Supplement of

Atmospheric histories, growth rates and solubilities in seawater and other natural water of the potential transient tracers HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-125, HFC-23, PFC-14 and PFC-116

Pingyang Li [1], Jens Mühle [2], Stephen A. Montzka [3], David E. Oram [4], Benjamin R. Miller [3], Ray F. Weiss [2], Paul J. Fraser [5] and Toste Tanhua [1]

[1]GEOMAR Helmholtz Centre for Ocean Research Kiel, Marine Biogeochemistry, 24105 Kiel, Germany
[2] Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California 92093, USA
[3]Earth System Research Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colorado 80305, USA
[4]National Centre for Atmospheric Science, Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, UK
[5]Climate Science Centre, Commonwealth Scientific and Industrial Research Organization Oceans and Atmosphere, Aspendale, Victoria, 3195, Australia

Correspondence to: Toste Tanhua (ttanhua@geomar.de)

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Section S1. Smoothing spline fit method

After the data containing replicate times have been converted into a value at each replicate time, the data were sorted as $x_1 < x_2 <\ldots< x_i <\ldots< x_n$.

Set $x_i, y_i, \delta y_i$ $(i = 1, 2, \ldots, n)$ to be the decimal time, the corresponding atmospheric mole fractions and the standard deviation.

Normalize the *x* vector

$$t_i = (x_i - min(x_i))/(max(x_i) - min(x_i)) \tag{1}$$

The smoothing function $f(t)$ to be constructed shall

$$\text{Minimize } p\sum_{i=1}^{n}[\tfrac{g(t_i)-y_i}{\delta y_i}]^2 + \int g''(t)^2 dt \tag{2}$$

The solution of the minimum principle is a spline. By introducing the auxiliary variable *z* together with the Lagrangian parameter *p*, we have to look for the minimum of the function

$$\int_{t_1}^{t_n} g''(t)^2 dt + p[\sum_{i=1}^{n}\left(\frac{g(t_i) - y_i}{\delta y_i}\right)^2 + z^2] \tag{3}$$

From the corresponding Euler-Lagrange equations, we determine the optimal function $f(t)$.

$$f(t) = a_i + b_i(t - t_i) + c_i(t - t_i)^2 + d_i(t - t_i)^3, \quad t_i \le t < t_{i+1} \tag{4}$$

We obtain the spline coefficients (Reinsch, 1967).

$$c_i = \frac{pQ^T y}{B}, c = [0;\ c_i;\ 0]^T \tag{5}$$

$$a = y - W^2 Qc/p \tag{6}$$

$$d_i = (c_{i+1} - c_i)/(3h_i) \tag{7}$$

$$b_i = (a_{i+1} - a_i)/h_i - c_i h_i - d_i h_i^2 \tag{8}$$

$$coeffs = [d, c, b, a] \tag{9}$$

Here, the following notation is used:

$$h_i = t_{i+1} - t_i, \tag{10}$$

$$W = diag(\delta y_1, \ldots, \delta y_n), \tag{11}$$

T is the $(n - 1) \times (n - 1)$ dimensional positive tridiagonal matrix with entries t_{ij} $(i, j = 1, 2, \ldots, \mathrm{n} - 1)$ given by

$$t_{ii} = 2(h_{i-1} + h_i)/3, \quad t_{i,i+1} = t_{i+1,i} = h_i/3 \tag{12}$$

Q is the $(n) \times (n - 2)$ dimensional tridiagonal matrix with with entries q_{ij} $(i = 1, 2, \ldots, n;\ j = 1, 2, \ldots, n - 2)$ given by

$$q_{i-1,i} = 1/h_{i-1}, \qquad q_{i,i} = -1/h_{i-1} - 1/h_i, \qquad q_{i+1,i} = 1/h_i \tag{13}$$

The elements in the ith column of Q given by the coefficients of the 2th order divided differences based on $t_i, \ldots, t_{i+2}$. Let the coefficient matrix be denoted by

$$B_p = Q^T W^2 Q + pT \tag{14}$$

The *influence matrix* associated with the smoothing spline is the unique $n \times n$ symmetric matrix A_p satisfying

$$a = A_p y \tag{15}$$

The error

$$error = y - a = W^2 Q B_p^{-1} Q^T y \tag{16}$$

So that

$$I - A_p = W^2 Q B_p^{-1} Q^T \tag{17}$$

The weighted residual sum of squares

$$RSS = \left\| (I - A_p) y / W \right\|^2 = \left\| W^2 Q B_p^{-1} Q^T y \right\|^2 \tag{18}$$

The estimate value of the generalized cross-validation (*GCV*) minimization function V of p used in the experiments below is the minimizer of the GCV function V_p defined

$$V_p = \frac{n \left\| (I - A_p) y / W \right\|^2}{[Tr(I - A_p)]^2} \tag{19}$$

The estimated degrees of freedom (Hutchinson and De Hoog, 1985)

$$Tr(I - A_p) = n - 2 - pTr(T/B) \tag{20}$$

The estimated variance

$$VAR = RSS / Tr(I - A_p) \tag{21}$$

The estimated 95% Bayesian confidence intervals (*CI*) for the cross-validated smoothing spline (Wahba, 1983) are given by

$$CI = 1.96 \sqrt{VAR * diag(A_p)} \tag{22}$$

Table S1a. Collected data used for HCFC-22

Data	Network	Station	Latitude °N	Longitude °E	Instrument	Data availability	Scale	Reference
NH								
In situ	AGAGE	Mace Head	53.3	-9.9	ADS	1999.01-2004.12	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
In situ	AGAGE	Mace Head	53.3	-9.9	Medusa	2003.11-2017.09	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
Flask	NOAA	Mace Head	53.3	-9.9	GC-MS	1998.10-2018.08	NOAA-2006	(Montzka et al., 1996a; Montzka et al., 2015)
In situ	AGAGE	Trinidad Head	41.0	-124.1	Medusa	2005.05-2017.09	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
Flask	NOAA	Trinidad Head	41.0	-124.1	GC-MS	2002.03-2018.08	NOAA-2006	(Montzka et al., 1996a; Montzka et al., 2015)
Model	NOAA	NH	30-90	-	2-D box	1944-2009	NOAA-2006	(Montzka et al., 2010)
SH								
In situ	AGAGE	Cape Grim	-40.7	144.7	ADS	1998.03-2004.12	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
In situ	AGAGE	Cape Grim	-40.7	144.7	Medusa	2004.01-2017.09	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
Flask	NOAA	Cape Grim	-40.7	144.7	GC-MS	1991.11-2018.08	NOAA-2006	(Montzka et al., 1996a; Montzka et al., 2015)
Archived air	AGAGE	Cape Grim	-40.7	144.7	Medusa	1978.04-1996.12	SIO-93	(Miller et al., 1998)
Model	NOAA	SH	-30 ~ -90	-	2-D box	1944-2009	NOAA-2006	(Montzka et al., 2010)

Table S1b. Collected data used for HCFC-141b

Data	Network	Station	Latitude °N	Longitude °E	Instrument	Data availability	Scale	Reference
NH								
Archived air	NOAA	Niwot Ridge	40.0	-	GC-MS	1987.01-1994.03	NOAA-1994	(Thompson et al., 2004)
In situ	AGAGE	Mace Head	53.3	-9.9	ADS	1994.11-2004.12	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
In situ	AGAGE	Mace Head	53.3	-9.9	Medusa	2003.11-2017.09	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
Flask	NOAA	Mace Head	53.3	-9.9	GC-MS	1998.10-2018.08	NOAA-1994	(Montzka et al., 1996a; Montzka et al., 2015)
In situ	AGAGE	Trinidad Head	41.0	-124.1	Medusa	2005.03-2017.09	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
Flask	NOAA	Trinidad Head	41.0	-124.1	GC-MS	2002.02-2018.08	NOAA-1994	(Montzka et al., 1996a; Montzka et al., 2015)
SH								
Firn air	AGAGE	Antarctic	-90.0	-4.8	ADS	1935.06-1991.11	UB-98	(Sturrock et al., 2002)
Archived air	NOAA	-	-29.4	-	GC-MS	1987.06	NOAA-1994	(Thompson et al., 2004)
Archived air	UEA	Cape Grim	-40.7	144.7	GC-MS	1978.04-2011.06	NOAA-1994	(Oram et al., 1995);
In situ	AGAGE	Cape Grim	-40.7	144.7	ADS	1998.03-2004.12	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
In situ	AGAGE	Cape Grim	-40.7	144.7	Medusa	2004.01-2017.09	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
Flask	NOAA	Cape Grim	-40.7	144.7	GC-MS	1994.10-2018.08	NOAA-1994	(Montzka et al., 1996a; Montzka et al., 2015)

Table S1c. Collected data used for HCFC-142b

Data	Network	Station	Latitude °N	Longitude °E	Instrument	Data availability	Scale	Reference
NH								
Archived air	NOAA	Niwot Ridge	40.0	-	GC-MS	1987.01-1994.03	NOAA-1994	(Thompson et al., 2004)
In situ	AGAGE	Mace Head	53.3	-9.9	ADS	1994.10-2004.12	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
In situ	AGAGE	Mace Head	53.3	-9.9	Medusa	2003.11-2017.09	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
Flask	NOAA	Mace Head	53.3	-9.9	GC-MS	1998.10-2018.07	NOAA-1994	(Montzka et al., 1996a; Montzka et al., 2015)
In situ	AGAGE	Trinidad Head	41.0	-124.1	Medusa	2005.03-2017.09	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
Flask	NOAA	Trinidad Head	41.0	-124.1	GC-MS	2002.02-2018.08	NOAA-1994	(Montzka et al., 1996a; Montzka et al., 2015)
SH								
Firn air	AGAGE	Antarctic	-90.0	-4.8	ADS	1936.06-1992.05	UB-98	(Sturrock et al., 2002)
Archived air	NOAA	-	-29.4	-	GC-MS	1987.06	NOAA-1994	(Thompson et al., 2004)
Archived air	UEA	Cape Grim	-40.7	144.7	GC-MS	1978.04-2011.06	NOAA-1994	(Oram et al., 1995);
In situ	AGAGE	Cape Grim	-40.7	144.7	ADS	1998.03-2004.12	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
In situ	AGAGE	Cape Grim	-40.7	144.7	Medusa	2004.01-2017.09	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
Flask	NOAA	Cape Grim	-40.7	144.7	GC-MS	1992.01-2018.08	NOAA-1994	(Montzka et al., 1996a; Montzka et al., 2015)

Table S1d. Collected data used for HFC-134a

Data	Network	Station	Latitude °N	Longitude °E	Instrument	Data availability	Scale	Reference
NH								
Archived air	AGAGE	La Jolla and other	32.87	-117.25	Medusa	1973.06-2016.04	SIO-05	this study
Archived air	NOAA	Niwot Ridge	40.0	-	GC-MS	1976.01-1999.04	NOAA-1995	(Montzka et al., 1996b)
In situ	AGAGE	Mace Head	53.3	-9.9	ADS	1994.10-2004.12	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
In situ	AGAGE	Mace Head	53.3	-9.9	Medusa	2003.11-2017.09	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
Flask	NOAA	Mace Head	53.3	-9.9	GC-MS	1998.10-2018.06	NOAA-1995	(Montzka et al., 1996a; Montzka et al., 2015)
In situ	AGAGE	Trinidad Head	41.0	-124.1	Medusa	2005.03-2017.09	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
Flask	NOAA	Trinidad Head	41.0	-124.1	GC-MS	2002.02-2018.06	NOAA-1995	(Montzka et al., 1996a; Montzka et al., 2015)
SH								
Archived air	AGAGE	Cape Grim	-40.7	144.7	Medusa	1978.04-2011.06	SIO-05	this study
Archived air	NOAA	-	-29.4	-	GC-MS	1987.06	NOAA-1995	(Montzka et al., 1996b)
Archived air	UEA	Cape Grim	-40.7	144.7	GC-MS	1990.05-2012.12	NOAA-1995	(Oram et al., 1996)
In situ	AGAGE	Cape Grim	-40.7	144.7	ADS	1998.02-2004.12	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
In situ	AGAGE	Cape Grim	-40.7	144.7	Medusa	2004.01-2017.09	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
Flask	NOAA	Cape Grim	-40.7	144.7	GC-MS	1994.10-2018.08	NOAA-1995	(Montzka et al., 1996a; Montzka et al., 2015)

Table S1e. Collected data used for HFC-125

Data	Network	Station	Latitude °N	Longitude °E	Instrument	Data availability	Scale	Reference
NH								
Archived air	AGAGE	La Jolla and other	32.87	-117.25	Medusa	1973.06-2015.11	SIO-14	(O'Doherty et al., 2009)
Archived air	AGAGE	La Jolla and other	32.87	-117.25	Medusa	1973.06-2011.06	UB-98	(O'Doherty et al., 2009)
In situ	AGAGE	Mace Head	53.3	-9.9	ADS	1998.02-2004.12	SIO-14	(Prinn et al., 2018a; Prinn et al., 2018b)
In situ	AGAGE	Mace Head	53.3	-9.9	Medusa	2003.11-2017.09	SIO-14	(Prinn et al., 2018a; Prinn et al., 2018b)
In situ	AGAGE	Trinidad Head	41.0	-124.1	Medusa	2005.03-2017.09	SIO-14	(Prinn et al., 2018a; Prinn et al., 2018b)
Flask	NOAA	Trinidad Head	41.0	-124.1	GC-MS_ M2	2007.01-2015.04	NOAA-2008	(Montzka et al., 2015)
SH								
Archived air	AGAGE	Cape Grim	-40.7	144.7	Medusa	1978.04-2011.06	SIO-14	(O'Doherty et al., 2009)
Archived air	AGAGE	Cape Grim	-40.7	144.7	Medusa	1995.02-2001.09	UB-98	(O'Doherty et al., 2009)
In situ	AGAGE	Cape Grim	-40.7	144.7	ADS	1998.02-2004.12	SIO-14	(Prinn et al., 2018a; Prinn et al., 2018b)
In situ	AGAGE	Cape Grim	-40.7	144.7	Medusa	2004.02-2017.09	SIO-14	(Prinn et al., 2018a; Prinn et al., 2018b)
Flask	NOAA	Cape Grim	-40.7	144.7	GC-MS_ M2	2007.01-2015.04	NOAA-2008	(Montzka et al., 2015)

Table S1f. Collected data used for HFC-23

Data	Network	Station	Latitude °N	Longitude °E	Instrument	Data availability	Scale	Reference
NH								
In situ	AGAGE	Mace Head	53.3	-9.9	Medusa	2007.10-2017.09	SIO-07	(Prinn et al., 2018a; Prinn et al., 2018b)
In situ	AGAGE	Trinidad Head	41.0	-124.1	Medusa	2007.09-2017.09	SIO-07	(Prinn et al., 2018a; Prinn et al., 2018b)
Model	AGAGE	NH	30-90	-	2-D 12-box	1978.01-2009.12	SIO-07	(Miller et al., 2010)
SH								
Archived air	AGAGE	Cape Grim	-40.7	144.7	Medusa3	2005.04-2009.11	SIO-07	(Miller et al., 2010)
Archived air	AGAGE	Cape Grim	-40.7	144.7	Medusa9	1978.04-2006.12	SIO-07	(Miller et al., 2010)
In situ	AGAGE	Cape Grim	-40.7	144.7	Medusa	2007.01-2017.09	SIO-07	(Prinn et al., 2018a; Prinn et al., 2018b)
Model	AGAGE	SH	-30 ~ -90	-	2-D 12-box	1978.01-2009.12	SIO-07	(Miller et al., 2010)

Table S1g. Collected data used for PFC-14

Data	Network	Station	Latitude °N	Longitude °E	Instrument	Data availability	Scale	Reference
NH								
In situ	AGAGE	Mace Head	53.3	-9.9	Medusa	2006.05-2017.09	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
In situ	AGAGE	Trinidad Head	41.0	-124.1	Medusa	2006.04-2017.09	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
Model	AGAGE	NH	30-90	-	2-D 12-box	1900-2015	SIO-05	(Trudinger et al., 2016)
SH								
In situ	AGAGE	Cape Grim	-40.7	144.7	Medusa	2006.05-2017.09	SIO-05	(Prinn et al., 2018a; Prinn et al., 2018b)
Model	AGAGE	SH	-30 ~ -90	-	2-D 12-box	1900-2015	SIO-05	(Trudinger et al., 2016)

Table S1h. Collected data used for PFC-116

Data	Network	Station	Latitude °N	Longitude °E	Instrument	Data availability	Scale	Reference
NH								
In situ	AGAGE	Mace Head	53.3	-9.9	Medusa	2003.11-2017.09	SIO-07	(Prinn et al., 2018a; Prinn et al., 2018b)
In situ	AGAGE	Trinidad Head	41.0	-124.1	Medusa	2005.05-2017.09	SIO-07	(Prinn et al., 2018a; Prinn et al., 2018b)
Model	AGAGE	NH	30-90	-	2-D 12-box	1900-2015	SIO-07	(Trudinger et al., 2016)
SH								
In situ	AGAGE	Cape Grim	-40.7	144.7	Medusa	2004.04-2017.09	SIO-07	(Prinn et al., 2018a; Prinn et al., 2018b)
Model	AGAGE	SH	-30 ~ -90	-	2-D 12-box	1900-2015	SIO-07	(Trudinger et al., 2016)

Table S3. Ostwald solubility function of PFC-14 in seawater estimated by the method I

Compound	a_1	a_2	a_3	c_1	c_2	c_3	T_{min} (K)	T_{max} (K)	L_0 at 1 atm, 25 °C (L L^{-1})	L at 1 atm, 25 °C, 35.0 ‰ (L L^{-1})
PFC-14	-113.8218	162.6686	49.4215	$6.60 \cdot 10^{-5}$	0.003341	0.21307	273.15	328.15	0.00513	0.004027

$$lnL = \left[a_1 + a_2 \cdot (\frac{100}{T}) + a_3 \cdot ln(\frac{T}{100})\right] \times exp[-(c_1(T - 273.15)^2 + c_2(T - 273.15) + c_3) \times \frac{0.03600}{1.80655} \times S \times \rho(T,S)]$$

Table S4. Comparison among the calculated Ostwald solubility coefficients (L_0, L L^{-1}) by the poly-parameter linear free energy relationships (pp-LFERs) based on V, V_c and log L^{16}, observed ones and calculated ones by the Clark-Glew-Weiss (CGW) model fit of target compounds and CFC-12 in water at 298.15 K and 310.15 K

Species	T (K)	Calculated log L_0_V by the pp-LFERs [a]	Calculated L_0_V by the pp-LFERs [a]	Calculated log $L_0\_V_c$ by the pp-LFERs [b]	Calculated $L_0\_V_c$ by the pp-LFERs [b]	Calculated log $L_0\_L^{16}$ by the pp-LFERs [c]	Calculated $L_0\_L^{16}$ by the pp-LFERs [c]	Observed log L_0 [d]	Observed L_0 [d]	Calculated L_0 by the CGW fit [e]
HCFC-22	298.15	-0.017	0.961	-0.052	0.888	-0.025	0.944	-0.091	0.811	0.844
HCFC-141b	298.15	-0.136	0.731	-0.154	0.702	-0.152	0.705	-0.148	0.711	0.711
HCFC-142b	298.15	-0.405	0.394	-0.440	0.363	-0.405	0.394	-0.449	0.356	0.352
HFC-134a	298.15	-0.326	0.472	-0.407	0.392	-0.326	0.472	-0.408	0.391	0.381
HFC-125	298.15	-1.003	0.099	-1.130	0.074	-0.989	0.103	-1.059	0.087	0.086
HFC-23	298.15	-0.453	0.352	-0.505	0.313	-0.469	0.340	-0.510	0.309	0.313
PFC-14	298.15	-2.241	0.00574	-2.296	0.00505	-0.250	0.00562	-2.306	0.00494	0.00513
PFC-116	298.15	-2.658	0.00220	-2.763	0.00173	-2.716	-	-	-	0.00143
CFC-12	298.15	-1.120	0.076	-1.155	0.070	-1.145	0.072	-1.129	0.074	0.069
HCFC-22	310.15	-0.161	0.691	-0.203	0.626	-0.210	0.617	-	-	0.598
HCFC-141b	310.15	-0.306	0.494	-0.327	0.471	-0.348	0.449	-0.336	0.461	0.484
HCFC-142b	310.15	-0.571	0.269	-0.614	0.243	-0.591	0.256	-0.605	0.248	0.246
HFC-134a	310.15	-0.563	0.274	-0.621	0.239	-0.636	0.231	-0.547	0.284	0.269
HFC-125	310.15	-1.208	0.062	-1.339	0.046	-0.241	0.057	-1.203	0.063	0.062
HFC-23	310.15	-0.618	0.241	-0.683	0.208	-0.685	0.207	-0.622	0.239	0.225
PFC-14	310.15	-2.310	0.00490	-2.382	0.00415	-2.413	0.00386	-2.386	0.00411	0.00437
PFC-116	310.15	-2.755	0.00176	-2.883	0.00131	-2.851	-	-	-	0.00110
CFC-12	310.15	-1.213	0.061	-1.256	0.055	-1.257	0.055	-1.275	0.053	0.048

[a] Calculated log L_0_V and L_0_V are calculated by the pp-LFERs, which are obtained from Table 6,7,9,12-15 in Abraham et al. (2001) and Table 2 in Abraham et al. (2012)

[b] Calculated log $L_0\_V_c$ and $L_0\_V_c$ are calculated by the pp-LFERs based on the V_c

[c] Calculated log $L_0\_L^{16}$ and $L_0\_L^{16}$ are calculated by the pp-LFERs, which are obtained from Table 6,7,9,12-15 in Abraham et al. (2001) and Table 2 in Abraham et al. (2012)

[d] Observed log L_0 and L_0 are measured by experiments, which are also obtained from Table 6,7,9,12-15 in Abraham et al. (2001) and Table 2 in Abraham et al. (2012)

[e] Calculated L_0 by the CGW fit are calculated based on the combined method for water solubility

Table S5. Ostwald solubility functions of target compounds and CFC-12 in seawater estimated by the (revised) method II at 298.15 K and 310.15 K

Species	Chemical Formula	*T* (K)	*c*	*e*	*s*	*a*	*b*	*v*	K_s	L_0 at 1 atm, 25 °C (L L^{-1})	*L* at 1 atm, 25 °C, 35.0 ‰ (L L^{-1})
HCFC-22	$CHClF_2$	298.15	-0.994	0.577	2.549	3.813	4.841	-0.869	0.169 ± 0.022	0.888	0.703
HCFC-141b	$C_2H_3Cl_2F$	298.15	-0.994	0.577	2.549	3.813	4.841	-0.869	0.204 ± 0.023	0.702	0.530
HCFC-142b	$C_2H_3ClF_2$	298.15	-0.994	0.577	2.549	3.813	4.841	-0.869	0.198 ± 0.022	0.363	0.277
HFC-134a	CH_2FCF_3	298.15	-0.994	0.577	2.549	3.813	4.841	-0.869	0.193 ± 0.022	0.392	0.300
HFC-125	C_2HF_5	298.15	-0.994	0.577	2.549	3.813	4.841	-0.869	0.224 ± 0.021	0.091	0.067
HFC-23	CHF_3	298.15	-0.994	0.577	2.549	3.813	4.841	-0.869	0.168 ± 0.021	0.313	0.248
PFC-14	CF_4	298.15	-0.994	0.577	2.549	3.813	4.841	-0.869	0.202 ± 0.022	0.00505	0.00382
PFC-116	C_2F_6	298.15	-0.994	0.577	2.549	3.813	4.841	-0.869	0.244 ± 0.022	0.00173	0.00123
CFC-12	CCl_2F_2	298.15	-0.994	0.577	2.549	3.813	4.841	-0.869	0.204 ± 0.021	0.070	0.053
HCFC-22	$CHClF_2$	310.15	-0.966	0.698	2.412	3.393	4.577	-1.072	0.169 ± 0.022	0.626	0.530
HCFC-141b	$C_2H_3Cl_2F$	310.15	-0.966	0.698	2.412	3.393	4.577	-1.072	0.204 ± 0.023	0.471	0.385
HCFC-142b	$C_2H_3ClF_2$	310.15	-0.966	0.698	2.412	3.393	4.577	-1.072	0.198 ± 0.022	0.243	0.200
HFC-134a	CH_2FCF_3	310.15	-0.966	0.698	2.412	3.393	4.577	-1.072	0.193 ± 0.022	0.239	0.198
HFC-125	C_2HF_5	310.15	-0.966	0.698	2.412	3.393	4.577	-1.072	0.224 ± 0.021	0.059	0.047
HFC-23	CHF_3	310.15	-0.966	0.698	2.412	3.393	4.577	-1.072	0.168 ± 0.021	0.208	0.176
PFC-14	CF_4	310.15	-0.966	0.698	2.412	3.393	4.577	-1.072	0.202 ± 0.022	0.00415	0.00340
PFC-116	C_2F_6	310.15	-0.966	0.698	2.412	3.393	4.577	-1.072	0.244 ± 0.022	0.00131	0.00103
CFC-12	CCl_2F_2	310.15	-0.966	0.698	2.412	3.393	4.577	-1.072	0.204 ± 0.021	0.055	0.045

$L = 10^\wedge\left[-K_S \cdot \frac{S}{M_{NaCl}} + c + eE + sS + aA + bB + vV_c\right]$, (*V* for HFC-125, V_c for other compounds)

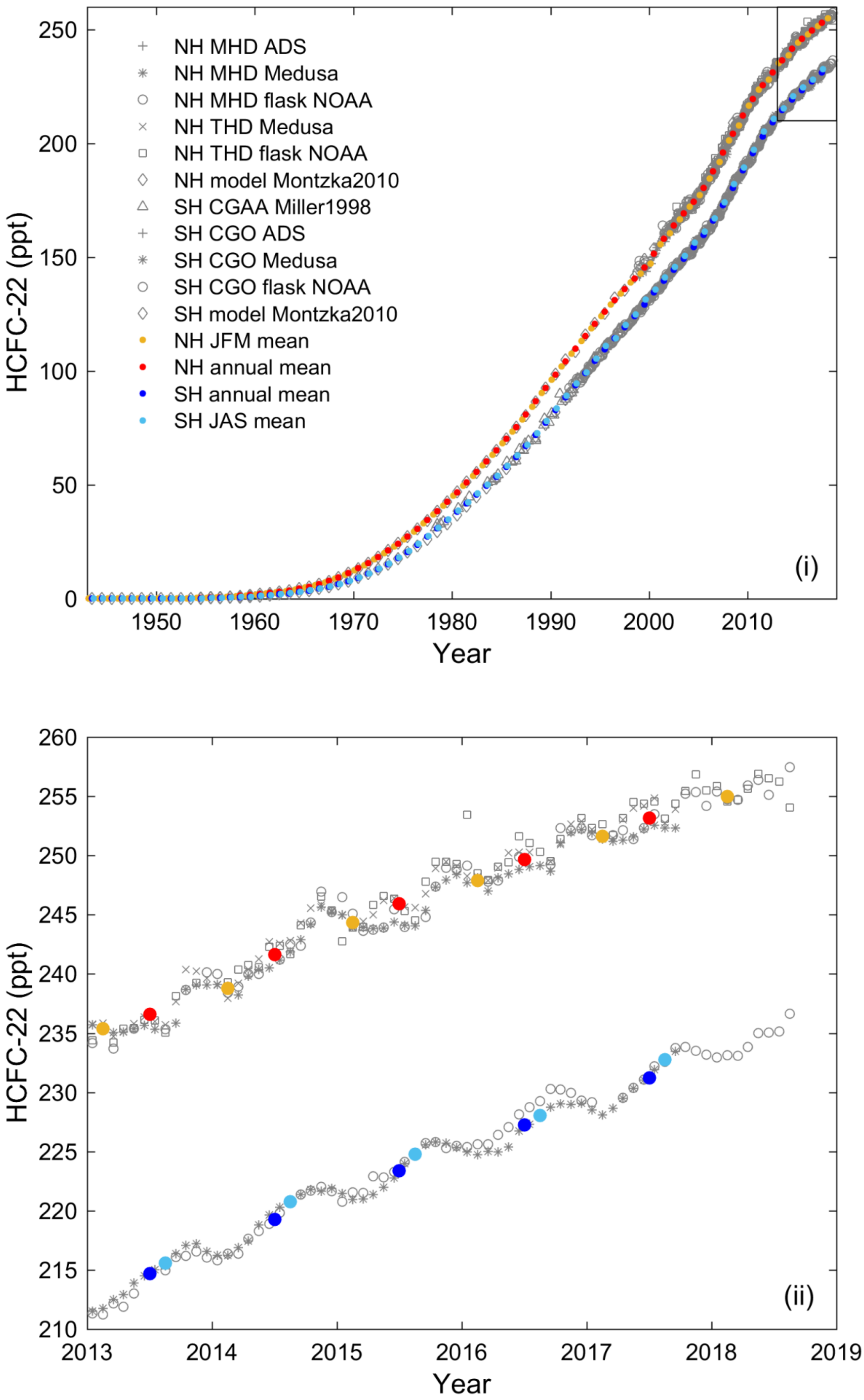

Fig. S1a. HCFC-22: Atmospheric mole fractions in the NH and SH based on collected data (Table S2a) in the range of (i) 1943-2019; (ii) 2013-2019. Fig. (ii) is the enlarged figure of the square in Fig. (i).

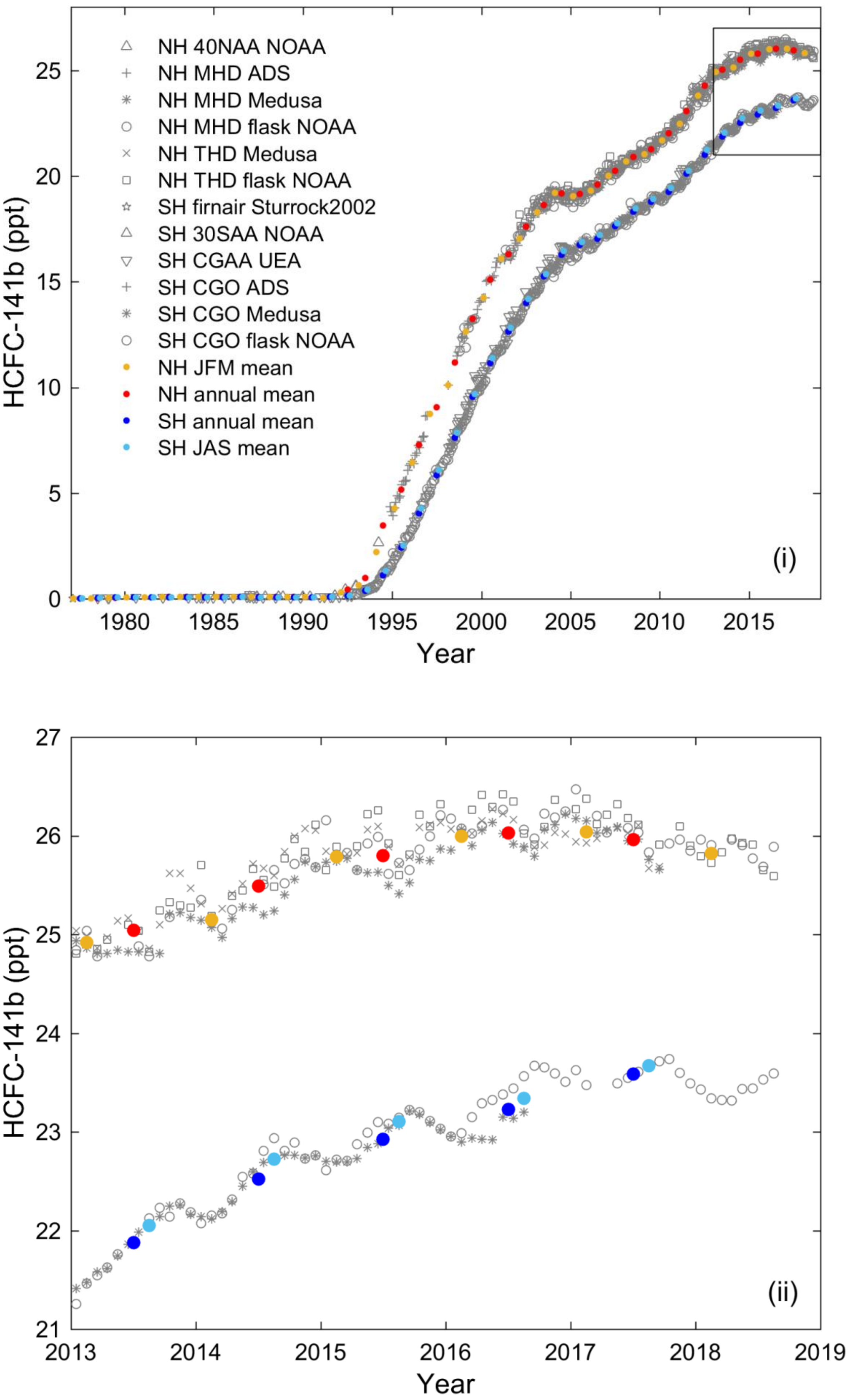

Fig. S1b. HCFC-141b: Atmospheric mole fractions in the NH and SH based on collected data (Table S2b) in the range of (i) 1977-2019; (ii) 2013-2019. Fig. (ii) is the enlarged figure of the square in Fig. (i).

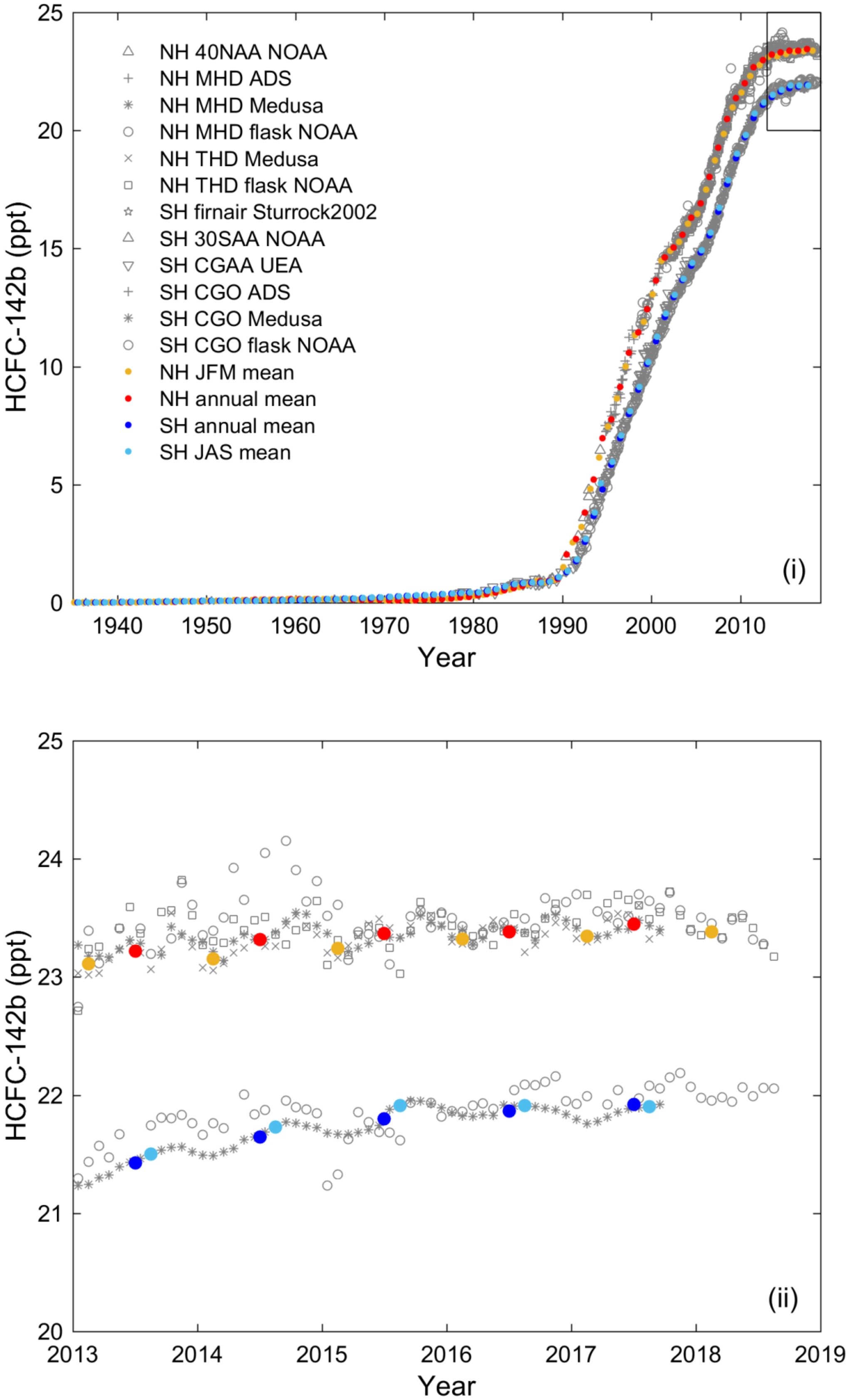

Fig. S1c. HCFC-142b: Atmospheric mole fractions in the NH and SH based on collected data (Table S2c) in the range of (i) 1935-2019; (ii) 2013-2019. Fig. (ii) is the enlarged figure of the square in Fig. (i).

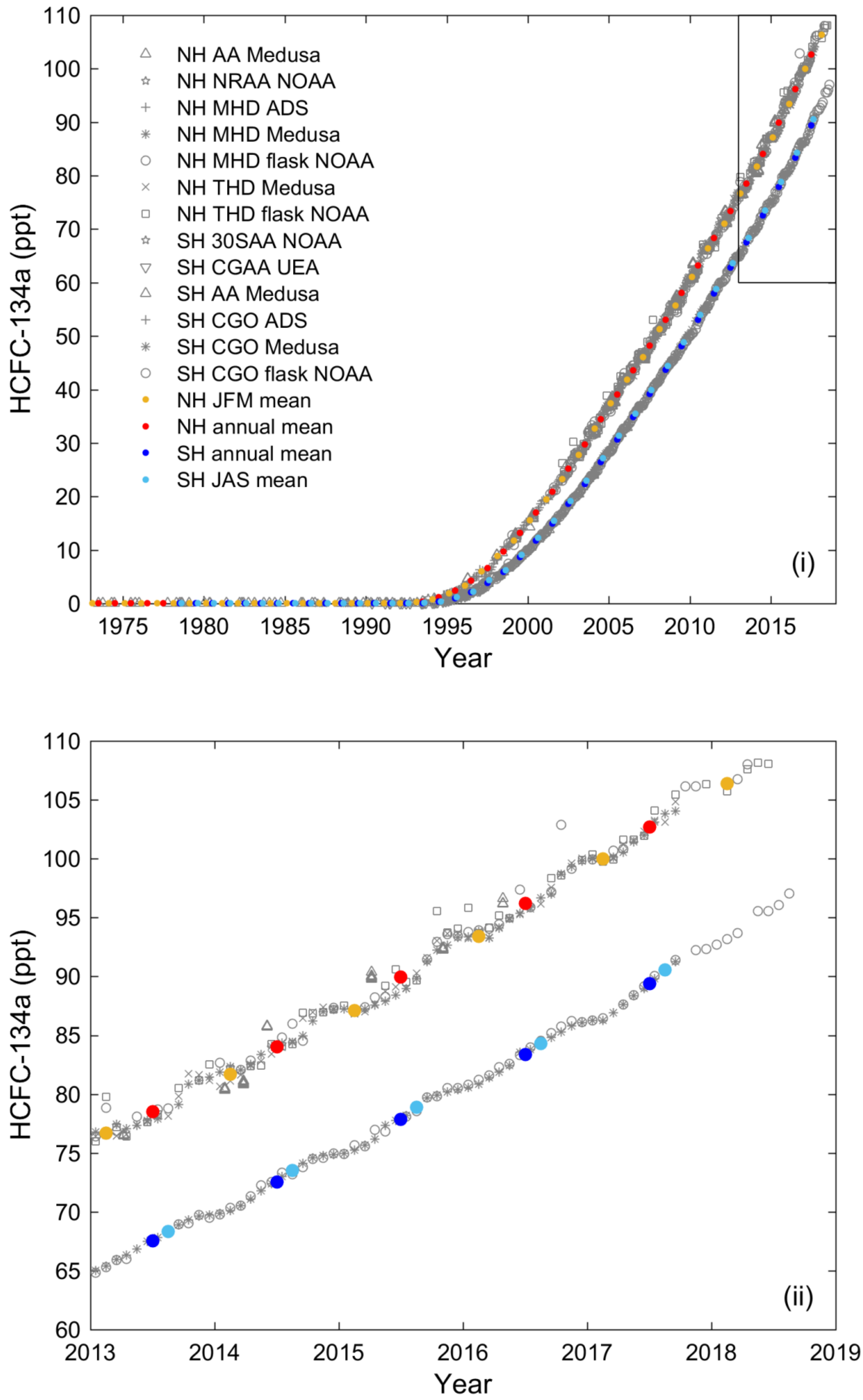

Fig. S1d. HFC-134a: Atmospheric mole fractions in the NH and SH based on collected data (Table S2d) in the range of (i) 1973-2019; (ii) 2013-2019. Fig. (ii) is the enlarged figure of the square in Fig. (i).

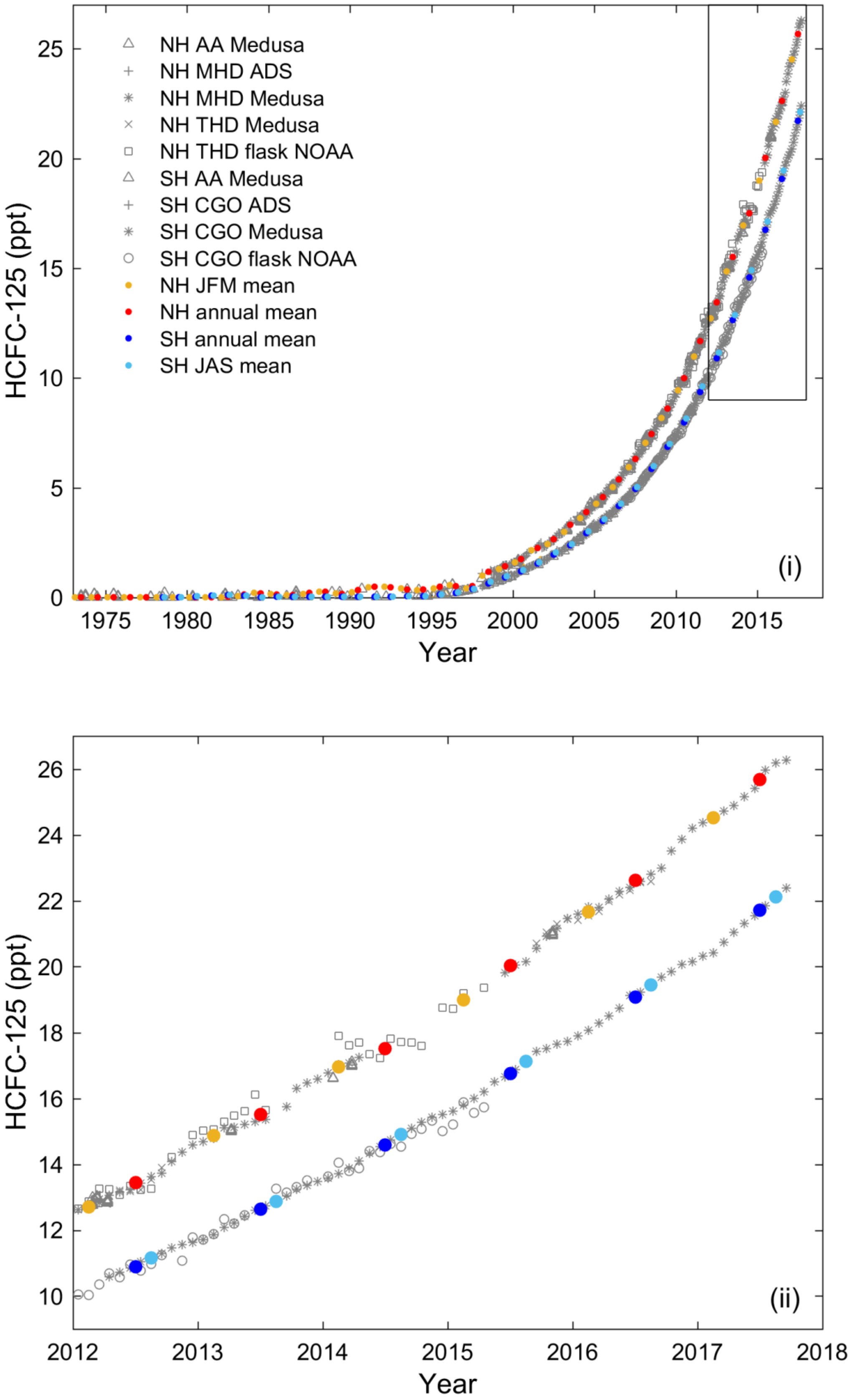

Fig. S1e. HFC-125: Atmospheric mole fractions in the NH and SH based on collected data (Table S2e) in the range of (i) 1973-2018; (ii) 2012-2018. Fig. (ii) is the enlarged figure of the square in Fig. (i).

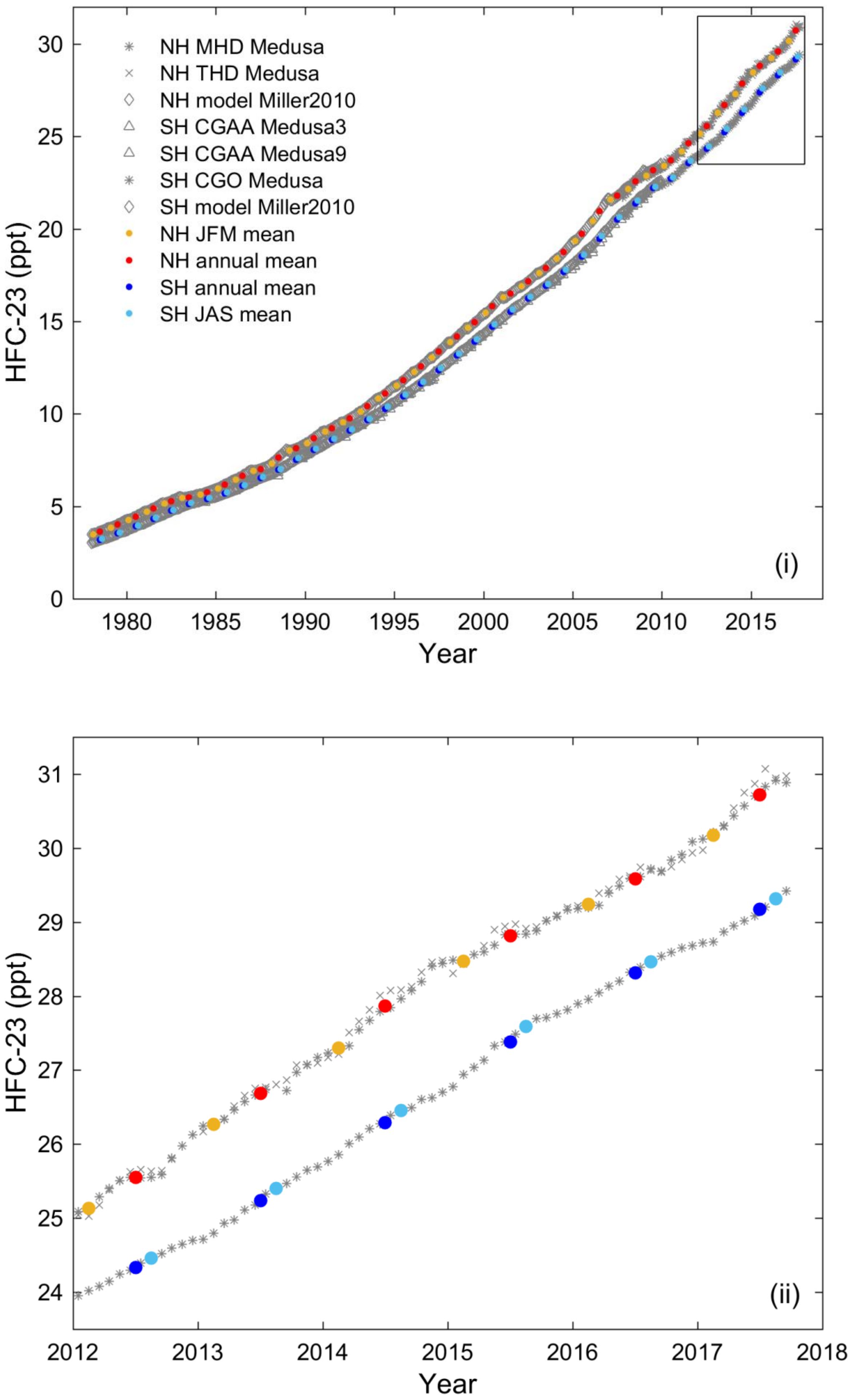

Fig. S1f. HFC-23: Atmospheric mole fractions in the NH and SH based on collected data (Table S2f) in the range of (i) 1978-2018; (ii) 2012-2018. Fig. (ii) is the enlarged figure of the square in Fig. (i).

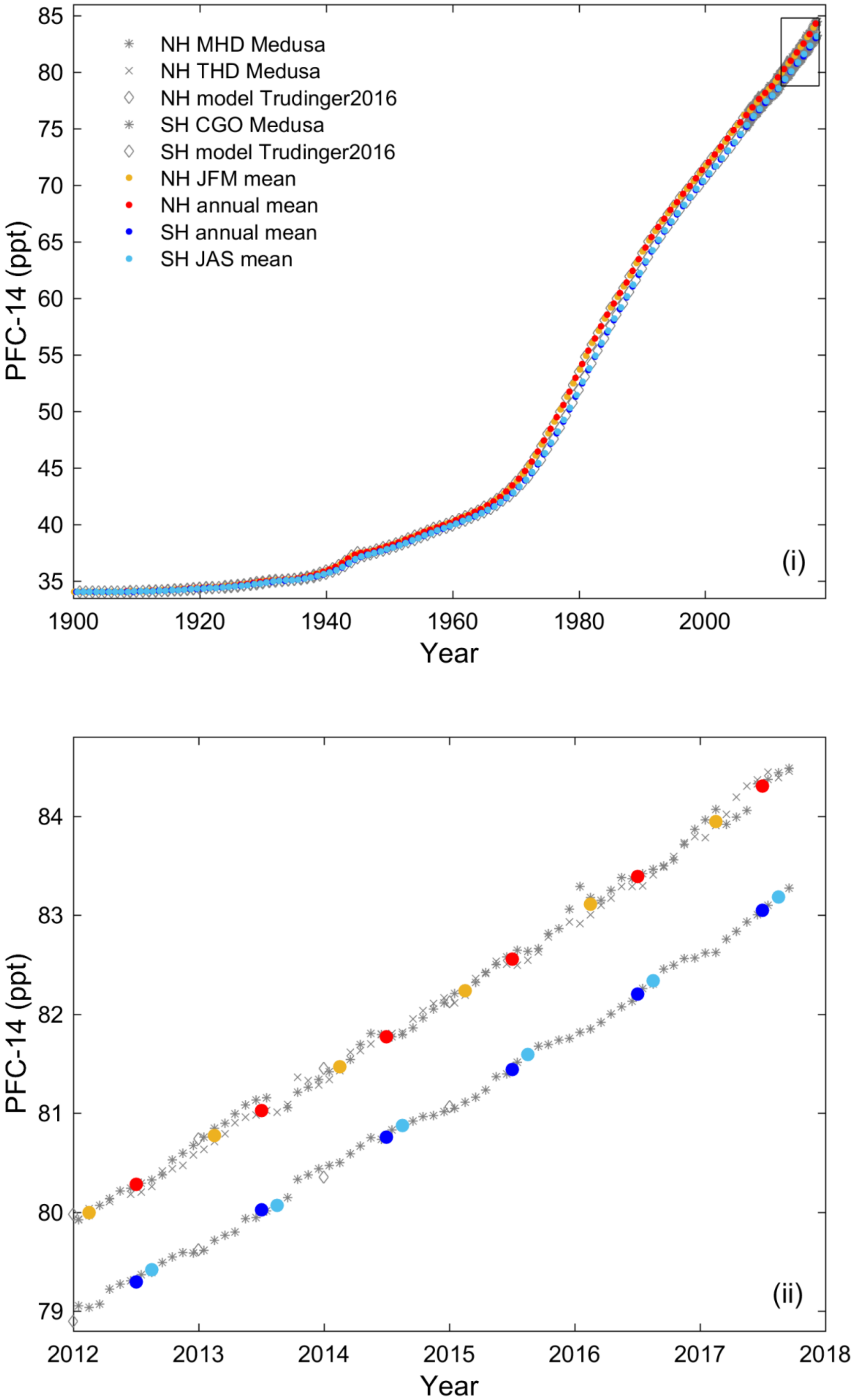

Fig. S1g. PFC-14: Atmospheric mole fractions in the NH and SH based on collected data (Table S2g) in the range of (i) 1900-2018; (ii) 2012-2018. Fig. (ii) is the enlarged figure of the square in Fig. (i).

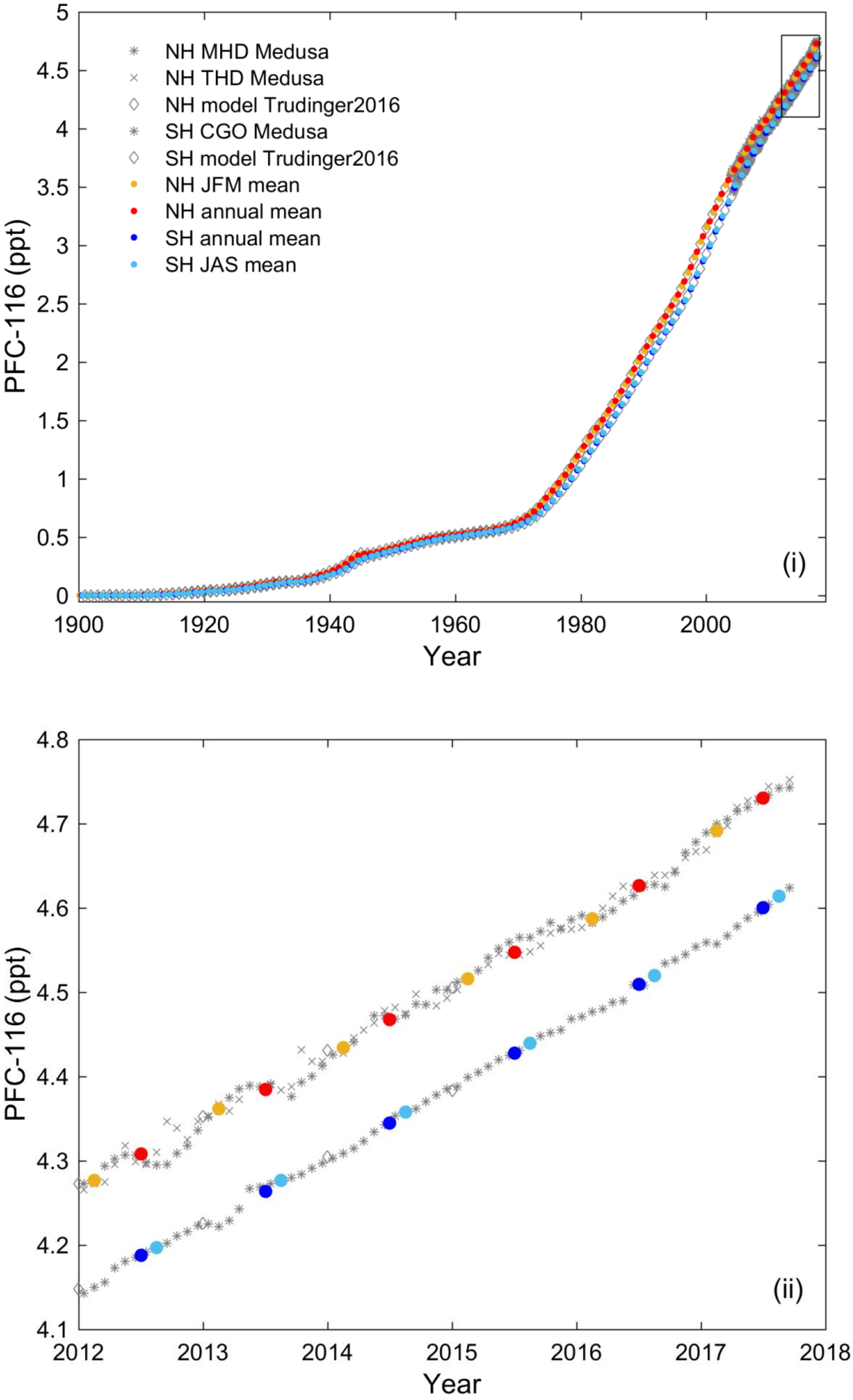

Fig. S1h. PFC-116: Atmospheric mole fractions in the NH and SH based on collected data (Table S2h) in the range of (i) 1900-2018; (ii) 2012-2018. Fig. (ii) is the enlarged figure of the square in Fig. (i).

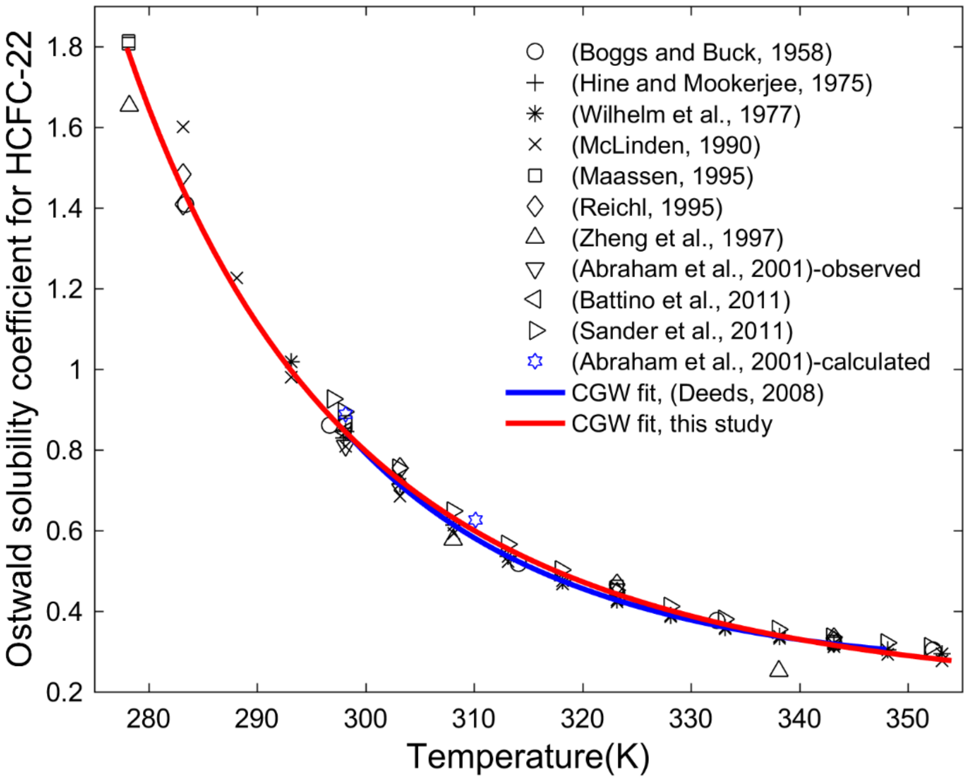

Fig. S2a. HCFC-22 freshwater solubility (Ostwald solubility coefficients) as a function of temperature based on previous studies (Abraham et al., 2001; Battino et al., 2011; Boggs and Buck Jr, 1958; Hine and Mookerjee, 1975; Maaßen, 1995; Mclinden, 1990; Reichl, 1996; Sander et al., 2011; Wilhelm et al., 1977; Zheng et al., 1997). The Clarke-Glew-Weiss (CGW) model is used to fit the data (black markers) and compared with the results from Deeds (2008) and from (Abraham et al., 2001)-calculated (blue Hexagram, calculated by the revised method II). The CGW fit in this study agrees to within 4.0 % with two-thirds of the data.

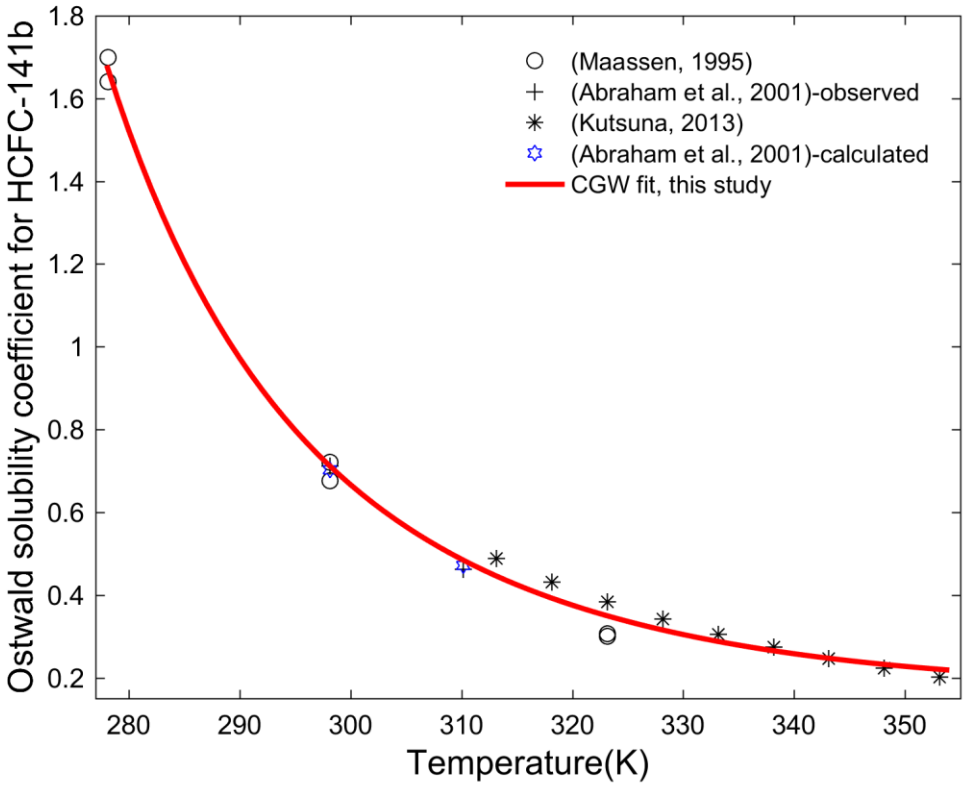

Fig. S2b. HCFC-141b freshwater solubility (Ostwald solubility coefficients) as a function of temperature based on previous studies (Abraham et al., 2001; Kutsuna, 2013; Maaßen, 1995). The Clarke-Glew-Weiss (CGW) model is used to fit the data (black markers) and compared with the results from (Abraham et al., 2001)-calculated (blue Hexagram, calculated by the revised method II). The CGW fit in this study agrees to within 7.8 % with two-thirds of the data.

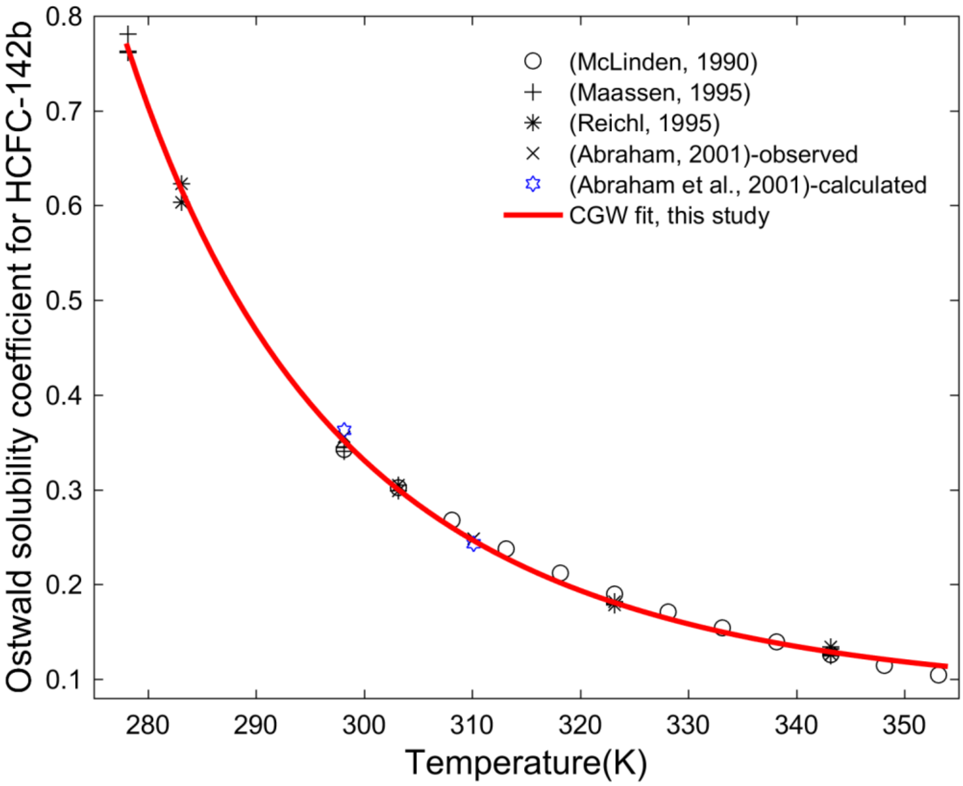

Fig. S2c. HCFC-142b freshwater solubility (Ostwald solubility coefficients) as a function of temperature based on previous studies (Abraham et al., 2001; Maaßen, 1995; Mclinden, 1990; Reichl, 1996). The Clarke-Glew-Weiss (CGW) model is used to fit the data (black markers) and compared with the results from (Abraham et al., 2001)-calculated (blue Hexagram, calculated by the revised method II). The CGW fit in this study agrees to within 2.5 % with two-thirds of the data.

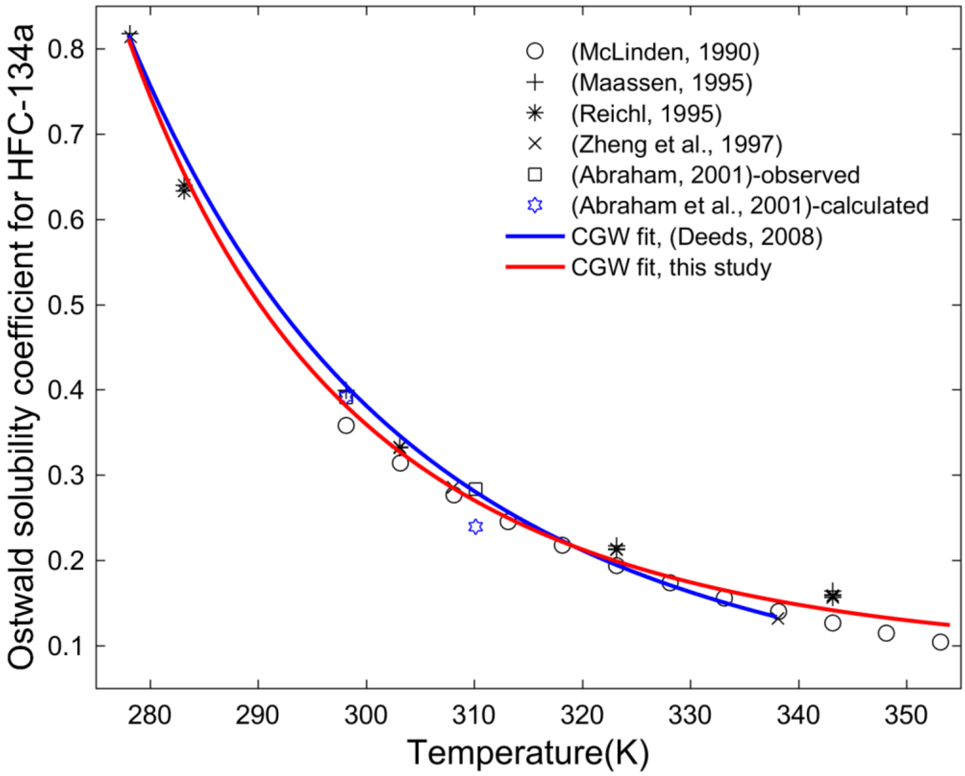

Fig. S2d. HFC-134a freshwater solubility (Ostwald solubility coefficients) as a function of temperature based on previous studies (Abraham et al., 2001; Maaßen, 1995; Mclinden, 1990; Reichl, 1996; Zheng et al., 1997). The Clarke-Glew-Weiss (CGW) model is used to fit the data (black markers) and compared with the results from Deeds (2008) and from (Abraham et al., 2001)-calculated (blue Hexagram, calculated by the revised method II). The CGW fit in this study agrees to within 6.8 % with two-thirds of the data.

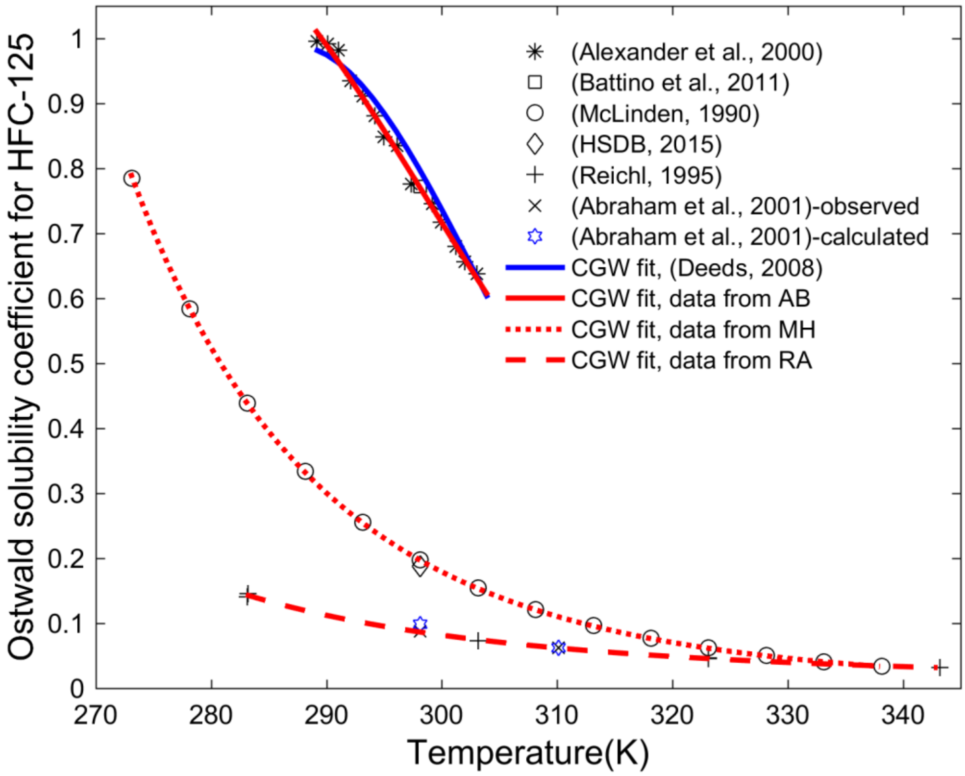

Fig. S2e. HFC-125 freshwater solubility (Ostwald solubility coefficients) as a function of temperature based on previous studies (Abraham et al., 2001; Battino et al., 2011; HSDB, 2015; Mclinden, 1990; Miguel et al., 2000; Reichl, 1996). The Clarke-Glew-Weiss (CGW) model is used to fit the data (black markers) and compared with the results from Deeds (2008) and from Abraham et al. (2001)-calculated (blue Hexagram, calculated by the method II based on Eq. (12)). The CGW fit in this study agrees to within 2.1 % with all data. Unfortunately, the data from previous studies is not described by one CGW fit, but by three. Curve 1 is the upper and red solid line fitted the data (Battino et al., 2011; Miguel et al., 2000) in the temperature range of 289.15-303.15 K. This fit agrees to within 1.0 % with 2/3 data. Curve 2 is the middle and red dotted line fitted the data (HSDB, 2015; Mclinden, 1990) from 273.15 K to 338.15 K. This fit agrees to within 0.75 % with 2/3 data. Curve 3 is the bottom and red dashed line fitted the data (Abraham et al., 2001; Reichl, 1996) in the temperature range of 283.15-343.15 K. This fit agrees to within 3.3 % with two-thirds of the data. The discrepancy of the three fits is discussed in the text.

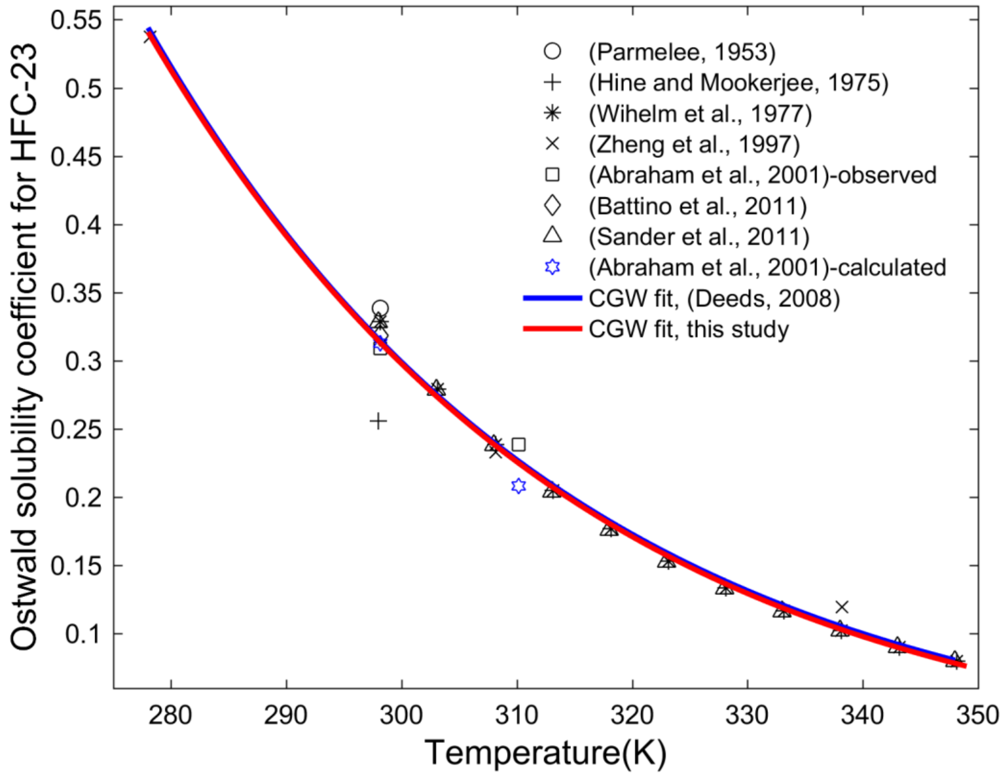

Fig. S2f. HFC-23 freshwater solubility (Ostwald solubility coefficients) as a function of temperature based on previous studies (Abraham et al., 2001; Battino et al., 2011; Hine and Mookerjee, 1975; Parmelee, 1953; Sander et al., 2011; Wilhelm et al., 1977; Zheng et al., 1997). The Clarke-Glew-Weiss (CGW) model is used to fit the data (black markers) and compared with the results from Deeds (2008) and from (Abraham et al., 2001)-calculated (blue Hexagram, calculated by the revised method II). The CGW fit in this study agrees to within 2.3 % with two-thirds of the data.

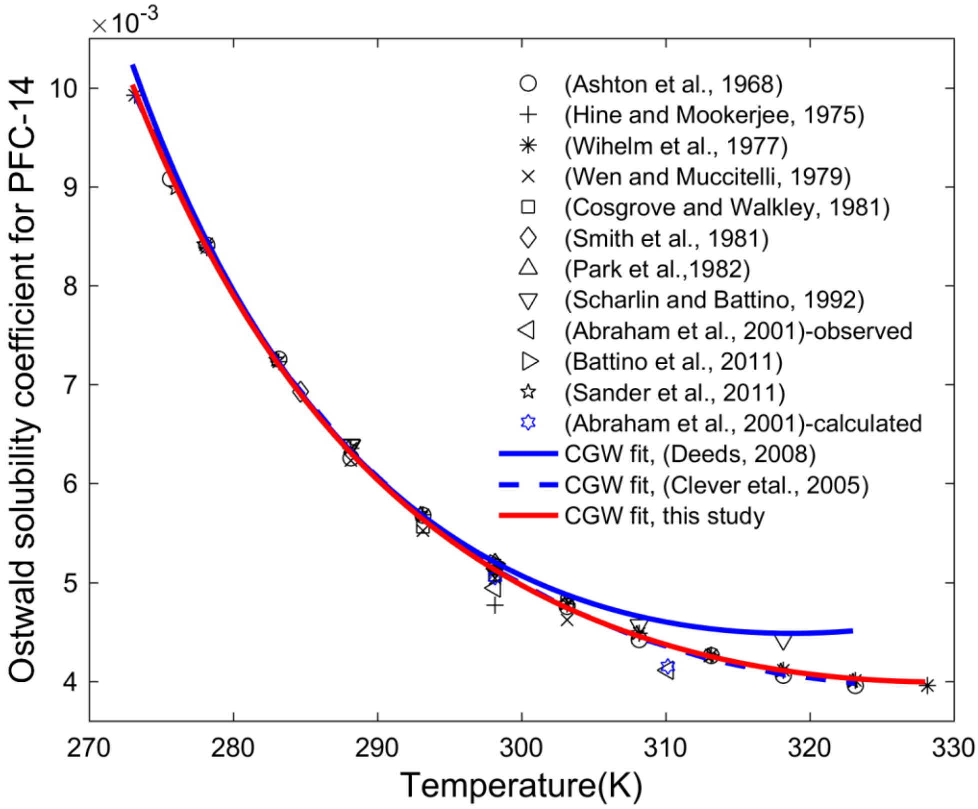

Fig. S2g. PFC-14 freshwater solubility (Ostwald solubility coefficients) as a function of temperature based on previous studies (Smith et al., 1981; Park et al., 1982; Scharlin and Battino, 1992; Abraham et al., 2001; Battino et al., 2011; Sander et al., 2011). The Clarke-Glew-Weiss (CGW) model is used to fit the data (black markers) and compared with the results from Deeds (2008), from Clever et al. (2005) and from (Abraham et al., 2001)-calculated (blue Hexagram, calculated by the revised method II). The CGW fit in this study agrees to within 0.95 % with two-thirds of the data.

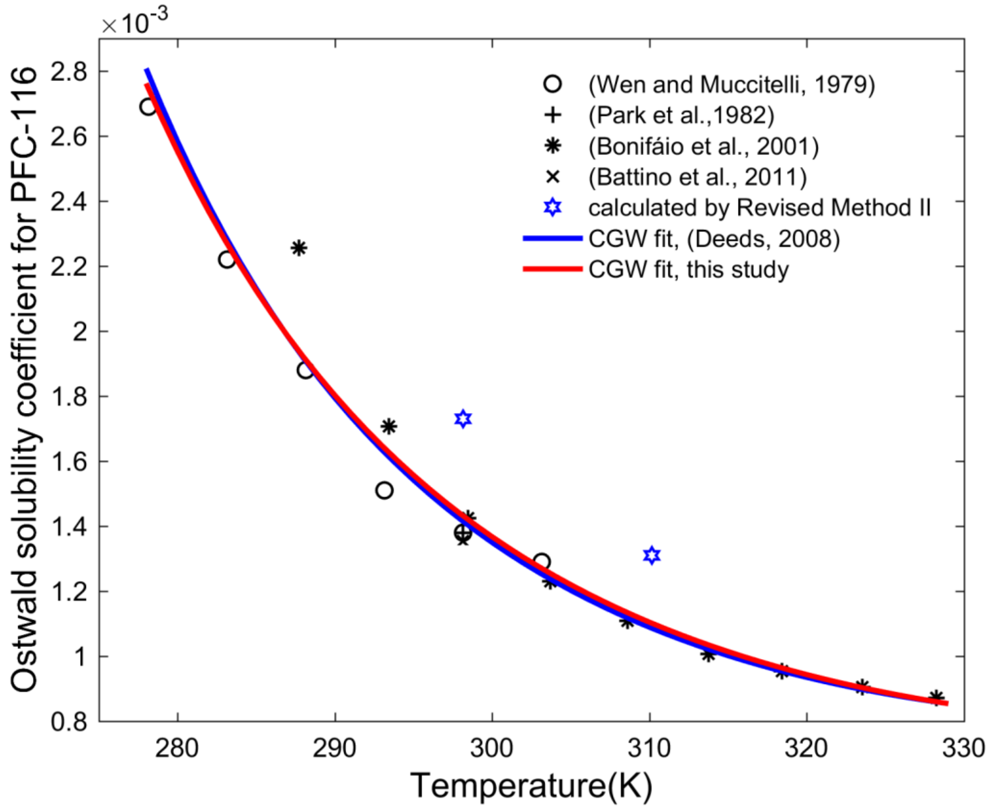

Fig. S2h. PFC-116 freshwater solubility (Ostwald solubility coefficients) as a function of temperature based on previous studies (Battino et al., 2011; Bonifácio et al., 2001; Park et al., 1982; Wen and Muccitelli, 1979). The Clarke-Glew-Weiss (CGW) model is used to fit the data (black markers) and compared with the fit results from Deeds (2008) and from the data calculated by the revised method II (blue Hexagram). The CGW fit in this study agrees to within 3.5 % with two-thirds of the data.

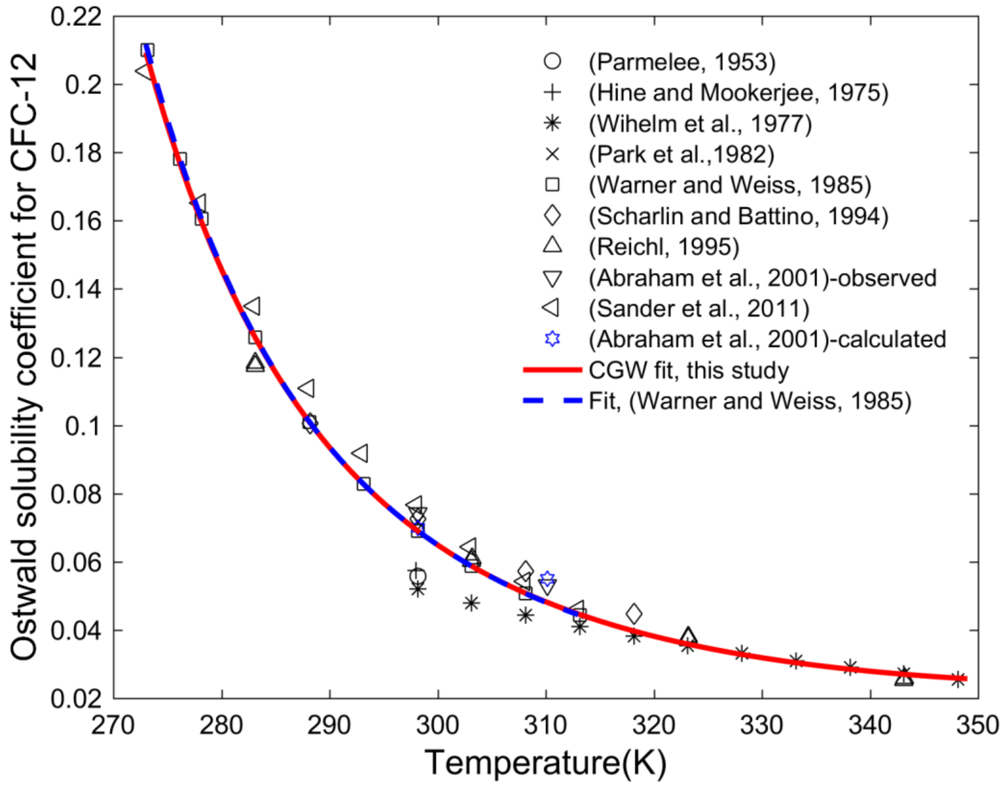

Fig. S2i. CFC-12 freshwater solubility (Ostwald solubility coefficients) as a function of temperature based on previous studies (Abraham et al., 2001; Hine and Mookerjee, 1975; Park et al., 1982; Parmelee, 1953; Reichl, 1996; Sander et al., 2011; Scharlin and Battino, 1994; Warner and Weiss, 1985; Wilhelm et al., 1977). The Clarke-Glew-Weiss (CGW) model is used to fit the data (black markers) and compared with the fit results from Warner and Weiss (1985) and the data from (Abraham et al., 2001)-calculated (blue Hexagram, calculated by the revised method II). The CGW fit in this study agrees to within 6.6 % with two-thirds of the data.

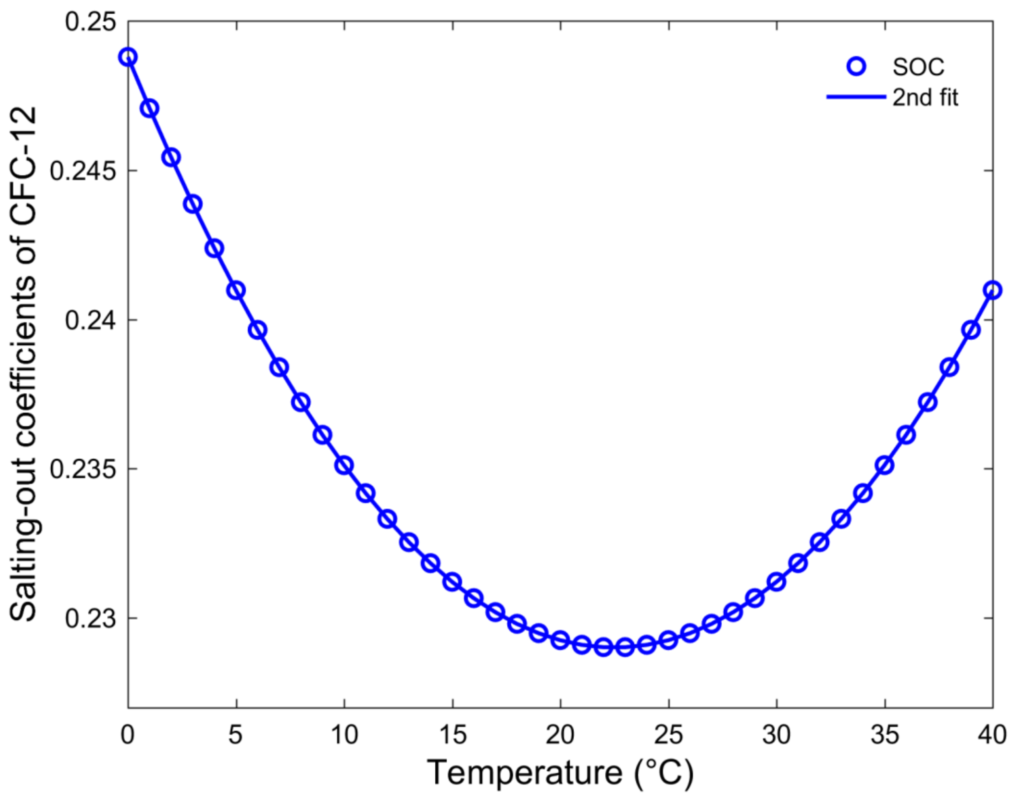

Fig. S3. The relationship between salting-out coefficients (SOC) and temperature for CFC-12 calculated by Eq. (16) based on the data from Warner and Weiss (1985).

References

Abraham, M. H., Gil-Lostes, J., Corr, S., and Acree, W. E.: Determination of partition coefficients of refrigerants by gas liquid chromatographic headspace analysis, J. Chromatogr. A, 1265, 144-148, 2012.

Abraham, M. H., Gola, J. M., Cometto-Muñiz, J. E., and Cain, W. S.: Solvation properties of refrigerants, and the estimation of their water-solvent and gas-solvent partitions, Fluid Phase Equilib., 180, 41-58, 2001.

Battino, R., Seybold, P. G., and Campanell, F. C.: Correlations Involving the Solubility of Gases in Water at 298.15 K and 101325 Pa, Journal of Chemical & Engineering Data, 56, 727-732, 2011.

Boggs, J. E. and Buck Jr, A. E.: The solubility of some chloromethanes in water, J. Phys. Chem., 62, 1459-1461, 1958.

Bonifácio, R. P., Pádua, A. A. H., and Costa Gomes, M. F.: Perfluoroalkanes in water: Experimental Henry's law coefficients for hexafluoroethane and computer simulations for tetrafluoromethane and hexafluoroethane, J. Phys. Chem. B, 105, 8403-8409, 2001.

Clever, H. L., Battino, R., Clever, H. L., Jaselskis, B., Clever, H. L., Yampol'skii, Y. P., Jaselskis, B., Scharlin, P., and Young, C. L.: IUPAC-NIST Solubility Data Series. 80. Gaseous Fluorides of Boron, Nitrogen, Sulfur, Carbon, and Silicon and Solid Xenon Fluorides in all Solvents, J. Phys. Chem. Ref. Data, 34, 201-438, 2005.

Deeds, D. A.: The Natural Geochemistry of Tetrafluoromethane and Sulfur Hexafluoride : Studies of Ancient Mojave Desert Groundwaters, North Pacific Seawaters and the Summit Emissions of Kilauea Volcano, PhD thesis, 2008.

Hine, J. and Mookerjee, P. K.: Structural effects on rates and equilibriums. XIX. Intrinsic hydrophilic character of organic compounds. Correlations in terms of structural contributions, J. Org. Chem., 40, 292-298, 1975.

HSDB: Hazardous Substances Data Bank, TOXicology data NETwork (TOXNET), National Library of Medicine (US), available at: http://toxnet.nlm.nih.gov/newtoxnet/hsdb.htm, last access: 10 April 2015.

Hutchinson, M. F. and De Hoog, F.: Smoothing noisy data with spline functions, Numer. Math., 47, 99-106, 1985.

Kutsuna, S.: Determination of Rate Constants for Aqueous Reactions of HCFC-123 and HCFC-225ca with OH- Along with Henry's Law Constants of Several HCFCs, Int. J. Chem. Kinet., 45, 440-451, 2013.

Maaßen, S.: Experimentelle Bestimmung und Korrelierung von Verteilungskoeffizienten in verdünnten Lösungen, PhD thesis, Shaker, 1995.

Mclinden, M. O.: Physical properties of alternatives to the fully halogenated chlorofluorocarbons, United States, 1990.

Miguel, A. A. F., Ferreira, A. G. M., and Fonseca, I. M. A.: Solubilities of some new refrigerants in water, Fluid Phase Equilib., 173, 97-107, 2000.

Miller, B. R., Huang, J., Weiss, R. F., Prinn, R. G., and Fraser, P. J.: Atmospheric trend and lifetime of chlorodifluoromethane (HCFC-22) and the global tropospheric OH concentration, J. Geophy. Res., 103, 13237-13248, 1998.

Miller, B. R., Rigby, M., Kuijpers, L. J. M., Krummel, P. B., Steele, L. P., Leist, M., Fraser, P. J., McCulloch, A., Harth, C., Salameh, P., Mühle, J., Weiss, R. F., Prinn, R. G., Wang, R. H. J., O'Doherty, S., Greally, B. R., and Simmonds, P. G.: HFC-23 (CHF_3) emission trend response to HCFC-22 ($CHClF_2$) production and recent HFC-23 emission abatement measures, Atmos. Chem. Phys., 10, 7875-7890, 2010.

Montzka, S. A., Butler, J. H., Myers, R. C., Thompson, T. M., Swanson, T. H., Clarke, A. D., Lock, L. T., and Elkins, J. W.: Decline in the tropospheric abundance of halogen from halocarbons: Implications for stratospheric ozone depletion, Science, 272, 1318-1322, 1996a.

Montzka, S. A., Kuijpers, L., Battle, M. O., Aydin, M., Verhulst, K. R., Saltzman, E. S., and Fahey, D. W.: Recent increases in global HFC-23 emissions, Geophys. Res. Lett., 37, L02808, 2010.

Montzka, S. A., McFarland, M., Andersen, S. O., Miller, B. R., Fahey, D. W., Hall, B. D., Hu, L., Siso, C., and Elkins, J. W.: Recent trends in global emissions of hydrochlorofluorocarbons and hydrofluorocarbons: Reflecting on the 2007 adjustments to the Montreal Protocol, J. Phys. Chem. A, 119, 4439-4449, 2015.

Montzka, S. A., Myers, R. C., Butler, J. H., Elkins, J. W., Lock, L. T., Clarke, A. D., and Goldstein, A. H.: Observations of HFC-134a in the remote troposphere, Geophys. Res. Lett., 23, 169-172, 1996b.

O'Doherty, S., Cunnold, D. M., Miller, B. R., Mühle, J., McCulloch, A., Simmonds, P. G., Manning, A. J., Reimann, S., Vollmer, M. K., Greally, B. R., Prinn, R. G., Fraser, P. J., Steele, L. P., Krummel, P. B., Dunse, B. L., Porter, L. W., Lunder, C. R., Schmidbauer, N., Hermansen, O., Salameh, P. K., Harth, C. M., Wang, R. H. J., and Weiss, R. F.: Global and regional emissions of HFC-125 (CHF_2CF_3) from in situ and air archive atmospheric observations at AGAGE and SOGE observatories, J. Geophy. Res., 114, D23304, 2009.

Oram, D. E., Reeves, C. E., Penkett, S. A., and Fraser, P. J.: Measurements of HCFC-142b and HCFC-141b in the Cape Grim air Archive: 1978–1993, Geophys. Res. Lett., 22, 2741-2744, 1995.

Oram, D. E., Reeves, C. E., Sturges, W. T., Penkett, S. A., Fraser, P. J., and Langenfelds, R. L.: Recent tropospheric growth rate and distribution of HFC-134a (CF_3CH_2F), Geophys. Res. Lett., 23, 1949-1952, 1996.

Park, T., Rettich, T. R., Battino, R., Peterson, D., and Wilhelm, E.: Solubility of gases in liquids. 14. Bunsen coefficients for several fluorine-containing gases (Freons) dissolved in water at 298.15 K, J. Chem. Eng. Data, 27, 324-326, 1982.
Parmelee, H. M.: Water solubility of Freon refrigerants, Refrigerating Engineering, 61, 1341, 1953.
Prinn, R. G., Weiss, R. F., Arduini, J., Arnold, T., DeWitt, H. L., Fraser, P. J., Ganesan, A. L., Gasore, J., Harth, C. M., and Hermansen, O.: History of chemically and radiatively important atmospheric gases from the Advanced Global Atmospheric Gases Experiment (AGAGE), Earth System Science Data, 10, 985-1018, 2018a.
Prinn, R. G., Weiss, R. F., Arduini, J., Arnold, T., Fraser, P. J., Ganesan, A. L., Gasore, J., Harth, C. M., Hermansen, O., Kim, J., Krummel, P. B., Li, S., Loh, Z. M., Lunder, C. R., Maione, M., Manning, A. J., Miller, B. R., Mitrevski, B., Mühle, J., O'Doherty, S., Park, S., Reimann, S., Rigby, M., Salameh, P. K., Schmidt, R., Simmonds, P. G., Steele, L. P., Vollmer, M. K., Wang, R. H., and Young, D.: The ALE/GAGE/AGAGE Network (DB 1001), http://cdiac.essdive.lbl.gov/ndps/alegage.html, doi: 10.3334/CDIAC/atg.db1001, 2018b.
Reichl, A.: Messung und Korrelierung von Gaslöslichkeiten halogenierter Kohlenwasserstoffe, PhD thesis, Shaker, 1996.
Reinsch, C. H.: Smoothing by spline functions, Numer. Math., 10, 177-183, 1967.
Sander, S., Abbatt, J., Barker, J., Burkholder, J., Golden, D., Kolb, C., Kurylo, M., Moortgat, G., Wine, P., Huie, R., and Orkin, V.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies Evaluation Number 17, Pasadena, CA: Jet Propulsion Laboratory, National Aeronautics and Space Administration, 2011.
Scharlin, P. and Battino, R.: Solubility of CCl_2F_2, $CClF_3$, CF_4 and c-C_4F_8 in H_2O and D_2O at 288 to 318 K and 101.325 kPa. Thermodynamics of transfer of gases from H_2O to D_2O, Fluid Phase Equilib., 95, 137-147, 1994.
Sturrock, G. A., Etheridge, D. M., Trudinger, C. M., Fraser, P. J., and Smith, A. M.: Atmospheric histories of halocarbons from analysis of Antarctic firn air: Major Montreal Protocol species, J. Geophy. Res.: Atmos., 107, 4765, 2002.
Thompson, T. M., Butler, J. H., Daube, B. C., Dutton, G. S., Elkins, J. W., Hall, B. D., Hurst, D. F., King, D. B., Kline, E. S., and Lafleur, B. G.: Halocarbons and other atmospheric trace species, 115-135 pp., 2004.
Trudinger, C. M., Fraser, P. J., Etheridge, D. M., Sturges, W. T., Vollmer, M. K., Rigby, M., Martinerie, P., Mühle, J., Worton, D. R., and Krummel, P. B.: Atmospheric abundance and global emissions of perfluorocarbons CF_4, C_2F_6 and C_3F_8 since 1800 inferred from ice core, firn, air archive and in situ measurements, Atmos. Chem. Phys., 16, 11733-11754, 2016.
Wahba, G.: Bayesian" confidence intervals" for the cross-validated smoothing spline, Journal of the Royal Statistical Society. Series B (Methodological), 1983. 133-150, 1983.
Warner, M. J. and Weiss, R. F.: Solubilities of chlorofluorocarbons 11 and 12 in water and seawater, Deep Sea Res. Part A. Oceanogr. Res. Pap., 32, 13, 1985.
Wen, W. and Muccitelli, J. A.: Thermodynamics of Some Perfluorocarbon Gases in Water, J. Solution Chem., 8, 22, 1979.
Wilhelm, E., Battino, R., and Wilcock, R. J.: Low-Pressure Solubility of Gases in Liquid Water, Chem. Rev., 77, 44, 1977.
Zheng, D., Guo, T., and Knapp, H.: Experimental and modeling studies on the solubility of CO_2, $CHClF_2$, CHF_3, $C_2H_2F_4$ and $C_2H_4F_2$ in water and aqueous NaCl solutions under low pressures, Fluid Phase Equilib., 129, 197-209, 1997.