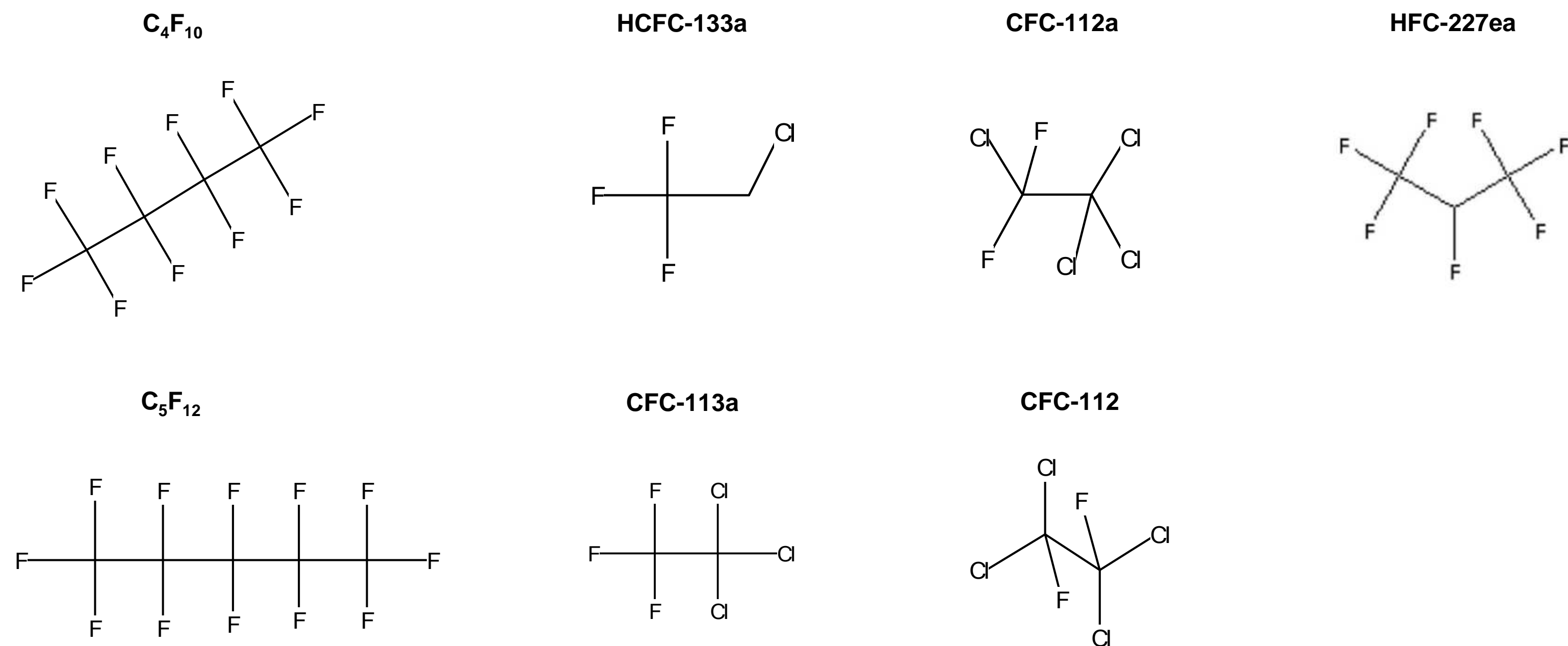


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## Which are the "new" compounds?



- All compounds are expected to be strong greenhouse gases with Greenhouse Warming Potentials (GWPs) hundreds to thousands times higher than that of CO<sub>2</sub>
- Four compounds also have the potential to deplete ozone in the stratosphere: the CFCs and HCFC-133a

## Where does the data come from?

Results are based on high-sensitivity GC-MS measurements of air samples collected from:



1) The Geophysica high altitude aircraft; stratospheric flights in mid-latitudes in late 2009 and in high latitudes in early 2010



2) Lufthansa passenger aircraft flights in the UT/LS from Germany to South Africa in 2009, 2010 & 2011 (CARIBIC project)



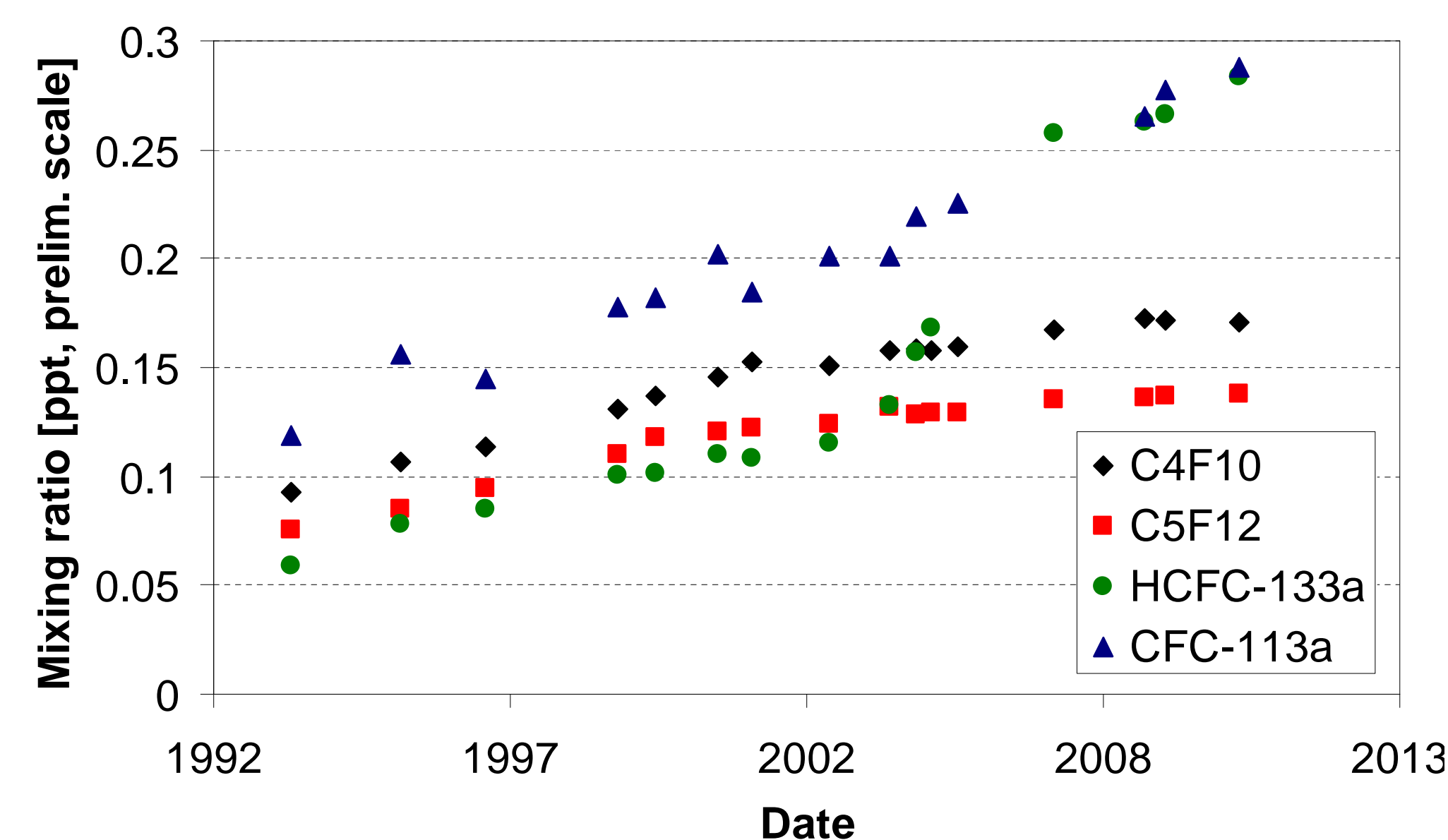
3) Deep firn in the Arctic and Antarctic dating back to the early 20<sup>th</sup> century (NEEM project in Greenland; photo by Helle Astrid Kjær)



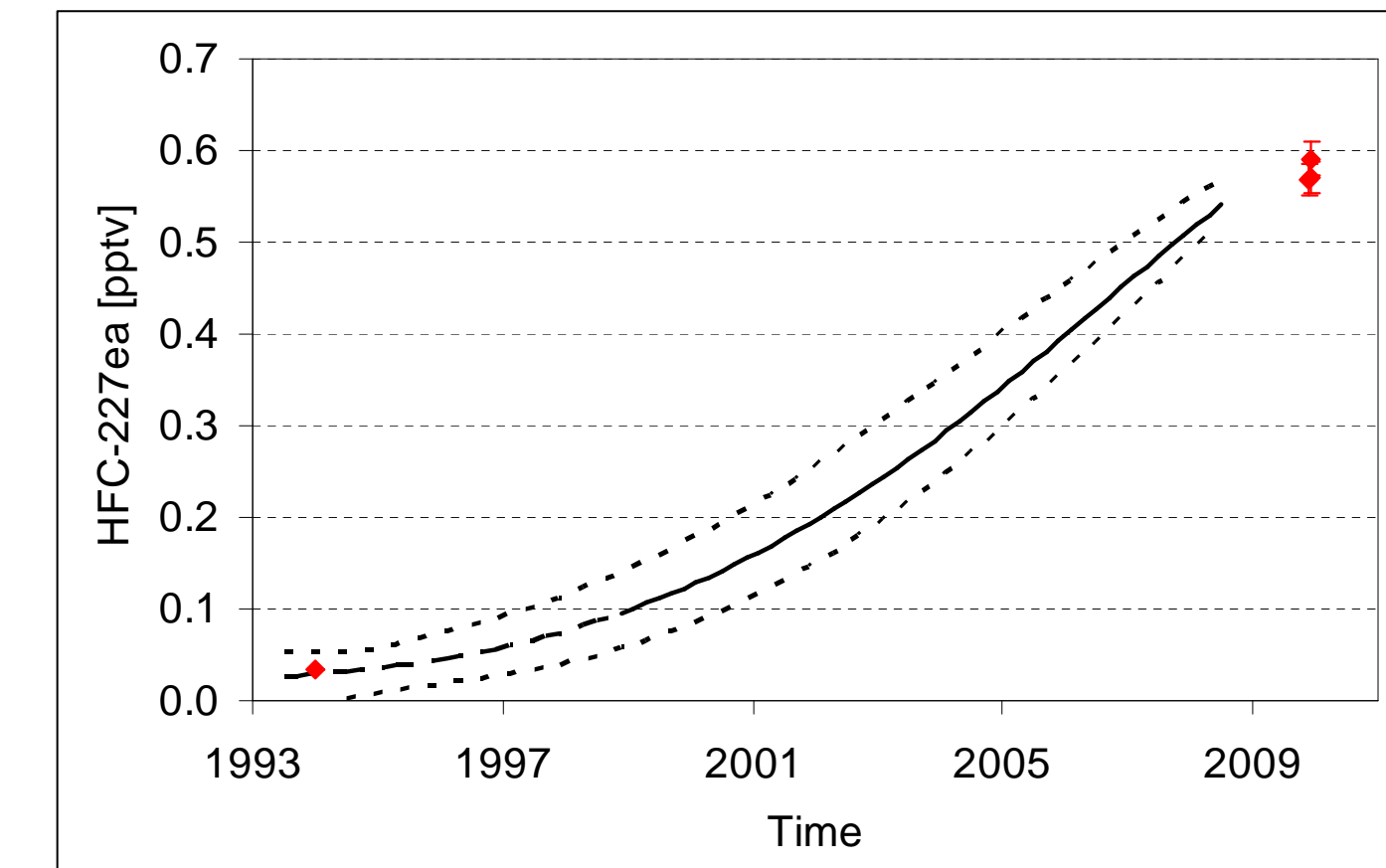
4) A remote ground-based observatory at Cape Grim, Tasmania archived samples dating back to 1978

## Tropospheric trends from Cape Grim

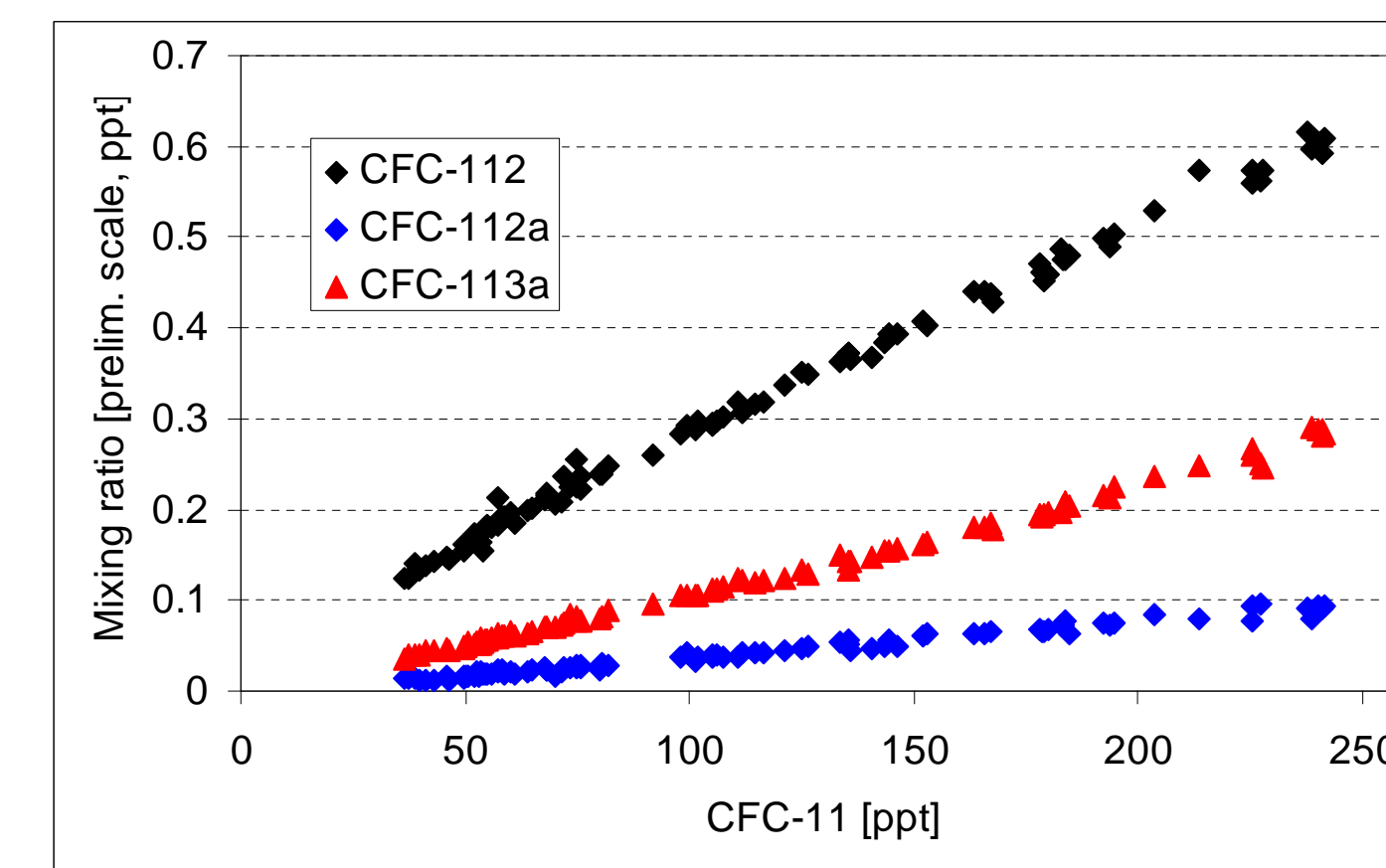
At Cape Grim, Tasmania the air contains gases at concentrations representative of the unpolluted Southern Hemisphere and is thus ideal to measure long term trends. The figure shows the reanalysis of archived air samples for the strong greenhouse gases C<sub>4</sub>F<sub>10</sub> and C<sub>5</sub>F<sub>12</sub> as well as two of the ozone-depleting compounds. **All four show continuing growth.** The other two CFCs are decreasing, while HFC-227ea shows accelerating growth (not shown).



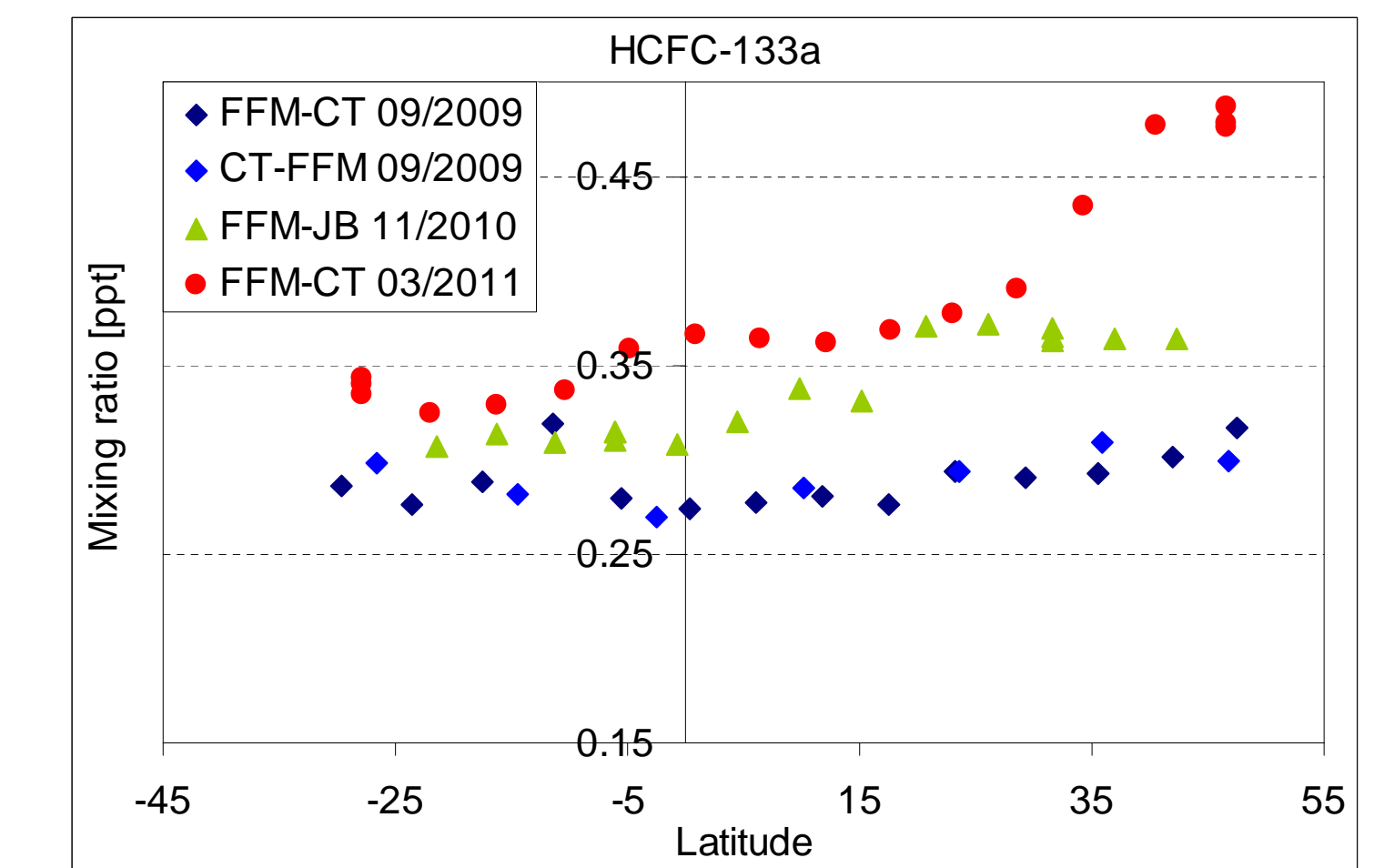
## Results



Air trapped in **firn (deep snow)** provides a natural archive which can be used to reconstruct atmospheric histories of trace gases back to the early 20<sup>th</sup> century. Growth of atmospheric HFC-227ea - a CFC replacement compound and strong greenhouse gas - was recently discovered<sup>1</sup> (top left). **All compounds presented here are not found in deep firn, meaning they are entirely man-made.**



Data from the upper troposphere from the CARIBIC aircraft give indications of growth rates and hemispheric distributions. The figure on the right shows mixing ratios of HCFC-133a during flights from Germany to South Africa: almost directly from the mid Northern to the mid Southern Hemisphere. **Emissions are higher in the Northern Hemisphere. Growth from 2009 to 2011 can be observed.**



The stratospheric data from the Geophysica can be used to estimate stratospheric lifetimes. The lifetime  $\tau_{strat}$  can be inferred from the slope of the correlation with a trace gas of known stratospheric lifetime (here: CFC-11). **We estimate stratospheric lifetimes similar to that of CFC-11 for the CFCs, and on the order of centuries for HFC-227ea and HCFC-133a.** These are shown in the Table below.

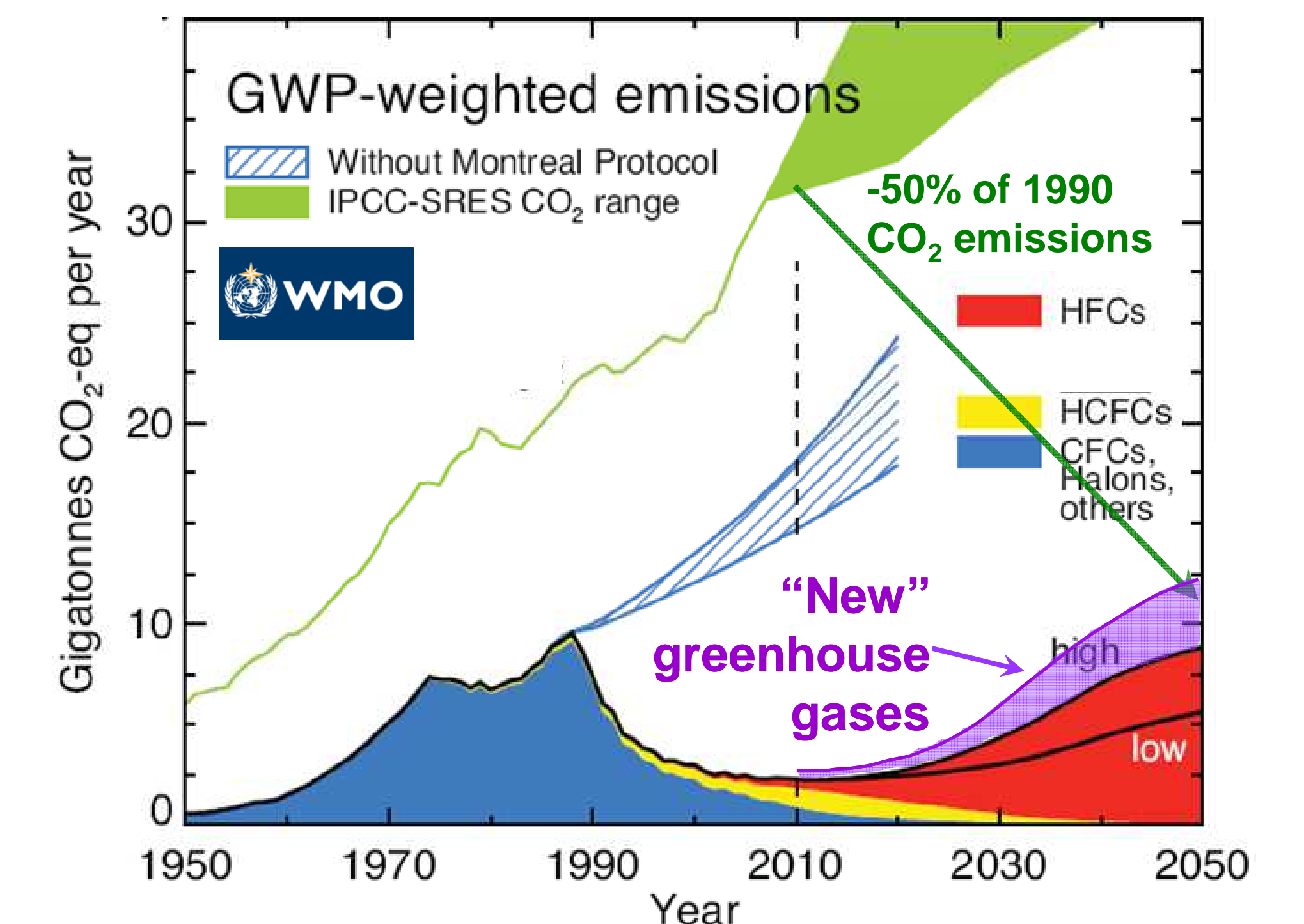
## Emissions of strong greenhouse gases

Gas	Lifetime (y)	100-y GWP	Emissions (Gg yr <sup>-1</sup> )
HFC-227ea	52	6,180	1.8 (2007) [1]
HFC-23	222	14,200	2.8 (2007) [2]
CF <sub>4</sub>	50,000	7,390	12 (2003) [3]
C <sub>2</sub> F <sub>6</sub>	10,000	12,200	2.6 (2003) [3]
C <sub>3</sub> F <sub>8</sub>	2,600	8,830	0.76 (2005-08) [4]
c-C <sub>4</sub> F <sub>8</sub>	3,200	10,300	1.1 (2007) [5]
C <sub>4</sub> F <sub>10</sub>	2,600	8,850	?
C <sub>5</sub> F <sub>12</sub>	4,100	9,150	?
NF <sub>3</sub>	500	17,500	0.62 (2008) [6]
SO <sub>2</sub> F <sub>2</sub>	36	4,740	1.9 (2007) [7]
SF <sub>6</sub>	3,200	22,800	7.16 (2008) [8]
CFC-112	49 - 55	6,000?	?
CFC-112a	42 - 46	6,000?	?
CFC-113a	49 - 53	6,000?	?
"Others"		6,000	1 (2010) [See text]

In red: first reported in the atmosphere by UEA  
In green: lifetimes from this study (stratospheric = global for CFCs)

The figure right is adapted from WMO (2011)<sup>9</sup> with the addition of an envelope representing the contribution to CO<sub>2</sub>-equivalent emissions that would occur if the emission rates of the gases in the Table above grew ten-fold by 2050 (HFC-23 was not included as its emissions are expected to decline). Adding this to the projected estimate for the contribution of other HFC gases in 2050 suggests that **unconstrained growth could seriously undermine** the benefits from present international efforts to substantially reduce future CO<sub>2</sub> emissions.

One way of visualising the potential impact of strong greenhouse gases emissions is to calculate an equivalent emission of CO<sub>2</sub>; i.e. "Global Warming Potential (GWP)-weighted emissions". The GWP and emission rates of the "new" gases, along with other recently-reported important halocarbons, are compiled in the Table left. Since the GWPs and emission rates of some of the "new" gases are not yet well known, a generic contribution of "Other" gases has been assumed.



**Summary** We have detected seven new fluorinated organic compounds in the atmosphere, all at low abundance, but likely to be strong greenhouse gases. Several are increasing. The present contribution to global warming is very small. However, taken together with other recently-discovered gases, a picture of a potentially serious threat to the climate system emerges if such gases were allowed unconstrained future growth.

### References

<sup>1</sup>Laube, J. C., et al., *Atmos. Chem. Phys.*, 10, 5903-5910, 2010; <sup>2</sup>Montzka et al., *Geophys. Res. Lett.*, 37, L02808, 2010; <sup>3</sup>Worton et al., *Environ. Sci. Technol.*, 41, 2184-2189, 2007; <sup>4</sup>Mühle et al., *Atmos. Chem. Phys.*, 10, 5145-5164, 2010; <sup>5</sup>Oram et al., *Atmos. Phys. Chem. Disc.*, 11, 19089-19111, 2011; <sup>6</sup>Weiss et al., *Geophys. Res. Lett.*, 35, L20821, 2008; <sup>7</sup>Mühle et al., *Geophys. Res. Lett.*, 114, D05306, 2009; <sup>8</sup>Levine et al., *Atmos. Chem. Phys.*, 10, 2655-2662, 2010; <sup>9</sup>Daniel, J.S. and Velders, G.J.M., Chapter 5 in *Scientific Assessment of Ozone Depletion: 2010*, WMO, 5.1-5.56, 2011.

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