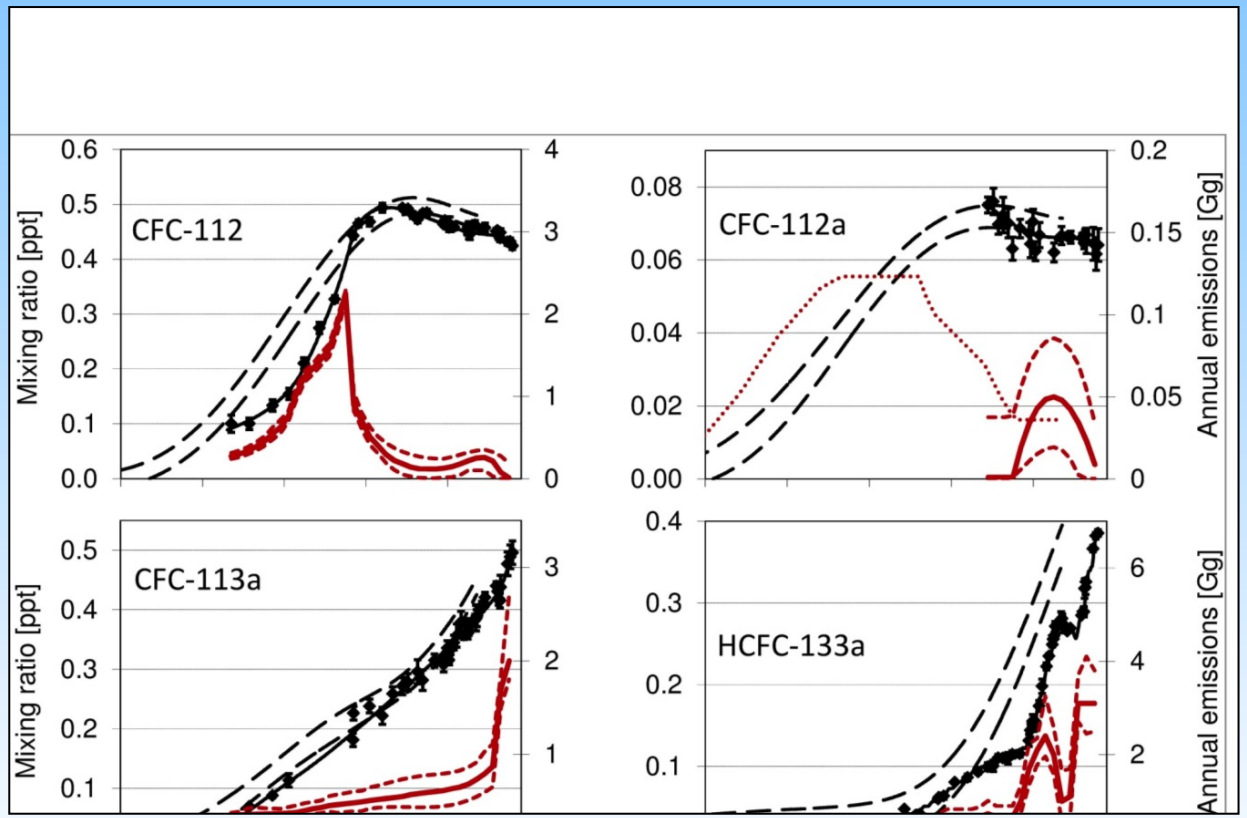


CFC-113a



HCFC-133a





- Manuscript published in Nature GeoScience in March 2014

Update on 'new' CFCs & HCFC

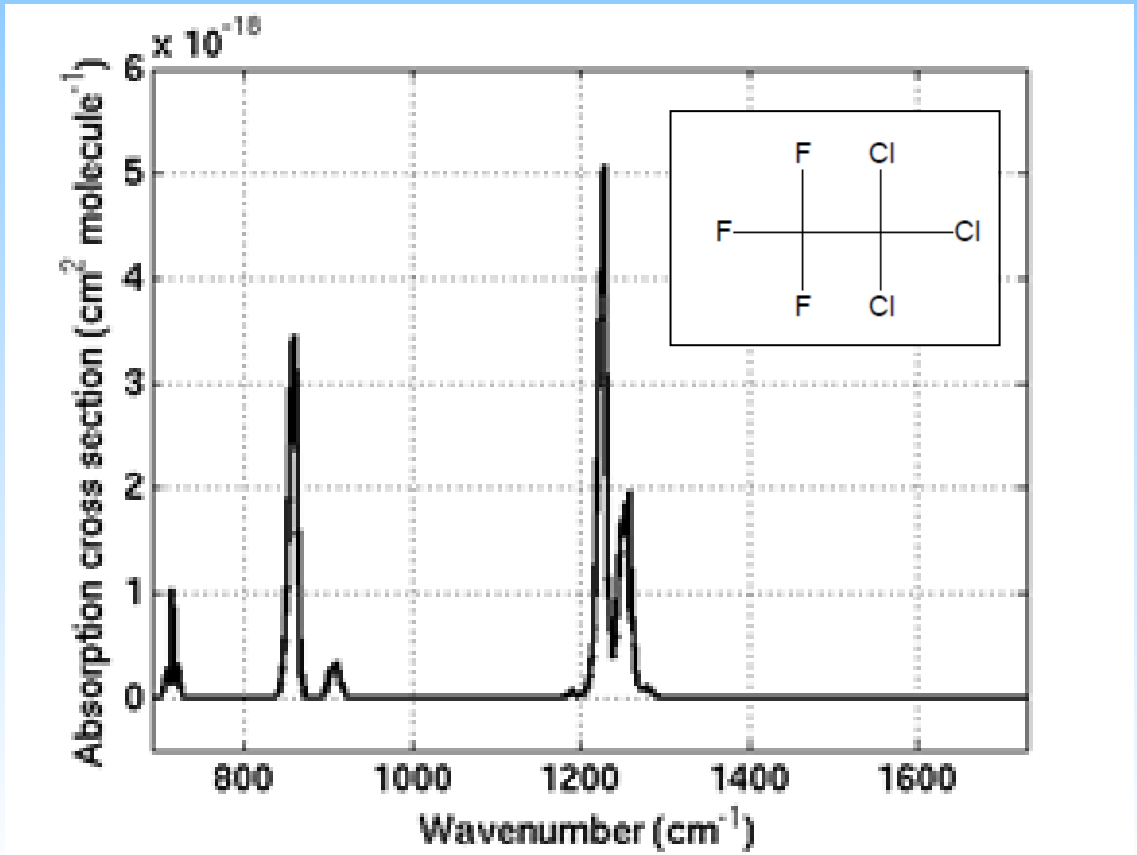
CFC-112 CFC-112a CFC-113a HCFC-133a

Media coverage:

Mysterious new man-made gases pose threat to ozone layer, ***BBC News***
Four banned ozone depleters detected in the atmosphere, ***New Scientist***
Four new gases found in ozone layer, ***Global News***
Four new gases that harm ozone layer found, despite bans, ***Thomson Reuters***
Four New Mystery Gases Are Harming the Ozone Layer, ***Science AAAS News***
Four new ozone depleting gases in atmosphere: scientists, ***Times LIVE***
Four new ozone-depleting gases detected, ***ABC News***
Four New Ozone-Depleting Gases Found in Atmosphere, ***Wall Street Journal***
New ozone-killing chemicals found, ***The Guardian***
Vier Ozonkiller neu nachgewiesen, ***Tagesanzeiger***
Neue Ozonkiller in Atmosphäre gefunden, ***ORF***
New gases threat to ozone layer, ***Gulf News***
New ozone-depleting gas discovered in the atmosphere, ***Planet Earth Online***
New Ozone-Killing Gases Found in Atmosphere, ***Discovery News***
Forscher weisen Ozon-Killer erstmals nach, ***Die Welt***
Quatre nouveaux gaz nocifs pour la couche d'ozone détectés…, ***Le Monde***
New gases attack ozone layer, ***Financial Times***
Plus Radio & TV interviews, e.g. for BBC Radio, ITV, CBC, Voice of Russia

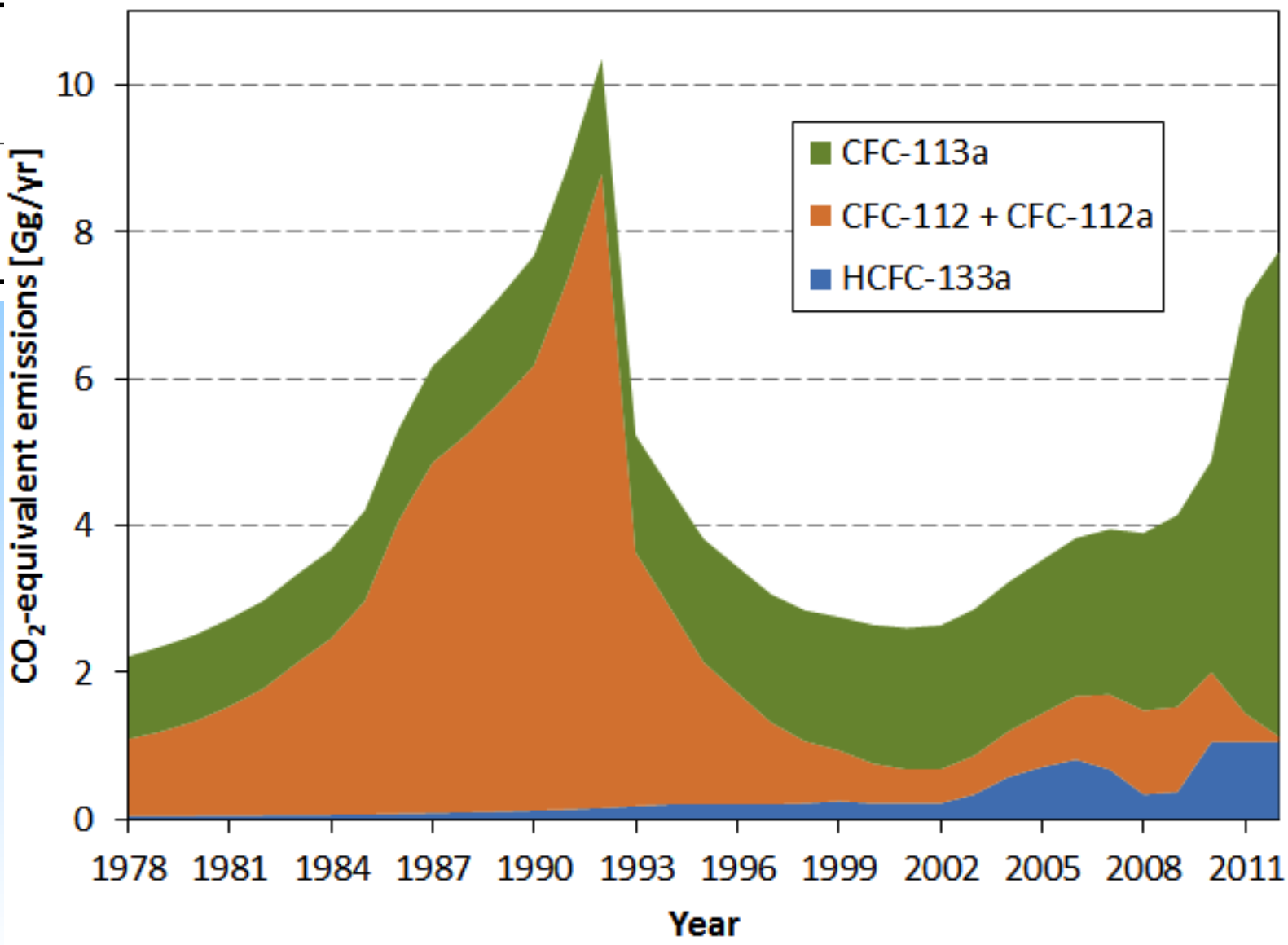
Update on 'new' CFCs & HCFC: GWPs

- **Also published this year**: M. Etminan, E. J. Highwood, J. C. Laube, R. McPheat, G. Marston, K. P. Shine and K. M. Smith., Infrared Absorption Spectra, Radiative Efficiencies, and Global Warming Potentials of Newly-Detected Halogenated Compounds: CFC-113a, CFC-112 and HCFC-133a, Atmosphere 5, 473, 2014.



Update on 'new' CFCs & HCFC: CO_2-eq. emissions

Gas
CFC-113a
CFC-112
HCFC-133a



More 'new' gases

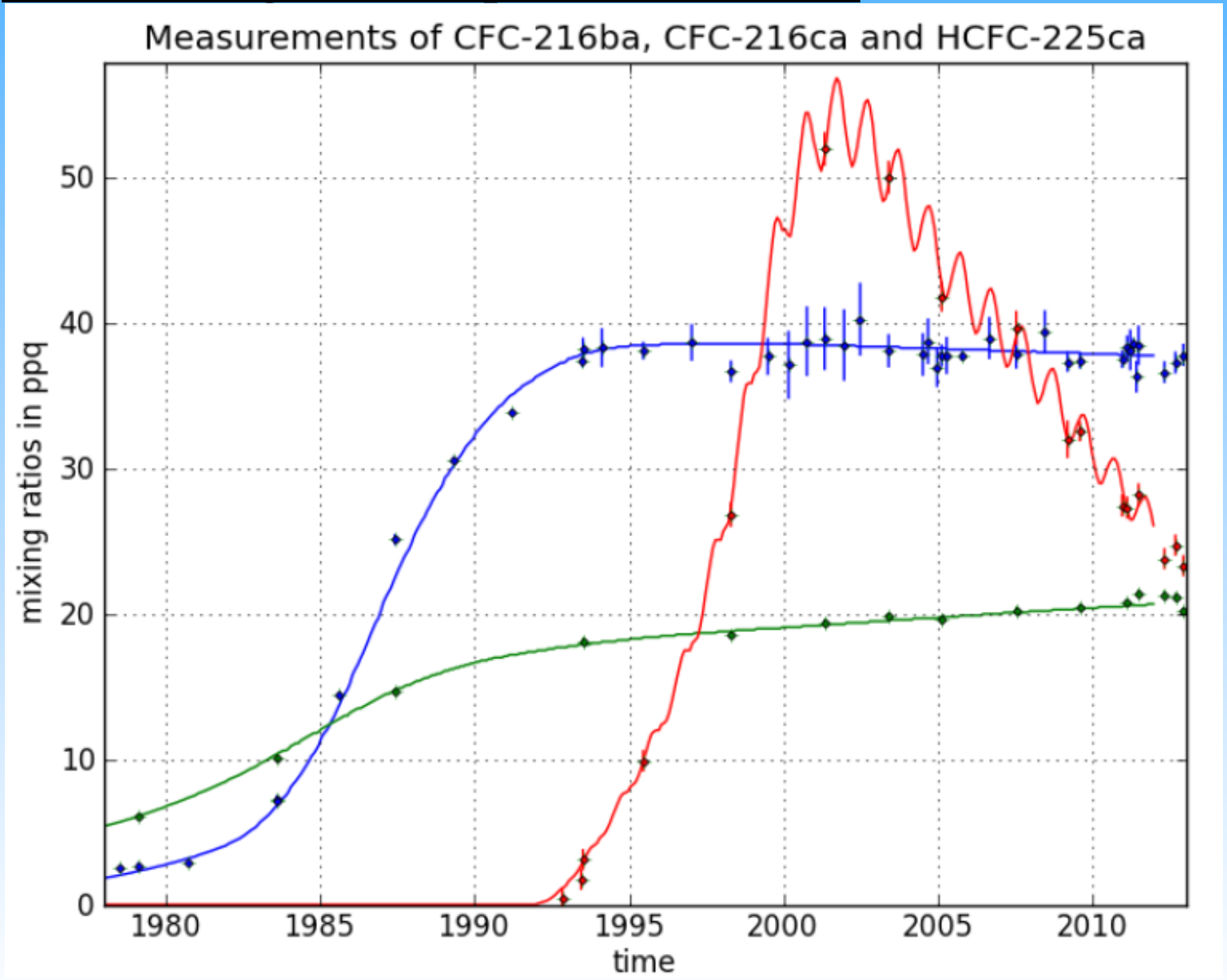
- **CFC-216ba: 1,2-Dichlorohexafluoropropane**
- **CFC-216ca: 1,3-Dichlorohexafluoropropane**
- **HCFC-225ca: 3,3-Dichloropentafluoropropane**

- Master thesis of Corinna Kloss (2013):
  - Calibration of CFC-216ca and HCFC-225ca
  - limited Cape Grim record (all)

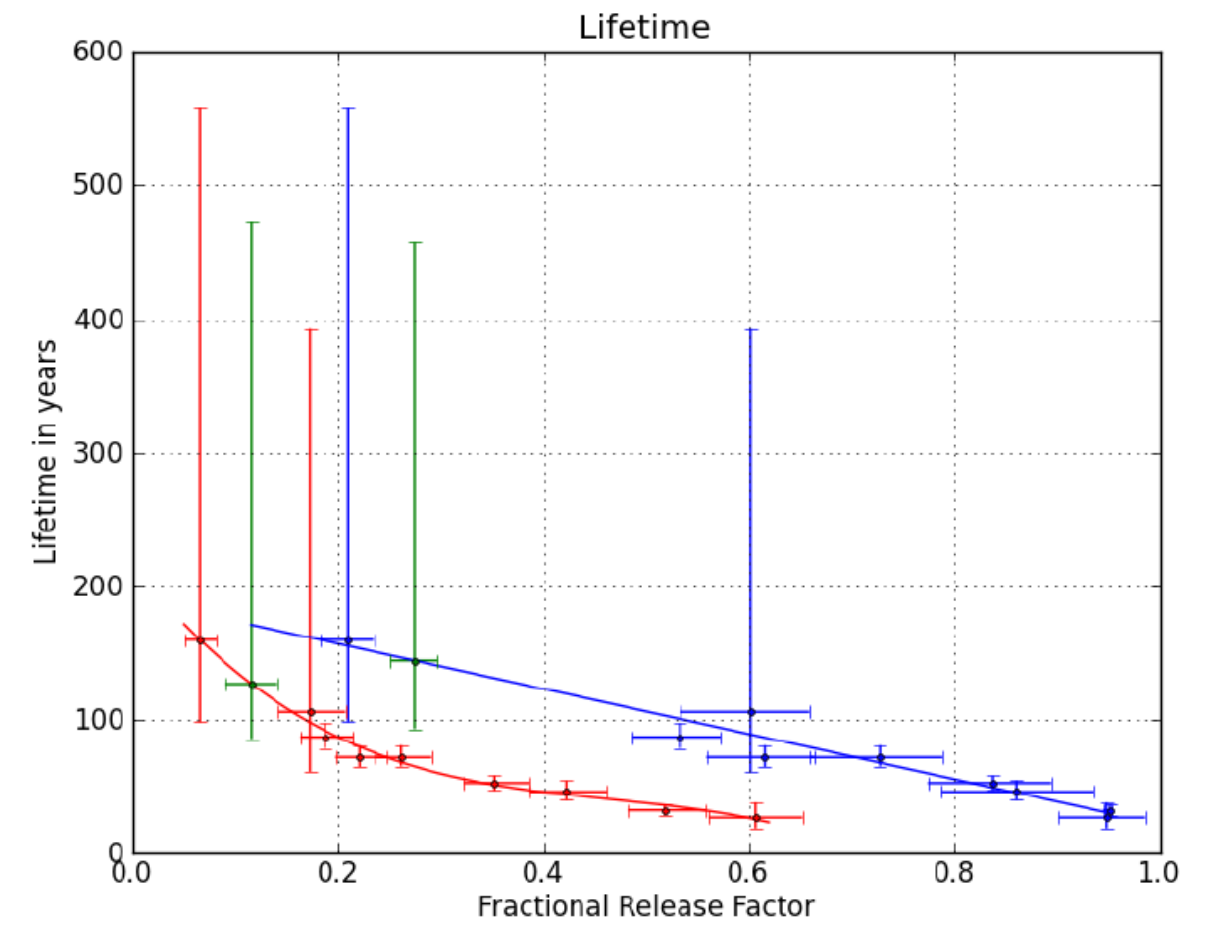
- Additional data sets: Stratospheric (216ba only), CARIBIC UT/LS data (all)

- **Also published this year**: Kloss, C, Newland, MJ, Oram, DE, Fraser, PJ, Brenninkmeijer, CAM., Röckmann, T, and Laube, JC (2014) Atmospheric Abundances, trends and emissions of CFC-216ba, CFC-216ca and HCFC-225ca, Atmosphere 5, pp. 420-434.

More 'new' gases – Cape Grim histories



More 'new' gases: CFC-216ba lifetime

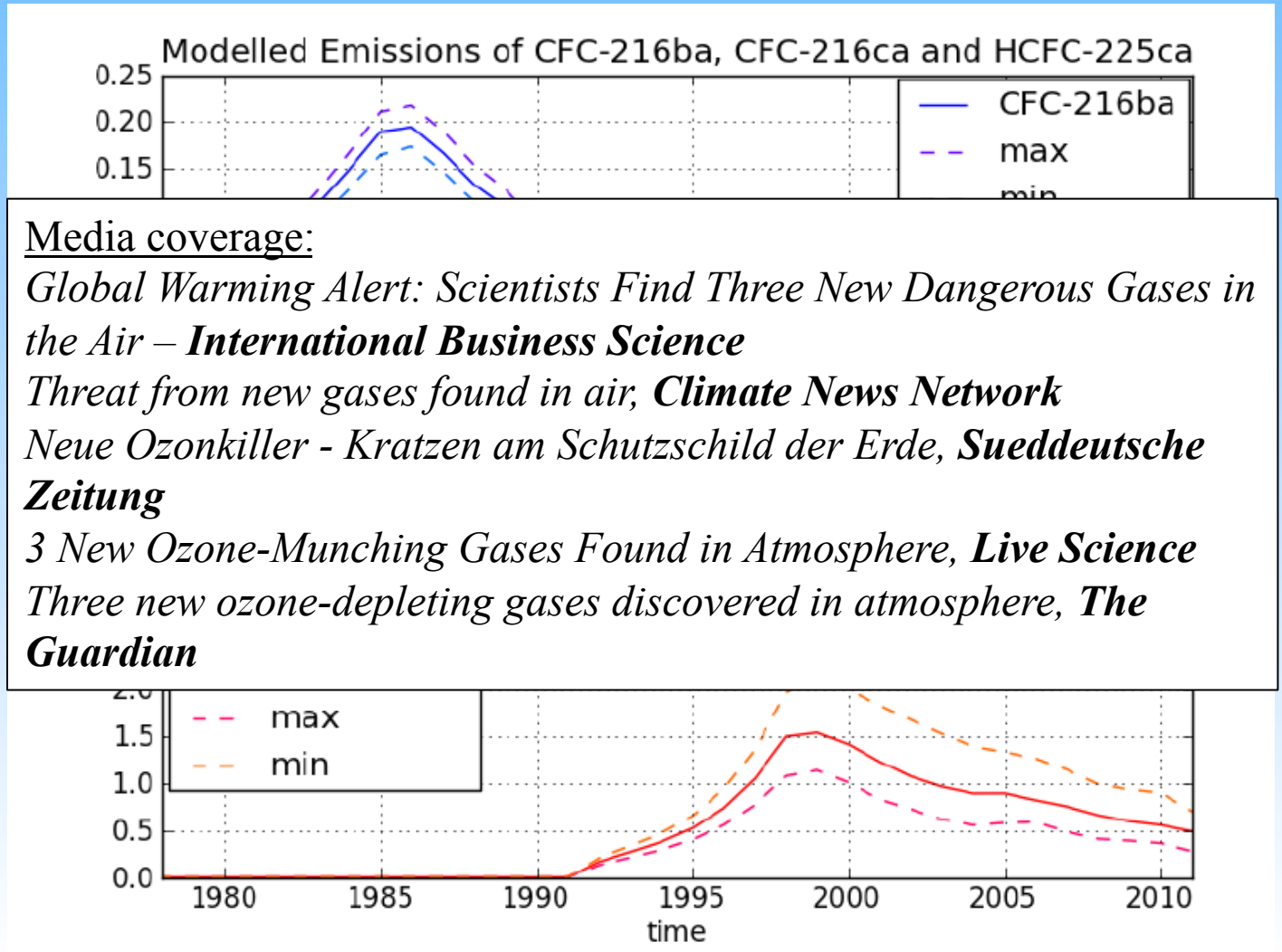


- Estimation method via Fractional Release Factors (FRF) in comparison with compounds with known stratospheric lifetimes
- CFC-216ba lifetime: 135 (85-472) years (same assumed for 216ca isomer)

Emissions: CFC-216ba, CFC-216ca, and HCFC-225ca

- HCFC-225ca: - lifetime known: 2.7 years (Zerefos et al., 2009)

  - still significant emissions according to 2D model



Media coverage:

Global Warming Alert: Scientists Find Three New Dangerous Gases in the Air – ***International Business Science***

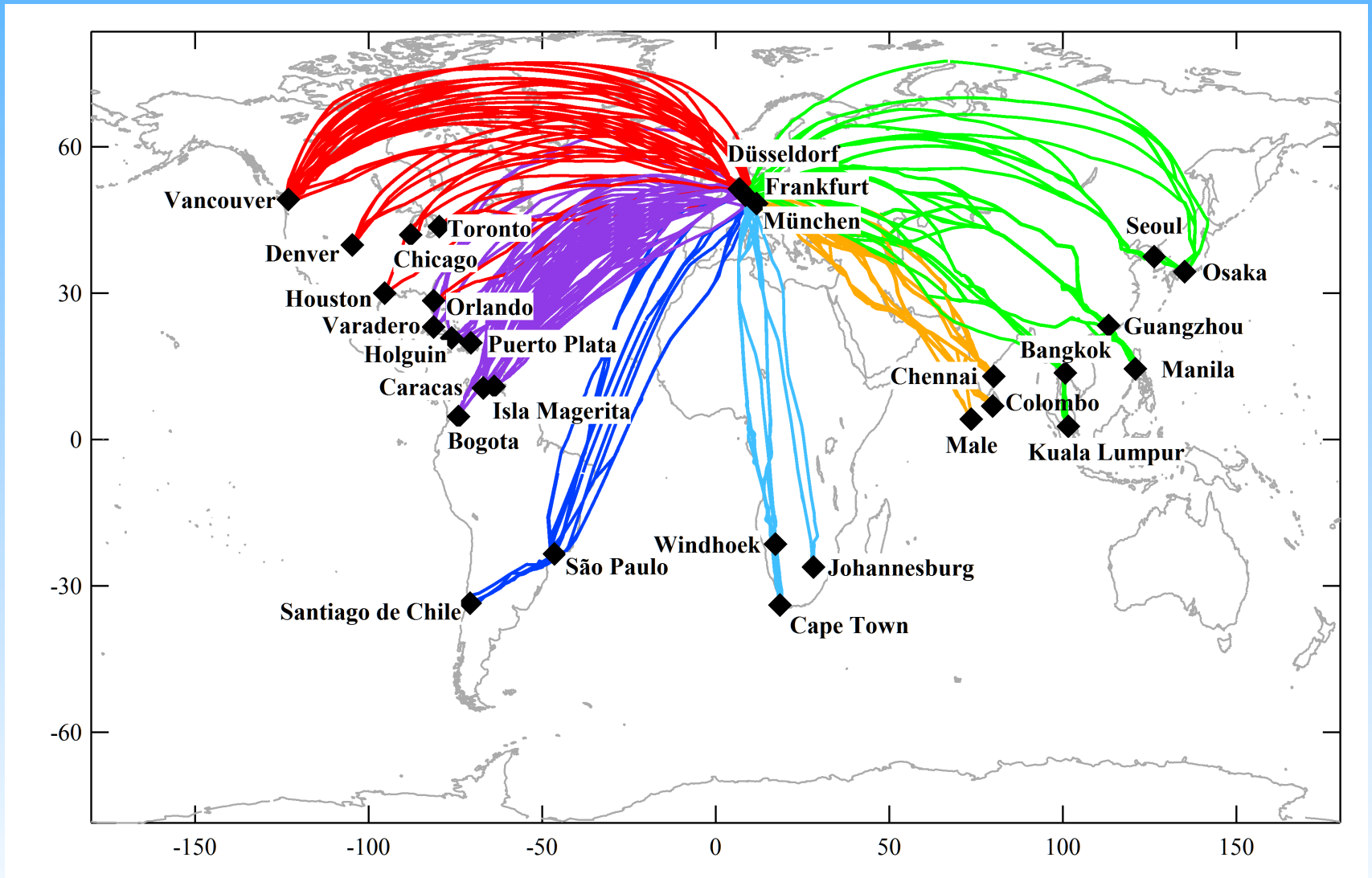
Threat from new gases found in air, ***Climate News Network***

Neue Ozonkiller - Kratzen am Schutzschild der Erde, ***Sueddeutsche Zeitung***

3 New Ozone-Munching Gases Found in Atmosphere, ***Live Science***

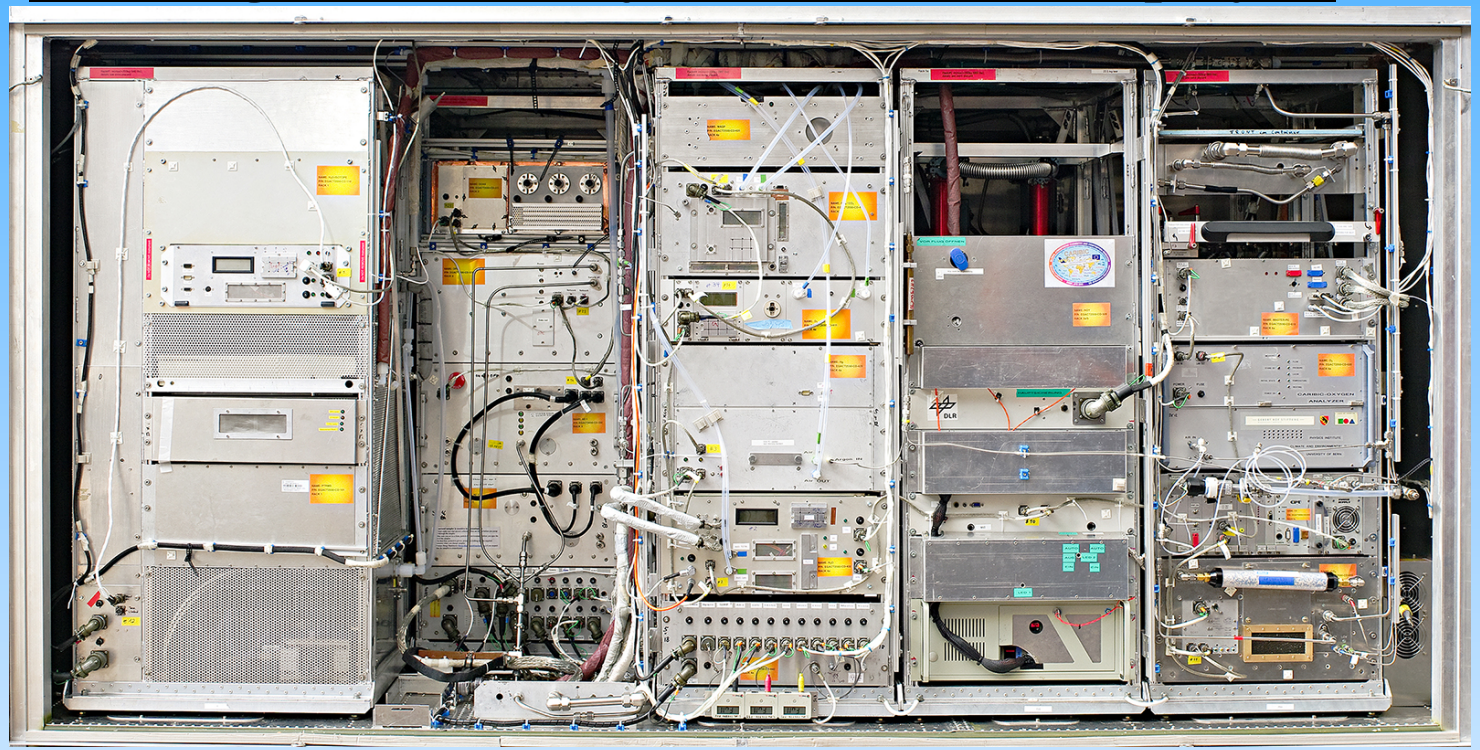
Three new ozone-depleting gases discovered in atmosphere, ***The Guardian***

Related gases: Results from the CARIBIC project



Air samples collected since 1998

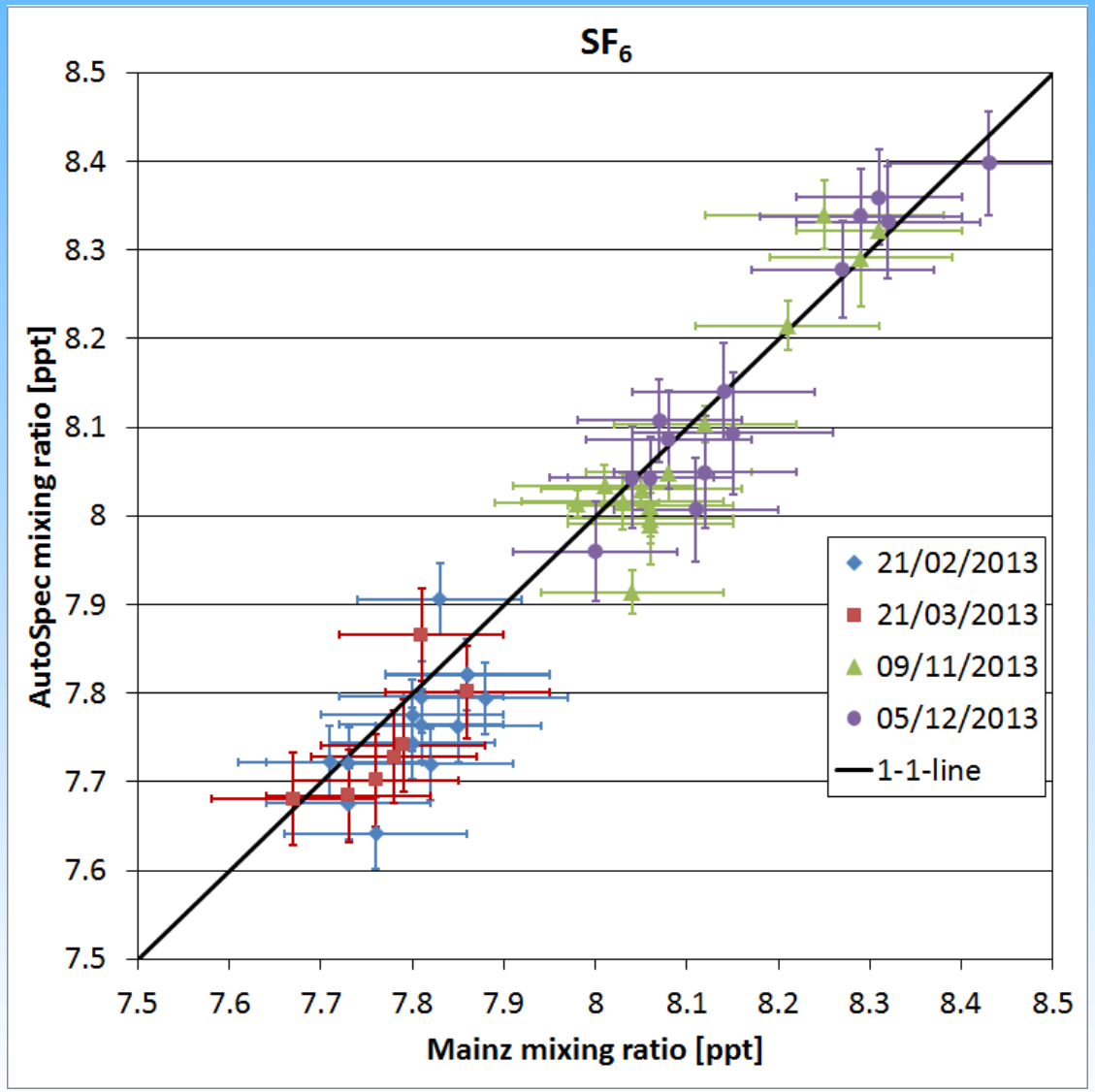
Related gases: Results from the CARIBIC project



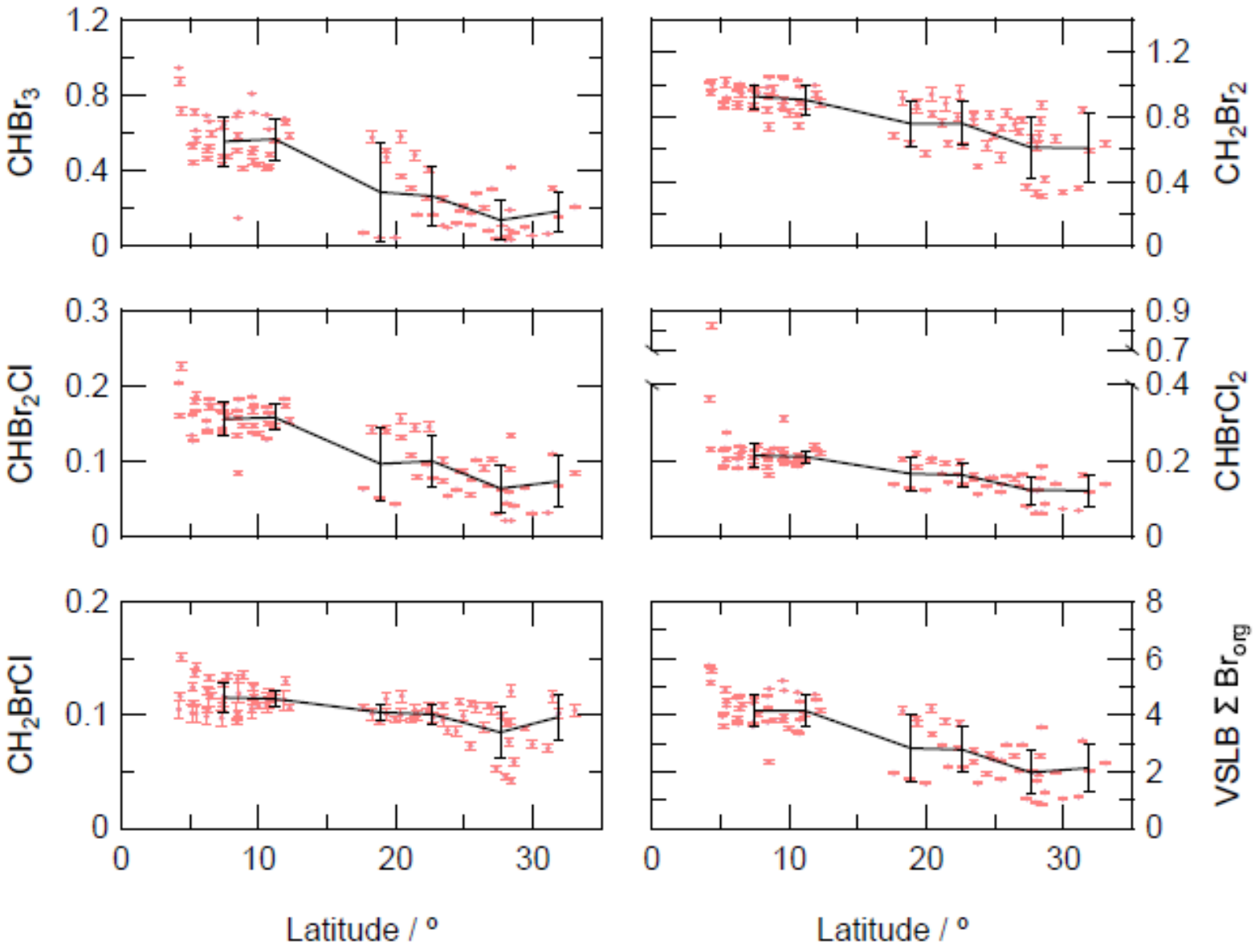
Two recent UEA publications on halocarbons from whole-air-sampler:

1) Wisher et al., 2014, ACP, **Very short-lived bromomethanes** measured by the CARIBIC observatory over the North Atlantic, Africa and Southeast Asia during 2009–2013
2) Leedham et al., 2014, ACPD, Increasing concentrations of **dichloromethane** inferred from CARIBIC air samples collected 1998–2012

Quality assurance within CARIBIC



Related gases: Short-lived bromocarbons

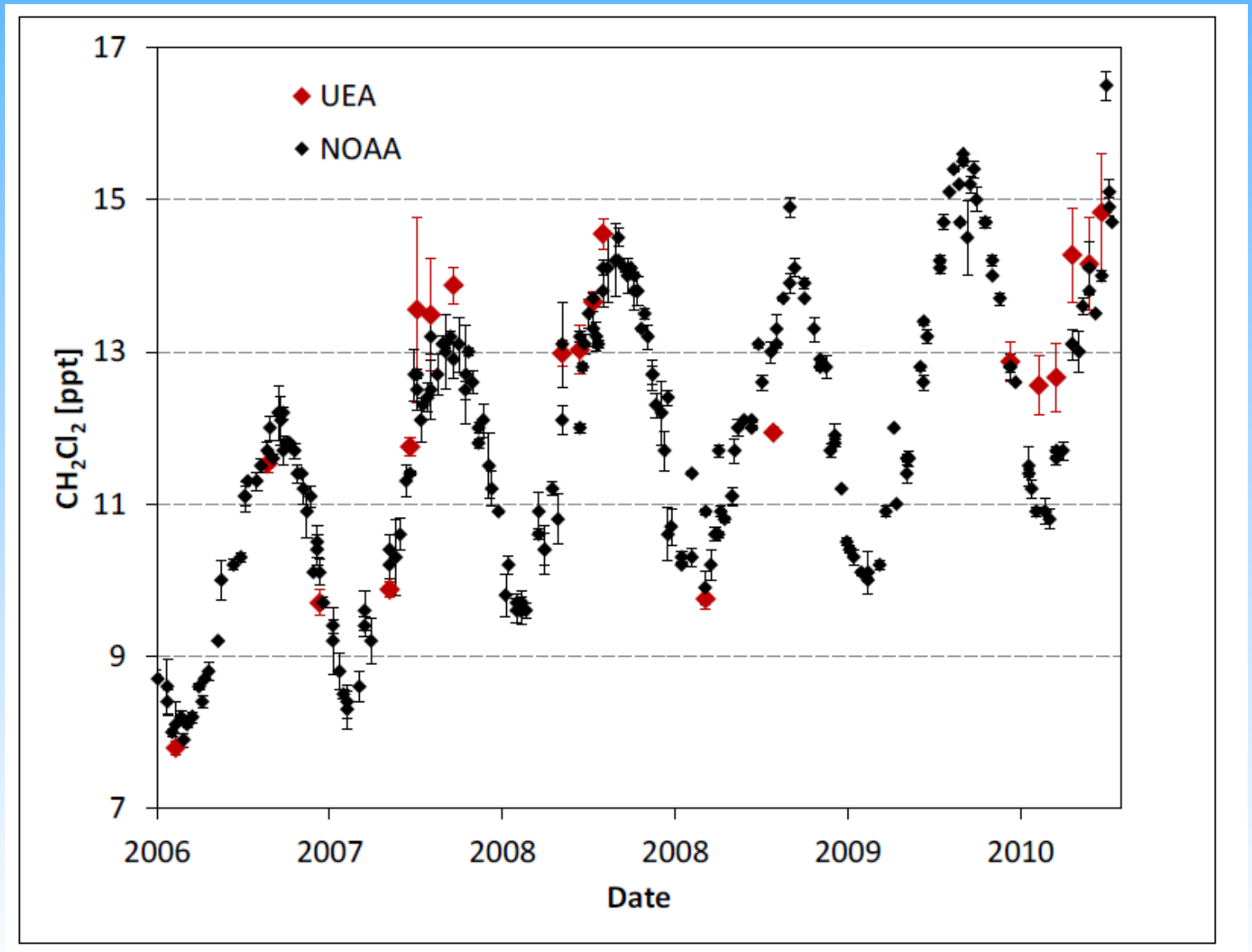


Related gases: Short-lived bromocarbons

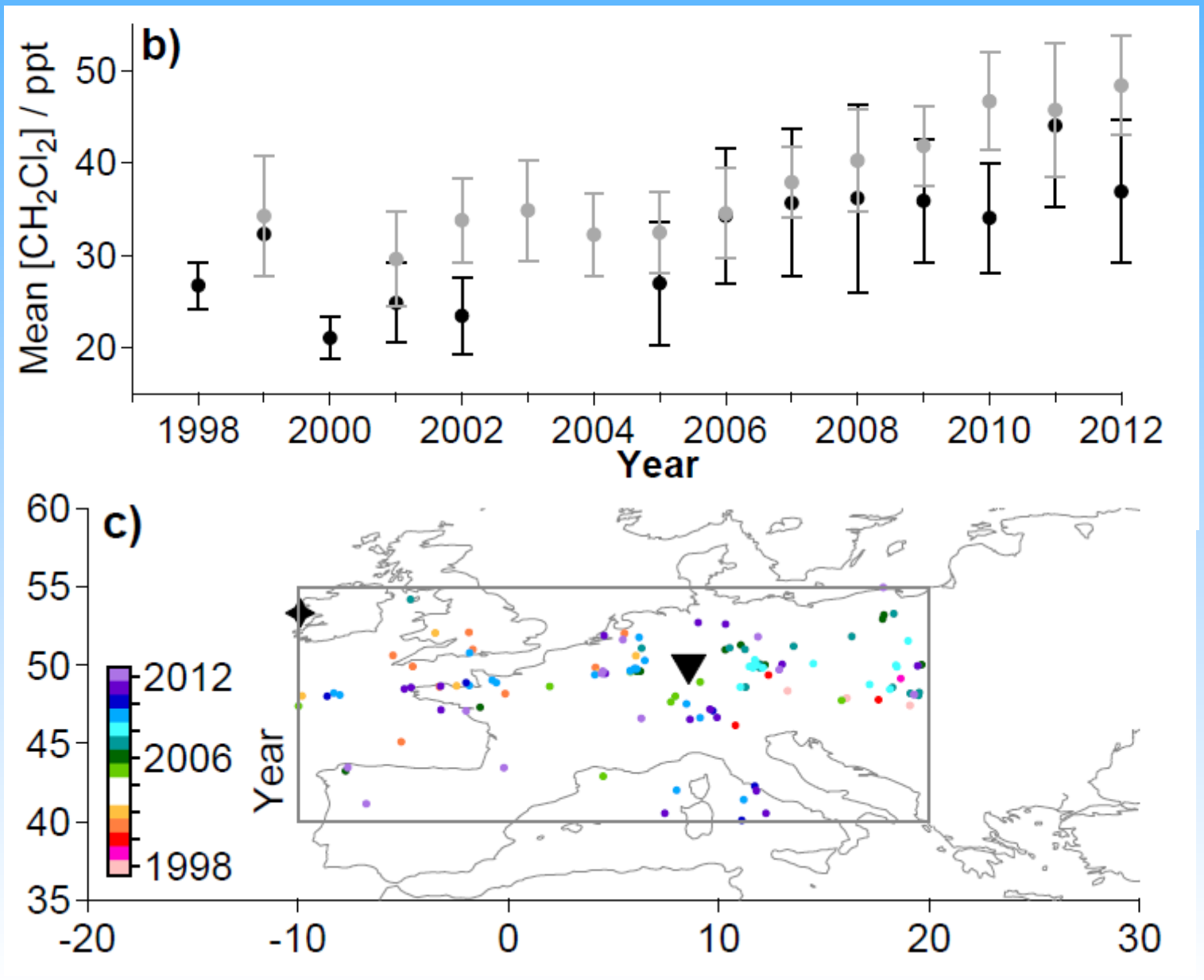
	Campaign		$CHBr_3$	CH_2Br_2	$CHBr_2Cl$	$CHBrCl_2$	CH_2BrCl	VSLB Σ Br_{org}
CARIBIC [1]	C. America	Ex. Trop. [58]	0.52 ± 0.27 {0.45} (0.14–1.4)	0.71 ± 0.11 {0.70} (0.42–0.98)	0.15 ± 0.05 {0.15} (0.08–0.27)	0.23 ± 0.05 {0.22} (0.15–0.38)	0.12 ± 0.02 {0.11} (0.01–0.15)	3.6 ± 1.1 {3.4} (1.7–7.2)
		Tropical [36]	0.52 ± 0.26 {0.49} (0.02–1.1)	0.72 ± 0.14 {0.71} (0.38–1.1)	0.17 ± 0.16 {0.14} (0.04–1.1)	0.27 ± 0.32 {0.21} (0.12–2.1)	0.11 ± 0.03 {0.10} (0.0–0.24)	3.7 ± 1.5 {3.5} (1.4–9.7)
	S. Africa	Tropical [26]	0.48 ± 0.54 {0.35} (0.03–2.8)	0.68 ± 0.14 {0.69} (0.40–0.87)	0.14 ± 0.10 {0.12} (0.05–0.55)	0.24 ± 0.10 {0.22} (0.10–0.56)	0.10 ± 0.02 {0.10} (0.04–0.14)	3.4 ± 2.1 {2.9} (1.4–12)
	S.E. Asia FRA-BKK	Tropical $> 15°$ N [18]	0.28 ± 0.19 {0.25} (0.05–0.58)	0.76 ± 0.14 {0.79} (0.49–0.95)	0.10 ± 0.04 {0.10} (0.04–0.16)	0.17 ± 0.03 {0.16} (0.11–0.22)	0.10 ± 0.01 {0.10} (0.09–0.12)	2.8 ± 0.93 {2.8} (1.6–4.2)
	S.E. Asia BKK-KUL	Tropical 0–15° N [39]	0.56 ± 0.12 {0.56} (0.15–0.81)	0.92 ± 0.08 {0.93} (0.74–1.0)	0.16 ± 0.02 {0.16} (0.08–0.19)	0.21 ± 0.03 {0.21} (0.16–0.31)	0.12 ± 0.01 {0.12} (0.09–0.14)	4.2 ± 0.56 {4.1} (2.4–5.2)
WMO2010 [4]		Tropical	0.50 (0.12–1.21)	0.86 (0.63–1.21)	0.11 (0.01–0.36)	0.11 (0.02–0.28)	0.09 (0.03–0.16)	3.5 (1.7–7.4)

[1] 10–12.3 km mid-upper tropospheric means $\pm 1\sigma$ and ranges.
[2] Wofsy et al. (2012). Averages at 9–12 km altitude. VSLB Σ Br_{org} does not include $CHBrCl_2$ and CH_2BrCl.
[3] VSLB Σ Br_{org} derived from $CHBr_3$, CH_2Br_2 and $CHBr_2Cl$ only.
[4] 10–12 km. Montzka and Reimann (2011)

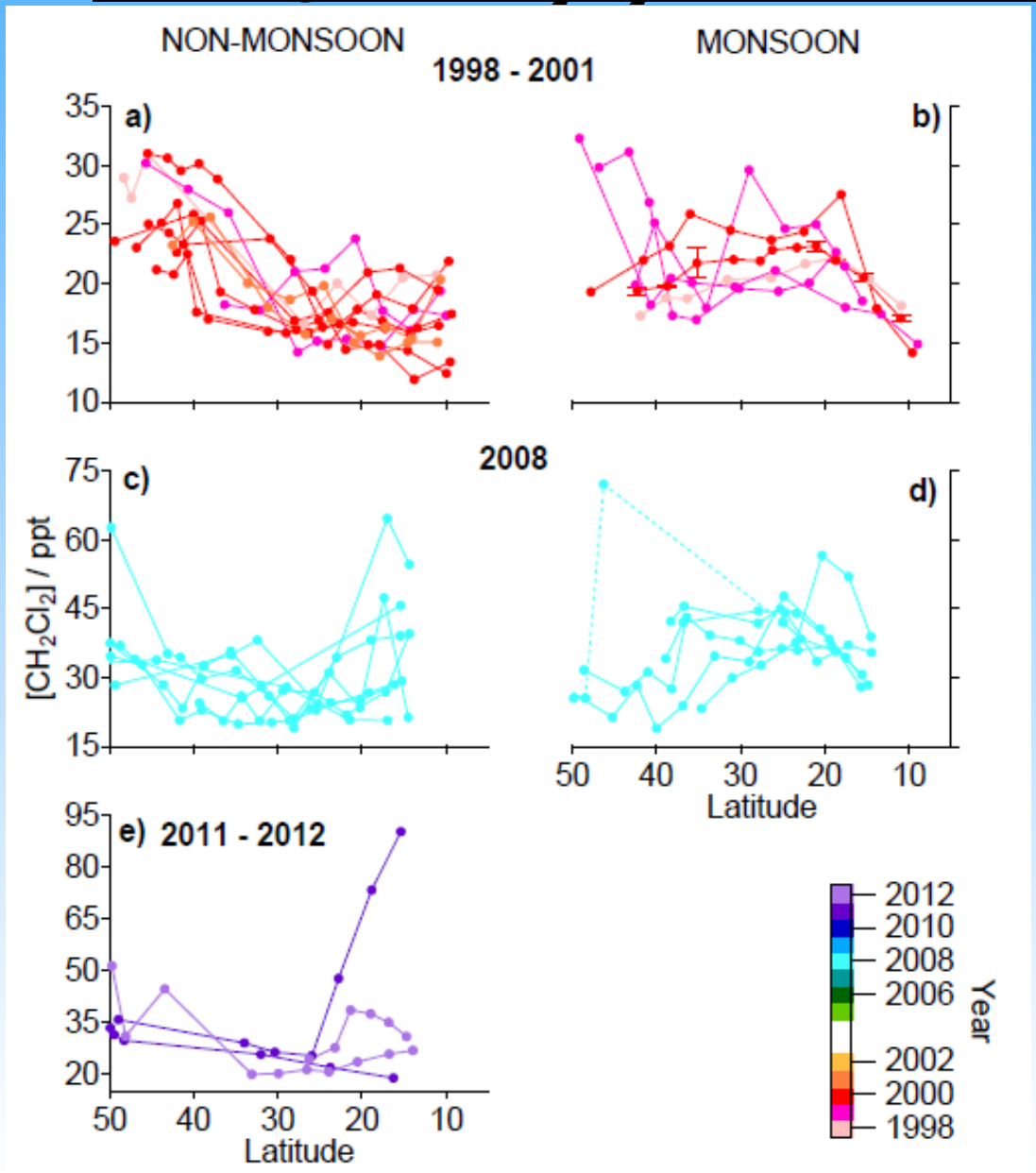
Related gases: CH_2Cl_2 trends (NOAA & UEA)



Related gases: CH_2Cl_2 trends (NOAA & CARIBIC)

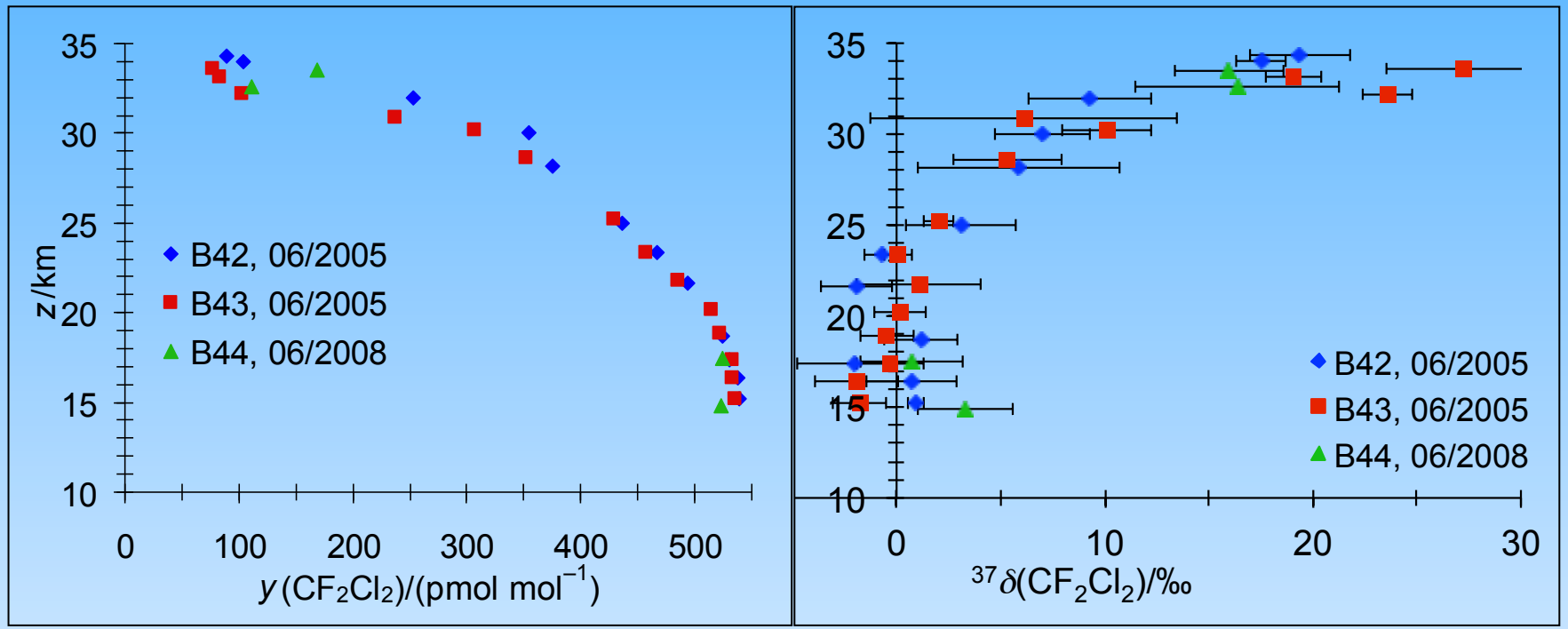


Related gases: CH_2Cl_2 and the Indian monsoon



Samples collected between Frankfurt and India until the end of 2012

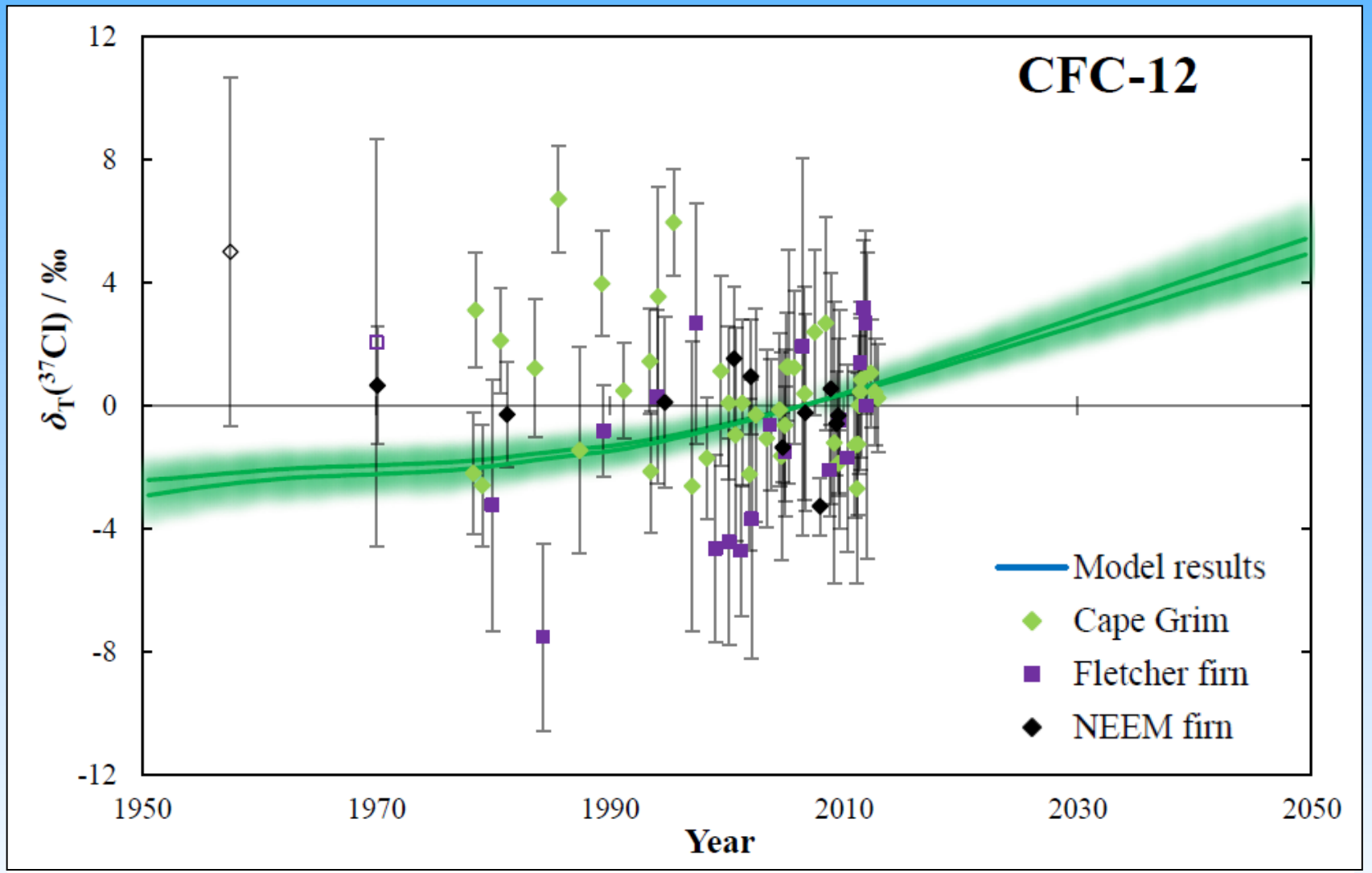
Chlorine isotopes in CFCs: Stratospheric effects



- Caused by faster decomposition of $CF_2{}^{35}Cl_2$ relative to $CF_2{}^{37}Cl^{35}Cl$ and $CF_2{}^{37}Cl_2$
- Similar effects found for CFC-11 and CFC-113, but less pronounced:

	CFC-11 (ε_{app}) / ‰	CFC-12 (ε_{app}) / ‰	CFC-113 (ε_{app}) / ‰
Mid latitude	-2.4 ± 0.5	-12.2 ± 1.5	-3.5 ± 1.6
High latitude	-2.4 ± 0.3	-6.8 ± 1.0	-3.3 ± 1.4

Chlorine isotopes in CFCs: Long-term trends



- No significant trends for Cl isotopes in CFCs except for CFC-12 at Cape Grim

Summary and outlook

- **Paper published** on CFC-112, CFC-112a, CFC-113a, and HCFC-133a
- **Paper published** on high resolution IR spectra and GWPs of CFC-112/CFC-112a, CFC-113a, and HCFC-133a **(**collaboration with Uni Reading and the Molecular Spectroscopy Facility)
- **Paper published** atmospheric histories, lifetimes, ODPs and emissions for 2 further CFCs and 1 further HCFC
- **Related papers** on short-lived bromocarbons (**published**) and dichloromethane (**in review**) in the mid/upper troposphere from the CARIBIC project
- **Next steps:**
    - **Finalise paper on chlorine isotopes in CFC-11, CFC-12, & CFC-113**: stratospheric observations, long-term trends from Cape Grim & firn air
    - **Under investigation**: ^{13}C isotope trends in CFCs