Supplement 1. PFC emissions from UNFCCC data

Perfluorocarbon (PFC) emission are reported to UNFCCC by 34 Annex I countries as part of their obligations as signatories to the Kyoto Protocol (UNFCCC, 2009). Emissions are reported for CF_4, C_2F_6, C_3F_8, c-C_4F_8, C_4F_{10}, C_5F_{12} and C_6F_{14} in Gg for individual PFCs, and total PFC emissions are reported in Gg (CO_2-e, using the GWP_{100}s (100-yr period) 6500 (CF_4), 9200 (C_2F_6), 7000 (C_3F_8), 8700 (c-C_4F_8), 7000 (C_4F_{10}), 7500 (C_5F_{12}), and 7400 (C_6F_{14}). Some countries also or solely (in particular the UK) report emissions of an unspecified mix of PFCs in CO_2-e. To derive total individual PFC emissions in any one year (T), the global total of unspecified PFC emissions is assumed to contain the same PFC mix as the global total of specified PFC emissions in that year (S).

Table S1 shows global emissions (in Gg) of specific PFCs as reported to UNFCCC (S), and total emissions (T) where any unspecified mix of PFCs has been distributed according to the global total of specified PFC emissions. The UNFCCC data contain emissions from the 27 member countries of the European Community (EUC, Austria, Belgium, Bulgaria, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, and the UK) as well as other individual European countries. The global totals reported below contain emissions from all reporting countries and the EUC excluding individual countries which also report under the EUC sum. Portugal, Ukraine and the UK (3) report total PFC emissions only. Australia, Austria, Belgium, Canada, Croatia, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Japan, Monaco, Netherlands, New Zealand, Norway, Poland, Romania, Russia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the USA (31) report individual PFC emissions. Austria, Finland, Germany, Japan, and the Netherlands (5) also report an unspecified PFC mix.

Table S1. PFC emission from UNFCCC (2009) data

	Year	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
CF_4	S	8.58	7.86	7.16	6.77	6.19	6.16	6.31	6.04	5.87	5.74	5.59	4.63	4.47	4.08	3.86	3.8	3.6
	T	9.34	8.7	7.99	7.9	7.71	7.93	8.15	8.05	7.52	7.06	6.79	5.65	5.37	4.95	4.78	4.66	4.43
C_2F_6	S	1.27	1.18	1.11	1.1	1.06	1.03	1.07	1.03	1.03	1.03	0.93	0.78	0.81	0.72	0.67	0.64	0.64
	T	1.38	1.3	1.23	1.29	1.33	1.32	1.38	1.37	1.32	1.26	1.14	0.95	0.98	0.88	0.83	0.79	0.78
C_3F_8	S	0.025	0.024	0.026	0.026	0.03	0.036	0.041	0.043	0.035	0.021	0.046	0.049	0.044	0.06	0.046	0.046	0.049
	T	0.027	0.026	0.029	0.03	0.037	0.046	0.054	0.058	0.045	0.025	0.055	0.06	0.053	0.073	0.057	0.057	0.06

Supplement 2. CF_4 emissions from primary aluminum production

The International (Primary) Aluminium Institute (IAI) annually reports anode affect data to derive PFC emissions from the global aluminum (Al) smelting industry, using data on Al production and PFC (CF_4 and C_2F_6) smelting technology-specific emission factors (EF, Tier 1), emission coefficients (Tier 2) and, when available, facility-specific coefficients (Tier 3, confidential data) in their IAI Anode Effect surveys (1996; 2000, 2001, 2003-2008, 2009b, a). IAI uses median technologies EF/coefficients to estimate emissions from non-reporting facilities which currently produce ~40% of global Al (IAI, 2009a) and mainly use high performing Point Feed Prebake (PFPB) technology. Until the mid-2000s Chinese Al production was dominated by Horizontal Stud Soderberg (HSS) technology, but through the mid-2000s a transformation occurred and by the end of 2005 the China Non-Ferrous Metals Industry Association (CNIA) reported 100% use of PFPB technology. It seemed reasonable to assume that the time-dependent Chinese CF_4 EF were the same as the average deduced for PFPB smelters participating in the global IAI Anode Effect surveys (2009b, a) which declined from ~0.3 to ~0.04 kg/tonne Al from 1990 to 2006 (2009b). However, IAI recently found a median PFPB EF for 8 Chinese smelters 2.6 times larger than the global PFPB

technology average (2009a). Assuming the Chinese EF is constant in time, revised CF_4 emissions were calculated for Chinese and global Al smelting from 2006 to 2008 (Table S2).

Table S2. CF_4 emissions from primary aluminum production

	1990	1995	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008
1. Global CF_4 emissions (Gg)[a]	11.4	7.39	7.70	7.69	7.10	4.71	5.00	4.50	4.60	3.46	3.19	3.41	3.37
2. Chinese aluminum production (Mt)[b]				2.60	2.79	3.37	4.32	5.55	6.69	7.81	9.35	12.6	13.1
3. PFPB CF_4 emission factor (kg/tonne)[a]	0.310	0.097	0.080	0.091	0.080	0.080	0.061	0.053	0.047	0.038	0.038	0.038	0.038
4. Chinese CF_4 emissions (Gg)[c]											0.36	0.48	0.50
5. Global CF_4 emissions (excl. China)[d]											2.83	2.94	2.87
6. Revised Chinese CF_4 emissions (Gg)[e]											0.92	1.24	1.29
7. Revised global CF_4 emission (Gg)[f]											3.75	4.18	4.16

[a]International (Primary) Aluminium Institute (1996; 2000, 2001, 2003-2008, 2009b, a)

[b]International Aluminium Institute (IAI) http://www.world-aluminium.org/Statistics/Historical+statistics)

[c]Chinese CF_4 emissions = Chinese aluminum production * standard PFPB emission factor (= 2 * 3)

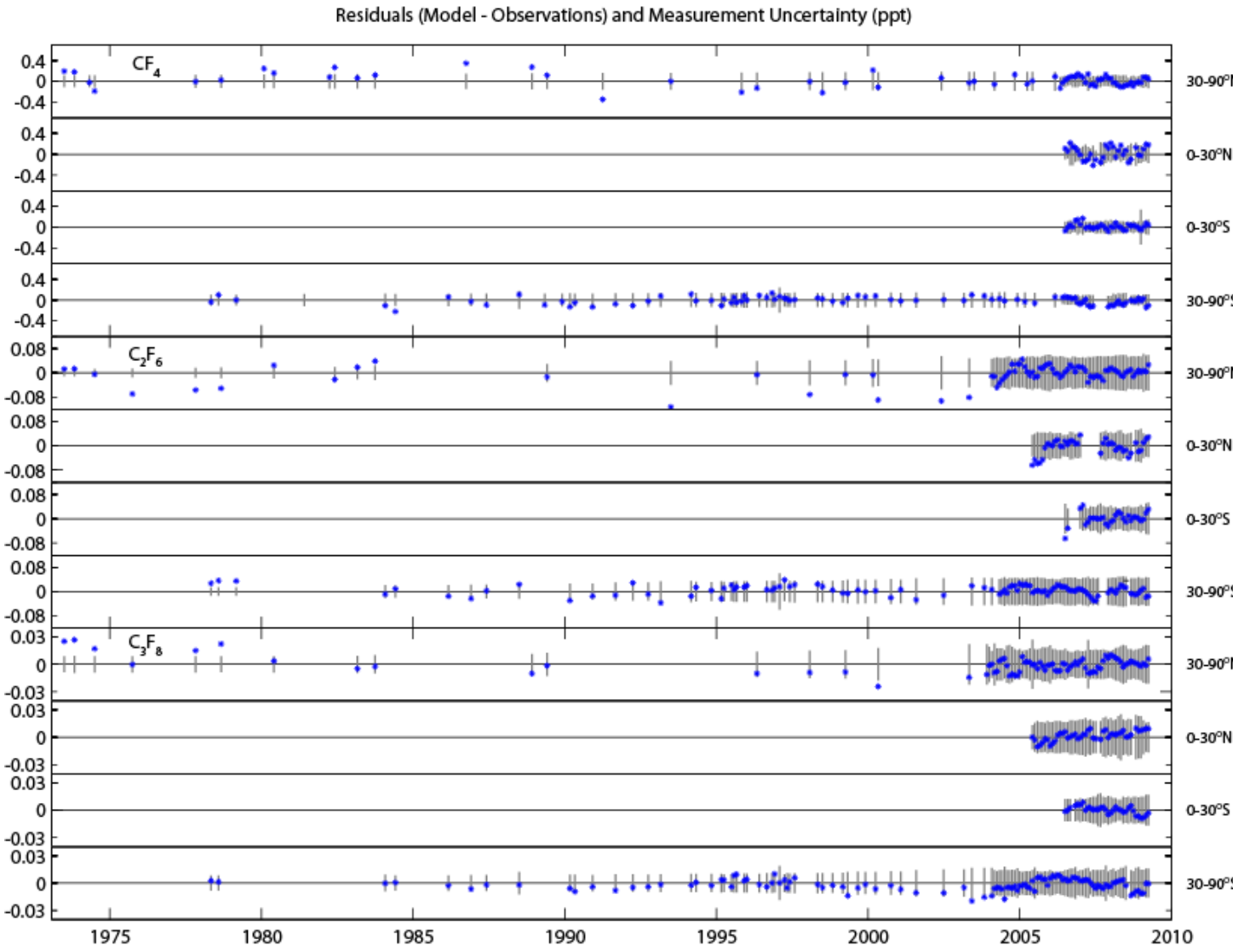
[d]Global CF_4 emissions (excl. China) = global – China (= 1 – 4)

[e]Revised CF_4 Chinese emissions = Chinese CF_4 emissions * 2.6 (= 4 * 2.6)

[f]Revised global CF_4 emissions = Global CF_4 emissions (excluding China) + Revised Chinese CF_4 emissions (= 5 + 6)

Supplement 3. Residuals and Measurement Uncertainty

Figure S3. Residuals (Model – Observations) and Measurement Uncertainty (ppt)



Residuals as modeled minus observed mixing ratios (blue dots) vs. measurement uncertainty (gray bars) for CF_4, C_2F_6, and C_3F_8 in each semi-hemispheric model box. Residuals are generally smaller than the measurement uncertainty indicating that the derived emissions are consistent with the measurements. Residuals that lie outside of the measurement uncertainty may have occurred when the sampled air was not truly representative of the semi-hemispheric background.