Supplementary information to

Distributions, long term trends and emissions of four perfluorocarbons in remote parts of the atmosphere and firn air

J. C. Laube[1], C. Hogan[1], M. J. Newland[1], F. S. Mani[1,2], P. J. Fraser[3], C. A. M. Brenninkmeijer[4], P. Martinerie[5], D. E. Oram[6], T. Röckmann[7], J. Schwander[8], E. Witrant[9], G. P. Mills[1], C. E. Reeves[1] and W. T. Sturges[1]

[1]{School of Environmental Sciences, University of East Anglia, Norwich, United Kingdom}

[2]{School of Applied Sciences, Fiji National University, Suva, Fiji}

[3]{Centre for Australian Weather and Climate Research, Commonwealth Scientific and

Industrial Research Organisation, Aspendale, Victoria 3195, Australia}

[4]{Max Planck Institute for Chemistry, Air Chemistry Division, Mainz, Germany}

[5]{Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE), CNRS / Université Joseph Fourier, BP 96, 38 402 Saint Martin d'Hères, France}

[6]{National Centre for Atmospheric Science, School of Environmental Sciences, University of East Anglia, Norwich, United Kingdom}

[7]{Institute for Marine and Atmospheric Research, Utrecht University, Utrecht, Netherlands}

[8]{Physics Institute, University of Berne, Bern, Switzerland}

[9]{Grenoble Image Parole Signal Automatique (GIPSA-lab), Université Joseph Fourier / CNRS, BP 46, 38 402 Saint Martin d'Hères, France}

Correspondence to: J. C. Laube (j.laube@uea.ac.uk)

Details of analysis, calibration and instrument linearity

The GC-MS and pre-concentration system was used in the exact same setup as described in Laube et al., 2010a. Table S1 displays the retention time, ions and respective mass-to-charge (m/z) ratios used to identify and quantify the perfluorocarbons. No chromatographic interferences were found for the quantifier ions at the given retention time windows. It should be noted, however, that n-C_6F_{14} is measured on m/z 168.99 but co-elutes with $CF_2ClCFCl_2$ (CFC-113) which represents a comparably large signal and forms an ion with a similar m/z ratio ($C_2F_2{}^{35}Cl_2{}^{37}Cl^+$, m/z 168.90). However, the ratio of m/z 218.99 to m/z 168.99 remained constant except for two samples with very low mixing ratios in the Cape Grim air archive where the signal on m/z 218.99 was close to detection limit. Considering the gradient in CFC-113 mixing ratios over the last three decades the ratio between m/z 218.99 to m/z 168.99 should have changed significantly if the latter was influenced by m/z 168.90. We therefore conclude that the influence of the $C_2F_2{}^{35}Cl_2{}^{37}Cl^+$ ion on n-C_6F_{14} mixing ratios is negligible.

For compound identity confirmation and quantification we utilised and later modified an existing two-step static dilution system previously described in Laube et al., 2010a. All compounds were diluted in Oxygen-free Nitrogen (OFN) obtained from BOC Gases, UK. For n-C_4F_{10} (obtained from Fluorochem Ltd. UK, purity 98 %) and n-C_5F_{12} (also from Fluorochem Ltd. UK, purity 99 %) we added CF_2Cl_2 (CFC-12) as an internal reference compound. n-C_6F_{14} (from Apollo Scientific, purity 98.5 %) and n-C_7F_{16} (from Sigma-Aldrich, technical grade, 85% n-isomer) are liquids at room temperature and thus more likely to experience losses from condensation inside the dilution system. To prevent this, all parts of the dilution system except for the pressure sensors and the two 100-litre drums were heated to 80°C using two Agilent 5971 GC ovens as well as rope heaters (OMEGALUX®) controlled by 1/16 DIN Autotune controllers from Omega Engineering Ltd., UK. In addition $CFCl_3$ (CFC-11) was used as an alternative internal standard for the liquids. The mixing ratios derived from the internal standards (CFC-11 and CFC-12) showed deviations of less than 5.5 % from their internationally recognised NOAA-ESRL scales (NOAA-2008 for CFC-12 and NOAA-1993 for CFC-11). We assign a calibration scale uncertainty of less than 7 % (similar to Oram et al., 2011) at the mixing ratios levels in the dilutions prepared here. The calibration results including the mixing ratios of the dilutions and those assigned to the standards (remote tropospheric air sampled in 2006) are also shown in Table S1. The standard deviation of the calibrations was only higher than 7 % in the case of C_7F_{16} which is due to the limited precision of the GC-MS analysis of this compound at the time of those measurements. The calibration system operates at high temperatures and low pressures of pure compounds thus minimising influence from non-ideal gas behaviour. It has been previously demonstrated that a) virial coefficients have no significant influence on the derived mixing ratios and b) the complete analytical setup shows linear response behaviour over several orders of magnitude (Laube et al., 2010a). However, one significant uncertainty specific to the calibrations of the higher perfluorocarbons remains. Although we observed similar ratios of quantifier to qualifier ions in atmospheric samples as compared to dilutions of pure compounds we can not rule out the presence of other isomeric perfluorocarbons in either of these samples. These isomers have very similar mass spectra and physicochemical properties and the used gas chromatographic setup is unlikely to be capable of separating them. This is especially true in the case of n-C_7F_{16} which we could only obtain as a technical mixture of isomers with 85 % n-isomer basis. In fact dilutions of this mixture resulted in a double peak with the dominant part of it at the exact retention time of n-C_7F_{16}. As we can not distinguish between these isomers we assign an additional 15 % uncertainty to the calibration scale of this molecule. We are not able to estimate similar uncertainties to the other perfluorocarbons but have found no indications for isomeric or other impurities in these compounds (pure and atmospheric) to date.

To determine the linearity of the response behaviour of the analytical system a static dilution series was prepared by diluting an unpolluted NH air sample collected in 2009 at Niwot Ridge near Boulder, USA (containing 0.177 ppt of C_4F_{10}, 0.136 ppt of C_5F_{12}, 0.257 ppt of C_6F_{14}, and 0.103 ppt of C_7F_{16}) with Research Grade Nitrogen (obtained from BOC Gases, UK) in stainless steel canisters. Five dilutions were prepared with dilution factors of 1.00, 0.672, 0.458, 0.236 and 0.00. Within the uncertainties of the dilution factors and measurement uncertainties (less than 5 % in all cases) the analytical system was found to respond linearly for all four compounds.

Table S1. Additional information on the identification and quantification of the reported perfluoroalkanes.

Compound	n-C_4F_{10}	n-C_5F_{12}	n-C_6F_{14}	n-C_7F_{16}
Retention time [min]	13.7	16.4	18.7	20.8
Identification ions m/z	31.00 50.00 70.00 93.00 99.99 118.99	31.00 50.00 70.00 93.00 99.99 118.99	70.00 74.00 81.00 93.00 99.99 111.99	70.00 74.00 81.00 93.00 99.99 111.99

	130.99 149.99 168.99 218.99	130.99 149.99 168.99 180.99 218.99	118.99 123.99 130.99 142.99 149.99 161.99 168.99 180.99 192.99 218.99	118.99 123.99 130.99 142.99 149.99 161.99 168.99 180.99 218.99
Quantifier ion (m/z)	$C_2F_5^+$ (118.99)	$C_2F_5^+$ (118.99)	$C_3F_7^+$ (168.99)	$C_3F_7^+$ (168.99)
Qualifier ion (m/z)	$C_3F_5^+$ (130.99)	$C_3F_5^+$ (130.99)	$C_4F_9^+$ (218.99)	$C_4F_7^+$ (180.99)
Deviation of internal std from NOAA scales [%]	1.0 to 2.7	-1.4 to 2.8	-2.7 to -0.7	-5.5 to -0.8
Mixing ratio range prepared [ppt]	13.9-33.7	12.9-13.5	7.2-7.9	5.0-9.1
Mixing ratio assigned to standard [ppt]	0.169	0.135	0.238	0.096
Standard deviation of calibrations [%]	1.68	5.13	4.86	7.35

Details of firn reconstruction and Cape Grim growth rates

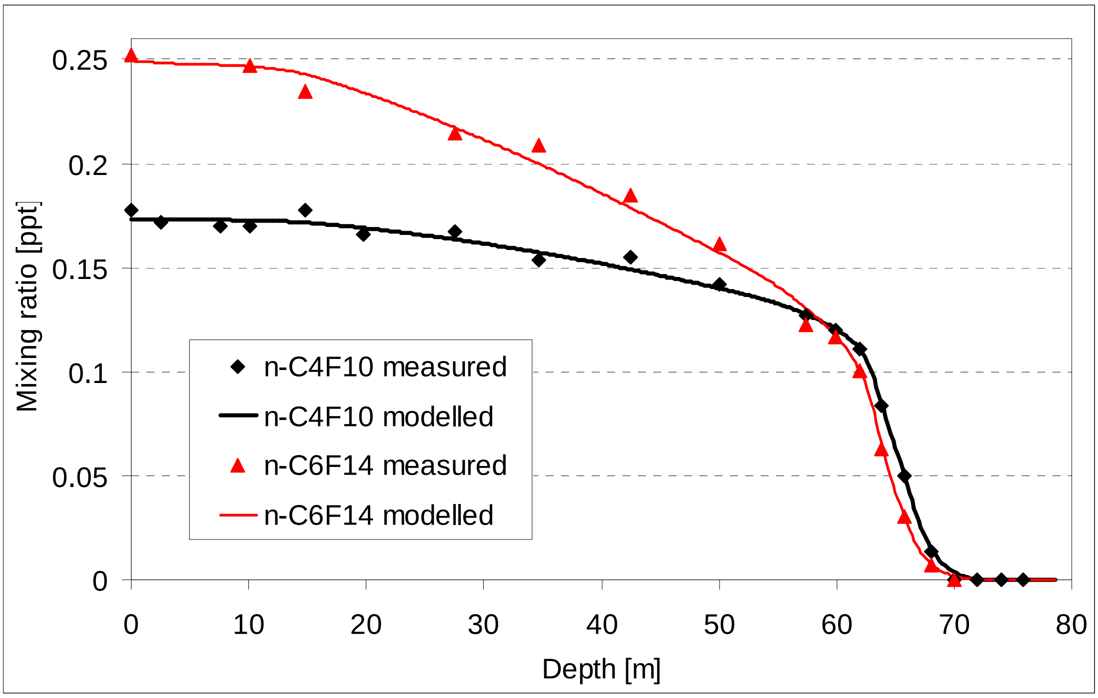

Figure S1. Measured firn depth profiles in comparison to firn model results for n-C_4F_{10} and n-C_6F_{14}.

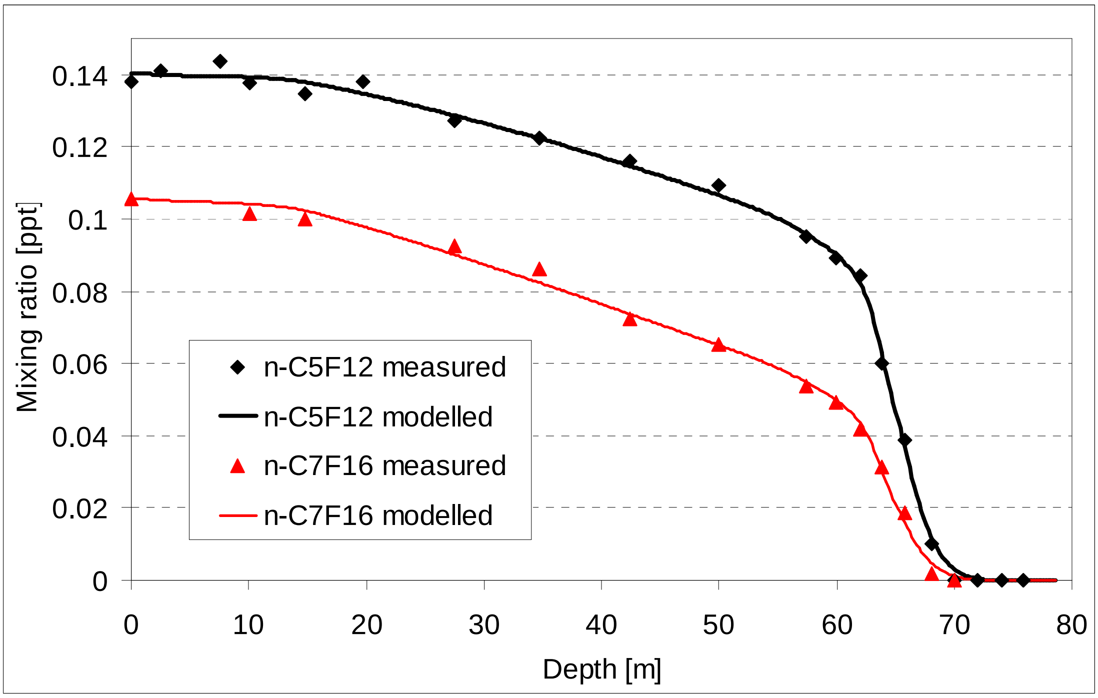

Figure S2. The same as in Figure S1 but for n-C_5F_{12} and n-C_7F_{16}.

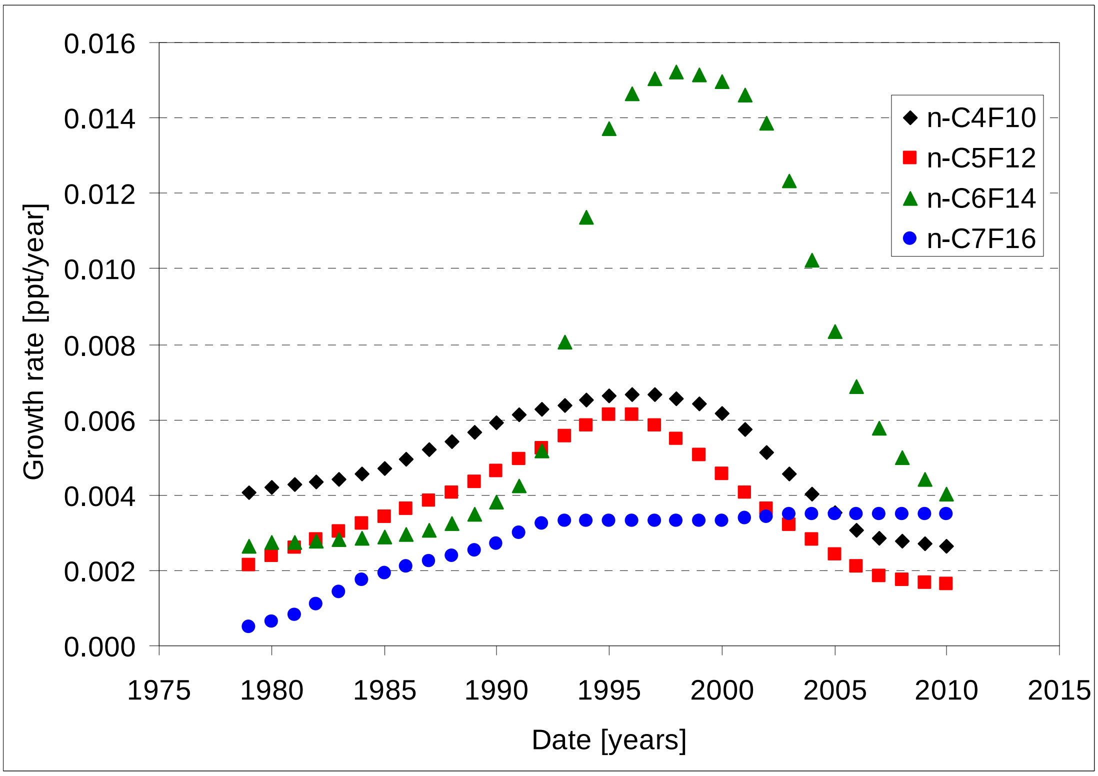

Figure S3. Growth rates of all four perfluoroalkanes as inferred from the sigmoidal expressions fitted to the Cape Grim data set.

Table S2. Trends and emissions inferred from the Cape Grim record.

Date	Cape Grim mixing ratio from fit [ppt]	Measurement uncertainty average [ppt]	Global emissions [Gg]	Emission uncertainty [Gg]
n-C_4F_{10}				
1978	0.019	0.002	0.17	0.04
1979	0.023	0.002	0.17	0.04
1980	0.027	0.002	0.17	0.04
1981	0.031	0.002	0.18	0.04
1982	0.035	0.002	0.18	0.04
1983	0.040	0.002	0.19	0.04
1984	0.044	0.003	0.19	0.04
1985	0.049	0.003	0.20	0.05
1986	0.054	0.003	0.21	0.05
1987	0.059	0.003	0.22	0.05
1988	0.065	0.003	0.23	0.05
1989	0.070	0.003	0.24	0.05
1990	0.076	0.004	0.25	0.05
1991	0.082	0.005	0.26	0.05
1992	0.089	0.004	0.26	0.05
1993	0.095	0.004	0.27	0.05
1994	0.102	0.004	0.27	0.05
1995	0.108	0.004	0.27	0.05
1996	0.115	0.003	0.27	0.05
1997	0.122	0.003	0.27	0.05
1998	0.128	0.004	0.26	0.05
1999	0.134	0.006	0.25	0.05
2000	0.141	0.005	0.23	0.04
2001	0.146	0.003	0.21	0.04
2002	0.152	0.003	0.18	0.03
2003	0.156	0.004	0.16	0.03
2004	0.160	0.003	0.14	0.02
2005	0.164	0.003	0.12	0.02
2006	0.167	0.003	0.12	0.02
2007	0.170	0.003	0.11	0.02
2008	0.172	0.004	0.11	0.02
2009	0.175	0.005	0.11	0.02
2010	0.178	0.002	-	-
n-C_5F_{12}				
1978	0.018	0.002	0.11	0.03
1979	0.020	0.002	0.12	0.04
1980	0.022	0.002	0.13	0.04
1981	0.025	0.002	0.14	0.04
1982	0.028	0.002	0.15	0.04
1983	0.031	0.002	0.16	0.04
1984	0.034	0.003	0.17	0.04
1985	0.037	0.003	0.18	0.05
1986	0.041	0.003	0.19	0.05
1987	0.045	0.003	0.20	0.05

1988	0.049	0.003	0.22	0.05
1989	0.053	0.003	0.23	0.05
1990	0.058	0.004	0.25	0.06
1991	0.063	0.004	0.26	0.06
1992	0.068	0.003	0.28	0.06
1993	0.074	0.003	0.29	0.06
1994	0.079	0.003	0.31	0.06
1995	0.086	0.003	0.30	0.06
1996	0.092	0.003	0.29	0.06
1997	0.098	0.002	0.27	0.05
1998	0.103	0.003	0.25	0.05
1999	0.108	0.003	0.22	0.04
2000	0.113	0.003	0.20	0.04
2001	0.117	0.003	0.18	0.03
2002	0.120	0.003	0.16	0.03
2003	0.124	0.002	0.14	0.03
2004	0.126	0.003	0.12	0.02
2005	0.129	0.003	0.10	0.02
2006	0.131	0.003	0.09	0.02
2007	0.133	0.003	0.09	0.02
2008	0.134	0.003	0.08	0.02
2009	0.136	0.004	0.08	0.02
2010	0.138	0.002	-	-
n-C_6F_{14}				
1978	0.012	0.009	0.16	0.16
1979	0.015	0.008	0.16	0.13
1980	0.018	0.007	0.16	0.11
1981	0.021	0.007	0.16	0.09
1982	0.023	0.007	0.16	0.09
1983	0.026	0.007	0.16	0.08
1984	0.029	0.007	0.17	0.07
1985	0.032	0.007	0.17	0.07
1986	0.035	0.007	0.18	0.07
1987	0.038	0.007	0.19	0.07
1988	0.041	0.007	0.20	0.08
1989	0.045	0.007	0.22	0.08
1990	0.048	0.007	0.25	0.09
1991	0.053	0.007	0.28	0.10
1992	0.058	0.007	0.50	0.17
1993	0.066	0.007	0.70	0.23
1994	0.077	0.007	0.83	0.26
1995	0.091	0.007	0.85	0.26
1996	0.106	0.007	0.87	0.26
1997	0.121	0.007	0.88	0.25
1998	0.136	0.007	0.87	0.24
1999	0.151	0.007	0.86	0.23
2000	0.166	0.007	0.84	0.22
2001	0.181	0.007	0.80	0.21
2002	0.194	0.007	0.70	0.18
2003	0.207	0.007	0.56	0.15

2004	0.217	0.007	0.46	0.12
2005	0.225	0.007	0.38	0.10
2006	0.232	0.007	0.32	0.08
2007	0.238	0.007	0.28	0.07
2008	0.243	0.007	0.25	0.06
2009	0.247	0.007	0.23	0.06
2010	0.251	0.007	-	-
n-C_7F_{16}				
1978	0.015	0.005	0.04	0.02
1979	0.016	0.004	0.05	0.03
1980	0.016	0.004	0.06	0.04
1981	0.017	0.004	0.08	0.05
1982	0.018	0.004	0.10	0.06
1983	0.020	0.004	0.12	0.07
1984	0.021	0.005	0.13	0.08
1985	0.023	0.005	0.14	0.08
1986	0.025	0.005	0.15	0.09
1987	0.028	0.005	0.16	0.09
1988	0.030	0.005	0.17	0.10
1989	0.033	0.005	0.18	0.10
1990	0.035	0.007	0.20	0.12
1991	0.038	0.009	0.22	0.14
1992	0.041	0.007	0.22	0.13
1993	0.045	0.005	0.22	0.11
1994	0.048	0.005	0.22	0.11
1995	0.051	0.005	0.22	0.11
1996	0.055	0.005	0.22	0.11
1997	0.058	0.004	0.22	0.10
1998	0.061	0.004	0.22	0.10
1999	0.065	0.004	0.22	0.10
2000	0.068	0.006	0.22	0.10
2001	0.071	0.007	0.23	0.10
2002	0.075	0.006	0.23	0.11
2003	0.078	0.004	0.23	0.10
2004	0.082	0.004	0.23	0.10
2005	0.085	0.004	0.23	0.10
2006	0.089	0.004	0.23	0.10
2007	0.092	0.004	0.23	0.10
2008	0.096	0.004	0.23	0.10
2009	0.099	0.005	0.23	0.10
2010	0.103	0.005	-	-