Atmospheric lifetime implications for SF_6 from stratospheric observations

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Why care about SF_6?

- IPCC, 2013: One of the strongest GHGs in the atmosphere

Species	Lifetime (yr)	RE (W m^{-2} ppb^{-1})
CO_2 (ppm)		1.37×10^{-5}
CH_4 (ppb)	9.1	3.63×10^{-4}
N_2O (ppb)	131	3.03×10^{-3}
SF_6	3200	0.575
CF_4	50,000	0.1
C_2F_6	10,000	0.26
HFC-125	28.2	0.219
HFC-134a	13.4	0.159
HFC-143a	47.1	0.159
HFC-152a	1.5	0.094
HFC-23	222	0.176
CFC-11	45	0.263
CFC-12	100	0.32

Why care about SF_6?

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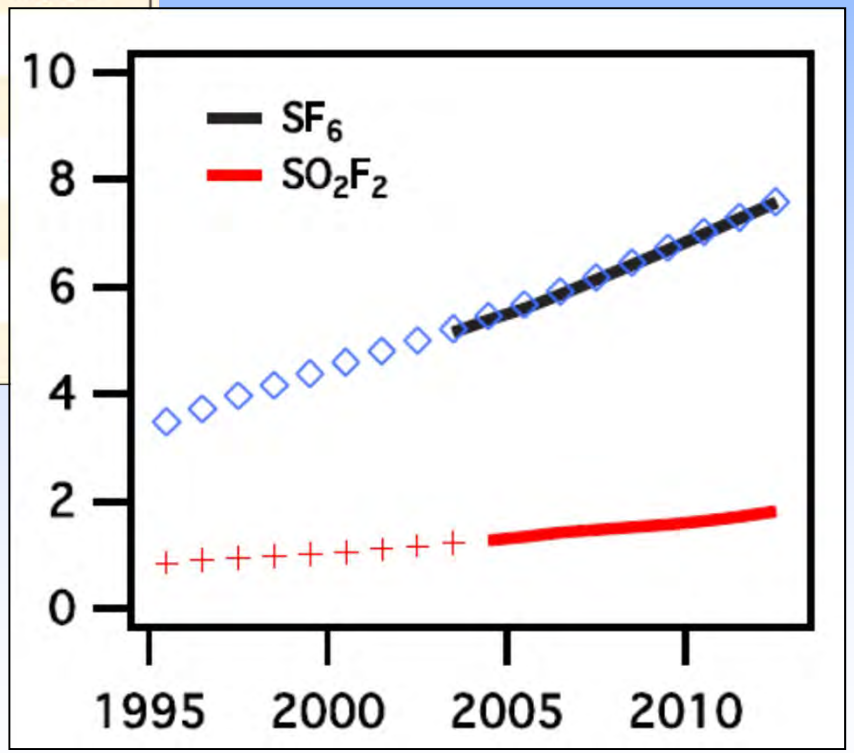
Nitrogen trifluoride	16,100
Sulphur hexafluoride	23,500
(Trifluoromethyl) sulphur pentafluoride	17,400
Sulphuryl fluoride	
PFC-14	
PFC-116	
PFC-c216	
PFC-218	
PFC-318	

…and concentrations steadily increasing!

Sources: Electricity distribution systems, magnesium production, semi-conductor manufacturing

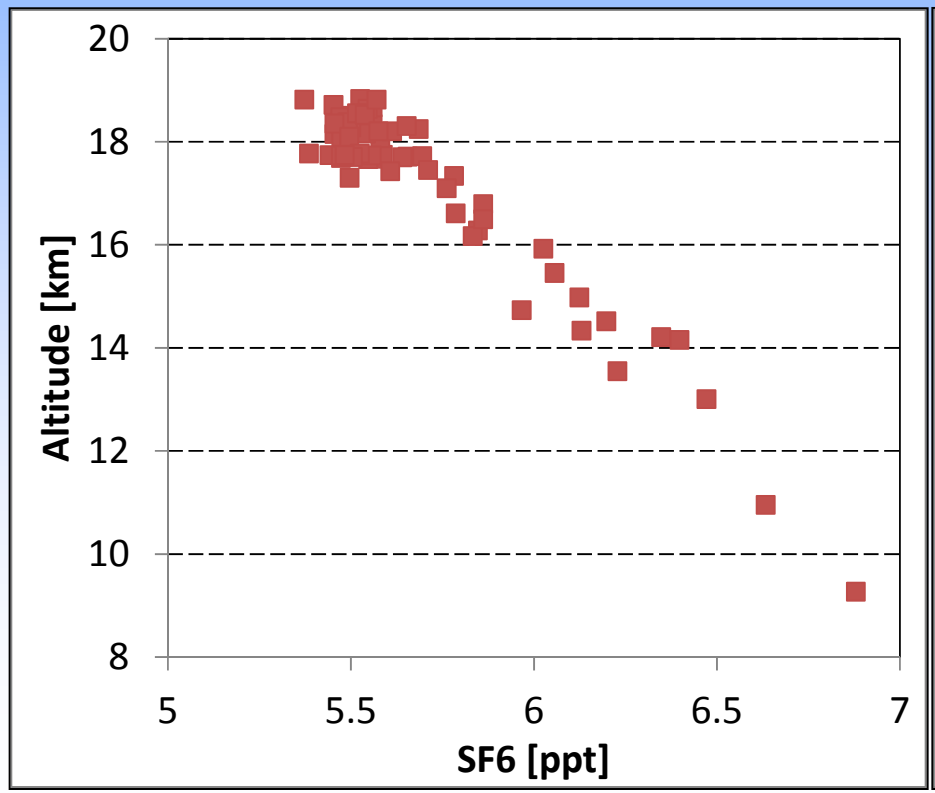


Source: WMO, 2014

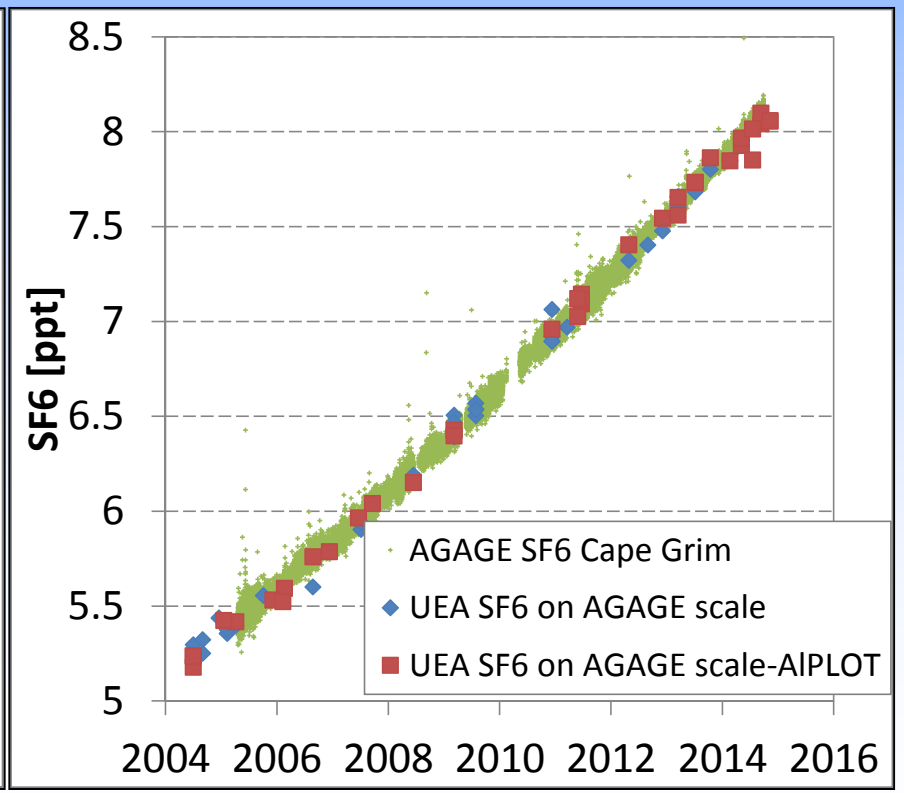
Why care about SF_6?

- Sufficient tropospheric growth rates and the long lifetime make it an ideal tracer of transport in groundwater, the oceans, and the **stratosphere**

Stratospheric altitude profile (2010)



Tropospheric time trend

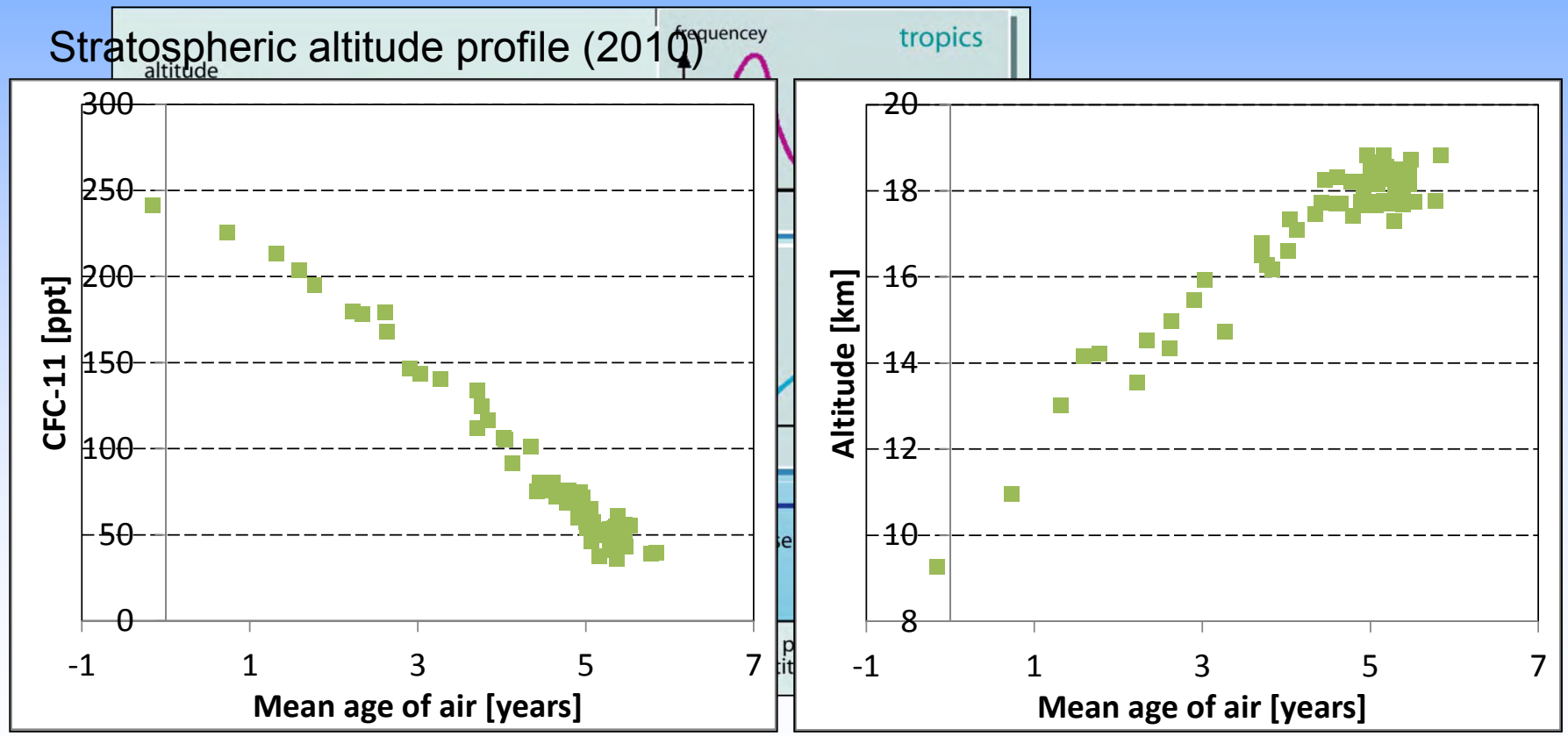


Source: cdiac.ornl.gov

Why care about SF_6?

- Sufficient tropospheric growth rates and the long lifetime make it an ideal tracer of transport in the **stratosphere**

Stratospheric altitude profile (2010)



- The less SF_6 you find, the older the air

Why care about SF_6?

- Many papers have been using SF_6 to diagnose stratospheric transport and chemistry:

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 102, NO. D21, PAGES 25,543–25,564, NOVEMBER 20, 1997

LETTERS
PUBLISHED ONLINE: 14 DECEMBER 2008 | DOI: 10.1038/NGEO388
nature geoscience

Atmos. Chem. Phys., 12, 3311–3331, 2012
www.atmos-chem-phys.net/12/3311/2012/
doi:10.5194/acp-12-3311-2012

Atmospheric Chemistry and Physics

Atmos. Chem. Phys., 13, 2779–2791, 2013
www.atmos-chem-phys.net/13/2779/2013/
doi:10.5194/acp-13-2779-2013

Atmospheric Chemistry and Physics

Observed temporal for the 2002 to 2010

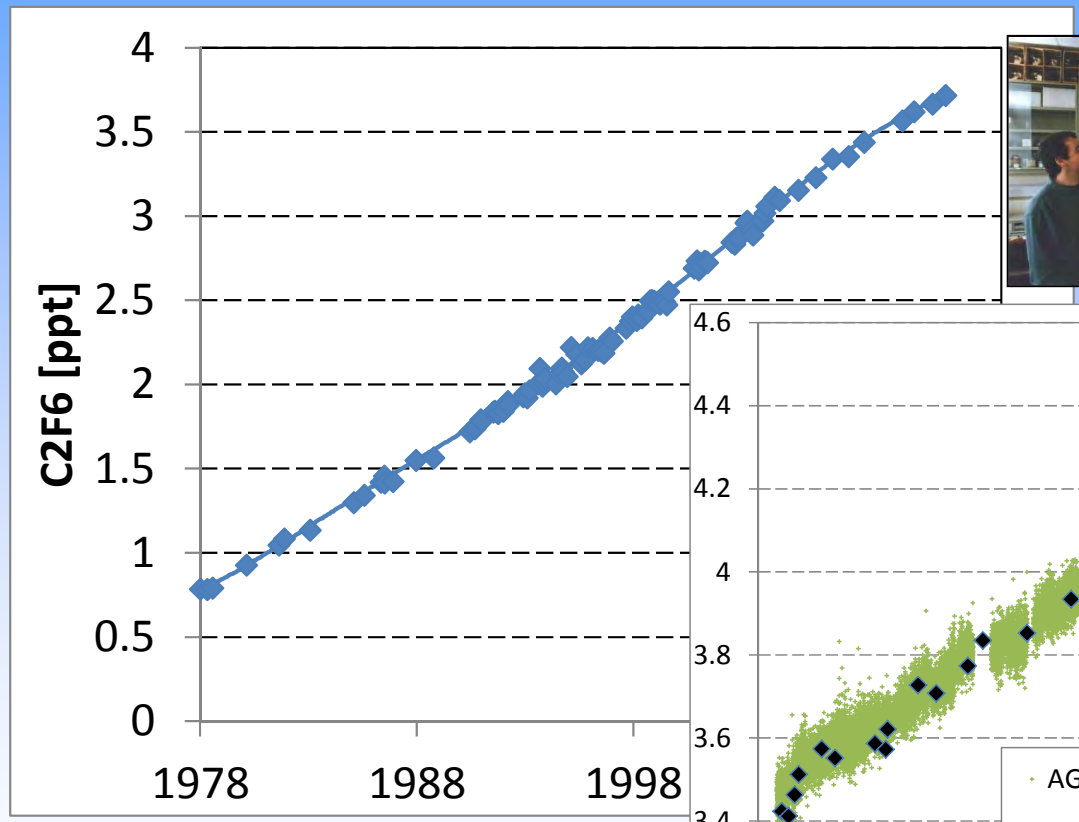
G. P. Stiller[1], T. von Clarmann[1], F.
A. Linden[1], S. Lossow[1], and M. Ló

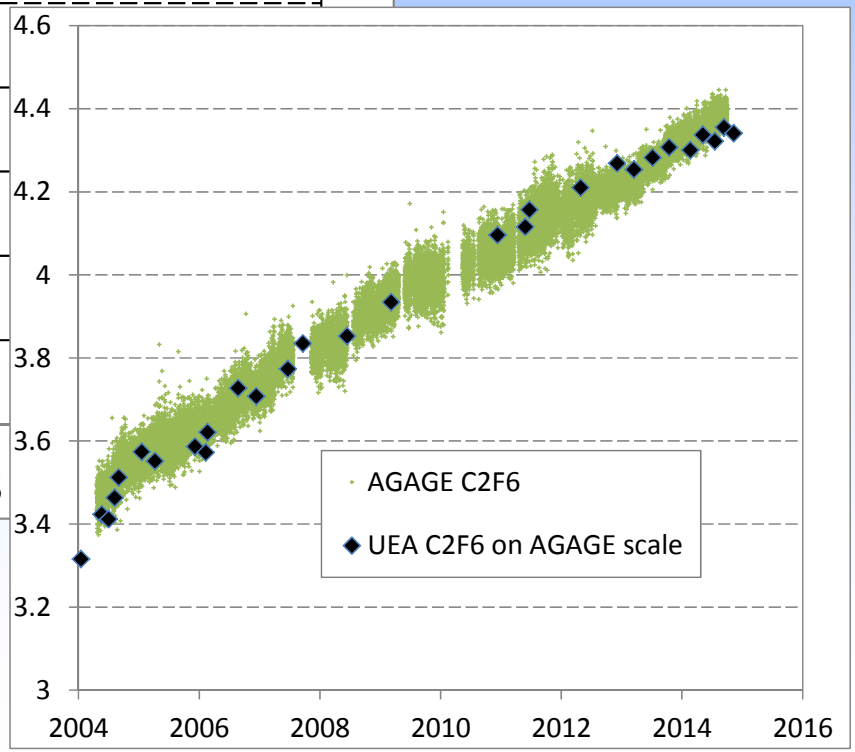
Observation-based assessment of stratospheric fractional release, lifetimes, and ozone depletion potentials of ten important source gases

J. C. Laube[1], A. Keil[2], H. Bönisch[2], A. Engel[2], T. Röckmann[3], C. M. Volk[4], and W. T. Sturges[1]

SF_6 age tracer alternatives

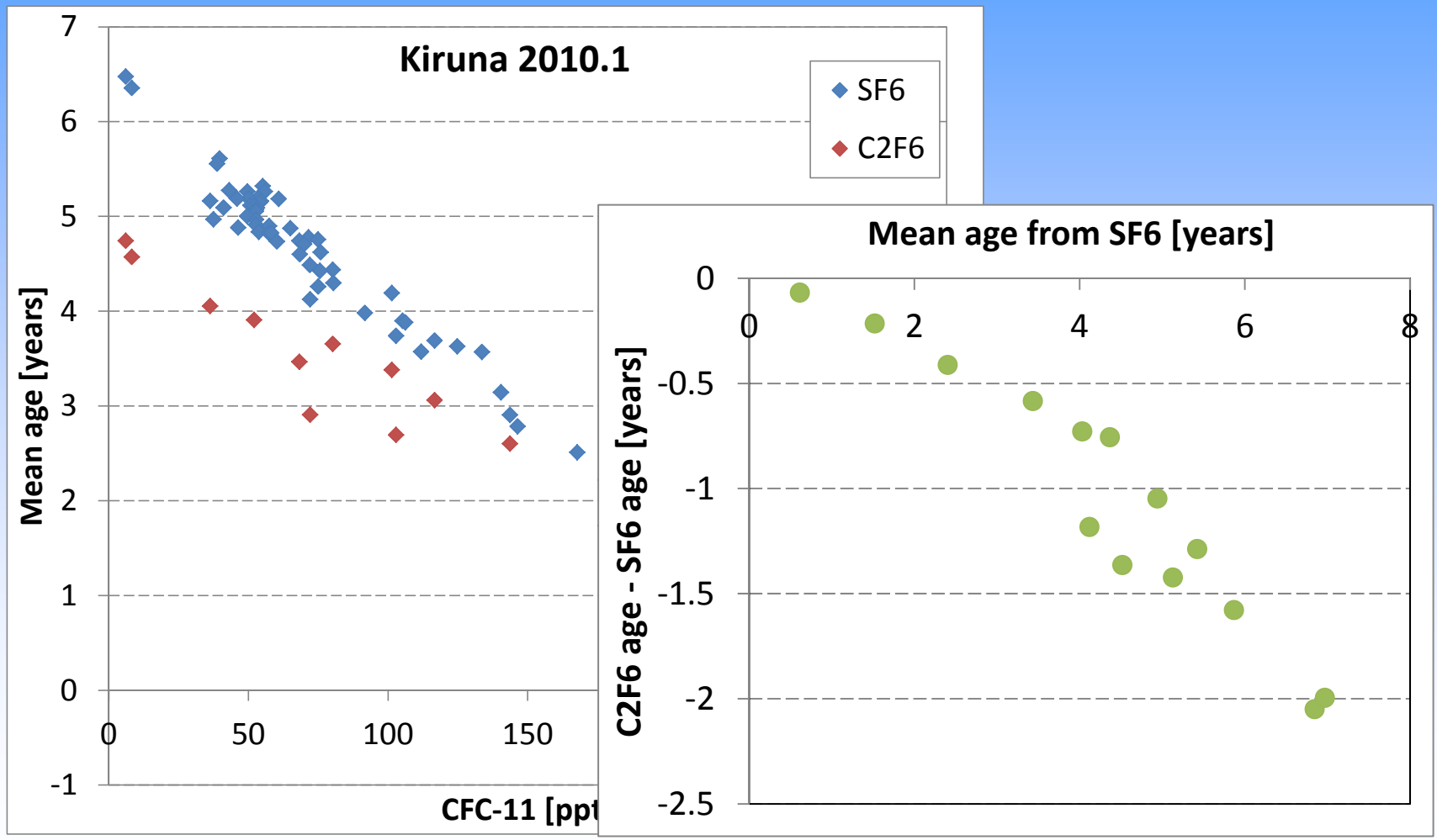
- Sufficient tropospheric growth rates and long lifetime (>10,000 years): C_2F_6





SF_6 age tracer alternatives

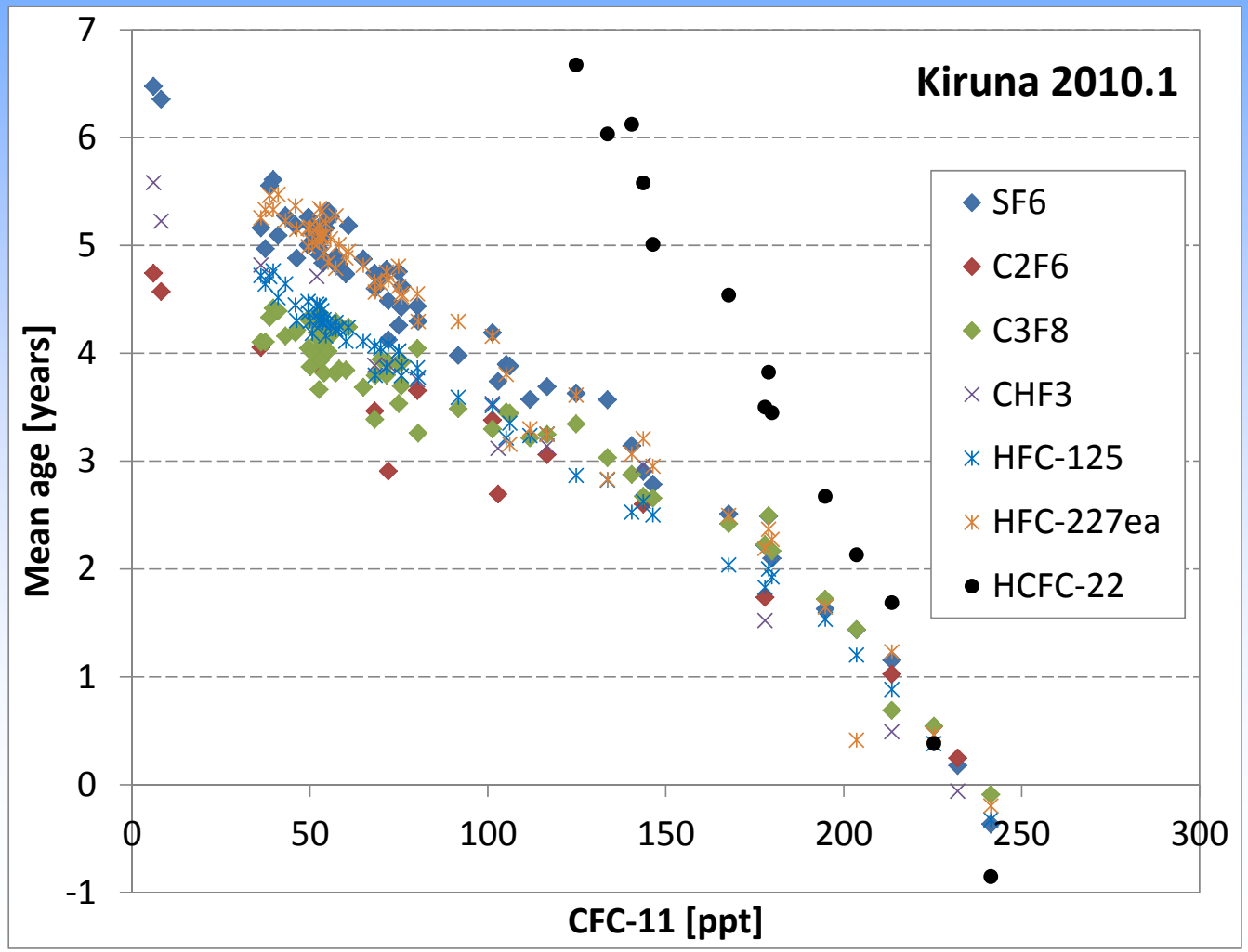
Stratospheric data (2010)



…gives lower mean age from C_2F_6 and discrepancy increases with altitude

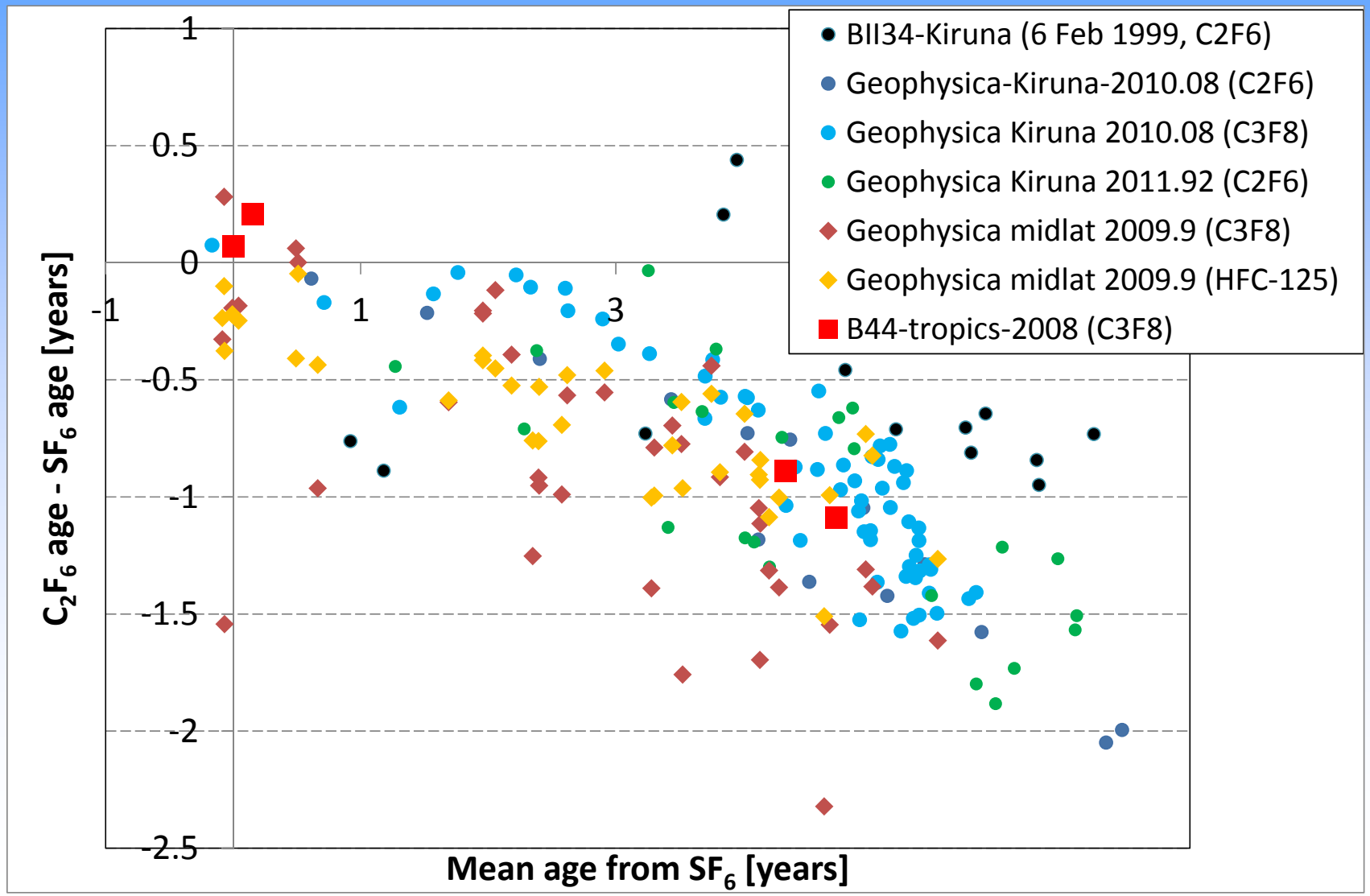
SF_6 age tracer alternatives

Trace gas	C_2F_6	C_3F_8	CHF_3 (HFC-23)	CHF_2CF_3 (HFC-125)	CF_3CHFCF_3 (HFC-227ea)	CHF_2Cl (HCFC-22)
Stratospheric lifetime (WMO 2014)	>10,000	7000	4420	351	673	161



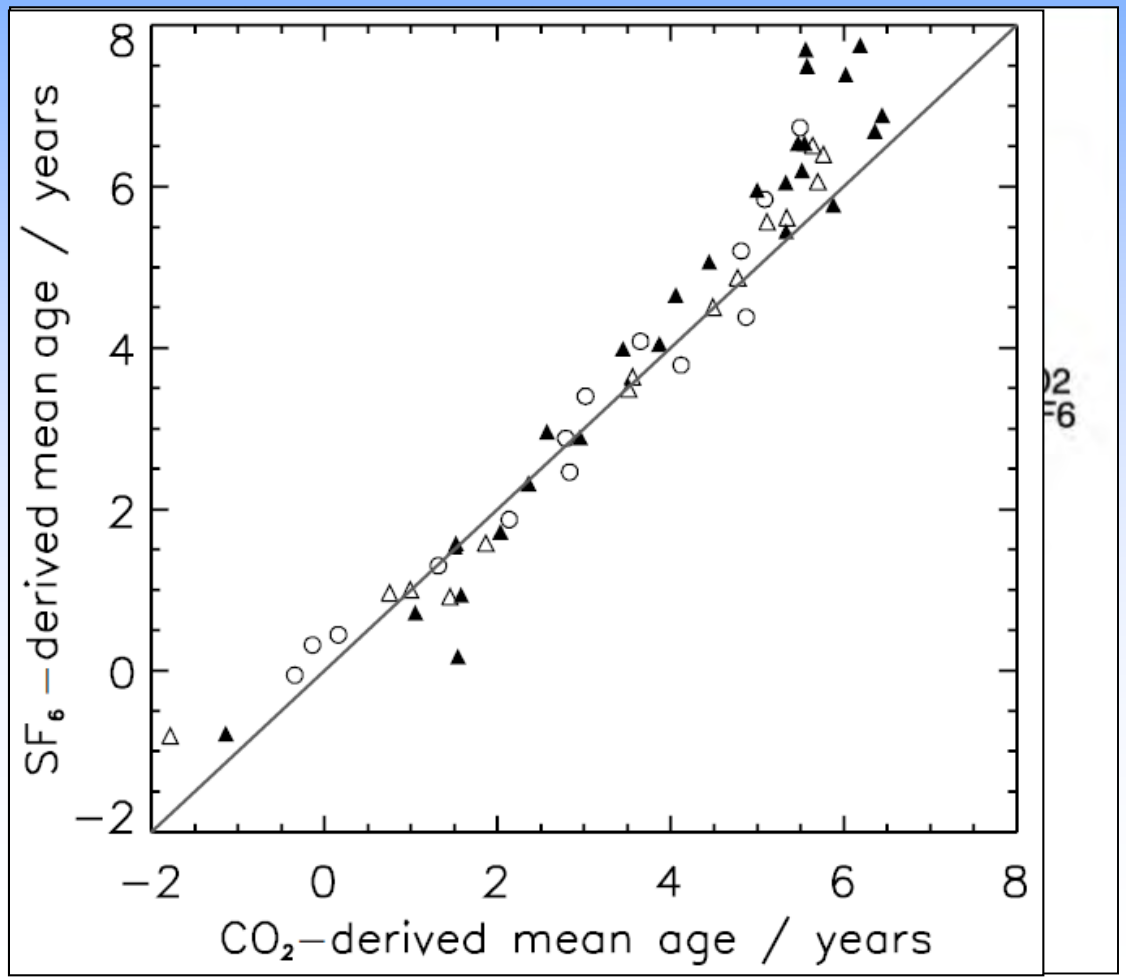
SF_6 age tracer alternatives: other field campaigns

- Similar discrepancies also observed in other campaigns including in mid latitudes and tropics



SF_6 age tracer alternatives: CO_2

- Similarities and differences have been seen using CO_2 as age tracer
- But: CO_2 comes with a whole range of other problems
  (e.g. sinusoidal trend with variable annual growth rate, and production in the stratosphere from oxidation of CH_4)

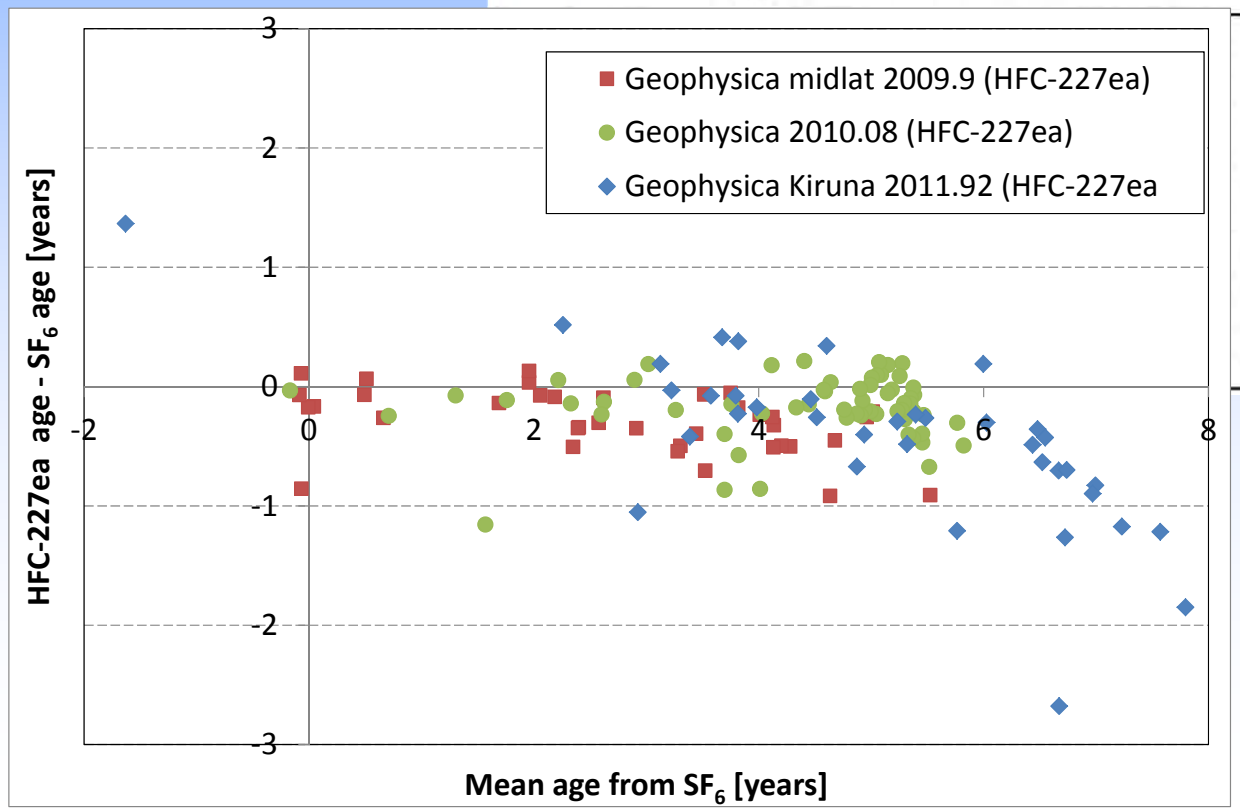


Engelet al., 2002; Hall et al. (1999)

SF_6 lifetime

- 3,200 years come from Ravishankara et al., Science, 1993 with significant sink reactions only occurring in the mesosphere:

Molecule	Fractional loss due to: Photolysis at 121.6 nm	Fractional loss due to: $O(^1D)$ reaction	Fractional loss due to: Other paths	τ (combust)	τ (H atoms)	τ (lower limit)	τ (best)
CF_4					>1.7 (5)	>2.5 (4)	>5.0 (4)
C_2F_6					>1.1 (5)	>1.0 (4)	>1.0 (4)
C_3F_8					>2.2 (4)	1.0 (3)	3.2 (3)
C_4F_{10}						2.6 (3)	
C_5F_{12}						1.9 (3)	4.1 (3)
C_6F_{14}					>1.0 (4)	1.0 (3)	3.1 (3)
C_7F_{16}					>1.0 (4)	850	2.9 (3)
C_8F_{18}						380	640
C_4F_8						1.1 (3)	1.7 (3)
C_5F_{10}						90	300
SF_6						>5.8 (2)	3.2 (3)

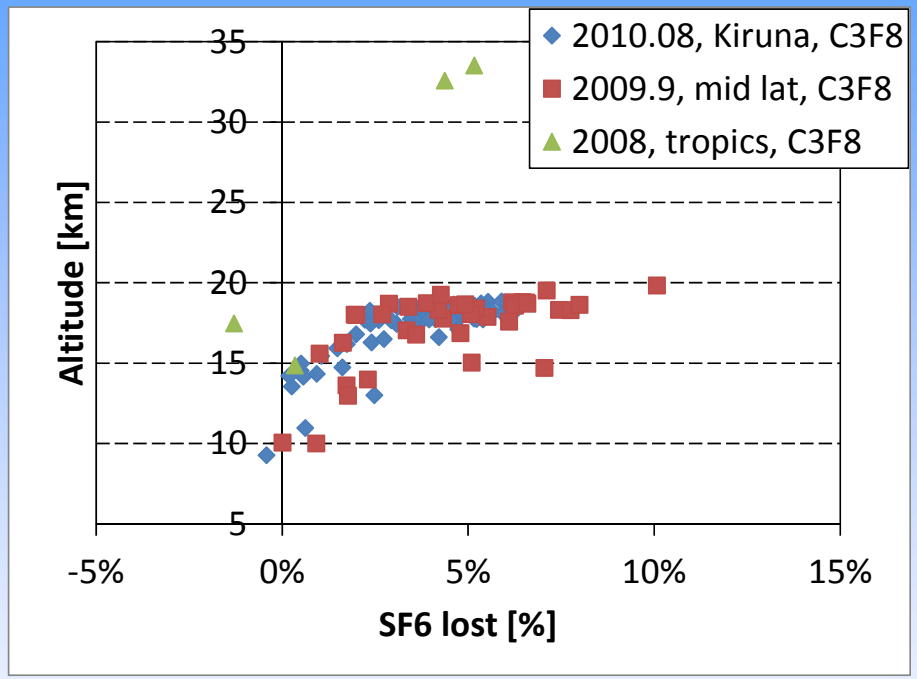


HFC-227ea

Stratospheric lifetime: 673 years

Conclusions

- Mean age from SF_6 is biased with differences to other age tracers increasing with altitude – **a thorough uncertainty analysis is however still outstanding!**



- **Known unknowns**: Reliance on age spectra shapes, e.g. more recirculation?
- SF_6 lifetime vs. other stratospheric lifetimes: significantly longer than HCFC-22, likely similar to HFC-227ea, and likely shorter than C_2F_6, C_3F_8, CHF_3 and CF_3CHF_2
- SF_6 is still a good tracer for the oceans, freshwater, and the troposphere and lower stratosphere, but there are **indications for a stratospheric sink**
- Its **GWP-100 and emissions will not change significantly** should the lifetime change