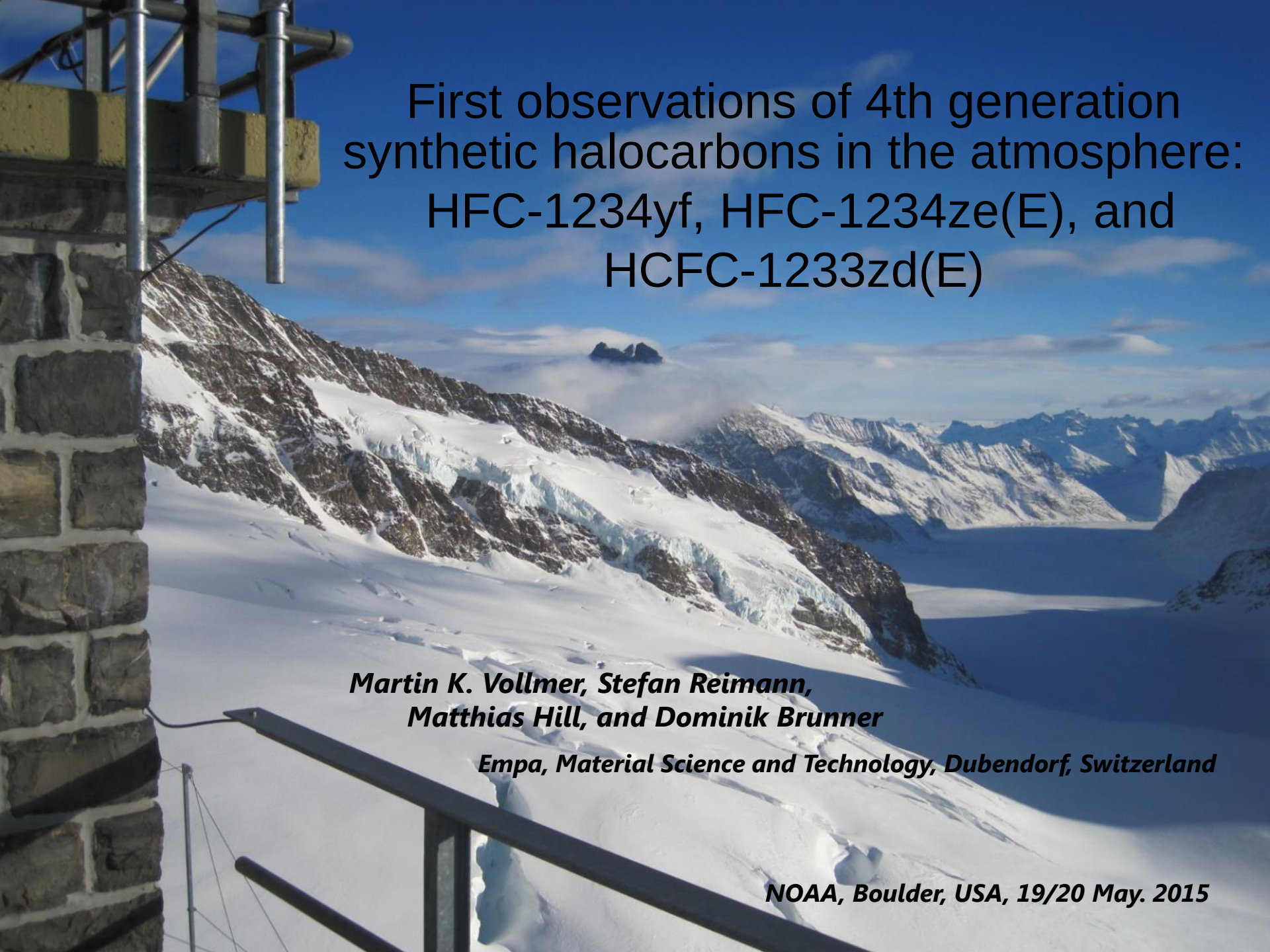


First observations of 4th generation synthetic halocarbons in the atmosphere: HFC-1234yf, HFC-1234ze(E), and HCFC-1233zd(E)

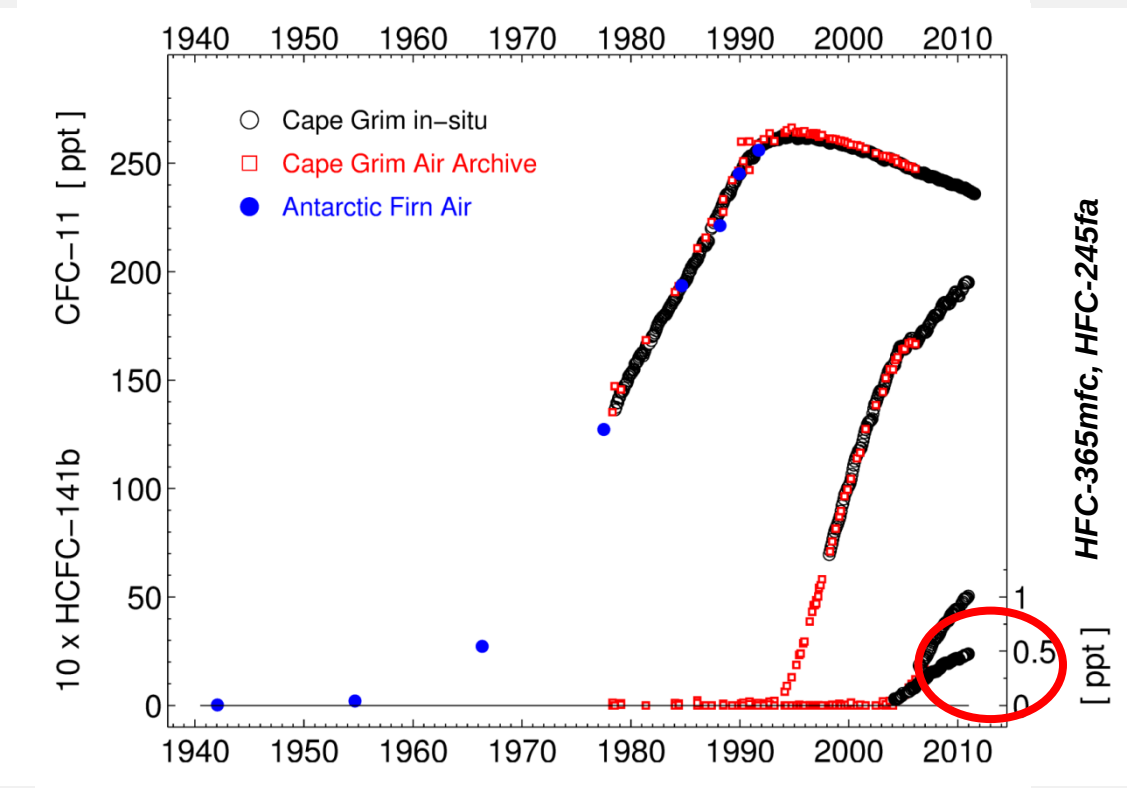
Martin K. Vollmer, Stefan Reimann, Matthias Hill, and Dominik Brunner

Empa, Material Science and Technology, Dubendorf, Switzerland

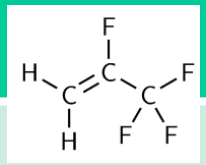
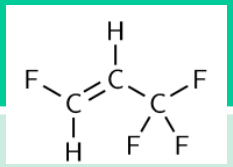
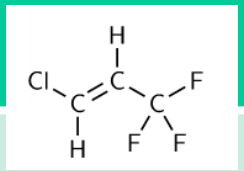
NOAA, Boulder, USA, 19/20 May. 2015

History of synthetic halogenated compounds

- 1950s: 1st generation: chlorofluorocarbons (CFCs), halons: Cl, F, Br, -
- 1990s: 2nd generation: hydrochlorofluorocarbons (HCFCs): H, Cl, F, -
- 1990s: 3rd generation: hydrofluorocarbons (HFCs), perfluorocarbons (PFC): H, F, -
- 2010s: 4th generation hydrohaloalkenes (hydrohaloolefines, hydro-fluoroolefines, HFOs) H, Cl, F, =



Properties of hydrohaloalkenes

	HFC-1234yf	HFC-1234ze(E)	HCFC-1233zd(E)	For comparison: CFC-11
Chemical Formula	 CF_3-CF=CH_2	 trans-CF_3CH=CHF	 trans-CF_3CH=CHCl	CCl_3F
lifetime	10 – 16 days	14 – 19 days	26 – 46 days	52 years
ODP	0	0	0.0005	1
GWP (100 yr)	< 4	< 7.5	< 14	4’800
Current abundance	0 – few ppt	0 – few ppt	0 – 50 ppq	240 ppt
Use	refrigerant (mainly mobile)	foam blowing (Europe), solvent	solvent, foam blowing	foam blowing
Global Emissions	?	?	0.5	~70 kt/yr
Detection limits	2 – 4 ppq	2 – 4 ppq	0.5 – 1 ppq	<1 ppt

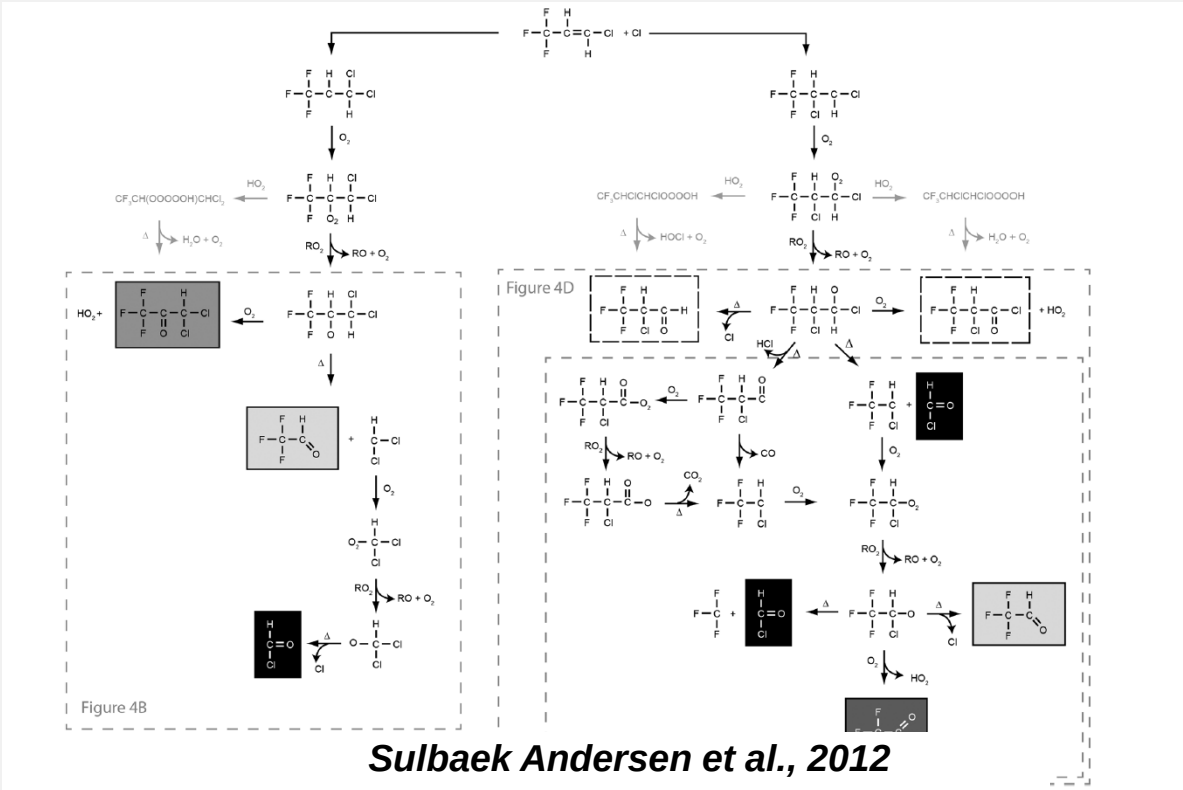
Why measure Hydrohaloalkenes?

Potentially huge amounts used in the future:

- potential replacement of:
  first + second generation (CFCs, HCFCs, halons etc)
  emissions: 650 Gg / yr
  third generation (HFCs, PFCs etc) emissions: 360 Gg / yr
  (ongoing activities to include HFCs in the Montreal Protocol)

- Decay products,
  fate in water
  and soils, toxicity:
  TFA issue

- Potential use as
  atmospheric tracers

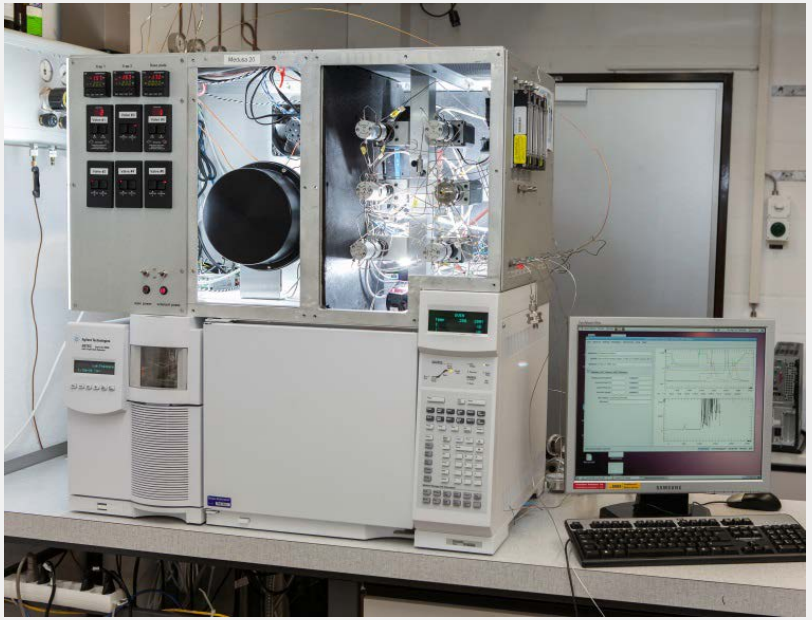


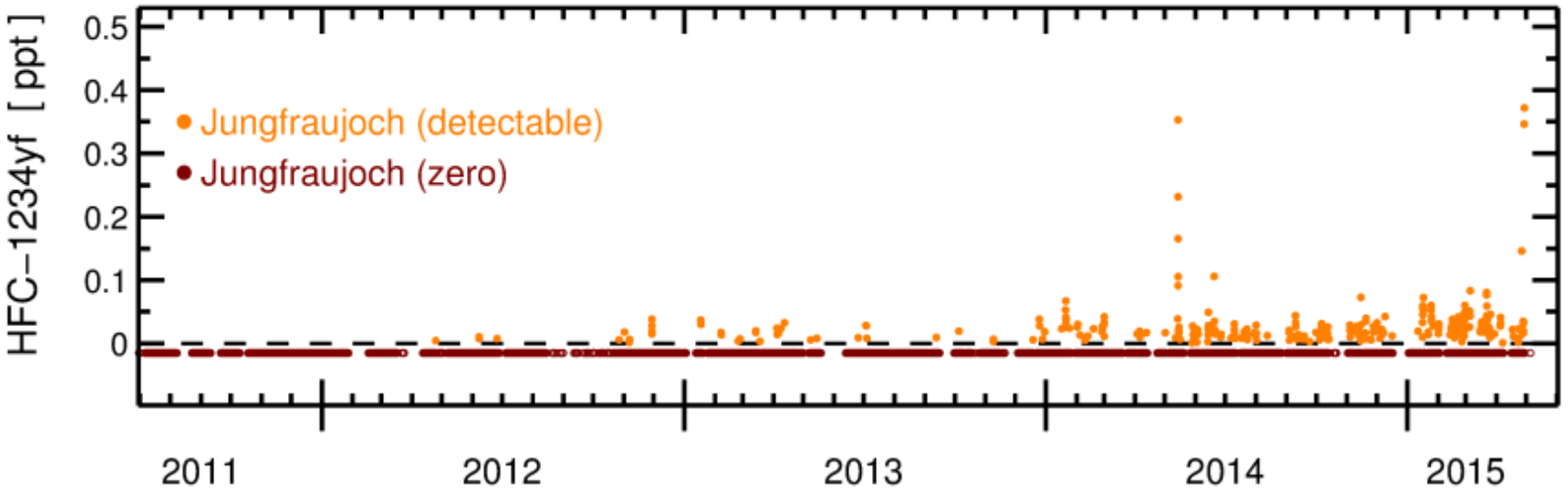
Sulbaek Andersen et al., 2012

Fig. 5 Proposed mechanism of the Cl atom initiated oxidation of *t*-$CF_3CH{=}CHCl$. Solid boxes indicate the experimentally observed products

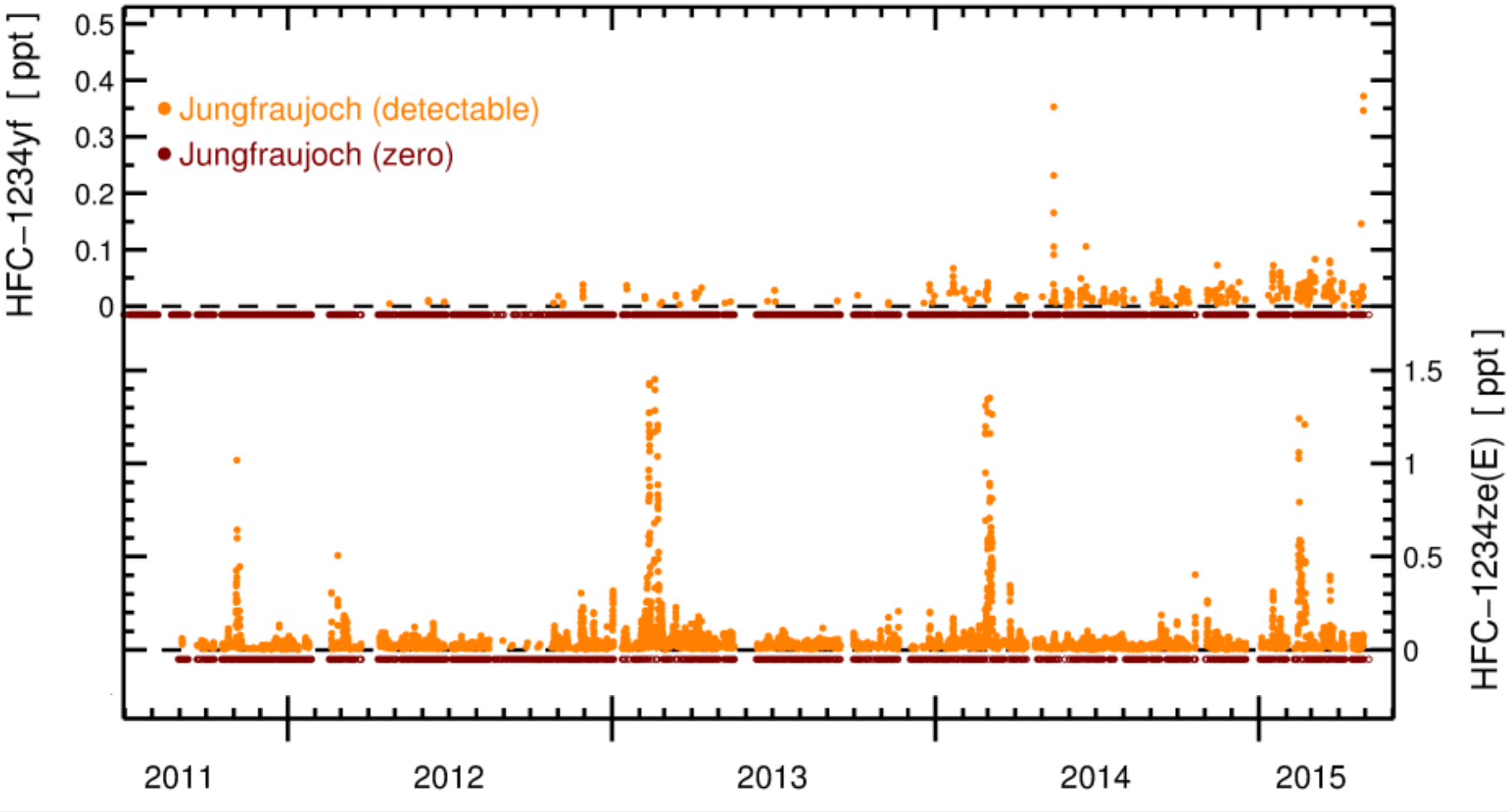
Analytical Techniques for hydrohaloalkenes

- Measure with Medusa GCMS technology (Miller et al., 2008)
- Measure at Jungfraujoch (Switzerland) at 3545 m. a. s. l.





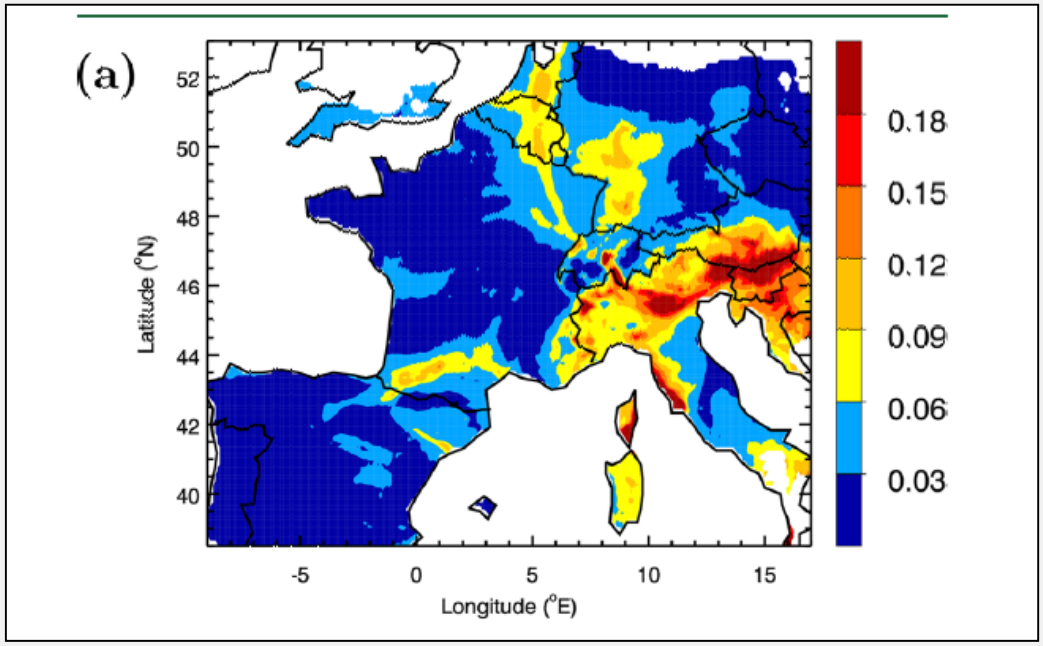
adopted from Vollmer et al., 2015, ES&T



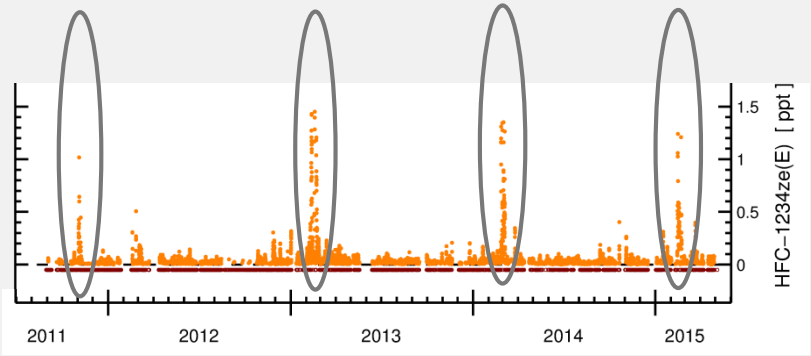
adopted from Vollmer et al., 2015, ES&T

EMPA
Materials Science & Technology

HFC-1234ze(E) source regions



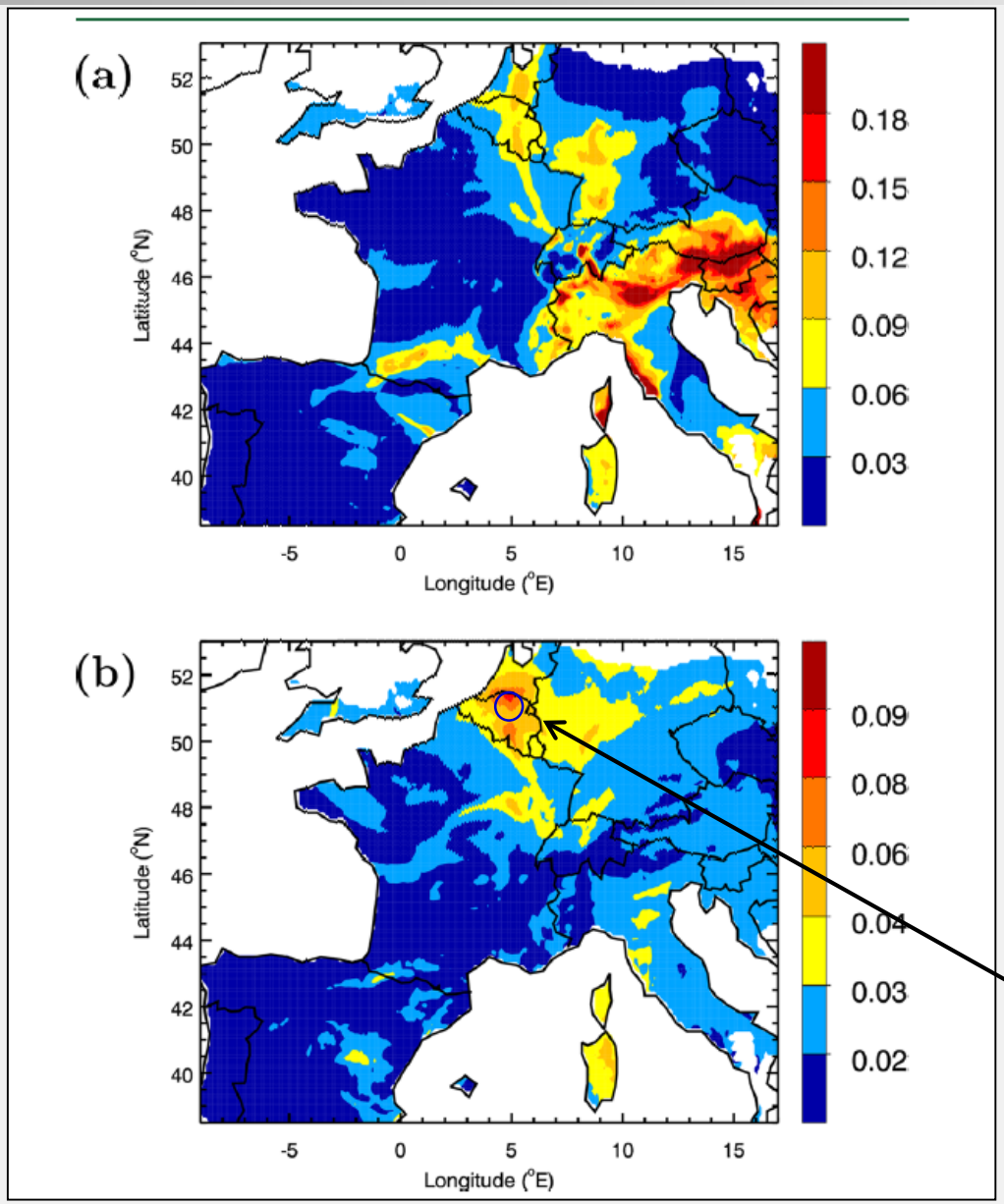
All data 2011 – 2014



adopted from Vollmer et al., 2015, ES&T

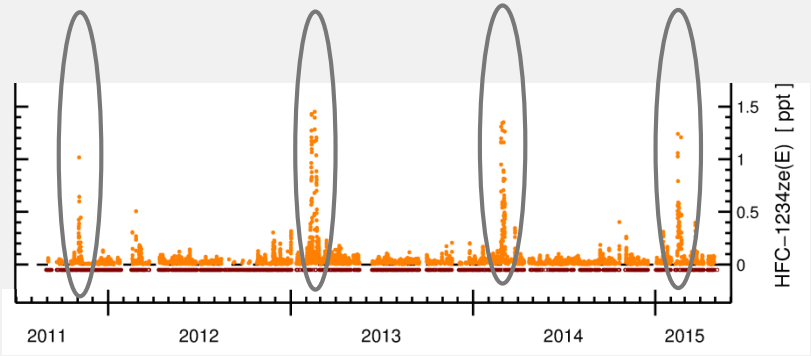
EMPA
Materials Science & Technology

HFC-1234ze(E) source regions



adopted from Vollmer et al., 2015, ES&T

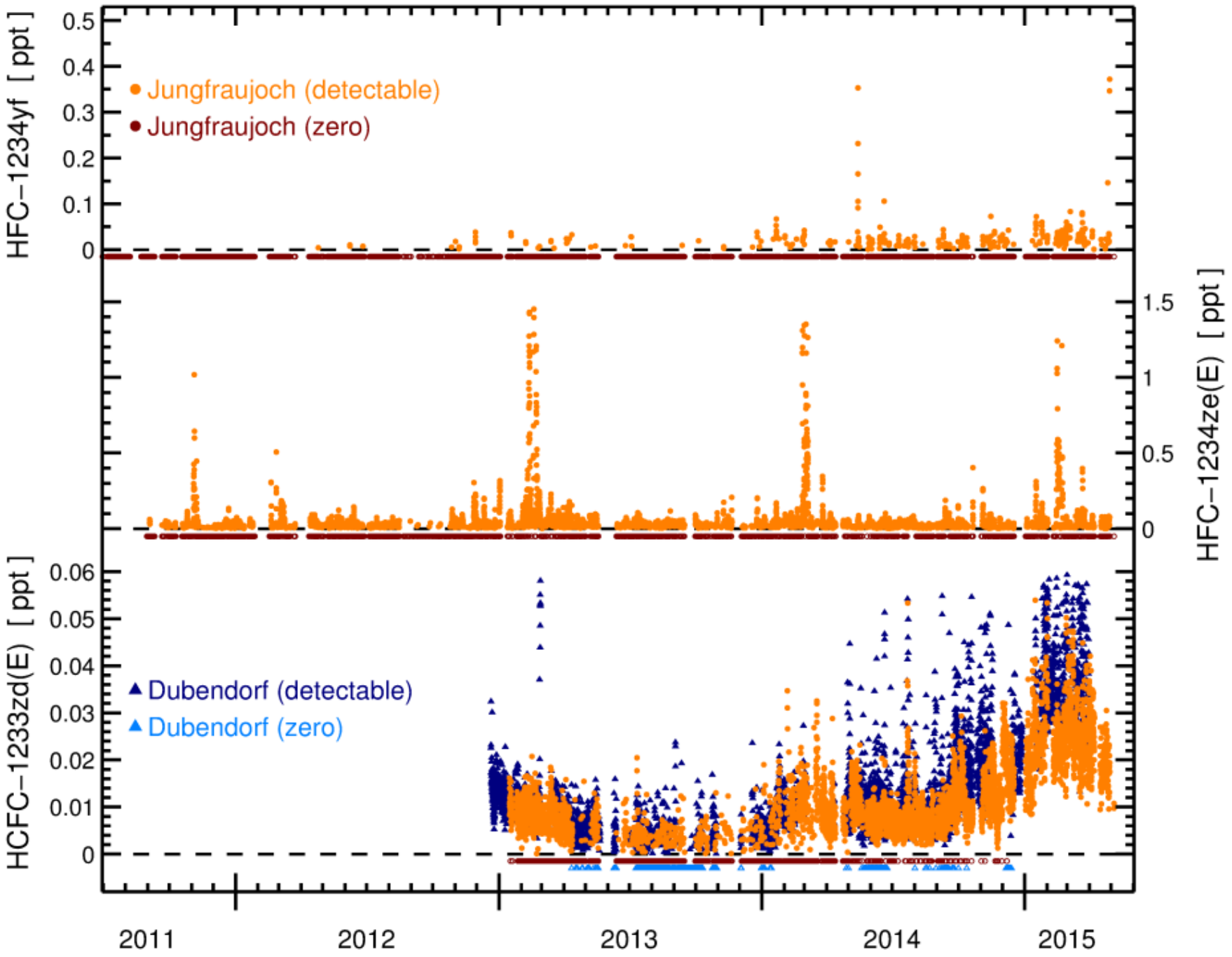
All data 2011 – 2014



Major events removed

Jackon, Olen/Antwerp: currently only large XPS manufacturer using 1234ze(E) [2014: 115 t]

EMPA
Materials Science & Technology



adopted from Vollmer et al., 2015, ES&T

Conclusions

- First measurements of three important hydrohaloalkenes: on the rise

- New challenges: Decay products, fate in water and soils, toxicity
  - potential replacement of 1'000 Gg/yr of 1st – 3rd generation:

Acknowledgments

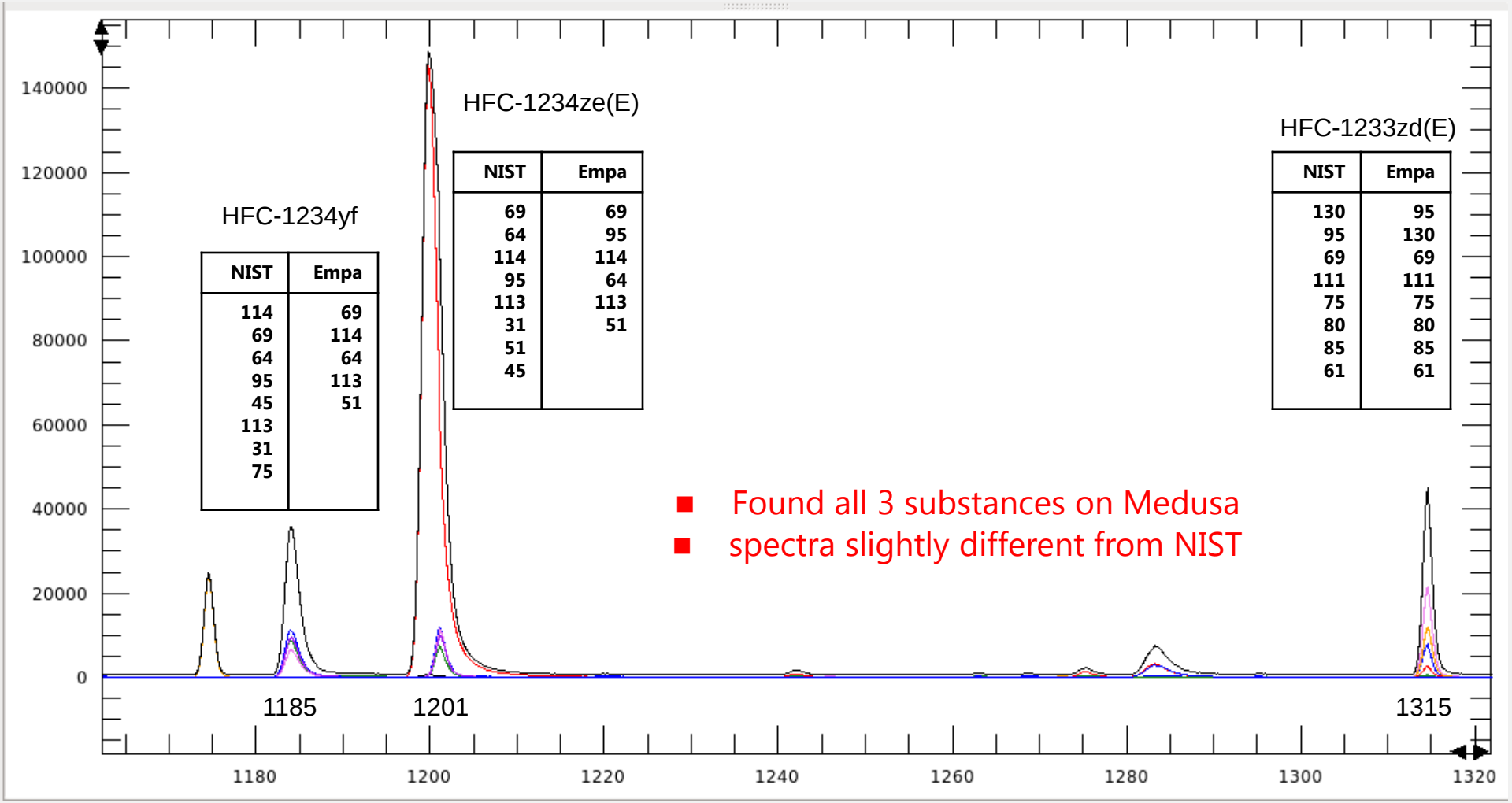
- Halclim (Swiss Federal Office for the Environment, FOEN)
- International Foundation High Altitude Research Station Jungfraujoch and Gornergrat (HFSJG)
- Integrated Non-CO_2 Greenhouse gas Observing System (InGOS, EU-FP-7)
- HIGHGAS, European Metrological Research Project ENV52 Metrology for high-impact greenhouse gases

- Station personnel at Jungfraujoch (Fischer and Otz families)
- Angelina Wenger, Fabian Schoenenberger, Christoph Zellweger, and Corinne Hoerger for help with preparation of primary calibration scale
- AGAGE / CSIRO, Ben Miller (NOAA): Cape Grim Records
- Rajiv R. Singh of Honeywell International for providing the pure compounds.


End

GCMS Identification

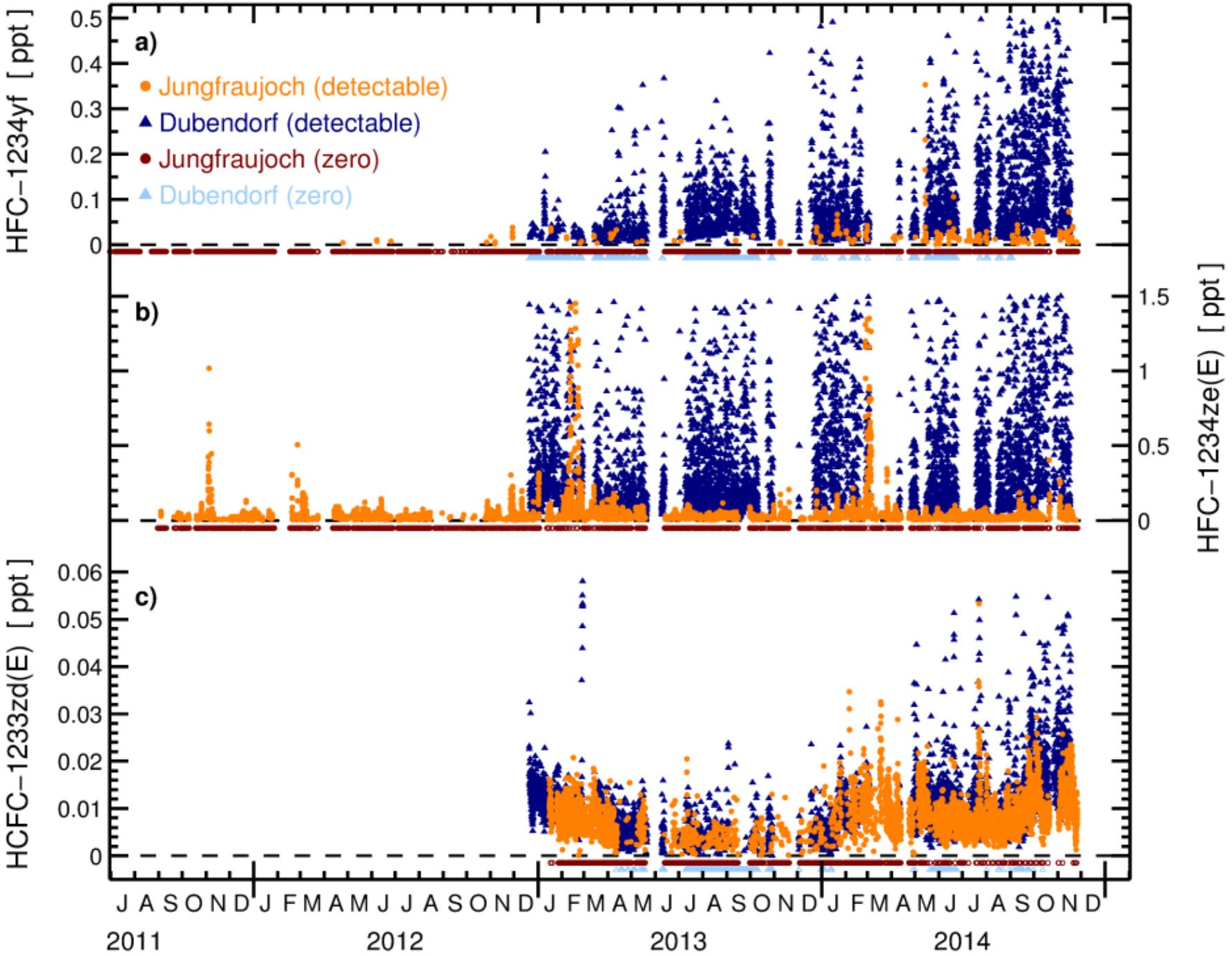
(CP-PoraBOND Q, 0.32 mm ID x 25 m, 5 µm Varian Chrompack, T-ramping)



For comparison: CH_3Cl $c\text{-}C_4F_8$ CFC-12 HFC-142b n-butane CH_2Cl_2

EMPA

Materials Science & Technology


a)
b)
c)
Jungfraujoch (detectable)
Dubendorf (detectable)
Jungfraujoch (zero)
Dubendorf (zero)
HFC−1234yf [ppt]
HFC−1234ze(E) [ppt]
HCFC−1233zd(E) [ppt]
0.5
0.4
0.3
0.2
0.1
0
1.5
1
0.5
0
0.06
0.05
0.04
0.03
0.02
0.01
0
J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D
2011
2012
2013
2014