Supplementary Material

Changing trends and emissions of hydrochlorofluorocarbons and their hydrofluorocarbon replacements.

Peter. G. Simmonds[1], Matthew. Rigby[1], Archibold. McCulloch[1], Simon. O'Doherty[1], Dickon. Young[1], Jens. Mühle[2], Paul. B. Krummel[3], L. Paul. Steele[3], Paul. J. Fraser[3], Alistair. J. Manning[4], Ray. F. Weiss[2], Peter. K. Salameh[2], Chris. M. Harth[2], Ray. H.J. Wang[5] and Ronald. G. Prinn[6].

[1] Atmospheric Chemistry Research Group, University of Bristol, Bristol, BS8 1TS, UK
[2] Scripps Institution of Oceanography (SIO), University of California San Diego, La Jolla, CA 92093, USA
[3] CSIRO Oceans and Atmosphere, Aspendale, VIC 3195, Australia
[4] Met Office Hadley Centre, Exeter, EX1 3PB, UK
[5] School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA
[6] Center for Global Change Science, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.

Correspondence to: P.G. Simmonds (petergsimmonds@aol.com)

1. Supplementary Material:

Table of global HCFC and HFC emissions (Gg) estimates from the AGAGE 12-box model.

	HCFC-22	HCFC-141b	HCFC-142b	HCFC-124	HFC-125	HFC-134a	HFC-143a	HFC- 32
1998	263.34	58.17	26.91		5.52	60.81		
1999	251.01	58.72	29.45		6.28	71.02		
2000	272.34	62.50	31.39		8.33	80.04		
2001	271.48	55.89	28.67		9.22	86.17		
2002	276.49	61.93	25.55		11.20	99.79		
2003	283.89	57.40	26.48		13.86	109.17	5.43	1.95
2004	289.13	49.54	25.43	5.92	14.51	117.04	11.66	3.80
2005	308.13	46.16	28.73	6.08	17.09	124.21	13.81	5.30
2006	333.22	51.28	34.20	5.82	19.47	127.93	15.51	6.73
2007	352.16	53.79	36.97	5.92	21.84	136.91	16.01	8.35
2008	370.05	54.19	39.36	5.05	26.42	148.31	18.50	9.72
2009	363.91	52.78	35.03	4.38	27.99	154.52	18.63	11.70
2010	382.67	60.47	35.19	4.23	35.54	168.92	20.52	15.09
2011	370.53	67.07	32.90	4.17	39.80	171.34	21.60	18.11
2012	369.84	68.43	29.10	4.11	44.51	177.13	23.08	21.09
2013	365.54	64.62	26.53	3.11	49.84	186.28	24.34	24.59
2014	369.91	63.01	25.77	3.36	57.20	199.64	25.65	29.56
2015	357.41	59.25	24.58	3.01	60.26	209.37	27.37	31.87

2. Supplementary Material: Calculation of Quantities Emitted using HCFC Consumption Data.

Consumption data for HCFCs are published only in aggregate, as the total quantity of all HCFCs, by the Montreal Protocol Secretariat of the United Nations Environment Programme [UNEP, 2016]. However, between 1990 and 2011, values for annual consumptions of HCFCs -22, -141b and -142b, individually, were provided in Figure 1.26 of WMO., 2014 **(**Chapter 1. Lead authors: L.T Carpenter and S. Reimann**)**. These constitute virtually all of the HCFCs consumed, as shown in Figure S1 comparing the sum of the data in WMO (2014) with the global total of HCFCs from UNEP (2016).

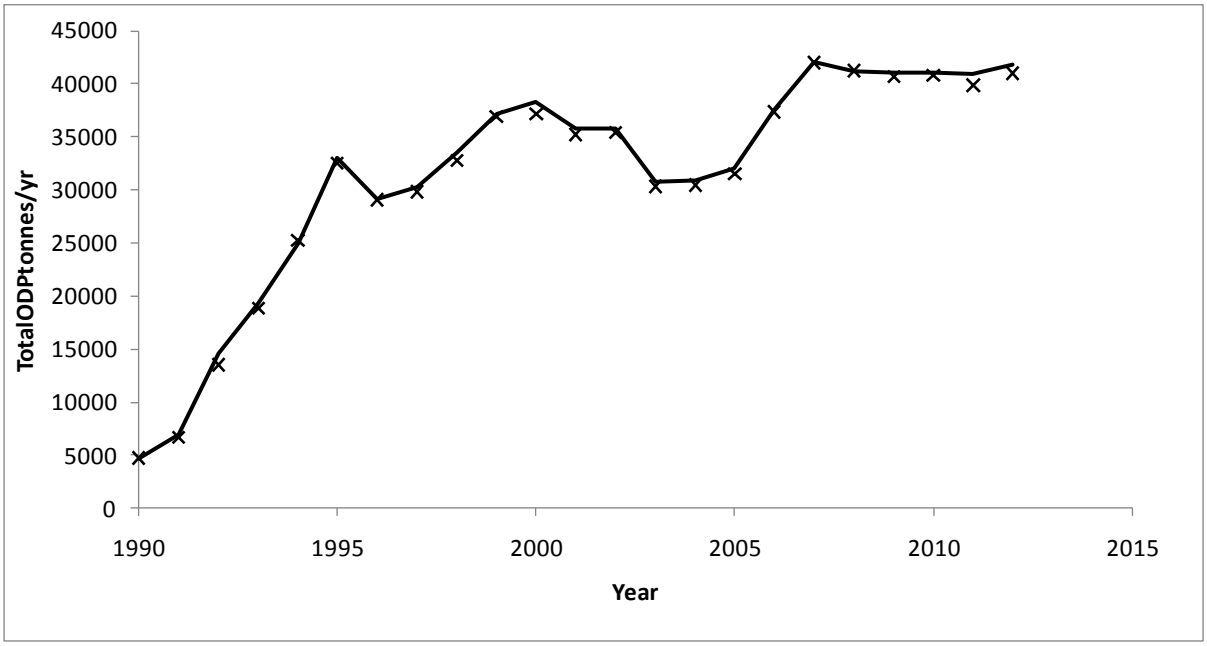

Figure S1. Comparison between HCFC global consumption databases expressed as mass multiplied by ozone depletion potential (ODPtonnes). Crosses are the totals of annual consumption of HCFC-22, HCFC-141b and HCFC-142b from WMO., 2014 (Chapter 1. Lead authors: L.T Carpenter and S. Reimann). Solid line is the total consumption of all Group C1 substances (HCFCs) reported under the Montreal Protocol (UNEP, 2016)

The differences between the points and the solid line show that the contribution from other HCFCs, such as HCFC-123 and HCFC-124 is very small (less than 2%, on average). Consequently, although the values in WMO (2014) do not extend beyond 2011, it was possible to extrapolate them for the three years to 2014 based on the annual totals and the prior contributions of individual HCFCs.

Emissions

Emissions of substances used in refrigeration or foam blowing generally conform to the pattern:

Initial loss, followed by loss during service and finally loss at disposal of the equipment containing the substance. [Ashford et al., 2004]

Values relevant to the most common uses of HCFCs-22, -141b and -142b are shown in Table S1.

In order to apply the emission functions provided by Ashford et al. (2004), information on the individual categories of end use would be required. The values from WMO (2014) are for total consumption and so the best that can be accomplished is a consistency test of these functions against emissions calculated from atmospheric measurements. These "measured" emissions compiled from this study are shown as the crosses in Figures S2 to S4.

Table S1. Emission functions expressed as loss rates. All data in percentages

	Ashford et al., 2004					This work	
	Short term		Medium to long term			Initial	Annual
	First year	Next year	Initial	Annual	Main use*	(± 1 st. dev.)	loss from bank
HCFC-22	83	17	37	6.3	RAC	41.3±5.8	9.8
HCFC-141b	83	17	15	4.5	CCF	34.5±4.0	2.2
HCFC-142b	83	17	33	3	CCF	30.0±6.8	12.9

* RAC represents refrigeration and air conditioning and CCF represents closed cell foam blowing.

Given the general form of the loss pattern in the historic data, it was postulated that emissions from total annual consumptions could be described as an initial loss plus a constant function of the bank remaining in equipment. Similar methodology has been used to examine the history of reported European emissions [McCulloch, 2009; McCulloch & Vink, 2010], in which it was demonstrated that the loss rate from the bank reduced towards a constant rate over several years after consumption commenced. Thus

$$E_y = I \times C_y + F \times B_y \quad (1)$$

where E is the mass emitted, I is the initial loss factor (%), C is the mass consumed and F is the annual emission factor from the bank B, all in year *y*.

The quantity in the bank each year being given by:

$$B_y = B_{y-1} + C_y - E_y \quad (2)$$

That is, the bank at the end of year *y* is equal to the previous year's bank plus the excess of consumption over emission for year *y*.

The equations were solved using the global emissions estimates reported in this study and the global consumption data in WMO (2014), over the period 1995 to 2014, for a series of emission functions from the bank to give a series of initial loss rates and their standard deviations. The annual banks were calculated explicitly, starting from the banks for each compound in the AFEAS database in 1990 [AFEAS, 2016]. Table S1 shows the values from these series with the lowest standard deviations of the initial losses. These are compared with the typical historic emission functions in Ashford et al (2004).

For HCFCs 22 and 142b, although the initial loss rates are similar to those previously estimated, long term emissions from the predominant uses are significantly faster. The rate of emission of HCFC-22 from the bank is 50% greater and that of HCFC-142b is greater by a factor of four. Consequently, the trends in

emissions follow trends in consumption more closely than would have been expected from Ashford et al. (2004).

Conversely, for HCFC-141b the initial loss rate is significantly greater than that proposed by Ashford et al. (2004) for the predominant use in foam blowing, with the possible inference of larger than expected use in short term release categories (such as solvent or cleaning agent). Furthermore, long term loss rates are half those previously assigned to foam blowing, calling into question the previous foam loss function.

Notwithstanding these, it appears that an initial loss with subsequent constant loss from the bank at a relatively low rate constitutes a viable model. Figures S2 to S4 show the range of annual emissions calculated using the values in Table S1, compared to the emissions calculated from atmospheric measurements and the consumption record. Mean values of these emissions are shown in Table S2.

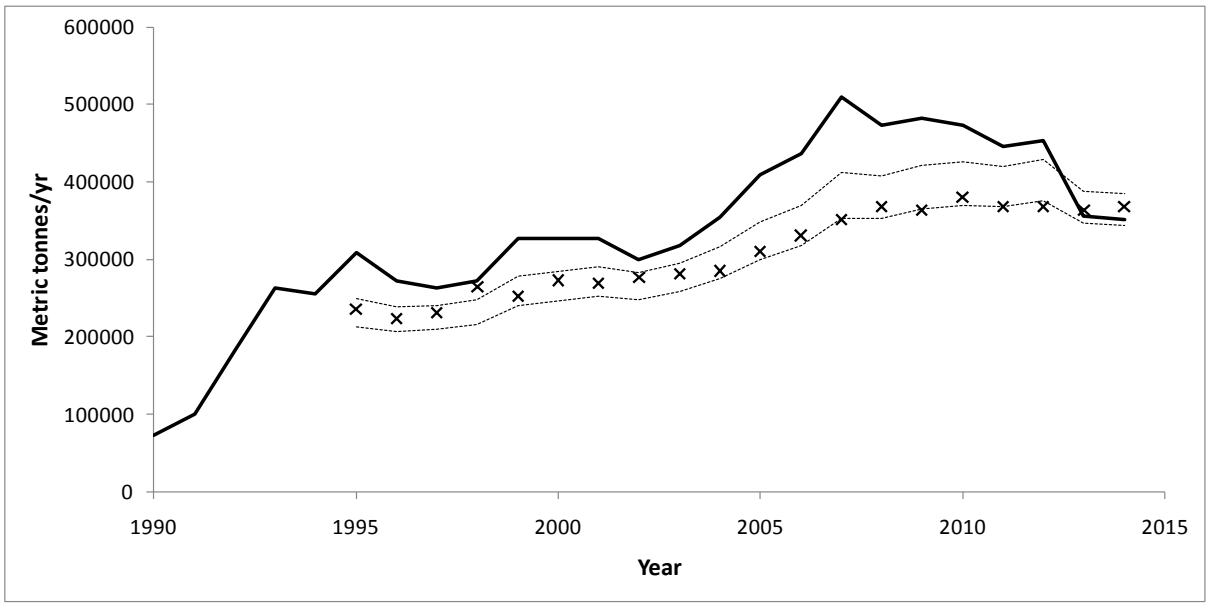

Figure S2. Annual consumptions of HCFC-22 from WMO., 2014 (Chapter 1. Lead authors: L.T Carpenter and S. Reimann), with annual emissions (X) and the range of emissions calculated from consumption (mean ± 1σ) (dotted lines).

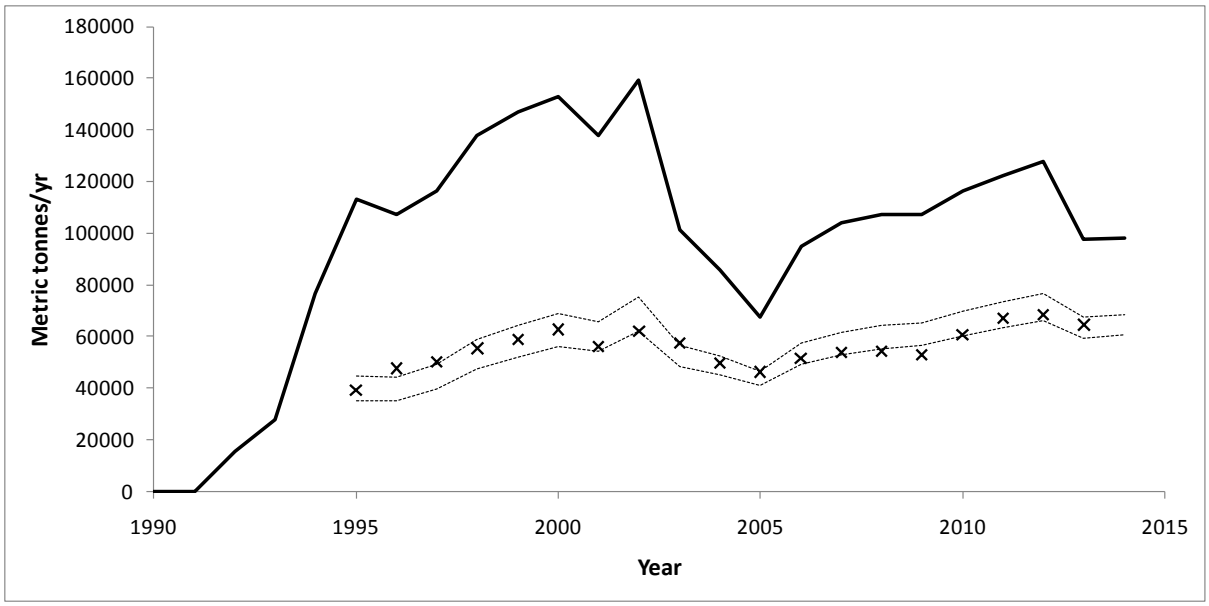

Figure S3. Annual consumptions of HCFC-141b from WMO., 2014 (Chapter 1. Lead authors: L.T Carpenter and S. Reimann), with annual emissions (X) and the range of emissions calculated from consumption (mean ± 1σ) (dotted lines).

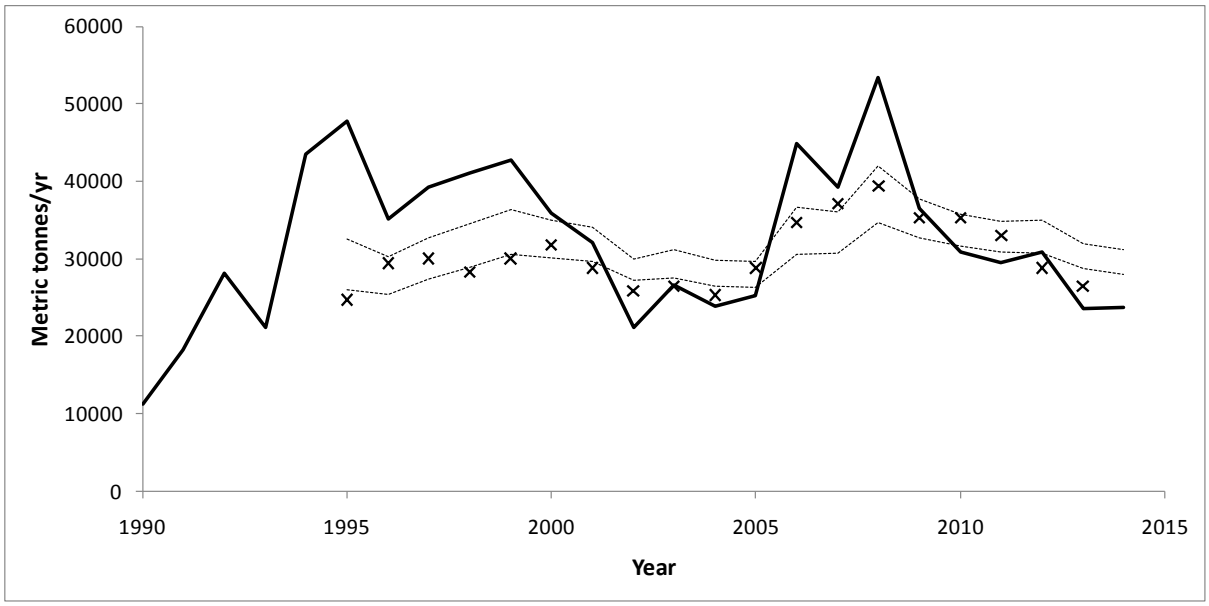

Figure S4. Annual consumptions of HCFC-142b from WMO., 2014 (Chapter 1. Lead authors: L.T Carpenter and S. Reimann), with annual emissions (X) and the range of emissions calculated from consumption (mean ± 1σ) (dotted lines).

Table S2. Mean annual emissions of HCFCs calculated from consumption data

Year	Emission metric tonnes/yr		
	HCFC-22	HCFC-141b	HCFC-142b
1995	230436	42070	29219
1996	223140	41525	27815
1997	224248	46136	30016
1998	231859	55068	31719
1999	258371	60054	33420
2000	265123	64076	32591
2001	271214	60757	31842
2002	265454	69839	28578
2003	276342	51750	29292
2004	295447	47556	28111
2005	323745	42063	27983
2006	343362	52119	33529
2007	382484	56226	33313
2008	379887	58335	38296
2009	392737	59408	35182
2010	397716	63625	33666
2011	393814	66896	32885
2012	402362	69882	32858
2013	366673	60806	30388
2014	363752	61823	29568

3. Supplementary Material: Reconciliation of the Quantities of Individual HFCs Released with the Compositions of Refrigerant Blends

- HFCs -32, -125 and -143a are used in refrigerant blends. It is assumed that this is their main use, although there is some HFC-125 that is also used in fire suppression systems.
- The blends, by weight %, are:

	R404A	**R407A**	**R407C**	**R407F**	**R410A**	**R438A**	**R507A**
125	44	40	25	30	50	45	50
134a	4	40	52	40		44.2	
143a	52						50
32		20	23	30	50	8.5	

- We can assume that most (almost all) of the HFC-143a is used in R404A. Hence the emission of R404A can be calculated from the HFC-143a emission, leading to a value for the HFC-125 emitted as R404A.
- The actual emission of HFC-125 minus that in R404A (*residual* HFC-125) is the result of:
  - emission of R407A and/or
  - emission of R407C, R407F and R410A (which could be counted as R410A) and/or
  - emission of HFC-125, on its own.
- We have two sources of data - UNFCCC (which is *NOT* global and covers only developed countries) and global values from this study of AGAGE data.

UNFCCC Data

Year	UNFCCC (all data in metric tonnes)						
	R404A based on HFC-143a	Residual HFC-125	HFC-32	HFC-125 Maximum R407A Needed	HFC-125 Maximum R407A Excess	HFC-125 Maximum R410A Needed	HFC-125 Maximum R410A Excess
2000.5	5524	1785	267	534	1251	267	1518
2001.5	6724	1996	431	862	1134	431	1565
2002.5	8020	2142	630	1260	882	630	1512
2003.5	9529	2395	932	1864	531	932	1463
2004.5	10748	2820	1373	2746	74	1373	1447
2005.5	12274	3259	1891	3782	-523	1891	1368
2006.5	13400	4242	2858	5715	-1473	2858	1384
2007.5	14810	5440	3988	7976	-2536	3988	1452
2008.5	16077	6721	5139	10279	-3558	5139	1582
2009.5	17731	8162	6306	12611	-4449	6306	1856
2010.5	19813	10436	8268	16535	-6100	8268	2168
2011.5	21640	12648	10309	20618	-7970	10309	2339
2012.5	23128	15051	12637	25275	-10224	12637	2414
2013.5	24826	17546	15190	30380	-12834	15190	2356
2014.5	0	0	0	0	0	0	0
2015.5	0	0	0	0	0	0	0

- If all of the HFC-125 emission were as R407A, the quantity required would be twice that of the HFC-32 emission; similarly if all were as R410A, the value would be the same as the HFC-32 emission.
- A positive value for the *excess* could indicate emission of HFC-125 on its own and a negative value could show that HFC-32 was emitted on its own.
- Up to 2005, the HFC-125 emissions exceed any that could be accountable to blends.
- However, from then on, the numbers are consistent with release of both R407A and R410A, without any need for emission of HFC-32 on its own.
- Depending on the extent to which HFC-125 is emitted on its own, the figures show a steady fall in the fraction of R407A, from about 70% in 2005, to 16% in 2013.

AGAGE Data

Year	Emissions (metric tonnes) calculated from AGAGE measurements							
	R404A based on HFC-143a	Residual HFC-125	HFC-32	HFC-125 Maximum R407A Needed	HFC-125 Maximum R407A Excess	HFC-125 Maximum R410A Needed	HFC-125 Maximum R410A Excess	R407A content
2000.5	16038	1402	985	1971	-568	985	417	42%
2001.5	16515	2019	1352	2704	-685	1352	667	49%
2002.5	17882	3339	1868	3736	-397	1868	1471	79%
2003.5	21783	4328	2720	5441	-1112	2720	1608	59%
2004.5	23054	4387	4189	8378	-3992	4189	198	5%
2005.5	26870	5288	5510	11020	-5732	5510	-222	-4%
2006.5	30025	6281	6802	13604	-7323	6802	-521	-8%
2007.5	30888	8269	8367	16734	-8465	8367	-98	-1%
2008.5	35599	10764	9720	19440	-8676	9720	1044	11%
2009.5	35882	12202	11687	23375	-11173	11687	515	4%
2010.5	39482	18176	15049	30098	-11922	15049	3127	21%
2011.5	41599	21520	18077	36153	-14634	18077	3443	19%
2012.5	44448	24979	21068	42137	-17158	21068	3910	19%
2013.5	46725	29251	24446	48892	-19641	24446	4805	20%
2014.5	49158	35694	28919	57839	-22145	28919	6774	23%
2015.5	52748	36509	31219	62439	-25929	31219	5290	17%

- These results are consistent with release of both R407A and R410A over the whole of the period.
- The apparent negative values in 2005 to 2007 are too small to be significant.
- Of more concern is the variability of the R407A fraction. It is possible that this shows three regimes - up to 2003, 2004 to 2009 and 2009 onwards although this is uncertain. Our conclusion is that the data are consistent with the proposition that the HFCs 32, 125 and 143a found in the atmosphere were released as blends.
- Because the GWPs of R407A and R410A are almost identical (2107 and 2088, respectively, 100-yr integration), the distribution of emissions between these two blends has little effect on their climate impacts.

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