Supplementary Material

Recent increases in the 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): 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.

S1. 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 (MP). 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 MP.

Table S1 shows the inventory of HCFC-22 production for all end uses, subdivided between developed countries (referred to in the MP as "non-Article 5 countries", that are not eligible for any support under the MP 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 S2), 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 MP(3) and the Technology and Economic

Assessment Panel of the MP[4]. From 2009 onwards, the total production reported to the Executive Committee of the MP 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 MP and TEAP data[3, 4].

Table S1. 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
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

China 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 MP 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 then, 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 MP were used[5].The resulting values agree within 4% with the numbers for 2013 to 2015 reported separately by the Chinese government[8].

S2. 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), Annex-1 countries, essentially the same set as the non-A5 countries, are required to report annual emissions of each HFC greenhouse gas individually and the emissions so recorded are shown in the first columns of Table S2[10]. The step changes that resulted either from closure of the HCFC-22 production facility, or from capture and thermal oxidation of the HFC-23, are clear. The data are consistent with pollutant reports to national authorities[11,12].

The second set of columns in Table S2 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 S2 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 MP[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].
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> 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.
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> 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.
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> 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 S2. National HFC-23 Emissions (metric tonnes, Mg)

Year	Countries Reporting to UNFCCC under CRF												Countries Reporting Data under CDM							Total Annual Emission Gg
	Australia	Canada	France	Germany	Greece	Italy	Japan	Netherlands	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*

[2] Stanford Research Institute, International, 1998: Fluorocarbons, Sections 543.7001 to 543.7005 of *Chemical Economics Handbook*, SRI International, Menlo Park, USA, updated using Will R. and H. Mori, Fluorocarbons, Chemical Economics Handbook 543.7000 of SRI Consulting, Access Intelligence (*www.sriconsulting.com*), 2008.

[3] Production and Consumption of Ozone Depleting Substances under the Montreal Protocol, 1986-2015, *United Nations Environment Programme*, available at *http://ozone.unep.org/en/data-reporting/data-centre*

[4]UNEP 2006 Assessment Report of the Technology and Economic Assessment Panel, *United Nations Environment Programme*, Nairobi, 2006.

[5] Key aspects related to HFC-23 by-product control technologies (Decision 78/5), Report to the Executive Committee of the Multilateral Fund for the Implementation of the Montreal Protocol, UNEP/OzL.Pro/ExCom/79/48 of 7 June 2017 available at *ozone.unep.org*

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[8] Wang Kaixiang, HCFCs/HFCs Production in China, Foreign Economic Cooperation Office, FECO/MEP, May 2015.

[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 *http://prtr.ec.europa.eu*

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

[13]Munnings C., B. Leard and A. Bento, The net emissions impact of HFC-23 offset projects from the Clean Development Mechanism, Resources for the Future, Discussion Paper 16-01, 2016.

[14] UNFCCC, Clean Development Mechanism Project Activities available at *http://cdm.unfccc.int/Projects/Index.html*

Supplementary Material (2): Firn Air Depth Profiles and Analyses of the CGAA

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. Three files are also available which tabulate 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.

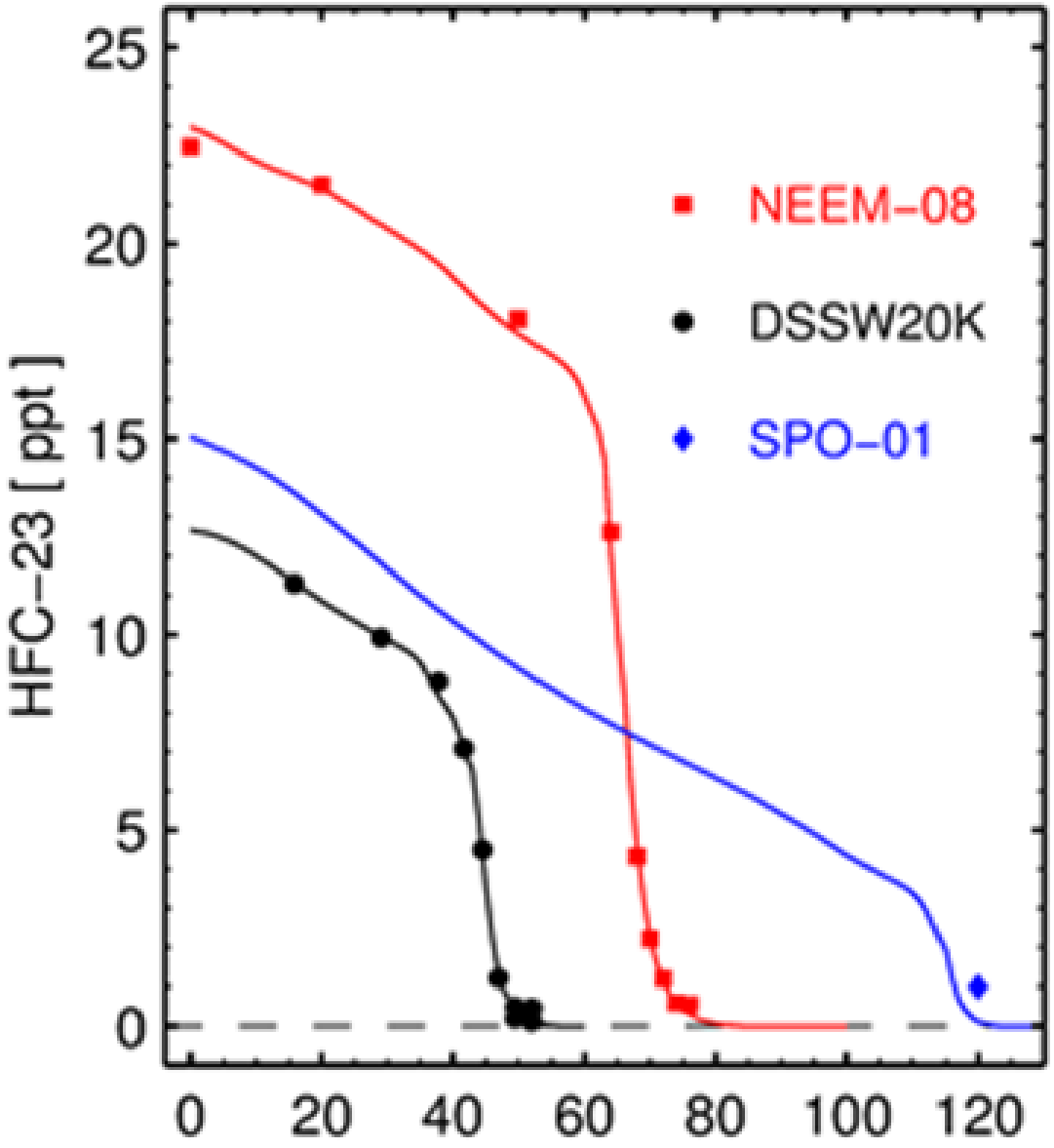
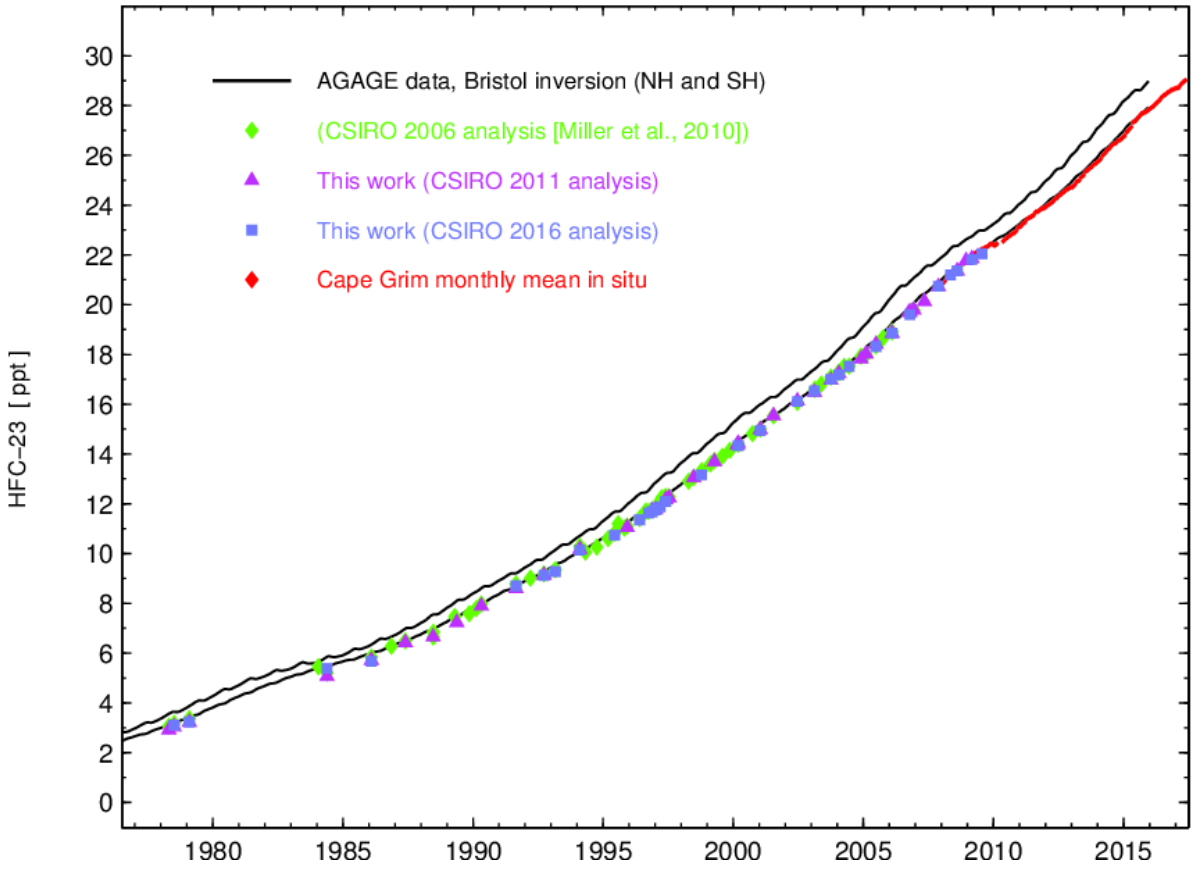


Figure S2. Comparison of three analysis sets of HFC-23 in the Cape Grim Air Archive



Supplementary Material (3): European Estimates Using FLEXPART and Empa Inversion

Methods

Transport model

Surface source sensitivities were computed with the Lagrangian Particle Dispersion Model (LPDM) FLEXPART (Stohl et al., 2005) driven by operational analysis/forecasts from the European Centre for Medium-Range Weather Forecasts (EMWF) IFS modelling system with a horizontal resolution of 0.2° x 0.2° for Central Europe and 1° x 1° elsewhere. 50,000 model particles were released for each 3-hourly time interval and followed backward in time for 10 days. Surface source sensitivities (concentration footprints) were obtained by evaluating the residence times of the model particles along the backward trajectories (Seibert and Frank, 2004).

Inversion system

A spatially resolved, regional-scale emission inversion, using the FLEXPART-derived source sensitivities and a Bayesian approach (Brunner et al., 2017; Henne et al., 2016), was applied to estimate European HFC-23 emissions for the years 2009 to 2016. The inversion relies on the continuous observations at the sites Jungfraujoch and Mace Head and requires *a priori* estimates of the emission distribution. The observations are split into a baseline concentration and above-baseline excursions of the signal that are attributed to recent emissions using the method of Ruckstuhl et al. (2012). The inversion estimates spatially distributed, annual mean emissions and a two-weekly concentration baseline. In the case of HFC-23 the baseline concentration is very well defined due to the relatively infrequent occurrence of larger pollution events. The inversion results were not significantly different when the baseline was not updated as part of the inversion. The spatial distribution was solved on a grid with different sized rectangular cells. The grid resolution depends on annual total source sensitivities and therefore finer close to the measurement sites and coarser in more remote regions that seldom influence the sites. In addition, the grid resolution was increased around known point emitters in order to better localise these large contributors.

A Priori emissions

Spatially distributed *a priori* emissions were generated from individual national inventory reports (NIR) to UNFCCC in 2017 (http://unfccc.int/national_reports/annex_i_ghg_inventories/national_inventories_submissions/items/10116.php). Most European countries separately list the emissions of HFC-23 by sector in Table 2(II) of their submission. Here we chose two different approaches how to spatially distribute these bottom-up estimates. First (UNFCCC), we directly follow the categorisation in each NIR and assign emission from ‘Fluorochemical production’ to individual production sites as taken from Keller et al. (2011), whereas emissions from ‘Electronics industry’ and ‘Product use’ were distributed according to population density (Center for International Earth Science Information Network, 2016). Countries reporting no

or zero HFC emissions were assigned a per capita emission factor equal to a tenth of the average per capita emission factor from reporting countries. This mostly impacts countries at the periphery of the inversion domain. In our second approach (UNFCCC r0.5), we used the same spatial disaggregation as before but assigning 50 % of the 'Electronics industry' and 'Product use' emissions in each country to the point source locations and distributed the remainder by population. Furthermore, inversions using the HFC-23 inventory provided by EDGAR (version 4.2) as *a priori* were tested. However, overall these inversions showed much weaker performance than those based on UNFCCC priors and, hence, were dropped from any further analysis.

Covariance matrices setup

We designed the *a priori* covariance matrix in such a way that the total *a priori* uncertainty for each of the regions/countries was 200 % and proportional to the emissions in each inversion grid cell. Off-diagonal elements of the matrix were filled with the assumption of exponentially decaying spatial correlation of the uncertainties with a length scale of 10 km. The choice of this rather small spatial correlation scale was motivated by the assumed strong contribution from point source emissions.

The data-mismatch covariance matrix contained uncertainty elements that describe the uncertainty of the observation and the transport model. The observation uncertainty was taken from target gas measurements, whereas the model uncertainty was estimated as the RMSE of the *a priori* simulations. The off-diagonal elements of the covariance matrix were again assumed to exponentially decay with the time between the data points. The according correlation time scale was estimated separately for each site from a fit to the auto-correlation function of the prior model residuals and was in the order of 0.2 to 0.3 days.

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. 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 regions listed in Table S3 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.

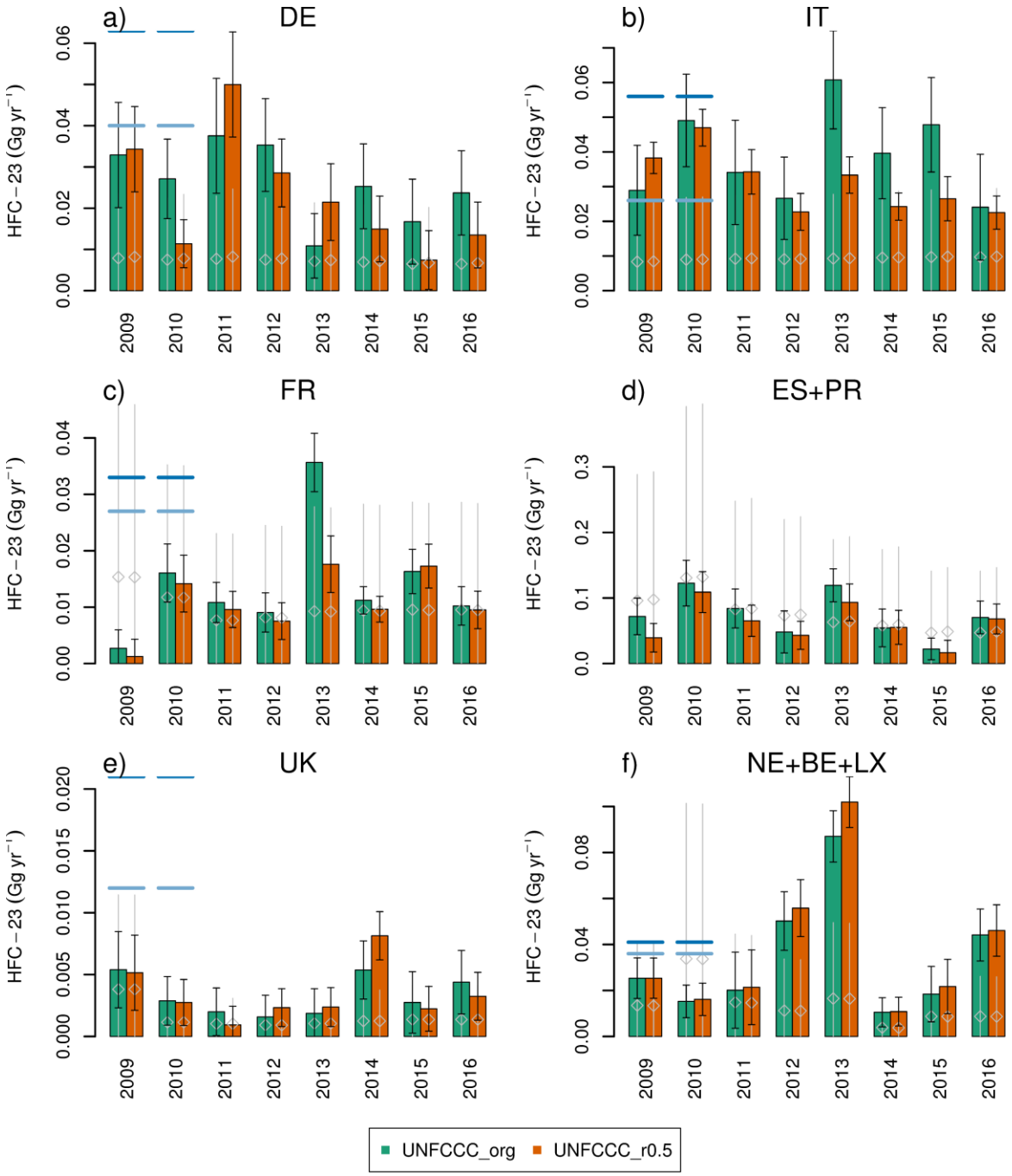


Figure S3: Temporal evolution of national/regional emissions of HFC-23: solid bars and error bars give *a posteriori* emissions using the two sets of *a priori* emissions (grey diamonds and lines). Blue horizontal lines give the estimates of Keller et al. (2011) for their Bayesian (light blue) and point source (dark blue) estimate. a) Germany, b) Italy, c) France, d) Spain and Portugal, e) United Kingdom, f) Benelux countries (Netherlands, Belgium, Luxembourg). Note: Same as Figure 6 in main article.

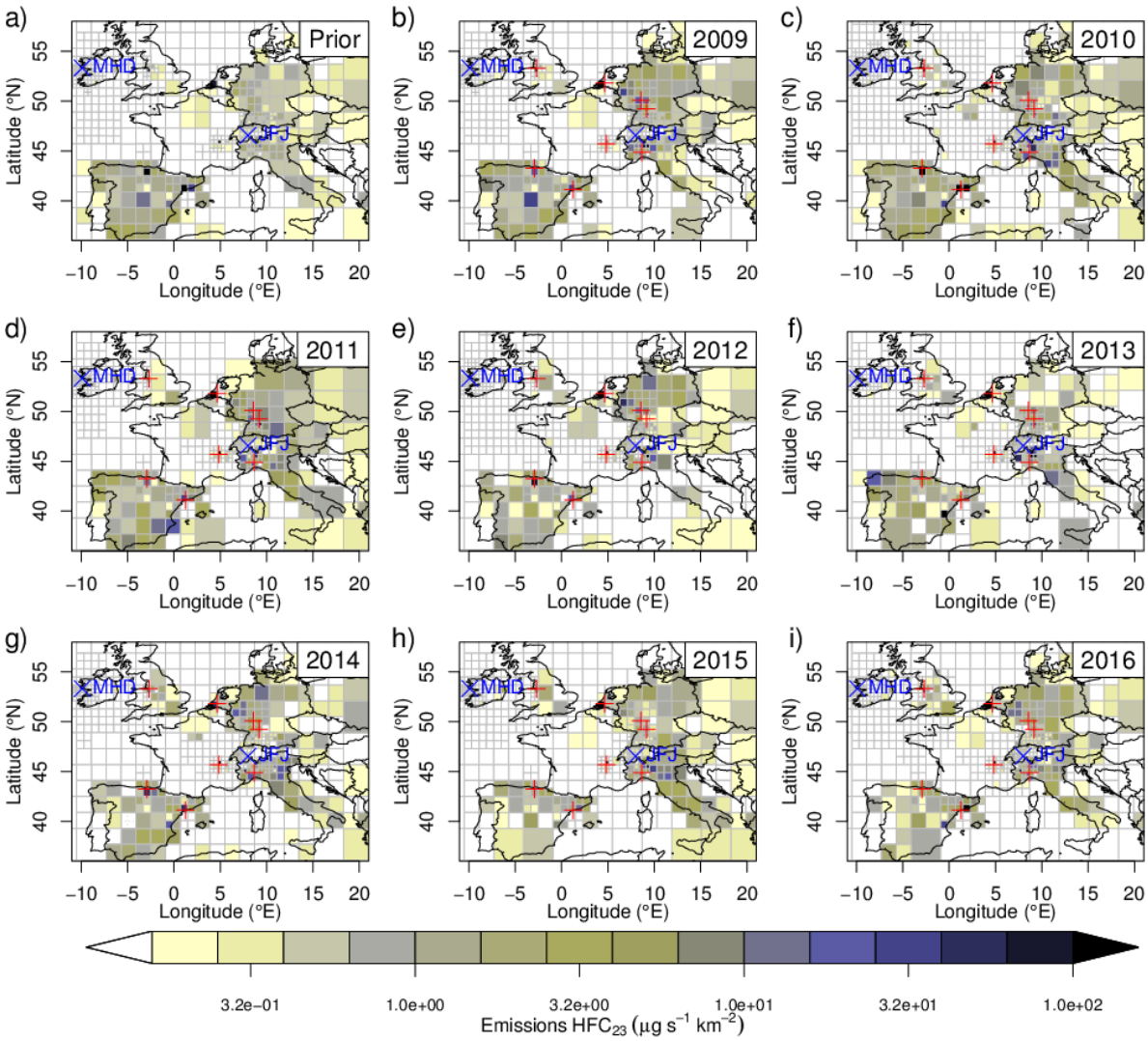


Figure S4: Spatial distribution of HFC-23 *a posteriori* emissions (b-i) as estimated when using the UNFCCC *a priori* emissions (a). Red crosses mark the location of past and present HCFC-22 production plants.

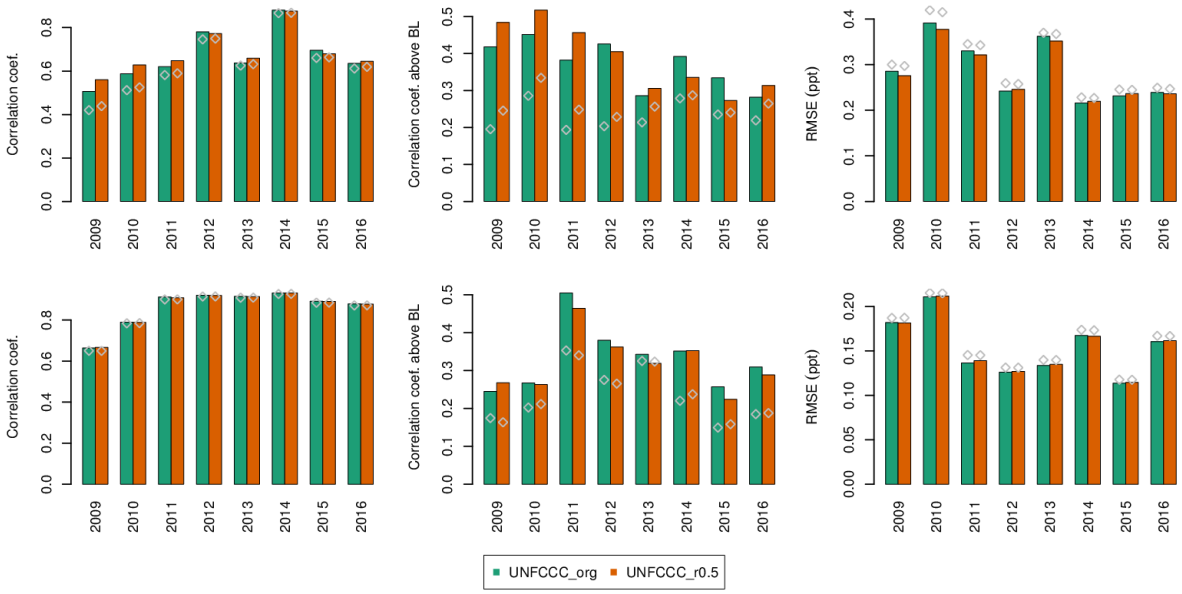


Figure S5: Regional scale transport model skills as evaluated against Jungfraujoch (top) and Mace Head (bottom) observations. *A priori* performance is shown as shaded bars and *a posteriori* performance as solid bars. (left) correlation coefficient for the complete time series, (center) correlation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

Table S3: European HFC-23 emissions by country/region: E_a *a priori*, E_b *a posteriori* emissions, f_a fraction of *a priori* emissions from factory locations, f_b fraction of *a posteriori* emissions from factory locations. All values represent averages from both inversions using different *a priori* distributions. Note: Same as Table 4 in main article.

	Germany				France				Italy			
year	E_a (Mg/yr)	E_b (Mg/yr)	f_a (%)	f_b (%)	E_a (Mg/yr)	E_b (Mg/yr)	f_a (%)	f_b (%)	E_a (Mg/yr)	E_b (Mg/yr)	f_a (%)	f_b (%)
2009	8±16	34±12	30	49	15±31	2±3.2	88	6	8.4±17	34±8.7	26	52
2010	7.6±15	19±14	27	13	12±23	15±5.1	84	86	9±18	48±9.3	26	45
2011	8±16	44±13	33	58	7.7±15	10±3.4	70	73	9.2±18	34±11	26	43
2012	7.6±15	32±9.7	30	40	8.1±16	8.3±3.4	76	73	9.1±18	25±8.6	26	31
2013	7.2±14	16±9.4	28	58	9.2±18	27±16	82	93	9.3±19	47±24	26	29
2014	7.1±14	20±9.2	30	27	9.4±19	10±2.3	84	85	9.5±19	32±14	26	32
2015	6.6±13	12±8.7	29	14	9.5±19	17±3.9	86	92	9.8±20	37±19	26	24
2016	6.6±13	19±9.1	29	26	9.5±19	9.9±3.4	86	85	9.8±20	23±10	26	39

	Benelux				United Kingdom				Iberian Peninsula			
year	E_a (Mg/yr)	E_b (Mg/yr)	f_a (%)	f_b (%)	E_a (Mg/yr)	E_b (Mg/yr)	f_a (%)	f_b (%)	E_a (Mg/yr)	E_b (Mg/yr)	f_a (%)	f_b (%)
2009	13±27	25±8.8	98	99	3.8±7.6	5.3±3.1	84	87	97±190	56±29	57	10
2010	34±67	16±7.1	99	98	1.2±2.3	2.8±1.9	48	71	130±260	120±33	66	52
2011	15±29	21±16	97	97	1±2.1	1.5±1.7	39	21	83±170	75±27	50	27
2012	11±22	53±13	96	99	0.92±1.8	2±1.6	26	46	74±150	46±27	45	43
2013	16±33	94±13	98	100	1.1±2.1	2.1±1.8	29	48	64±130	110±27	38	22
2014	3.8±7.6	11±6.3	85	94	1.3±2.5	6.8±2.4	35	73	59±120	55±27	35	45
2015	8.7±17	20±12	94	97	1.4±2.7	2.5±2.1	34	37	48±96	19±18	26	9
2016	8.7±17	45±11	94	99	1.4±2.7	3.8±2.2	34	42	48±96	69±24	26	33

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Supplementary Material (4): Additional HFC-23 emissions

Table S4. 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) Std. Dev	Year	HFC-23 Global annual emissions (Gg yr^{-1}) ±1 sigma (σ) Std. Dev
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
1954	0.06 ± 1.3	1979	3.92 ± 0.8