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Supplement of

Recent increases in the atmospheric growth rate and emissions of HFC-23 (CHF_3) and the link to HCFC-22 ($CHClF_2$) production

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Supplementary Material (1): AGAGE Instrumentation and Measurement Techniques

Typically for each measurement, the analytes from two litres of air are collected on the microtrap and, after fractionated distillation, purification and transfer, are desorbed onto a single main capillary chromatography column (CP-PoraBOND Q, 0.32 mm ID × 25 m, 5 µm, Agilent Varian Chrompack, batch-made for AGAGE applications) purged with helium (research grade 6.0) that is further purified using a heated helium purifier (HP2, VICI, USA). Separation and detection of the compounds are achieved by using Agilent Technology GCs (model 6890N) and quadrupole mass spectrometers in selected ion mode (initially model 5973 series, progressively converted to 5975C over the later years).

The quaternary standards are whole-air samples, pressurized into 34 L internally electropolished stainless steel canisters (Essex Industries, USA). They are filled by the responsible station scientist and/or on-site station personnel who are in charge of the respective AGAGE remote sites using modified oil-free diving compressors (SA-3 and SA-6, RIX Industries, USA) to ~60 bar (older canisters to ~40 bar). Cape Grim is an exception, where the canisters used for quaternary standard purposes are filled cryogenically. This method of cryogenically collecting large volumes of ambient air is the same as that is used for collecting air for the CGAA and measurements of many atmospheric trace species in air samples collected in this manner show that the trace gas composition of the air is well preserved (Fraser et al., 1991, 2016; Langenfelds et al., 1996, 2003). The on-site quaternary standards are compared weekly to tertiary standards from the central calibration facility at the Scripps Institution of Oceanography (SIO) in order to propagate the primary calibration scales and assess any long-term drifts. These tertiary standards are filled with ambient air in Essex canisters under “baseline” clean air conditions at Trinidad Head or at La Jolla (California) and are measured at SIO against secondary ambient air standards (to obtain an “out” value) before they are shipped to individual AGAGE sites. We define “baseline” as air masses that are representative of the unpolluted marine boundary layer, uninfluenced by recent local or regional emissions. After their on-site deployment they are again measured at SIO to obtain an “in” value, to assess any possible drifts. They are also measured on-site against the previous and next tertiaries. The secondary standards and the synthetic primary standards at SIO provide the core of the AGAGE calibration system (Prinn et al., 2000; Miller et al., 2008).

The GC-MS-Medusa measurement precisions for HFC-23 and HCFC-22 are determined as the precisions of replicate measurements of the quaternary standards over twice the time interval as for sample-standard comparisons (Miller et al., 2008). Accordingly, they are upper-limit estimates of the precisions of the sample-standard comparisons. Typical daily precisions for each compound vary with abundance and individual instrument performance over time.

Average percentage relative standard deviation (% RSD) between 2007 and 2016 were: HFC-23 (0.1%-1.9%, average 0.7%); and for HCFC-22 (0.1%-2.5%, average 0.6%).

Supplementary Material (2): Firn Air Depth Profiles, Analyses of the CGAA and old Northern Hemisphere (NH) air samples

In this section we illustrate in Figures S1 the depth profiles for HFC-23 in the polar firn and in Figure S2 we show three independent analyses of the data from the CGAA. Tables S1 and S2 also list the actual data used to construct these figures.

Figure S1. Depth profiles for HFC-23 in polar firn. DSSW20K and SPO-01 are Antarctic sites and NEEM-08 is from Greenland. The modelled mole fractions correspond to the optimized emissions history using an inversion and firn air model developed at CSIRO.

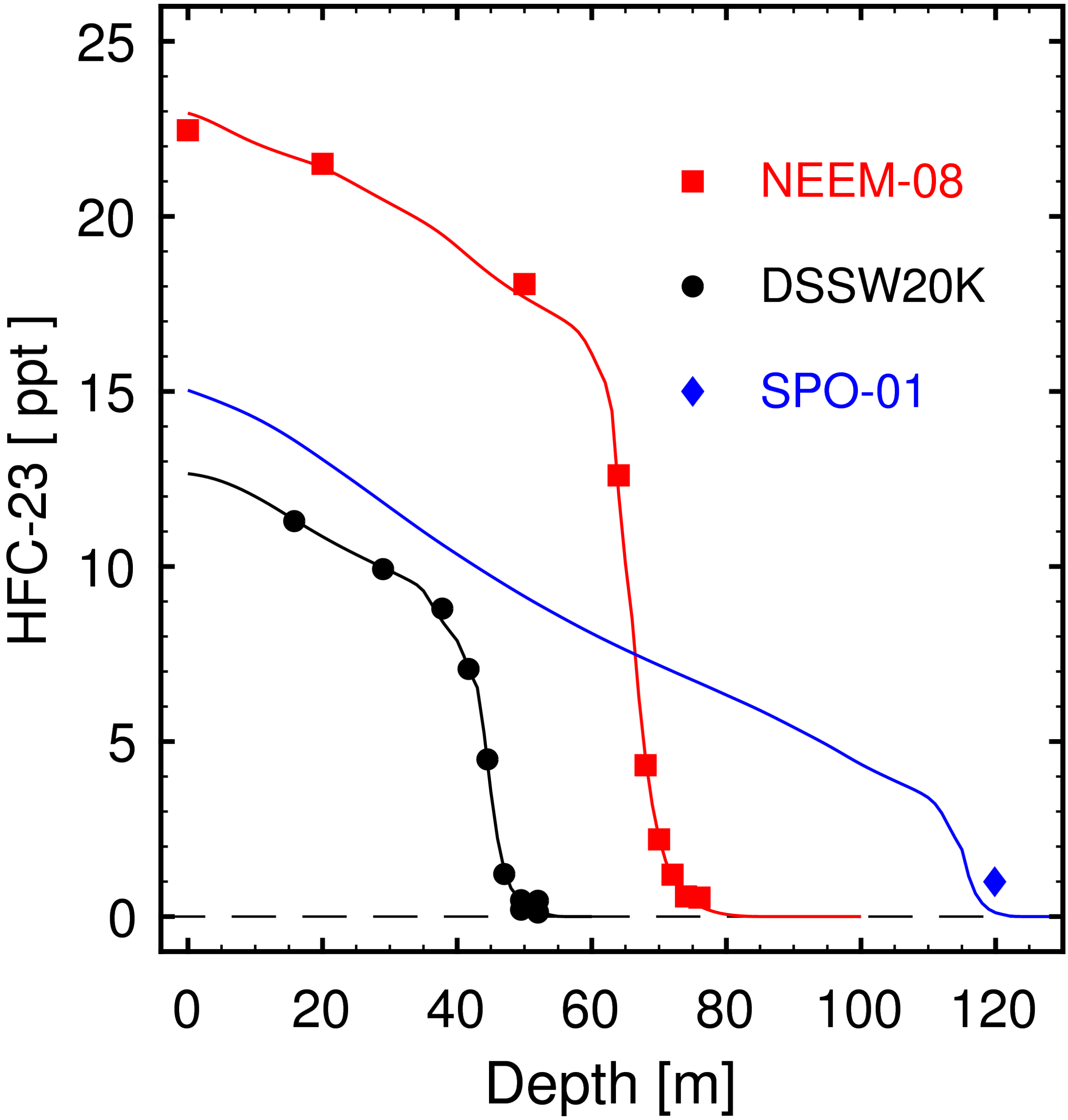
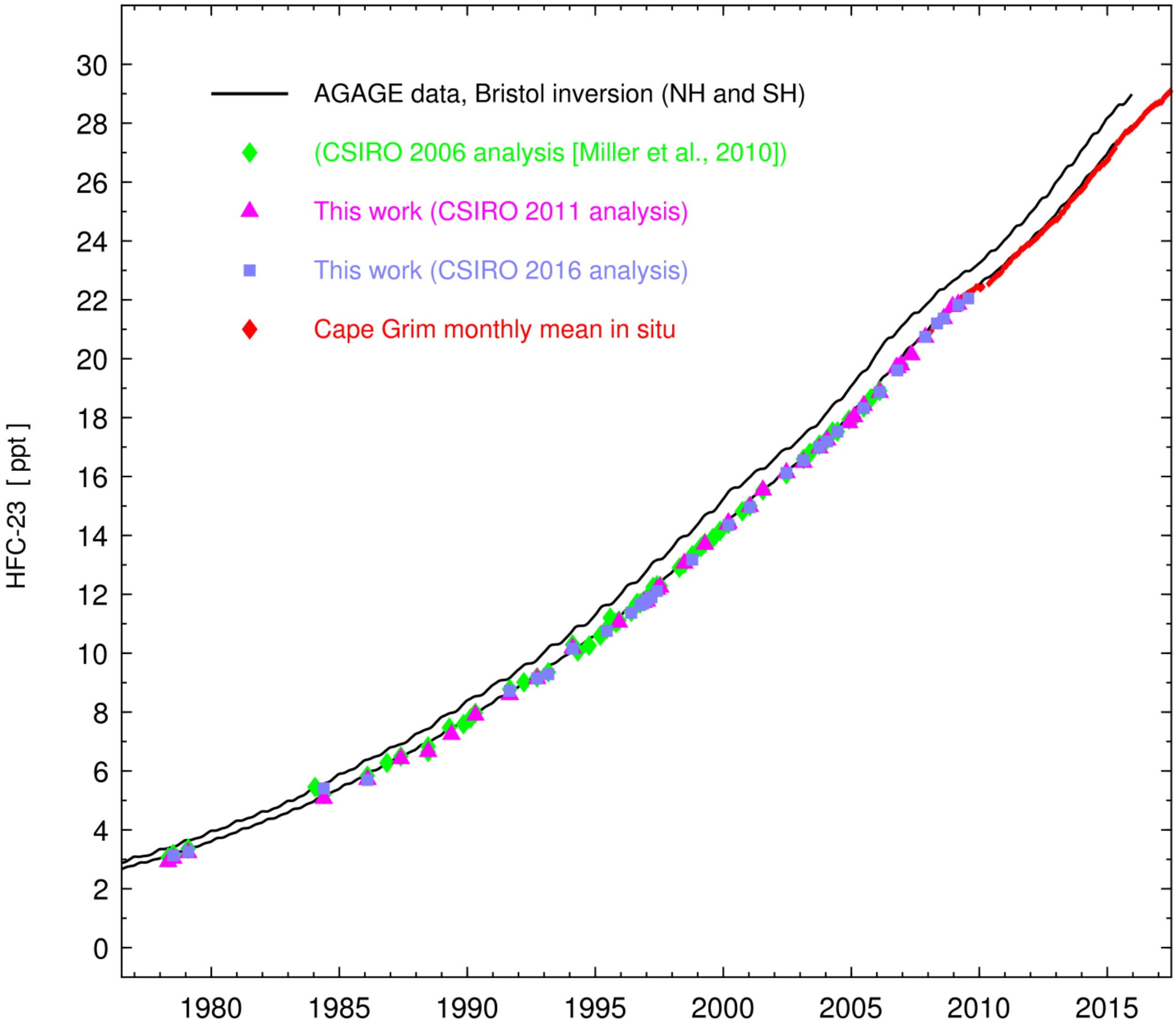


Figure S2. Comparison of three analysis sets of HFC-23 in the Cape Grim Air Archive



A series of old Northern Hemisphere (NH) air samples were mostly collected during clean air conditions but not with the purpose of creating a consistent air archive. Therefore, a stepwise tightening filtering algorithm was applied to the measurement results based on their deviations from a fit through all data (including in situ data). Due to the scarcity of the Northern Hemisphere HFC-23 data, the filtering of these samples used the fit through the filtered Southern Hemisphere samples as additional guide (with an appropriate time lag related to hemispheric transport). The remaining final NH HFC-23 data showed good agreement with concurrent in situ measurements. (Mühle et al., 2010; Vollmer et al., 2016)

Table S1

Firn air measurement and model results for HFC-23

Abbreviations: m: measured; mf: mole fraction; p: precision (measurement repeatability, 1 sigma); mod: firn air model output with uncertainties

Primary calibration scale for HFC-23: SIO-07

depth: depth in firn air hole from which sample was drawn

Sample Volume: volume of sample used in one analysis on the Medusa-GCMS

Flags used for the decisions on presence of the compound in the sample

Flag 1: Peak size large enough a non-zero positive mole fraction was calculated and reported.

Flag 2: Clear sign of a peak but very small. Mole fraction was calculated by GCWerks either using generally set parameters or using GCWerks special integration

Flag 3: Maybe a peak some baseline disturbance that point to a non-zero signal. In most cases a mole fraction assigned

Flag 4: no sign of a peak at all no change in baseline. Mole fraction definitely smaller than the estimated detection limit for that sample

					sample		HFC-23							
Site	Tank_ID	UAN	Parent_UAN	depth	volume	m-mf	m-p	n	Flag	mod-mf	mod-min	mod-max	mean	effect
				[m]	[L]	[ppt]	[ppt]			[ppt]	[ppt]	[ppt]	Age	Age
DSSW20K	S22L-002	UAN980141	UAN980141	15.8	3	11.295	0.071	3	1	11.335	11.282	11.449	1995.95	1996.26
DSSW20K	MC-05	UAN980780	UAN980142	29	2	9.924	0.098	2	1	9.968	9.856	10.1	1993.63	1994.04
DSSW20K	CA01674	UAN980143	UAN980143	37.8	3	8.796	0.041	4	1	8.431	8.327	8.624	1990.64	1991.23
DSSW20K	MC-08	UAN980783	UAN980144	41.7	2	7.074	0.06	2	1	7.075	6.954	7.307	1987.71	1988.85

DSSW20K	MC-09	UAN980784	UAN980145	44.5	2	4.49	0.018	2	1	4.425	4.221	4.54	1980.51	1982.51
DSSW20K	MC-06	UAN980781	UAN980146	47	2	1.215	0.021	2	1	1.323	1.195	1.411	1966.83	1970.73
DSSW20K	MC-04	UAN980779	UAN980147	49.5	2	0.196	0.033	2	1	0.478	0.414	0.53	1952.95	1953.44
DSSW20K	S22L-010	UAN980148	UAN980148	49.5	1.5	0.468	0.061	2	1	0.478	0.414	0.53	1952.95	1953.44
DSSW20K	MC-01	UAN980776	UAN980150	52	2	0.128	0.011	2	1	0.478	0.414	0.53	1952.95	1953.44
DSSW20K	MC-10	UAN980785	UAN980149	52	1	0.451	0.064	2	1	0.478	0.414	0.53	1952.95	1953.44
DSSW20K	S22L-007	UAN980151	UAN980151	52	2	0.115	0	1	1	0.137	0.137	0.292	1938.93	1937.62
NEEM-2008	S300-B15	UAN999698	UAN999698	0	1.5	22.462	0.104	2	1	0.137	0.137	0.292	1938.93	1937.62
NEEM-2008	S300-B13	UAN999697	UAN999697	20	1.5	21.502	0.189	2	1	0.137	0.137	0.292	1938.93	1937.62
NEEM-2008	S300-B11	UAN999695	UAN999695	50	1.5	18.067	0.067	2	1	0.137	0.137	0.292	1938.93	1937.62
NEEM-2008	S300-B12	UAN999696	UAN999696	64	1.5	12.602	0.1	2	1	0.137	0.137	0.292	1938.93	1937.62
NEEM-2008	S300-B16	UAN999699	UAN999699	68	1.5	4.322	0.012	2	1	0.137	0.137	0.292	1938.93	1937.62
NEEM-2008	S300-B18	UAN999701	UAN999701	70	1.5	2.204	0.051	2	1	0.137	0.137	0.292	1938.93	1937.62
NEEM-2008	S300-B19	UAN999702	UAN999702	72	1.5	1.196	0.047	2	1	0.137	0.137	0.292	1938.93	1937.62
NEEM-2008	S300-B17	UAN999700	UAN999700	74	1.5	0.575	0.05	2	1	0.137	0.137	0.292	1938.93	1937.62
NEEM-2008	S300-B20	UAN999703	UAN999703	76	1.5	0.541	0.011	2	1	NaN	NaN	NaN	NaN	NaN
SPO	S300-A23	UAN996580	UAN993582	119.87	1	0.994	0.04	2	1	21.391	21.182	21.537	2006.96	2007

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depth: depth in firn air hole from which sample was drawn

Sample Volume: volume of sample used in one analysis on the Medusa-GCMS

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					sample					HFC-23				
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DSSW20K	MC-10	UAN980785	UAN980149	52	1	0.451	0.064	2	1	0.478	0.414	0.53	1952.95	1953.44
DSSW20K	S22L-007	UAN980151	UAN980151	52	2	0.115	0	1	1	0.137	0.137	0.292	1938.93	1937.62
NEEM-2008	S300-B15	UAN999698	UAN999698	0	1.5	22.462	0.104	2	1	0.137	0.137	0.292	1938.93	1937.62
NEEM-2008	S300-B13	UAN999697	UAN999697	20	1.5	21.502	0.189	2	1	0.137	0.137	0.292	1938.93	1937.62
NEEM-2008	S300-B11	UAN999695	UAN999695	50	1.5	18.067	0.067	2	1	0.137	0.137	0.292	1938.93	1937.62
NEEM-2008	S300-B12	UAN999696	UAN999696	64	1.5	12.602	0.1	2	1	0.137	0.137	0.292	1938.93	1937.62
NEEM-2008	S300-B16	UAN999699	UAN999699	68	1.5	4.322	0.012	2	1	0.137	0.137	0.292	1938.93	1937.62
NEEM-2008	S300-B18	UAN999701	UAN999701	70	1.5	2.204	0.051	2	1	0.137	0.137	0.292	1938.93	1937.62
NEEM-2008	S300-B19	UAN999702	UAN999702	72	1.5	1.196	0.047	2	1	0.137	0.137	0.292	1938.93	1937.62
NEEM-2008	S300-B17	UAN999700	UAN999700	74	1.5	0.575	0.05	2	1	0.137	0.137	0.292	1938.93	1937.62
NEEM-2008	S300-B20	UAN999703	UAN999703	76	1.5	0.541	0.011	2	1	NaN	NaN	NaN	NaN	NaN
SPO	S300-A23	UAN996580	UAN993582	119.87	1	0.994	0.04	2	1	21.391	21.182	21.537	2006.96	2007

Table S2

Cape Grim Air Archive (CGAA) Results for HFC-23 from three analysis periods

Results are reported as dry air mole fractions for abundance (c) and precisions (p)

Measurements are conducted on the CSIRO Aspendale-9 GCMS-Medusa

Primary calibration scales: CFC-23: SIO-07

Notes for 2006: Measurements by B. R. Miller, L. Porter, L. P. Steele, P. B. Krummel. Results by peak area. Standard is G-141 with assigned values: CFC-23: 19.648 ppt

Notes for 2011: Measurements by D. Ivy, L. P. Steele, P. B. Krummel, M. Leist, Results by peak area. Standard is G-181 with assigned values: CFC-23: 23.1456 ppt

Notes for 2016: Measurements by M. K. Vollmer, L. P. Steele, B. Mitrevski, P. B. Krummel, Results by peak area. Standard is E-146S with assigned values: CFC-23: 31.4808 ppt

sampleID	time	year	month	day	c_mean	p_mean	c_2006	p_2006	n_2006	c_2011	p_2011	n_2011	c_2016	p_2016	n_2016
	fractional				[ppt]	[ppt]	[ppt]	[ppt]		[ppt]	[ppt]		[ppt]	[ppt]	
UAN780001	1978.315	1978	4	26	2.992	0.081	3.065	0.114	3	2.918	0.048	3	NaN	NaN	NaN
UAN780002	1978.512	1978	7	7	3.116	0.018	3.178	0.023	3	3.037	0.009	3	3.133	0.023	3
UAN790001	1979.099	1979	2	6	3.282	0.025	3.363	0.027	3	3.223	0.04	3	3.259	0.008	3
UAN910377	1984.053	1984	1	20	5.453	0.044	5.453	0.044	2	NaN	NaN	NaN	NaN	NaN	NaN
UAN840004	1984.391	1984	5	23	5.226	0.023	5.2	0.034	4	5.066	0.021	4	5.411	0.014	3
UAN860001	1986.099	1986	2	6	5.746	0.048	5.835	0.046	4	5.71	0.086	4	5.694	0.012	3
UAN860005	1986.863	1986	11	12	6.275	0.142	6.275	0.142	4	NaN	NaN	NaN	NaN	NaN	3

UAN870006	1987.403	1987	5	28	6.456	0.06	6.493	0.039	4	6.418	0.08	6	NaN	NaN	NaN
UAN880003	1988.47	1988	6	21	6.651	0.058	6.646	0.065	6	6.657	0.051	3	NaN	NaN	NaN
UAN880002	1988.47	1988	6	21	6.834	0.037	6.834	0.037	4	NaN	NaN	NaN	NaN	NaN	3
UAN890002	1989.299	1989	4	20	7.466	0.04	7.466	0.04	4	NaN	NaN	NaN	NaN	NaN	NaN
UAN890004	1989.378	1989	5	19	7.24	0.083	NaN	NaN	NaN	7.24	0.083	8	NaN	NaN	3
UAN890005	1989.852	1989	11	8	7.589	0.064	7.589	0.064	4	NaN	NaN	NaN	NaN	NaN	NaN
UAN900027	1990.127	1990	2	16	7.786	0.145	7.786	0.145	4	NaN	NaN	NaN	NaN	NaN	NaN
UAN900048	1990.315	1990	4	26	7.932	0.112	7.969	0.06	5	7.894	0.164	3	NaN	NaN	3
UAN910361	1991.658	1991	8	29	8.695	0.06	8.775	0.057	3	8.592	0.09	3	8.718	0.032	3
UAN920469	1992.211	1992	3	18	9.012	0.025	9.012	0.025	3	NaN	NaN	NaN	NaN	NaN	NaN
UAN920655	1992.727	1992	9	23	9.152	0.049	9.18	0.042	4	9.135	0.059	5	9.14	0.046	3
UAN930279	1993.164	1993	3	2	9.321	0.023	9.353	0.024	3	NaN	NaN	NaN	9.289	0.023	3
UAN940378	1994.112	1994	2	11	10.205	0.054	10.291	0.077	3	10.17	0.072	3	10.154	0.012	3
UAN940679	1994.318	1994	4	27	10.06	0.043	10.06	0.043	3	NaN	NaN	NaN	NaN	NaN	NaN
UAN941096	1994.759	1994	10	4	10.259	0.192	10.259	0.192	4	NaN	NaN	NaN	NaN	NaN	NaN
UAN950527	1995.195	1995	3	13	10.596	0.023	10.596	0.023	4	NaN	NaN	NaN	NaN	NaN	NaN
UAN950789	1995.447	1995	6	13	10.788	0.059	10.82	0.088	6	NaN	NaN	NaN	10.756	0.03	3
UAN950894	1995.584	1995	8	2	11.202	0.157	11.202	0.157	4	NaN	NaN	NaN	NaN	NaN	NaN
UAN960115	1995.811	1995	10	24	11.027	0.109	11.027	0.109	4	NaN	NaN	NaN	NaN	NaN	NaN
UAN960051	1995.923	1995	12	4	11.081	0.052	11.108	0.06	3	11.054	0.044	5	NaN	NaN	NaN
UAN960957	1996.404	1996	5	28	11.39	0.056	11.407	0.068	5	NaN	NaN	NaN	11.373	0.043	3

UAN961164	1996.637	1996	8	21	11.705	0.123	11.705	0.123	3	NaN	NaN	NaN	NaN	NaN	NaN
UAN961409	1996.754	1996	10	3	11.668	0.04	11.695	0.074	3	NaN	NaN	NaN	11.64	0.006	3
UAN970092	1996.885	1996	11	20	11.728	0.044	11.766	0.069	4	11.726	0.031	4	11.693	0.033	3
UAN970008	1997.016	1997	1	7	11.809	0.06	11.871	0.114	5	11.767	0.051	5	11.79	0.016	3
UAN970011	1997.016	1997	1	7	11.813	0.081	11.824	0.123	3	NaN	NaN	NaN	11.802	0.039	3
UAN970010	1997.017	1997	1	7	11.812	0.062	11.812	0.062	3	NaN	NaN	NaN	NaN	NaN	NaN
UAN970380	1997.195	1997	3	13	11.934	0.063	11.97	0.085	13	NaN	NaN	NaN	11.898	0.041	6
UAN970754	1997.255	1997	4	4	12.245	0.071	12.245	0.071	4	NaN	NaN	NaN	NaN	NaN	NaN
UAN970756	1997.408	1997	5	30	12.194	0.046	12.3	0.093	5	12.17	0.019	4	12.112	0.027	3
UAN971115	1997.534	1997	7	15	12.263	0.057	12.281	0.044	3	12.244	0.07	7	NaN	NaN	NaN
UAN980724	1998.285	1998	4	15	12.902	0.116	12.902	0.116	5	NaN	NaN	NaN	NaN	NaN	NaN
UAN980918	1998.479	1998	6	25	13.052	0.081	13.051	0.086	6	13.053	0.077	5	NaN	NaN	NaN
UAN981563	1998.786	1998	10	15	13.25	0.062	13.323	0.091	15	NaN	NaN	NaN	13.177	0.032	3
UAN991060	1999.129	1999	2	17	13.606	0.089	13.606	0.089	6	NaN	NaN	NaN	NaN	NaN	NaN
UAN991062	1999.279	1999	4	13	13.717	0.067	13.737	0.026	4	13.696	0.108	5	NaN	NaN	NaN
UAN991381	1999.59	1999	8	4	13.904	0.088	13.904	0.088	3	NaN	NaN	NaN	NaN	NaN	NaN
UAN992045	1999.874	1999	11	16	14.152	0.11	14.152	0.11	5	NaN	NaN	NaN	NaN	NaN	NaN
UAN20101335	2000.164	2000	3	1	14.375	0.088	NaN	NaN	NaN	14.375	0.088	6	NaN	NaN	NaN
UAN992982	2000.199	2000	3	14	14.391	0.092	14.393	0.139	6	14.426	0.111	5	14.353	0.028	3
UAN993562	2000.744	2000	9	29	14.818	0.044	14.818	0.044	4	NaN	NaN	NaN	NaN	NaN	NaN
UAN993563	2001.038	2001	1	15	14.979	0.089	15.002	0.111	7	14.977	0.133	4	14.957	0.022	3

UAN994885	2001.545	2001	7	19	15.534	0.104	15.53	0.116	3	15.539	0.093	5	NaN	NaN	NaN
UAN994886	2002.466	2002	6	20	16.11	0.075	16.08	0.105	4	16.13	0.086	6	16.121	0.035	3
UAN995445	2003.129	2003	2	17	16.54	0.071	16.596	0.08	6	16.481	0.079	5	16.544	0.053	3
UAN996454	2003.384	2003	5	21	16.802	0.071	16.802	0.071	3	NaN	NaN	NaN	NaN	NaN	NaN
UAN996455	2003.753	2003	10	3	17.018	0.062	17.081	0.096	4	16.967	0.057	5	17.005	0.032	3
UAN996456	2004.053	2004	1	20	17.265	0.113	17.265	0.113	3	NaN	NaN	NaN	NaN	NaN	NaN
UAN998318	2004.057	2004	1	22	17.237	0.058	17.275	0.072	5	17.24	0.059	6	17.195	0.042	3
UAN996457	2004.268	2004	4	8	17.523	0.205	17.523	0.205	3	NaN	NaN	NaN	NaN	NaN	NaN
UAN996458	2004.459	2004	6	17	17.529	0.025	17.53	0.026	3	NaN	NaN	NaN	17.529	0.025	3
UAN997089	2004.915	2004	12	1	17.879	0.075	17.932	0.075	16	17.826	0.075	18	NaN	NaN	NaN
UAN997090	2005.11	2005	2	10	18.009	0.037	17.991	0.052	5	18.028	0.021	5	NaN	NaN	NaN
UAN998005	2005.488	2005	6	28	18.36	0.098	18.345	0.175	14	18.413	0.095	18	18.32	0.025	6
UAN998006	2005.759	2005	10	5	18.653	0.122	18.653	0.122	8	NaN	NaN	NaN	NaN	NaN	NaN
UAN998195	2006.11	2006	2	10	18.873	0.134	18.905	0.204	14	18.853	0.173	15	18.862	0.025	6
G-139	2006.756	2006	10	4	19.695	0.12	NaN	NaN	NaN	19.695	0.12	6	NaN	NaN	NaN
UAN998425	2006.797	2006	10	19	19.65	0.042	NaN	NaN	NaN	19.696	0.043	6	19.603	0.042	4
UAN998852	2006.942	2006	12	11	19.784	0.094	19.778	0.134	5	19.791	0.054	4	NaN	NaN	NaN
UAN998898	2007.348	2007	5	8	20.132	0.098	NaN	NaN	NaN	20.132	0.098	5	NaN	NaN	NaN
UAN999276	2007.89	2007	11	22	20.733	0.181	NaN	NaN	NaN	20.726	0.308	5	20.741	0.054	3
UAN999627	2008.347	2008	5	7	21.198	0.014	NaN	NaN	NaN	NaN	NaN	NaN	21.198	0.014	3
UAN999756	2008.612	2008	8	12	21.365	0.067	NaN	NaN	NaN	21.364	0.086	6	21.365	0.049	3

UAN20100047	2008.956	2008	12	16	21.773	0.071	NaN	NaN	NaN	21.773	0.071	5	NaN	NaN	NaN
UAN20100609	2009.175	2009	3	6	21.836	0.09	NaN	NaN	NaN	21.851	0.118	8	21.821	0.062	3
UAN20101456	2009.567	2009	7	27	22.051	0.031	NaN	NaN	NaN	NaN	NaN	NaN	22.051	0.031	3

Supplementary Material (3): Emissions Inventories

HFC-23 (trifluoromethane, fluoroform, CHF_3) is a by-product of the chemical process to manufacture HCFC-22 (chlorodifluoromethane, $CHClF_2$) from chloroform and hydrogen fluoride.

S3.1. HCFC-22 Production

HCFC-22 is used in two ways: the commercial product is used in the refrigeration and air conditioning industries, and is eventually emitted into the atmosphere; production and consumption for this are controlled under the Montreal Protocol . It is also a chemical feedstock, the raw material for the manufacture of PTFE (polytetrafluoroethylene) and other fluoropolymers, effectively being destroyed in the process with small, inadvertent emissions not controlled under the Montreal Protocol.

Table S3 shows the inventory of HCFC-22 production for all end uses, subdivided between developed countries (referred to in the Montreal Protocol as "non-Article 5 countries", that are not eligible for any support under the Montreal Protocol or United Nations Framework Convention on Climate Change (UNFCCC) mechanisms, and individual Article 5 countries that are eligible to receive support to reduce emissions of HFC-23.

In the case of the non-A5 countries (which are listed individually in Table S4), historical demand for dispersive uses was taken from the AFEAS database (1) up to 2007 and demand for fluoropolymer feedstock was derived from Stanford Research Institute data (2) that shows historical linear growth at 5800 tonnes/year from 2001 onwards and a requirement of about 50% of the reported dispersive demand up to that date. Production for dispersive use in 2008 was derived from the Parties submissions to the Montreal Protocol (3) and the Technology and Economic Assessment Panel of the Montreal Protocol (4). From 2009 onwards, the total production reported to the Executive Committee of the Montreal Protocol was used (5).

The same report to the Executive Committee (5) was used for production from individual Article 5 countries from 2009 onwards; prior to that year, the quantities produced in Argentina, India, South Korea, Mexico and Venezuela were estimated using the Montreal Protocol and TEAP data (3, 4).

Table S3. Estimated HCFC-22 production: Total for all uses Gg.

Year	Non-Article 5 Countries	Article 5 Countries							Global Total
		Argentina	China	India	Korea (N)	Korea (S)	Mexico	Venezuela	
1990	320.57	0	0	3.62	0	1.75	1.54	1.85	329.33
1990	320.57	0	0	3.62	0	1.75	1.54	1.85	329.33
1991	355.22	0	0	3.86	0	2.65	1.84	1.80	365.37
1992	368.57	0	0	3.72	0	3.97	1.86	2.04	380.16
1993	360.93	0.18	4.92	4.72	0	4.41	2.82	2.01	379.99
1994	359.17	0.21	9.83	4.50	0	4.51	2.14	1.43	381.79
1995	365.20	0.00	14.75	5.22	0	5.09	1.96	1.45	393.67
1996	406.86	0.00	19.66	4.54	0	8.27	4.80	1.39	445.53
1997	376.66	0.00	24.58	5.33	0	9.28	4.67	1.37	421.89
1998	391.76	0.00	37.14	8.34	0	7.88	3.42	0.95	449.48
1999	378.56	0.00	59.74	8.68	0	14.42	4.89	1.07	467.37
2000	365.77	0.11	77.79	11.18	0	11.29	3.43	1.20	470.77
2001	345.20	0.11	111.42	12.01	0	5.81	2.59	1.32	478.46
2002	331.76	0.58	103.37	11.26	0	10.22	3.81	1.44	462.44
2003	326.63	1.06	144.22	13.88	0	6.84	3.70	1.57	497.89
2004	334.73	1.54	191.06	17.99	0	5.53	3.73	1.69	556.26
2005	327.37	2.01	270.89	17.41	0	7.92	5.53	1.81	632.93
2006	322.29	2.49	325.28	21.06	0	5.23	7.33	1.94	685.61
2007	328.10	2.96	414.97	29.32	0	4.94	9.13	2.06	791.47
2008	333.92	3.44	373.17	38.49	0	5.93	10.93	2.18	768.05
2009	195.80	3.91	483.98	47.66	0.50	6.91	12.73	2.31	753.80
2010	229.86	4.25	549.27	47.61	0.50	7.63	12.62	2.17	853.91
2011	241.78	4.02	596.98	48.48	0.48	7.26	11.81	2.44	913.26
2012	219.91	4.19	644.49	48.18	0.52	5.70	7.87	2.91	933.77
2013	193.52	1.95	615.90	40.65	0.58	6.67	7.38	2.20	868.86
2014	210.04	2.29	623.90	54.94	0.53	6.83	9.21	1.57	909.30
2015	225.16	2.45	534.93	53.31	0.50	7.18	4.75	0.68	828.95

Chinese production now accounts for 65% of the global total, with a large demand for fluoropolymer feedstock, and was estimated separately. Production for dispersive uses and export was derived from the submission to the Montreal Protocol database and TEAP data (3, 4). Fluoropolymer (mainly polytetrafluoroethylene, PTFE) production from 1998 to 2002 was reported in China Chemical Reporter (CCR) (6) and showed growth of 33%/year. This growth was assumed to be maintained until 2007, implying production of over 69 Gg/year of PTFE in 2007, a value consistent with the capacity for fluoropolymers stated in the 11th Chinese 5 year plan to be 80 Gg/year in 2007/8 (7). Total production of HCFC-22 in China was also reported in CCR (6), with a growth rate of between 47% and 25% in the period 1998 to 2001. For the values calculated here, a subsequent growth rate of 15% / year was applied until 2008, and from 2009 onwards, the total annual productions reported to the Executive Committee of the Montreal Protocol were used (5).The resulting values agree within 4% with the numbers for 2013 to 2015 reported separately by the Chinese government (8).

S3.2. HFC-23 Emissions

Attempts to reduce HFC-23 formation by adjusting process conditions have important economic consequences for HCFC-22 production; the historic rate of HFC-23 production from a plant optimised for HCFC-22 production is 4% (9). In plants, constructed in the last 10 years, this has been reduced to about 3% (5). HFC-23 has few uses, some of which (for example, as a fire suppressing agent) will result in the eventual emission of most or all into the atmosphere. In the 21st century emissions from these uses have been almost constant at 133 ± 9 metric tonnes year^{-1}, a maximum of 10% of all emissions (10). Prevention of emissions of HFC-23 requires the capture and treatment of the process vent stream, generally accomplished by high temperature oxidation.

Developed country signatories to the United Nations Framework Convention on Climate Change (UNFCCC), essentially the same set as the non-A5 countries, are required to report emissions of each HFC greenhouse gas each year. The emissions reported by individual countries are shown in the first columns of Table S4 (10); changes in accounting procedure, such as happened in Germany from 2007 were accommodated by using the original contemporaneous data files (rather than the compendia published in 2017). This is consistent with the step changes, that resulted either from closure of the HCFC-22 production facility or from capture and thermal oxidation of the HFC-23, and with pollutant reports to national authorities (11, 12).

The second set of columns in Table S4 shows the estimated emissions of HFC-23 from those countries that are eligible for assistance under the Clean Development Mechanism (CDM) of the UNFCCC. Essentially, this rewarded destruction of HFC-23 at 11700 times the value of the same mass of CO_2, a gearing ratio that distorted the economics of HCFC-22 production (13) and led to the closure of the CDM to HFC-23 projects after 2009. The decision of the EU to ban the use of HFC-23 certified emission reduction (CER) credits in the European Union Emissions Trading System from 1 May 2013 effectively rendered these CERs valueless (5).

The emissions in Table S4 were calculated by estimating the annual production of HFC-23 for each country and then subtracting the quantity estimated to have been abated.

> Argentina and Mexico - from 1990 to 2011, production of HFC-23 was estimated at 3.6%, falling to 3% of HCFC-22 production; from 2012 to 2015, the actual productions reported by the Executive Committee of the Montreal Protocol (5) were used. This was abated up to the maximum claimed under the CDM (14) up to May 2013, after which the destruction facilities were apparently shut down and the HFC-23 was released into the atmosphere (5).
>
> China - from 1990 to 2006, a production rate of 3.6% was assumed, falling to 2.8% subsequently(5). Abatement at the maximum rate allowed for the 11 of 32 plants operating under the CDM was then assumed until 2012 with the other 21 plants operating without abatement. From 2012 onwards, the actual emissions reported by China were used (5). The quantities of HFC-23 destroyed in the period 2007 to 2015 varied between 28 and 47% of that produced.
>
> India - up to year 2000, a production rate of 3.6% was assumed, which then dropped to 2.9%. Apparently, all of the India plants have abatement technology and, after 2006, no emissions were estimated.
>
> South Korea - a production rate of 4%, falling to 3% was assumed for the period 1990 to 2008. Subsequently the production reported to the Executive Committee was used (5). This was abated at the maximum allowed within the CDM until 2012, when the destruction facility was shut down. Although the HFC-23 is recovered for sale, much of that will be emitted and this is reflected in the values shown for South Korea.
>
> North Korea - there are no data prior to 2009 and defaults of zero have been used. From 2009 onwards, the estimates here are those given in Reference 5, with total emission.
>
> Venezuela - the production rate throughout is set at 3%, with no abatement.

Table S4. National HFC-23 Emissions (Metric tonnes Mt or Mg)

Year	Countries Reporting to UNFCCC under CRF												Countries Reporting Data under CDM							Total Annual Emission Gg
	Australia	Canada	France	Germany	Greece	Italy	Japan	etherlands	Russia	Spain	UK	USA	Argentina	China	India	Korea (N)	Korea (S)	Mexico	Venezuela	
1990	48.1	65.6	142.0	373.4	79.9	30.0	717.6	378.8	2428.2	205.4	972.3	3127.6	0.0	0.0	130.4	0.0	70.0	55.5	55.4	8.88
1991	96.3	71.4	184.6	342.9	94.6	30.0	1140.3	295.0	2312.8	186.2	1012.3	2812.0	0.0	0.0	138.9	0.0	106.1	66.1	54.0	8.94
1992	93.2	56.1	173.7	342.4	77.6	30.0	1185.7	378.0	1904.6	236.1	1052.4	3123.9	0.0	0.0	134.0	0.0	158.6	67.1	61.2	9.07
1993	106.9	0.0	177.5	342.1	137.3	30.0	1173.0	424.2	1234.3	193.0	1092.4	2846.9	5.4	176.9	170.0	0.0	176.4	101.4	60.4	8.45
1994	96.5	0.0	79.4	342.6	183.2	30.0	1248.8	544.2	1044.1	295.5	1132.5	2716.1	6.3	353.9	162.1	0.0	180.4	77.0	42.8	8.54
1995	65.4	0.1	19.5	302.8	278.0	30.8	1432.0	503.0	1042.3	396.5	1192.6	2843.7	0.0	530.8	187.9	0.0	223.1	70.4	43.5	9.16
1996	30.7	0.1	32.9	263.6	320.2	1.2	1422.3	611.9	917.5	432.4	1220.7	2690.9	0.0	707.8	163.4	0.0	330.9	172.9	41.7	9.36
1997	0.0	0.9	31.6	254.7	338.9	1.6	1328.5	621.8	1212.3	495.9	1330.8	2601.3	0.0	884.7	192.0	0.0	278.3	168.0	41.1	9.78
1998	0.0	0.3	20.6	246.5	373.6	2.5	1245.3	711.3	1468.2	437.1	1030.2	3411.2	0.0	1337.0	300.2	0.0	166.1	122.9	28.5	10.90
1999	0.1	0.4	38.7	233.5	430.9	2.5	1233.2	318.5	1523.2	511.5	409.9	2636.6	0.0	2175.8	312.6	0.0	311.2	176.2	32.2	10.35
2000	0.1	0.5	31.9	109.1	321.7	3.0	1149.7	223.8	1783.7	557.2	219.1	2468.6	3.4	2827.1	402.6	0.0	276.7	123.4	35.9	10.54
2001	0.1	0.5	33.0	99.6	275.1	3.4	933.7	41.9	1680.8	270.0	196.8	1702.6	3.2	4036.4	353.0	0.0	47.6	93.1	39.6	9.81
2002	0.1	0.5	34.2	110.1	277.2	3.9	667.1	62.4	1268.3	120.4	165.4	1819.0	17.5	3780.5	330.9	0.0	145.0	137.3	43.3	8.98
2003	0.1	0.6	23.4	53.8	232.8	4.6	527.7	37.8	933.5	176.0	158.9	1066.3	31.8	5274.9	408.0	0.0	145.2	133.0	47.0	9.26
2004	0.2	0.6	30.3	53.2	224.1	5.3	261.6	31.9	1160.8	98.8	29.4	1488.3	46.1	6945.8	365.0	0.0	46.0	134.3	50.7	10.97
2005	0.2	0.6	35.4	53.8	191.4	6.0	85.5	17.6	1217.7	92.2	28.0	1368.9	60.3	9916.5	50.1	0.0	117.5	199.0	54.4	13.50
2006	0.2	0.6	42.3	35.9	7.7	6.7	90.3	25.0	1045.8	109.4	17.2	1201.1	74.6	11132.2	0.0	0.0	37.0	0.0	58.1	13.88
2007	0.3	0.6	26.8	10.6	11.6	7.5	63.8	21.8	943.0	98.8	8.3	1470.0	0.0	7872.6	0.0	0.0	28.1	33.5	61.8	10.66
2008	0.3	0.6	29.0	9.5	12.6	8.3	71.5	19.2	955.9	101.7	4.7	1180.3	0.0	5726.7	0.0	0.0	57.8	82.7	65.5	8.33
2009	0.3	0.5	15.2	8.2	12.9	8.4	36.7	13.8	571.9	90.9	3.8	473.3	0.0	7848.3	0.0	9.1	87.4	126.6	69.2	9.38
2010	0.3	0.6	11.6	7.8	15.0	9.0	9.6	34.9	572.8	122.9	1.1	559.1	0.0	9165.0	0.0	9.0	109.0	124.0	65.0	10.82
2011	0.4	0.7	7.5	8.3	13.3	9.3	6.1	15.0	317.1	78.2	1.0	607.9	0.0	9961.3	0.0	8.6	97.9	104.4	73.3	11.31
2012	0.4	0.7	8.0	7.8	14.9	9.2	4.3	11.3	637.1	69.9	0.9	386.2	0.0	10753.9	0.0	8.4	51.1	8.1	87.4	12.06
2013	0.4	0.7	9.1	7.4	15.1	9.4	4.3	17.5	798.7	60.6	1.0	290.1	29.3	10841.1	0.0	10.6	100.1	88.0	66.1	12.35
2014	0.5	0.6	9.2	7.2	12.2	9.6	5.2	3.9	912.2	55.7	1.2	364.2	68.6	12492.5	0.0	7.8	205.0	202.8	47.0	14.41
2015	0.5	0.6	9.3	6.7	11.9	9.8	6.7	9.1	665.6	46.4	1.4	313.0	73.4	7481.8	0.0	7.4	204.0	100.8	20.3	8.97

Notes.

[1] Production of HCFC-22 up to 2007 in non-Article 5 countries downloadable from *https://agage.mit.edu/data/agage-data*

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[9] Intergovernmental Panel on Climate Change. Revised 1996 Guidelines for National Greenhouse Gas Inventories, Reference manual, vol 3, *IPCC/IGES*, Kanagawa, Japan, 1996.

[10] Data reported under the *Common Reporting Format* and in *National Inventory Reports* available at *http://unfccc.int/national_reports/annex_i_ghg_inventories/national_inventories_submissions/items/10116.php*.

[11] US EPA Facility Level Greenhouse Gas Emissions Data available at *https://ghgdata.epa.gov/ghgp/main.do*

[12] European Pollutant Release and Transfer Register (E-PRTR) available at *http://prtr.ec.europa.eu*

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Supplementary Material (4): Influence of OH on the inversions.

Small differences were found in the derived emissions of HCFC-22, whereas, owing to its very long lifetime, negligible differences were found for HFC-23.

For HCFC-22, the magnitude of the difference when Rigby et al., (2017) OH was used versus an annually repeating OH concentration was much smaller than the derived uncertainty.

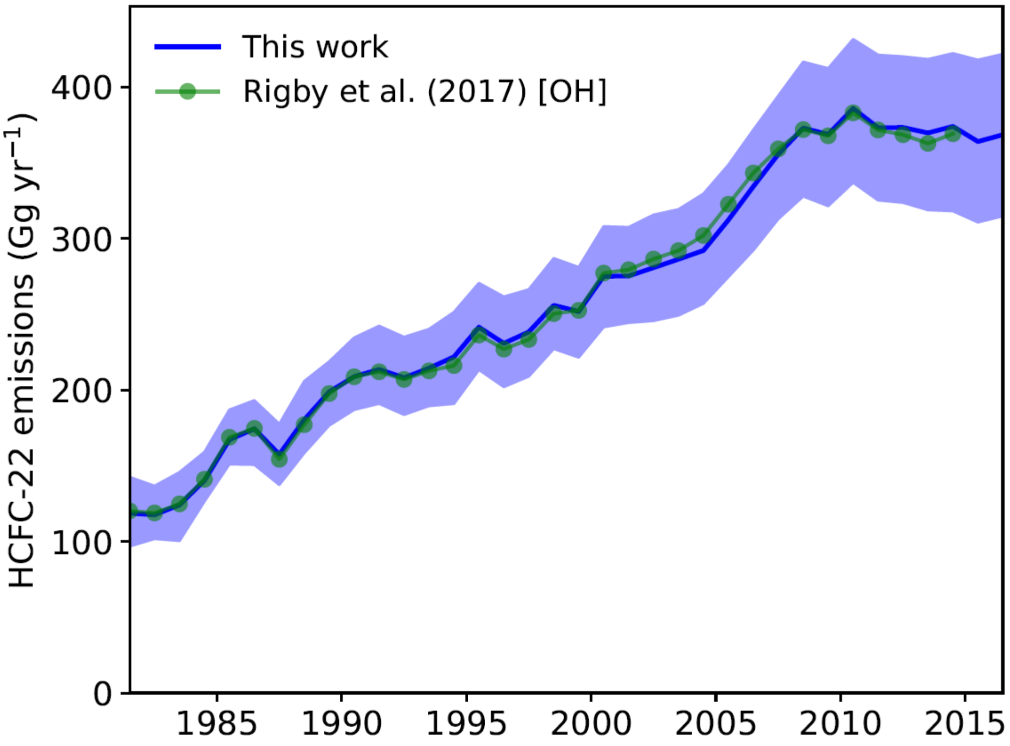

Figure S3. Potential variations in OH concentrations on the inversions

Supplementary Material (5): European Estimates Using FLEXPART and Empa Inversion

Detailed Results

The inversion results suggest that European emissions of HFC-23 in general were larger than reported to UNFCCC and exhibited considerable year-to-year variability. *A posteriori* estimates from the two inversions using different *a priori* emissions mostly agree with each other within the scope of their uncertainty limits (see Figure 6 in the main manuscript and Figure S4). Exceptions are the Italian estimates for the years 2013 and 2015, when the use of the UNFCCC a-priori resulted in much larger *a posteriori* emissions than the use of the 'UNFCCC r0.5' *a priori*. Furthermore, a large difference was also obtained for France in 2013, again the UNFCCC inversion yielding larger *a posteriori* emissions than the UNFCCCC r0.5 inversion. All regions except Spain exhibited larger *a posteriori* than *a priori* emissions for all years. These differences were most significant for Italy where average *a posteriori* emissions of 38±10 Mg/yr were estimated for the years 2009 to 2016. Although Italian *a posteriori* emissions were relatively low and closer to the *a priori* estimate in 2016 there is no clear negative trend in the emissions. Emissions from the Benelux region grew steadily until 2013 and dropped sharply afterwards, a tendency only partly reflected in the UNFCCC estimates. French *a posteriori* emissions agreed fairly well with the UNFCCC reports, with the exception of 2013 when at least one of the inversions yielded significantly higher emissions. A similar statement can be made for the United Kingdom, where only the *a posteriori* estimates for the year 2014 deviates more strongly form the UNFCCC values. The German *a posteriori* emissions were considerably larger than the *a priori* until 2012, thereafter they were closer to the reported UNFCCC values. Our *a posteriori* estimates for the Iberian Peninsula remained relatively close to the UNFCCC *a priori*. Total emissions for the six European regions listed in Table 4 (main manuscript) ranged from 108±30 Mg/yr in 2015 up to 293±43 Mg/yr in 2013 and showed a slightly negative, but insignificant trend for the period analysed here.

Compared to previous estimates by Keller et al. (2011) the estimates in this study for the years 2009 and 2010 are similar for Italy and the Benelux region, but were considerably smaller for Germany, France and the UK. The large difference for Germany may be explained by the much larger *a priori* estimate of 50 Mg/yr in Keller et al. (2011). For France and the UK similar *a priori* values were used and the differences may result from different selection of observation data. In Keller et al. (2011) the inversion was done for observations from July 2008 to July 2010, whereas here each inversion is based on one calendar year of observations.

The model performance was analysed at both Jungfraujoch and Mace Head with respect to correlations and root mean square error of simulated versus simulated time series (Figure S5). A large part of the correlation between simulation and observation is actually due to the increasing trend in HFC-23. Therefore, the correlation of the above-baseline signal can be seen as a better metric for the model performance. The latter increased considerably from a-priori to *a posteriori* for Jungfraujoch and only slightly for Mace Head. Again, there was year-to-year variability in the correlation coefficient and for Jungfraujoch a tendency to smaller correlation coefficients for later years can be seen.

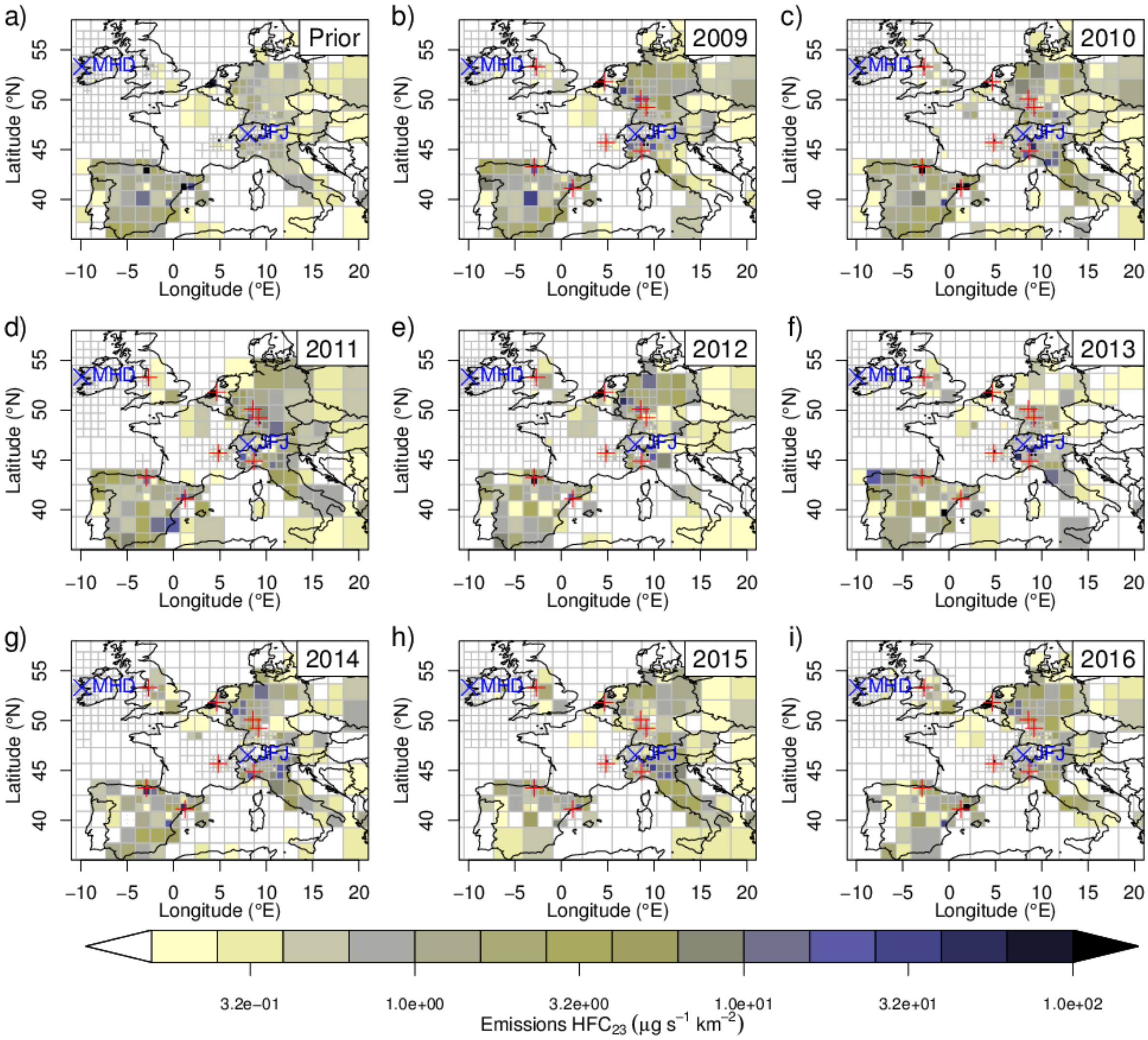

Figure S4: Spatial distribution of HFC-23 *a posteriori* emissions (b-i) as estimated when using the UNFCCC *a priori* emissions (a). Red crosses mark the location of past and present HCFC-22 production plants.

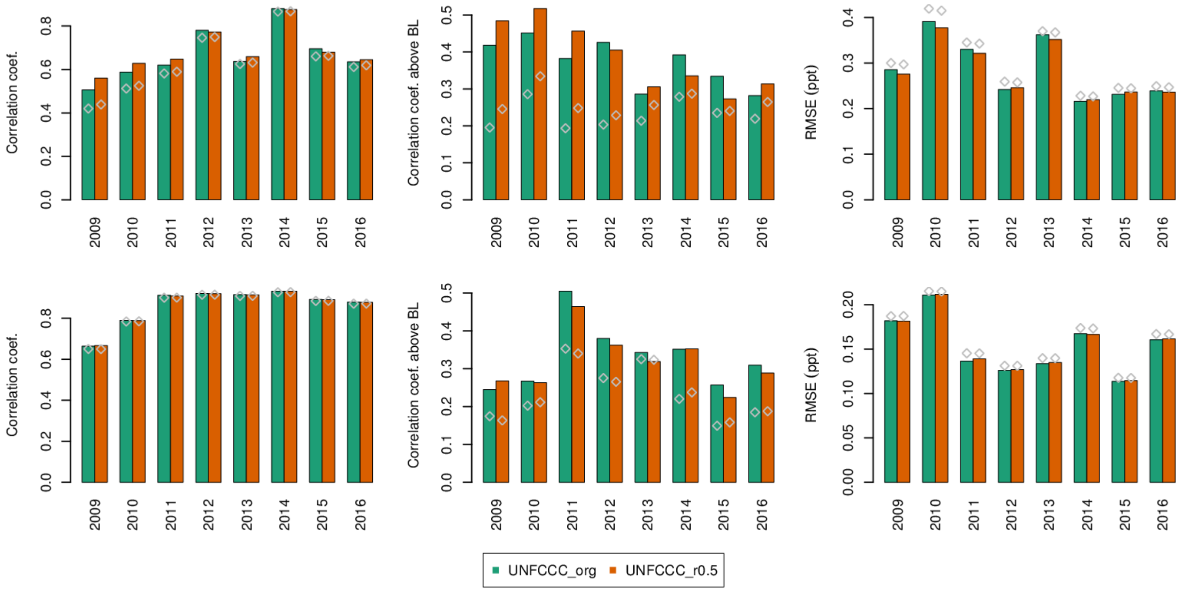

Figure S5: Regional scale transport model skills as evaluated against Jungfraujoch (top) and Mace Head (bottom) observations. *A priori* performance is shown as shaded bars and *a posteriori* performance as solid bars. (left) correlation coefficient for the complete time series, (centre) correlation coefficient for the regional (above baseline) part of the time series, (right) root mean square error.

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Supplementary Material (6): Additional HFC-23 emissions

Table S5. Annual mean global HFC-23 (CHF_3) emissions derived from the AGAGE 12-box model.

Year	HFC-23 Global annual emissions (Gg yr $^{-1}$) ±1 sigma (σ) SD.	Year	HFC-23 Global annual emissions (Gg yr $^{-1}$) ±1 sigma (σ) SD.
1930	0.54 ± 2.0	1955	0.11 ± 1.4
1931	0.52 ± 1.4	1956	0.16 ± 1.4
1932	0.50 ± 1.3	1957	0.20 ± 1.4
1933	0.47 ± 1.3	1958	0.29 ± 1.3
1934	0.44 ± 1.1	1959	0.39 ± 1.3
1935	0.41 ± 1.1	1960	0.43 ± 1.4
1936	0.37 ± 1.2	1961	0.50 ± 1.4
1937	0.34 ± 1.2	1962	0.62 ± 1.4
1938	0.30 ± 1.3	1963	0.76 ± 1.3
1939	0.27 ± 1.3	1964	0.92 ± 1.3
1940	0.24 ± 1.3	1965	1.10 ± 1.4
1941	0.20 ± 1.4	1966	1.33 ± 1.4
1942	0.17 ± 1.3	1967	1.60 ± 1.4
1943	0.15 ± 1.4	1968	1.94 ± 1.2
1944	0.12 ± 1.3	1969	2.15 ± 1.4
1945	0.09 ± 1.5	1970	2.24 ± 1.3
1946	0.07 ± 1.3	1971	2.38 ± 1.2
1947	0.05 ± 1.3	1972	2.61 ± 1.2
1948	0.04 ± 1.2	1973	2.95 ± 1.2
1949	0.03 ± 1.3	1974	2.98 ± 1.2
1950	0.02 ± 1.2	1975	2.99 ± 1.2
1951	0.01 ± 1.2	1976	2.95 ± 1.0
1952	0.02 ± 1.5	1977	3.17 ± 1.0
1953	0.04 ± 1.2	1978	3.62 ± 1.0
