



1 **Changing trends and emissions of hydrochlorofluorocarbons and their**  
2 **hydrofluorocarbon replacements.**

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17

18 **Abstract**

19 High frequency, *in situ* global observations of HCFC-22 (CHClF<sub>2</sub>), HCFC-141b (CH<sub>3</sub>CCl<sub>2</sub>F),  
20 HCFC-142b (CH<sub>3</sub>CClF<sub>2</sub>) and HCFC-124 (CHClF<sub>2</sub>CF<sub>3</sub>) and their main HFC replacements HFC-134a  
21 (CH<sub>2</sub>FCF<sub>3</sub>), HFC-125 (CHF<sub>2</sub>CF<sub>3</sub>), HFC-143a (CH<sub>3</sub>CF<sub>3</sub>), and HFC-32 (CH<sub>2</sub>F<sub>2</sub>) have been used to  
22 determine their changing global growth rates and emissions in response to the Montreal Protocol and its  
23 recent amendments. The 2007 adjustment to the Montreal Protocol required the accelerated phase-out of  
24 HCFCs with global production and consumption capped in 2013, to mitigate their environmental impact  
25 as both ozone depleting substances and important greenhouse gases. We find that this change has  
26 coincided with a reduction in global emissions of the four HCFCs with aggregated global emissions in  
27 2015 of 444 ± 75 Gg/yr, in CO<sub>2</sub> equivalent units (CO<sub>2</sub> e) 0.75 ± 0.1 Gt/yr, compared with 483 ± 70 Gg/yr  
28 (0.82 ± 0.1 Gt/yr CO<sub>2</sub> e) in 2010. (All quoted uncertainties in this paper are 1 sigma). About 80% of the  
29 total HCFC atmospheric burden in 2015 is HCFC-22, where global HCFC emissions appear to have been  
30 relatively constant in spite of the 2013 cap on global production and consumption. We attribute this to a  
31 probable increase in production and consumption of HCFC-22 in Montreal Protocol Article 5  
32 (developing) countries and the continuing release of HCFC-22 from the large banks which dominate  
33 HCFC global emissions. Conversely, the four HFCs all show increasing annual growth rates with  
34 aggregated global HFCs emissions in 2015 of 329 ± 70 Gg/yr (0.65 ± 0.12 Gt/yr CO<sub>2</sub> e) compared to  
35 2010 with 240 ± 50 Gg/yr (0.47 ± 0.08 Gt/yr CO<sub>2</sub> e). As HCFCs are replaced by HFCs we investigate the  
36 impact of the shift to refrigerant blends which have lower global warming potentials (GWPs). We also



37 note that emissions of HFC-125 and HFC-32 appear to have increased more rapidly during the 2011-2015  
38 5-yr period compared to 2006-2010.

39

## 40 1. Introduction

41

42 Hydrochlorofluorocarbons (HCFCs) were introduced between the 1940s and 1980s as alternatives to  
43 chlorofluorocarbons (CFCs) in some refrigeration and air conditioning applications. Production and  
44 consumption grew rapidly in “non-Article 5” developed countries until the mid-1990s. However, because  
45 they are ozone depleting substances (ODS), HCFCs were included in the 1992 Montreal Protocol  
46 amendment, with a view to eventual phase-out of production and consumption. Subsequently the 2007  
47 adjustments to the Montreal Protocol required an accelerated phase-out of HCFCs in both “non-Article 5”  
48 and “Article 5” developing countries, with a 2013 cap on global production and consumption of HCFCs.  
49 Historically, HCFCs-22, -141b and -142b account for >90% of the total consumption of all HCFCs in  
50 Article 5 countries.

51 A more rapid phase-out of the HCFCs should result in a faster recovery of the depleted  
52 stratospheric ozone layer, with the additional benefit of mitigating climate change, since these  
53 compounds are also potent greenhouse gases (GHGs). Detailed studies of the rates of atmospheric  
54 accumulation of the HCFCs indicate periods of rapid growth, temporary slowing followed by accelerated  
55 growth (Oram et al., 1995; Simmonds et al., 1998; O’Doherty et al., 2004; Reimann et al., 2004; Derwent  
56 et al., 2007; Montzka et al., 2009; Miller et al., 2010; Saikawa et al., 2012; Fortems-Cheiney et al., 2013;  
57 Rigby et al., 2014; Graziosi et al., 2015). More recently the global growth rates of HCFC-22 and HCFC-  
58 142b have slowed significantly and Montzka et al., (2015) reported that the 2007 adjustments to the  
59 Montreal Protocol had limited HCFC emissions significantly prior to the 2013 cap on global production,  
60 although the atmospheric growth rate of HCFC-141b had almost doubled between 2007 and 2012.

61 HFCs which have been introduced as replacements for the HCFCs and CFCs have grown rapidly  
62 in abundance since their introduction (Montzka et al., 1996, 2004; Oram et al., 1996; Reimann et al.,  
63 2004; O’Doherty et al., 2009, 2014; Carpenter et al., 2014; Rigby et al., 2014). As discussed by Velders  
64 et al., (2009, 2015) projected HFCs emissions may make a large contribution to future climate forcing if  
65 they are used in the transition away from ODSs.

66 In this study we focus on high frequency atmospheric measurements (6 -12 per day) of HCFC-22,  
67 HCFC-141b, HCFC-142b and HCFC-124 and their main replacements HFC-134a, HFC-125, HFC-  
68 143a, and HFC-32 from the five core globally-distributed Advanced Global Atmospheric Gases  
69 Experiment (AGAGE) sites with 10-20 year records (Prinn et al., 2000). We have previously estimated



70 global emissions of HFC-152a ( $\text{CH}_3\text{CHF}_2$ ) using the same modelling methods discussed in this paper  
 71 (Simmonds et al., 2015).

72 The Ozone Depletion Potential (ODP), Global Warming Potential (GWP) and atmospheric  
 73 lifetimes of these eight compounds are listed in Table 1.

74 Table 1. Lifetimes (yr), Ozone Depletion and Global Warming Potentials (100-yr time horizon) for the  
 75 HCFCs and HFCs reported in this study.

| Compound         | <sup>a</sup> ODP | <sup>b</sup> GWPs | <sup>c</sup> LIFETIME |
|------------------|------------------|-------------------|-----------------------|
| <b>HCFC-22</b>   | 0.055            | 1810              | 12                    |
| <b>HCFC-141b</b> | 0.11             | 725               | 9.4                   |
| <b>HCFC-142b</b> | 0.065            | 2310              | 18                    |
| <b>HCFC-124</b>  | 0.02             | 609               | 6                     |
| <b>HFC-134a</b>  | 0*               | 1430              | 14                    |
| <b>HFC-143a</b>  | 0*               | 4470              | 51                    |
| <b>HFC-125</b>   | 0*               | 3500              | 31                    |
| <b>HFC-32</b>    | 0*               | 675               | 5.4                   |

76 \* see Hurwitz et al., 2015.

77 Notes: <sup>a</sup> ODPs from the Montreal Protocol, <sup>b</sup> GWPs from (Forster et al., 2007),  
 78 <sup>c</sup> Lifetimes, from SPARC, (2013. Report No. 6, WCRP-15/2013).

79  
 80 We combine these observations with a 2-dimensional (12-box) atmospheric chemical transport  
 81 model whose circulation is based on observations and on tuning to provide good agreements with global  
 82 distributions of reactive and stable trace gases (Cunnold et al., 1983; Rigby et al., 2013; 2014). We then  
 83 estimate global emissions which we relate to the global phase-out and adoption schedules of HCFCs and  
 84 HFCs, respectively. We compare these estimated global emissions with HCFC and HFC emission  
 85 estimates compiled from national reports to the United Nations Environment Programme, UNEP  
 86 (consumption of HCFCs) and United Nations Framework Convention on Climate Change, UNFCCC  
 87 (emissions of HFCs), respectively, and Emissions Database for Global Atmospheric Research (EDGAR  
 88 v4.2; <http://edgar.jrc.ec.europa.eu/>, HFCs), using the same techniques reported earlier for these HCFCs  
 89 and HFCs (O'Doherty et al., 2009, 2014; Miller et al., 2010; Rigby et al., 2014). We recognise that due to  
 90 the historic range of use of these substances (refrigeration, foam blowing, and fire-fighting equipment),  
 91 the derivation of emissions from production and consumption data is difficult given the large and long-  
 92 lasting banks of these compounds.



93 We examine the evolution of the changing growth rates of the HCFCs with a view to determining  
94 if the 2013 cap on their production and consumption has been reflected in an accelerated phase-out.

95 Furthermore, we examine the rapid growth rates of the HFCs and whether these reflect manufacturers of  
96 air-conditioning and refrigeration equipment switching to HFC refrigerant blends with lower GWPs.

97 HCFC-22 is used in commercial and domestic refrigeration, air conditioning, extruded  
98 polystyrene foams and as a feedstock in the manufacture of fluoropolymers. HCFC-141b and HCFC-  
99 142b are primarily used as foam blowing agents; in addition, HCFC-141b is used as a solvent in  
100 electronics and precision cleaning applications; HCFC-142b is also used as an aerosol propellant and as a  
101 refrigerant. HCFC-124 has uses in specialized air conditioning equipment, refrigerant mixtures, fire  
102 extinguishers and as a component of sterilant mixtures.

103 HFC-134a has been used since the early 1990s in vehicle air conditioning systems and other  
104 refrigeration and air conditioning largely to replace CFC-12. Other uses include plastic foam blowing, as  
105 a cleaning solvent and as a propellant. HFCs-125 and -32 have been used as a 50:50 blend (R-410A) in  
106 residential air conditioning systems as well as in 3-component blends with HFC-134a. HFC-125 has also  
107 found application as a fire suppressant agent. HFC-143a is predominantly a component of refrigerant  
108 blends used in commercial refrigeration and in some air conditioning applications.

109 Although the HFCs are not significant ozone depleting substances (non-zero ODPs; Hurwitz et  
110 al., 2015), as GHGs the HFCs -143a, -125, -134a and -32 have global warming potentials (GWP 100-yr  
111 horizon) of 4470, 3500, 1430, and 675, respectively. The HCFCs, in addition to their ozone depletion  
112 potentials (ODPs), listed in Table 1, are also GHGs with GWPs comparable to the HFCs. This  
113 combination of ozone depletion and climate forcing has provided the impetus for the accelerated phase-  
114 out of the HCFCs.

## 115 2. Materials and Methods

116

### 117 2.1. AGAGE in situ measurements.

118 The data used here are compiled from *in situ* measurements at the core AGAGE sites, listed in  
119 Table 2, which shows the time frame when the measurements of individual HCFCs and HFCs began at  
120 each AGAGE site.

121

### 122 2.2. AGAGE Instrumentation and Measurement Techniques

123 Two similar measurement technologies have been used at AGAGE stations over time, both based  
124 on gas chromatography coupled with mass spectrometry (GC-MS) and cryogenic sample pre-  
125 concentration techniques. The earlier instrument, referred to as the GC-MS-ADS, incorporated an



126 Adsorption-Desorption-System (ADS) based on a Peltier-cooled microtrap maintained at  $-50^{\circ}\text{C}$  during  
127 the adsorption phase (Simmonds et al. 1995; Prinn et al., 2000) and was used for several years at the  
128 Mace Head and Cape Grim sites. These were replaced by another GC-MS instrument, the GC-MS-  
129 Medusa with doubled sampling frequency and enhanced cooling to  $\sim -180^{\circ}\text{C}$ , which uses the milder trap  
130 adsorbent HayeSep D, to extend compound selection, and improve measurement precisions (Miller et al.,  
131 2008; Arnold et al., 2012).

132 The GC-MS-Medusa system is currently deployed at all AGAGE sites used in this study (Table  
133 2). Typically for each measurement the analytes from two litres of air are collected on the sample traps  
134 and desorbed onto a single main capillary chromatography column (CP-PoraBOND Q, 0.32 mm ID  $\times$  25  
135 m, 5  $\mu\text{m}$ , Agilent Varian Chrompack, batch-made for AGAGE applications) purged with helium (grade  
136 6.0) that is further purified using a heated getter purifier (He-purifier HP2, VICI, USA). The separation  
137 and detection of the compounds are achieved using Agilent Technology GCs (model 6890N) and  
138 quadrupole mass spectrometers in selected ion mode (initially model 5973, progressively converted to  
139 5975C over the later years). For the field GC-MS-Medusa instruments, ambient air samples are analysed  
140 every 2 hours (c.f. 4 hours for the GC-MS-ADS) and are bracketed by measurements of quaternary  
141 standards to detect and correct for short-term drift in instrument response. The quaternary standards are  
142 whole-air pressurized into 34 L internally electropolished stainless steel canisters (Essex Industries,  
143 USA). They are filled by the groups who are in charge of the respective AGAGE stations using modified  
144 oil-free diving compressors (SA-3 and SA-6, RIX Industries, USA) to  $\sim 60$  bar (older tanks to  $\sim 30$  bar).  
145 Cape Grim is an exception, where the canisters used for quaternary standard purposes are typically filled  
146 cryogenically. The on-site quaternary standards are compared weekly to tertiary standards from the  
147 central calibration facility at the Scripps Institution of Oceanography (SIO) in order to propagate the  
148 primary calibration scales and to characterize any potential long-term drift of the measured compounds in  
149 the quaternary standards. Importantly, all of the stations report HCFC and HFC measurements relative to  
150 the SIO (SIO-05, SIO-07 and SIO-14) and University of Bristol (UB-98) calibration scales.

151 The GC-MS-Medusa measurement precisions for the four HCFCs and four HFCs are estimated  
152 based on the repeated measurements of the quaternary standards. They are typically for HCFC-22 (0.5  
153 ppt, 0.2%), -141b (0.05 ppt, 0.3%), -142b (0.05 ppt, 0.25%) and -124 (0.02 ppt, 1.6%) and for HFC-134a  
154 (0.2 ppt, 0.2%), -125 (0.05 ppt, 0.3%), -143a (0.1 ppt, 0.4%) and -32 (0.1 ppt, 0.8%).

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160 Table 2. Overview of the core AGAGE sites used in this study, their coordinates and periods for which  
161 data are available.

162

| Site                                  | Latitude | Longitude | ADS Data* | Medusa Data**      |
|---------------------------------------|----------|-----------|-----------|--------------------|
| <b>Mace Head, Ireland</b>             | 53.3° N  | 9.9° W    | 1994-2004 | June 2003-present  |
| <b>Trinidad Head, California, USA</b> | 41.0° N  | 124.1° W  |           | March 2005-present |
| <b>Ragged Point, Barbados</b>         | 13.2° N  | 59.4° W   |           | May 2005-present   |
| <b>Cape Matatula, American Samoa</b>  | 14.2° S  | 170.6° W  |           | May 2006-present   |
| <b>Cape Grim, Tasmania, Australia</b> | 40.7° S  | 144.7° E  | 1998-2004 | Jan 2004-present   |

163

164 \* Period of HCFC and HFC data records using GC-MS-ADS.

165 \*\* Period of HCFC and HFC data records using GC-MS-Medusa.

166

### 167 2.3. Calibration Scales

168 The estimated accuracy of the calibration scale for the various HCFCs and HFCs is reported  
169 below and a more detailed discussion of the measurement technique and calibration procedure have been  
170 reported elsewhere (Miller et al., 2008; O'Doherty et al., 2009; Mühle et al., 2010). The AGAGE  
171 measurements for the HCFCs-22, -141b, -142b, and HFC-134a, are reported relative to the Scripps  
172 Institution of Oceanography (SIO-05) calibration scale (as dry gas mole fractions in  $\text{pmol mol}^{-1}$ ). This  
173 scale is defined through the gravimetric preparation of 13 synthetic primary standards at near-ambient  
174 mole fractions (Prinn et al., 2000) at SIO in 2005. HCFC-124 is derived from the UB-98 calibration scale.  
175 HFCs -143a, -32 are reported relative to the SIO-07 and HFC-125 to the SIO-14 calibration scales.

176 The overall accuracies of these primary standards sets are liberally estimated at 2% for HCFC-22,  
177 -141b, and -142b, 10%, for HCFC-124 and 1.5% for HFC-134a, and 3% for HFC-125, -143a, and  
178 -32 with the largest fractional uncertainty contributed from the impurities in the starting reagents.

179

### 180 2.4. Selection of baseline data

181 Baseline *in situ* monthly mean HCFC and HFC mole fractions were calculated by excluding  
182 values enhanced by local and regional pollution influences, as identified by the iterative AGAGE  
183 pollution identification algorithm, (for details see Appendix in O'Doherty et al., 2001). Briefly, baseline  
184 measurements are assumed to have Gaussian distributions around the local baseline value, and an  
185 iterative process is used to filter out the points that do not conform to this distribution. A second-order  
186 polynomial is fitted to the subset of daily minima in any 121-day period to provide a first estimate of the  
187 baseline and seasonal cycle. After subtracting this polynomial from all the observations a standard  
188 deviation and median are calculated for the residual values over the 121-day period. Values exceeding  
189 three standard deviations above the baseline are thus identified as non-baseline (polluted) and removed



190 from further consideration. The process is repeated iteratively to identify and remove additional non-  
191 baseline values until the new and previous calculated median values agree within 0.1%.

192

### 193 3. Modelling studies

194

195 There are several sources of information on production and emissions of HCFCs and HFCs; none of  
196 which, on their own, provides a complete database of global emissions. The more geographically  
197 comprehensive source of information for HFC emissions is provided by the parties to the UNFCCC, but  
198 only includes Annex 1 countries (developed countries). The 2014 database covers years 1990 to 2012 and  
199 emissions are reported in Table 2(II) s1 in the Common Reporting Format (CRF) available at  
200 [http://unfccc.int/national-reports/annex\\_1ghg\\_inventories/national\\_inventories\\_submissions/items/8108.php](http://unfccc.int/national-reports/annex_1ghg_inventories/national_inventories_submissions/items/8108.php).

201 An alternative inventory estimate was also obtained from the Emissions Database for Global  
202 Atmospheric Research (EDGAR v4.2; <http://edgar.jrc.ec.europa.eu/>), a database that estimates global  
203 emission inventories of anthropogenic GHGs, including HFCs on a country, regional and gridded basis  
204 up to 2008.

205 Similar emission estimates are not available for HCFCs, but using HCFC consumption data  
206 published by the Montreal Protocol Secretariat of the United Nations Environment Programme (UNEP,  
207 2016a) we calculate HCFC emissions as described in the supplementary material (1).

208 Such bottom-up emission estimates of HFCs and HCFCs are based on industry production,  
209 imports, distribution and usage data for these compounds, reported to national governments and thence to  
210 UNEP and UNFCCC. We discuss these independent emission estimates because they are helpful as *a*  
211 *priori* data constraints on our model analysis and to compare them with our observation-based top-down  
212 estimates.

213

#### 214 3.1. Global emissions estimates using the AGAGE two-dimensional 12-box model.

215 To estimate global-average mole fractions and derive growth rates, a two-dimensional model of  
216 atmospheric chemistry and transport was employed. The AGAGE 12-box model simulates trace gas  
217 transport in four equal mass latitudinal sections (divisions at 30-90°N, 0-30°N, 30-0°S and 90-30°S) and  
218 at three heights (vertical divisions at 200, 500 and 1000 hPa). The model was originally developed by  
219 Cunnold et al. (1983) (nine-box version), with subsequent improvements by Cunnold et al. (1994) and  
220 Rigby et al. (2014). Emissions were estimated between 1998 and 2015 using a Bayesian method in which  
221 an *a priori* constraint (EDGAR v4.2) on the emissions growth rate was adjusted using the baseline-  
222 filtered AGAGE observations (Rigby et al., 2011, 2014). Global emissions were derived that included



223 estimates of the uncertainties due to the observations, the prior and the current best-estimate lifetimes of  
224 these compounds from SPARC (2013); as detailed in the supplementary material in Rigby et al. (2014).

225

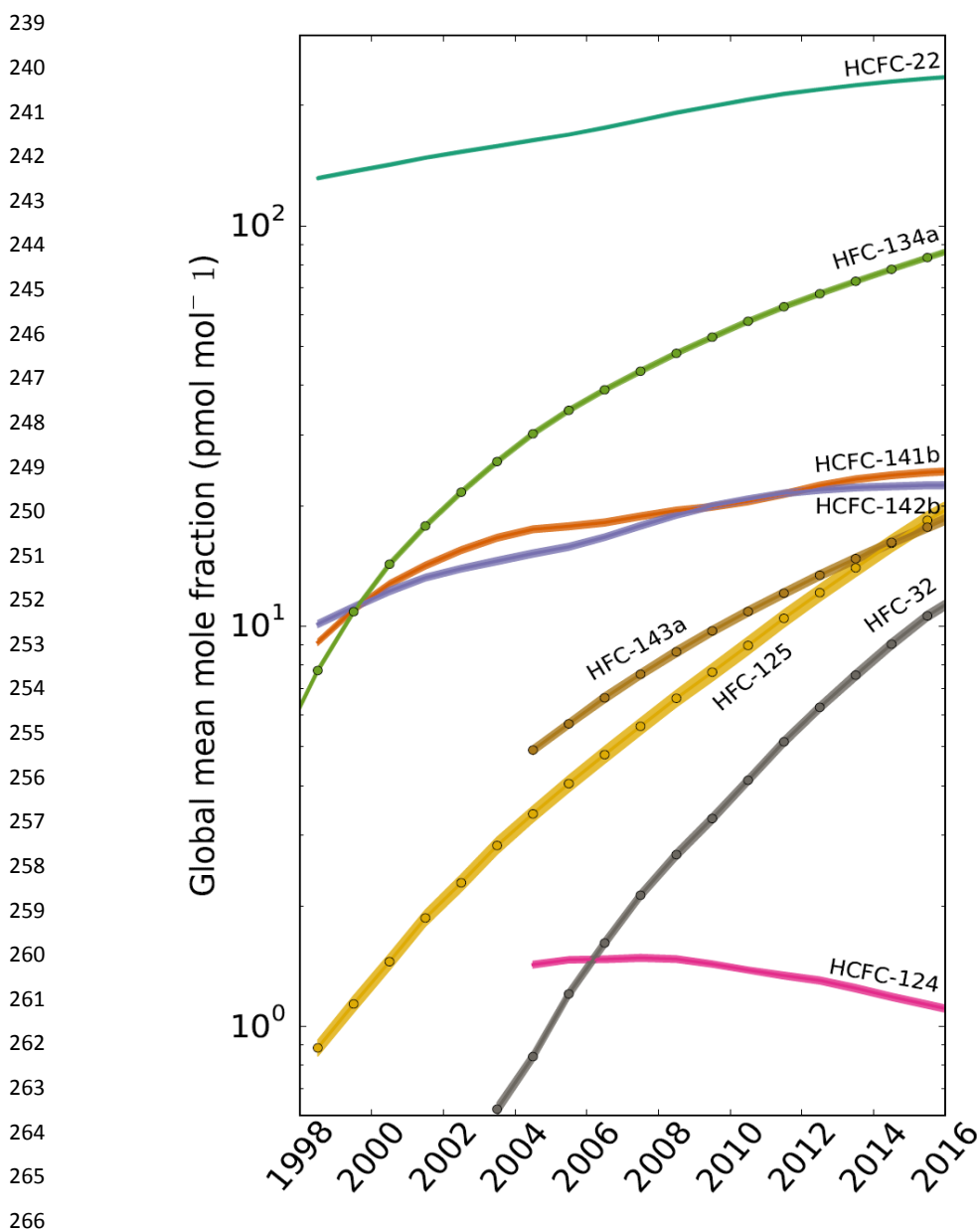
## 226 **4. Results and Discussion**

### 227 4.1. Atmospheric Mole Fractions

228 Based on the output from the 12-box model, into which AGAGE observations had been  
229 assimilated, Figure 1 illustrates the global mean mole fractions for the four HCFCs and the four HFCs,  
230 (the model output was used for “gap-filling” purposes). Figure 2 shows the average annual growth rates.  
231 Global mean mole fractions of HCFC-22, -141b, and -142b have increased throughout the observation  
232 period reaching 234, 24.3 and 22.4 pmol mol<sup>-1</sup>, respectively in 2015. HCFC-124 reached a maximum  
233 global mean mole fraction of 1.48 pmol mol<sup>-1</sup> in 2007 and has since declined by 23% to 1.14 pmol mol<sup>-1</sup>  
234 in 2015.

235 The HFCs all show increasing global mean mole fractions and growth rates over the entire period  
236 of observations. In 2015 the global mean mole fractions (pmol mol<sup>-1</sup>) in descending order of abundance  
237 are HFC-134a (83.3), HFC-125 (18.4), HFC-143a (17.7) and HFC-32 (10.5) with growth rates (pmol  
238 mol<sup>-1</sup> yr<sup>-1</sup>) for HFC-134a (5.6), HFC-125 (2.3), HFC-143a (1.5) and HFC-32 (1.6).





267 Figure 1. Global mean mole fractions for the four HCFCs and the four HFCs, (the model output was used  
268 for “gap-filling” purposes). Shading in the figure reflects the uncertainty on the mole fractions derived in  
269 the inversion and includes a contribution from random and scale-related measurement errors and  
270 modelling uncertainties (further details are provided in Rigby et al., 2014). Note that HCFC-124, HFC-  
271 143a and HFC-32 use only GC-MS-Medusa data for these calculations; all others use combined GC-MS-  
272 ADS and GC-MS-Medusa data. HFCs shown with individual annual mole fractions.

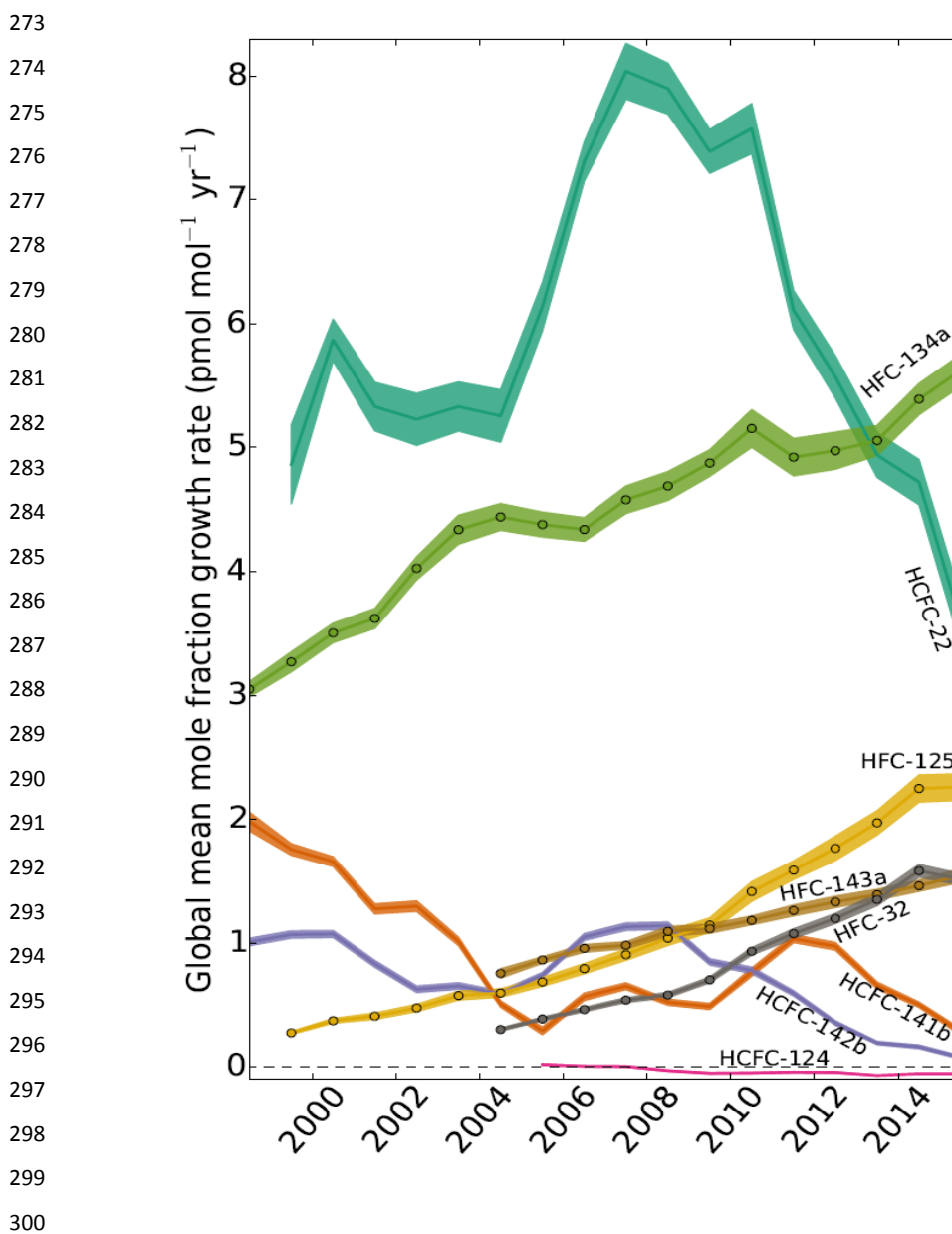


Figure 2. Annual average global mean mole fraction growth rates ( $\text{pmol mol}^{-1} \text{yr}^{-1}$ ) determined from the 12-box model for the HCFCs and HFCs. Note that HCFC-124, HFC-143a and HFC-32 use only Medusa data for these calculations; all others use combined GC-MS-ADS and GC-MS-Medusa data. HFCs shown with individual annual growth rates.

305  
306



307 Global mean HCFC-22 reached a maximum annual rate of increase of  $8.2 \text{ pmol mol}^{-1} \text{ yr}^{-1}$  in 2007  
308 and slowed by 54% to  $3.7 \text{ pmol mol}^{-1} \text{ yr}^{-1}$  in 2015. The global mean annual growth rates of HCFC-141b  
309 reached a first maximum of  $1.9 \text{ pmol mol}^{-1} \text{ yr}^{-1}$  in 1998, followed by a second maximum in 2011 of  $1.0$   
310  $\text{pmol mol}^{-1} \text{ yr}^{-1}$  and then slowed to  $\sim 0.3 \text{ pmol mol}^{-1} \text{ yr}^{-1}$  in 2015, a 70% decline. Similarly, HCFC-142b  
311 reached a maximum in 2008 of  $1.1 \text{ pmol mol}^{-1} \text{ yr}^{-1}$ , followed by a steep 90% decline to just  $0.11 \text{ pmol}$   
312  $\text{mol}^{-1} \text{ yr}^{-1}$ . These observations reflect substantial changes in the quantity of HCFCs emitted to the  
313 atmosphere over time with the rates of increase in 2015 considerably slower than their historical highs  
314 and broadly in response to the MP and its amendments.

315

## 316 4.2. Top-down Emission Estimates

317

### 318 4.2.1. Global estimates of HCFCs

319 Estimated annual global emissions (Gg/yr) of the HCFCs using the 12-box model (emissions  
320 listed in supplementary material 1) and those calculated from consumption reported by UNEP (2016a, see  
321 supplementary material 2) and EDGAR emission inventories are shown in Figure 3 a-d. The blue solid  
322 line represents our model-derived emissions, with the uncertainties shown by the shaded areas.

323

#### 324 4.2.1.1. HCFC-22

325 Model derived global emissions of HCFC-22 increased from  $234 \pm 35 \text{ Gg/yr}$  in 1995 to a  
326 maximum of  $383 \pm 54 \text{ Gg/yr}$  in 2010 increasing by  $\sim 10 \text{ Gg/yr}$ . Since 2010 global HCFC-22 emissions  
327 have declined by perhaps 6.6% to  $357 \pm 58 \text{ Gg/yr}$  in 2015. Figure 3a includes estimated emissions from  
328 UNEP and other reported global HCFC-22 emissions estimates (Saikawa et al., 2012; Xiang et al., 2014;  
329 Montzka et al., 2015) which all agree within the uncertainties of our estimates. Fortems-Cheiney et al.,  
330 (2013) using observations from multiple networks, an inversion and a new gridded bottom-up inventory  
331 estimated global emissions of  $387 \pm 9 \text{ Gg/yr}$  in 2010, very close to the estimated HCFC-22 emissions  
332 derived in this study.

333

#### 334 4.2.1.2. HCFC-141b and HCFC-142b

335 These two HCFCs have exhibited similar but fluctuating emissions with maxima in 2000 of  $63 \pm$   
336  $6 \text{ Gg/yr}$  (HCFC-141b) and  $31 \pm 6 \text{ Gg/yr}$  (HCFC-142b) followed by a decline during 2004-2005 to  $46 \pm 7$   
337  $\text{Gg/yr}$  (HCFC-141b) and  $29 \pm 5 \text{ Gg/yr}$  (HCFC-142b). HCFC-141b and HCFC-142b emissions then grew  
338 rapidly to new maxima of  $68 \pm 8 \text{ Gg/yr}$  (2012) and  $39 \pm 5 \text{ Gg/yr}$  (2008), respectively. These trends were  
339 again reversed with subsequent declines to  $59 \pm 10 \text{ Gg/yr}$  (HCFC-141b) and  $25 \pm 6 \text{ Gg/yr}$  (HCFC-142b)  
340 in 2015. Montzka et al., (2015), using an independent sampling network, also provided emissions  
341 estimates for HCFCs-141b and -142b in 2012 which are included in Figures 3 b,c and agree within the



342 uncertainties of our estimates. Inventory emissions estimates reported from EDGAR v4.2 are  
343 considerably lower than all other reported emissions post-2005. Global emissions of HCFC-141b and  
344 HCFC-142b have declined by 2.0% and 30%, respectively, from 2010 to 2015.

345

#### 346 4.2.1.3. HCFC-124

347 Global emissions of this less abundant HCFC had a maximum in 2005 of  $6.1 \pm 1.8$  Gg/yr,  
348 followed by a steady decline to  $3.0 \pm 0.9$  Gg/yr in 2015, a decrease in emissions over this 12-year time  
349 frame of 51%. There are no bottom-up estimates of HCFC-124 emissions or top-down global estimates to  
350 compare with our results. However, we note that HCFC-124 emissions make only a minor contribution to  
351 climate change in CO<sub>2</sub> equivalent units (CO<sub>2</sub> e) of 0.002 Gt/yr in 2015.

352 The combined model derived aggregated global emissions of these four HCFCs in 2015 were  $444$   
353  $\pm 75$  Gg/yr ( $0.75 \pm 0.1$  Gt/yr CO<sub>2</sub> e). We estimate that these four HCFCs contribute  $55 \pm 1$  mW/m<sup>2</sup> to  
354 climate forcing in 2015 with HCFC-22 accounting for 79% of this forcing.

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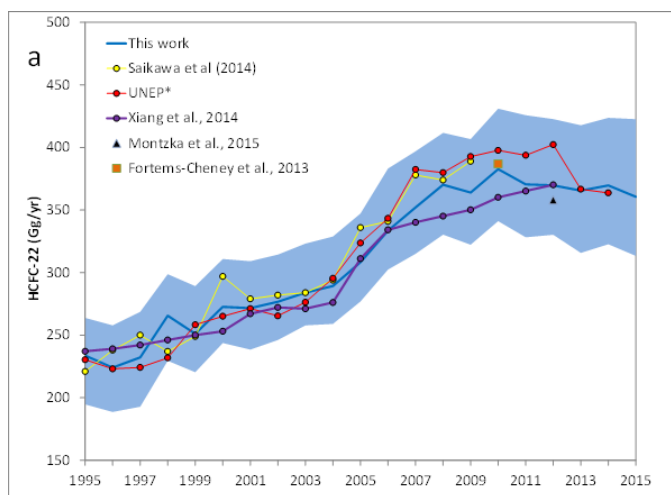
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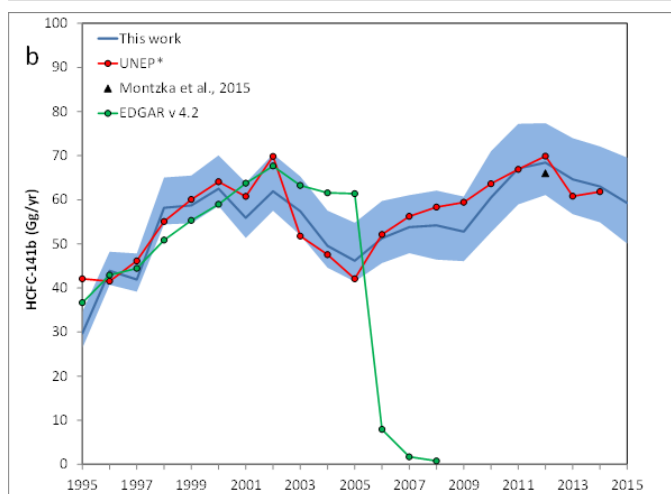
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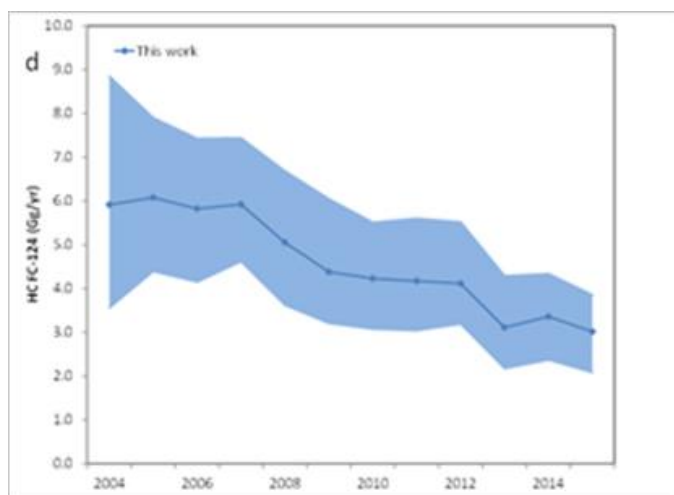
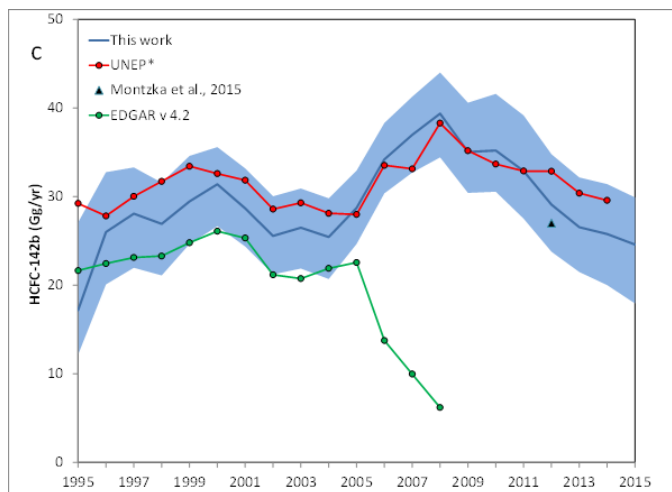
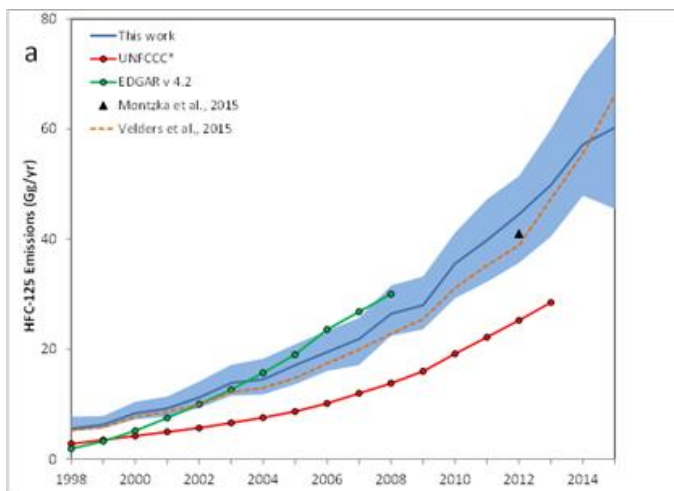
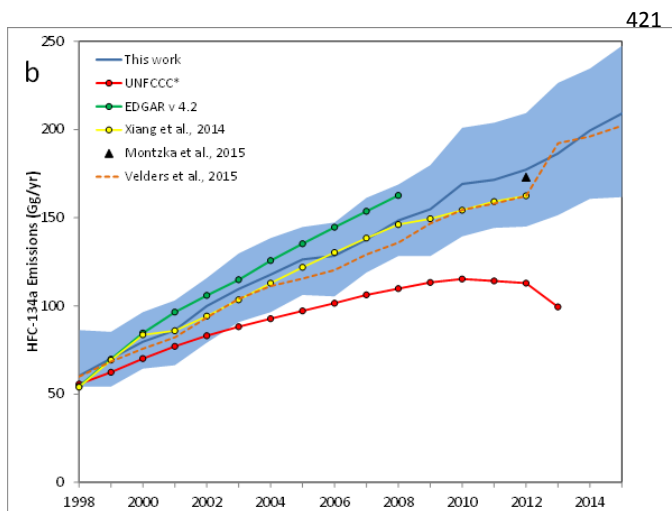


Figure 3 (a-d). Global HCFCs emissions (Gg/yr, blue line) from the 12-box model (solid blue line); shading, representing 1 sigma uncertainties; emissions derived from UNEP\* consumption data (- see supplementary material 2). EDGAR v4.2 and other works are also shown. Note that HCFC-124 uses only GC-MS-Medusa data for these calculations; all others use combined GC-MS-ADS and GC-MS-Medusa data.



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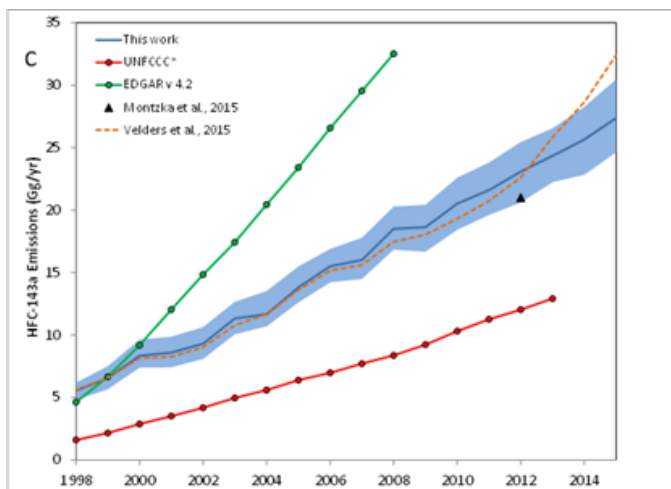
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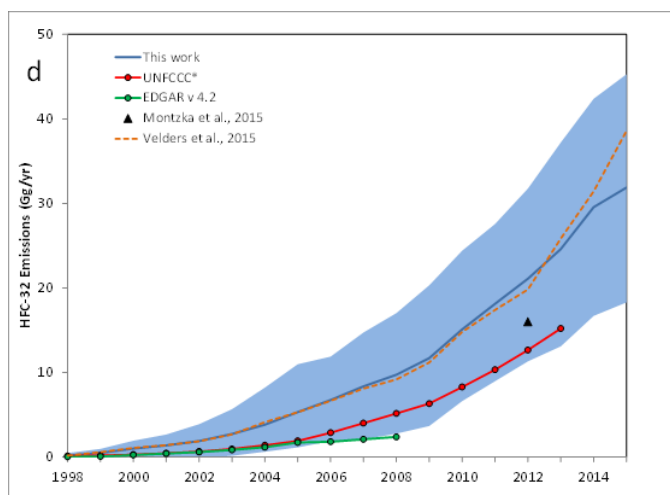


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470 Figure 4 (a-d). Global HFCs emissions (Gg/yr, blue line) from the 12-box model; shading represents 1  
471 sigma uncertainties; UNFCCC\* values are the global aggregate of national data reported in UNFCCC  
472 (2016). Note that HFC-143a and HFC-32 use only Medusa data for these calculations; all others use  
473 combined GC-MS-ADS and GC-MS-Medusa data.

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## 477 4.2.2. Global estimates of HFCs

478 In contrast to the HCFCs, estimates of HFCs emissions shown in Figure 4 (a-d) (see  
479 supplementary material 1 for actual values) have increased annually over the entire observational record,  
480 reaching maxima in 2015 of  $60 \pm 10$  Gg/yr (HFC-125),  $209 \pm 43$  Gg/yr (HFC-134a),  $27 \pm 3.0$  Gg/yr  
481 (HFC-143a) and  $32 \pm 14$  Gg/yr (HFC-32). UNFCCC emission estimates are consistently lower than our  
482 estimates, even for HFC-32 which barely agrees within our uncertainties. EDGAR v4.2 inventory  
483 emissions of HFC-143a post- 2000 are substantially larger than our estimates, but the other three HFCs  
484 are in reasonable agreement (within the uncertainties of our estimates). Recently published HFC  
485 emissions estimates by Velders et al., (2015) are in close agreement with the results from this work and  
486 within the uncertainties of our estimates, except for HFC-143a after 2014.

487 The combined model derived aggregated emissions of these four HFCs in 2015 were  
488  $329 \pm 70$  Gg/yr ( $0.65 \pm 0.14$  Gt/yr  $\text{CO}_2$  e). We estimate that these four HFCs contribute  $21.0 \pm 0.5$   
489  $\text{mW/m}^2$  to radiative forcing in 2015, less than half the combined forcing of the 4 HCFCs treated in this  
490 study.

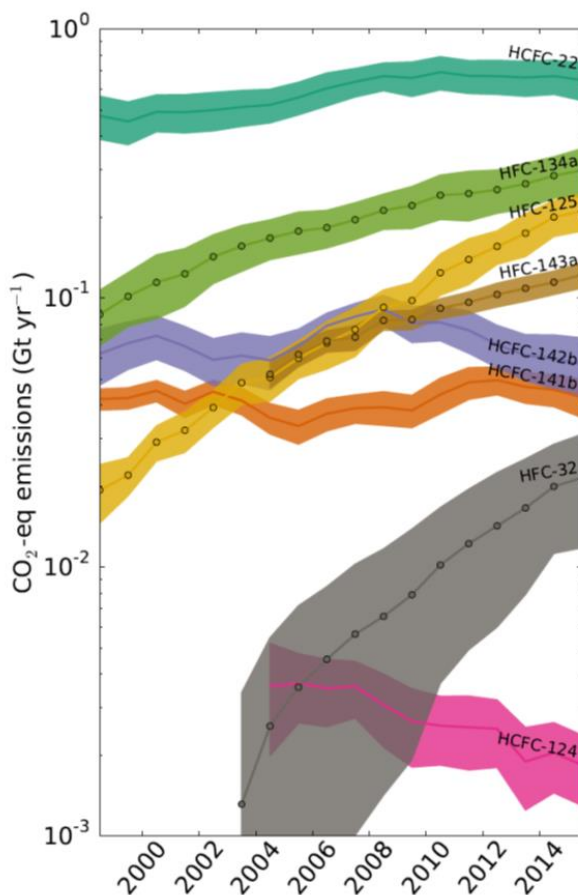
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## 492 4.3. Overall emissions trends

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494 In Figure 5 we plot individual HCFC and HFC in terms of  $\text{CO}_2$ -e emissions, noting that HCFC-22  
495 is the largest contributor to these emissions and they have declined relatively slowly since 2010. HCFC-  
496 141b and HCFC-142b exhibit declines in  $\text{CO}_2$ -e emissions after 2010, in spite of substantial changes in  
497 emissions over time and dramatic declines in their global mean mole fraction growth rates (see Figure 2).  
498 All of the HFCs have increasing  $\text{CO}_2$ -e emissions over time with HFC-125 and HFC-32 showing the  
499 most rapid increases in  $\text{CO}_2$ -e emissions.





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502 Figure 5. Individual HCFC and HFC carbon dioxide equivalent ( $\text{CO}_2\text{-e}$ ) emissions ( $\text{Gg/yr}$ ) derived from  
503 the 12-box model. Shading, representing 1 sigma uncertainties. Note that HCFC-124, HFC-143a and  
504 HFC-32 use only GC-MS-Medusa data for these calculations; all others use combined GC-MS-ADS and  
505 GC-MS-Medusa data.

506 Figure 6 shows the trends in  $\text{CO}_2\text{-e}$  emissions when the HCFCs and HFCs are aggregated  
507 together from 2005 to 2015. The figure indicates an increase in aggregate HCFC emissions until around  
508 2010, and subsequent reduction in emissions through 2015. HFC emissions were observed to increase  
509 throughout this period. Using 2010 as a “reference” year, we aimed to compare the relative trends in  
510 HCFC and HFC emissions and determine broadly whether a decline in HCFC emissions was being  
511 matched by acceleration in HFC usage. In order to determine a potential “business as usual” trajectory for  
512 HCFC and HFC emissions post-2010, we first assumed that emissions would continue to follow the 2005



513 – 2010 growth rates (dashed line). We also examined the potential change in emissions according to the  
514 projections of Velders et al., (2009) and WMO (2010), Chapter 1. S.A. Montzka and S. Reimann. Each of  
515 these projections suggests a growth in HCFC emissions during this period, whereas our observation-  
516 derived estimates show a decline. During this 5-year period, the accumulated difference between the top-  
517 down and projected emissions is -0.67, -0.71 and -0.66 Gt/yr CO<sub>2</sub>-e (with a 1-sigma uncertainty 0.25 Gt  
518 for each) for the linear projection, Velders et al., (2009) and WMO (2010), Chapter 1. S.A. Montzka and  
519 S. Reimann, respectively. For the HFCs, the linear projection shows more modest growth than we derive,  
520 with an accumulated difference of  $0.12 \pm 0.15$  Gt/yr CO<sub>2</sub>-e. However, the Velders et al., (2009)  
521 projection exhibits more rapid growth, leading to a difference of  $-0.27 \pm 0.15$ . When considered together,  
522 we find that the growth in HFC and HCFC emissions has been slower than these post-2010 projections by  
523 an accumulated total of  $-0.55 \pm 0.29$  Gt/yr CO<sub>2</sub>-e and  $-0.97 \pm 0.29$  Gt/yr CO<sub>2</sub>-e for the linear projection  
524 and Velders et al., (2009), respectively.

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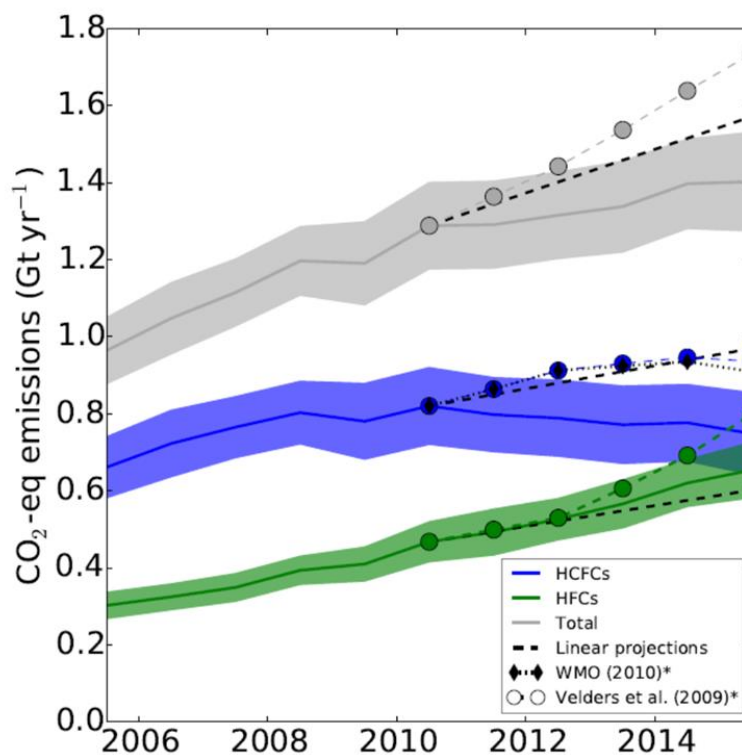
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546 Figure 6. Aggregated HCFCs and HFCs emissions as CO<sub>2</sub>-e (Gt yr<sup>-1</sup>) solid blue and green lines,  
547 respectively; shading representing 1 sigma uncertainties. The grey line and shading represents the total  
548 HCFC and HFC CO<sub>2</sub>-e emissions. The dashed line is a linear projection from 2010 to 2015, based on the  
549 2005 – 2010 emissions growth rate. The dashed lines with the circular data points are the Velders et al.  
550 (2009) projection, rescaled to the 2010 emissions rate, and the dashed line with the diamonds show the  
551 same but for HCFC emissions projections WMO (2010), Chapter 1. S.A. Montzka and S. Reimann.

552

553 In Table 3 we compare the cumulative emissions over two 5-years periods, 2006-2010 when  
554 HCFCs were still increasing (with the exception of HCFC-124) and 2011-2015 when all four HCFCs  
555 show declining emissions. From the percentage change in emissions between the two periods we note  
556 that HCFC-141b emissions have increased by 18% and HCFC-22 by 1.7%. In comparison HCFC-142b  
557 and -124 emissions have decreased by 23% and 30%, respectively. Aggregating the four HCFCs we  
558 observe a 1.4% increase in the combined emissions between the two 5-yr periods. However, over both 5-  
559 yr periods there is an equal contribution of 3.9 Gt CO<sub>2</sub>-e.

560 Conversely, global emissions of the HFCs have grown continuously throughout the period of  
561 observations with substantial increases between the two 5-yr periods. The largest increases were observed  
562 for HFC-32 (143%) and HFC-125 (92%) with smaller increases for HFC-143a (37%) and HFC-134a  
563 (28%). In terms of the aggregated HFC emissions we see a 43% increase representing a rise from 1.95 to  
564 2.87 Gt CO<sub>2</sub>-e, or an additional 0.92 Gt CO<sub>2</sub>-e between the two periods.

565 It is also apparent that emissions of HCFC-22 represent 79.3% of the global cumulative HCFC  
566 burden during 2011-2015 and HCFC-22 alone contributes 0.45 Gt CO<sub>2</sub>-e (13.5%) more than all HFCs  
567 cumulative emissions during 2011-2015.

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579 Table 3. Global emissions of HCFCs and HFCs in 2015 and a comparison of the cumulative emissions  
 580 and the percentage change in emissions over two 5-year periods (2006-2010 and 2011-2015).

581

| HCFCs        | 2015 Emissions (Gg) | 2006-2010 HCFCs Cumulative Emissions (Gg) and CO <sub>2</sub> - e Emissions (Gt CO <sub>2</sub> - e ) | 2011-2015 HCFCs Cumulative Emissions (Gg) and CO <sub>2</sub> - e Emissions (Gt CO <sub>2</sub> - e ) | % Change in cumulative emissions between 2006-2010 and 2011-2015 |
|--------------|---------------------|---|---|--|
| <b>22</b>    | 357.4 ± 58.1        | 1802.0 (3.26)   | 1833.2 (3.32)   | 1.7  |
| <b>141b</b>  | 59.3 ± 9.8          | 272.5 (0.20)  | 322.4 (0.23)  | 18.3   |
| <b>142b</b>  | 24.6 ± 6.3          | 180.8 (0.42)  | 138.9 (0.32)  | -23.2  |
| <b>124</b>   | 3.0 ± 0.89          | 25.4 (0.02)   | 17.8 (0.01)   | -29.9  |
| <b>Total</b> |                     | <b>2281 (3.9)</b>   | <b>2312 (3.9)</b>   | <b>1.4</b>   |
| HFCs         | 2015 Emissions (Gg) | 2006-2010 HFCs Cumulative Emissions (Gg) and CO <sub>2</sub> - e Emissions (Gt CO <sub>2</sub> - e )  | 2011-2015 HFCs Cumulative Emissions (Gg) and CO <sub>2</sub> - e Emissions (Gt CO <sub>2</sub> - e )  | % change in cumulative emissions between 2006-2010 and 2011-2015 |
| <b>125</b>   | 60.3 ± 9.5          | 131.3 (0.46)  | 251.2 (0.88)  | 91.7   |
| <b>134a</b>  | 209.4 ± 42.9        | 736.6 (1.05)  | 943.8 (1.35)  | 28.1   |
| <b>143a</b>  | 27.3 ± 3.0          | 89.2 (0.4)  | 122.0 (0.55)  | 36.9   |
| <b>32</b>    | 31.9 ± 14.4         | 51.6 (0.04)   | 125.2 (0.09)  | 142.7  |
| <b>Total</b> |                     | <b>1009 (1.9)</b>   | <b>1442 (2.9)</b>   | <b>43</b>  |

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Even though global production and consumption of HCFCs in Article 5 countries was capped in 2013 these developing countries have substantially increased their usage of HCFCs (Montzka et al., 2009) and are not required to phase-out potentially emissive consumption until 2040. As noted in Figure 2 the HCFCs show decreasing annual rates of growth with HCFC-142b declining by ~93% from 2007-2015, HCFC-141b by 53% and HCFC-22 by 54%. This is reflected in the aggregated HCFCs global CO<sub>2</sub>-e emissions (shown as in Figure 6) exhibiting a small but steady decline from 2010-2015. In spite of the 2013 cap on global production and consumption, the pace of decline has to some extent been moderated by the increased emissions of HCFC-22 and HCFC-141b in article 5 countries. HCFC-22 remains the dominant refrigerant used in Article 5 countries and it has been estimated that approximately 1 million tonnes of HCFC-22 are currently in use in air conditioners operating worldwide (UNEP, 2016b). As the HFCs have replaced HCFCs, their aggregated emissions in 2015 have risen to a level in CO<sub>2</sub>-e that is 13% less than the aggregated emissions of the HCFCs.

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Although there has been a shift in developed countries (non-Article 5) from HCFCs to high-GWP HFCs (Lunt et al., 2015; Montzka et al., 2015) the consumption of both HCFCs and HFCs in Article 5 countries has substantially increased, most notably in China (Fang et al., 2012; Zhang et al., 2014; Su et al., 2015; Velders et al., 2015). There has been a trend in recent years to move to refrigerant blends with

600



601 lower GWPs and in Japan in 2014 residential air-conditioners were switched to using HFC-32 (UNEP,  
602 2016b).

603 HFCs-134a, -125, -143a and -32 are the principal components of all alternative substitutes for the  
604 HCFCs and in the supplementary material (3) we examine the composition of the main refrigerant blends  
605 to determine if there is evidence for a significant use of single component refrigerants. In general, we find  
606 that the atmospheric mole fractions of HFCs -32, -125, and -143a are consistent with their release  
607 predominantly as blends.

608

## 609 5. Conclusions

610 This study confirms that the Montreal Protocol and its amendments have been effective in  
611 slowing the atmospheric accumulation of the HCFCs. If there had been no change in the emissions  
612 growth rate, we find that based on our linear projection there would have been an additional  $0.67 \pm 0.24$   
613 Gt CO<sub>2</sub>-e of aggregated HCFCs -22, -141b, -142b emitted to the atmosphere from 2010-2015. This  
614 compares with the forward projections of ‘business as usual’ in the Velders et al., 2009 and WMO (2010)  
615 scenario of an additional  $0.71 \pm 0.25$  Gt CO<sub>2</sub>-e and  $0.66 \pm 0.24$  Gt CO<sub>2</sub>-e, respectively, of total HCFCs  
616 that would have been emitted during this same period. However, we also calculate that the aggregated  
617 cumulative emissions of HCFCs-22, -141b, -142b, and -124 during the most recent 5-yr period (2011-  
618 2015) are slightly larger (1.4%) than in the previous five years (2006-2010). This increase has likely been  
619 driven by the substantial emissions of HCFCs-22 and -141b in Article 5 countries. HCFC-22 represents  
620 about 79% of total global HCFC emissions. As shown in Figure 2, the annual HCFC-22 growth rate has  
621 steadily declined since the introduction of the 2007 adjustment to the Montreal Protocol, yet global  
622 emissions have tended to remain approximately constant with only a modest decline in emissions post-  
623 2007 (see Figure 5). We also note the linkage between HCFC-22 and HFC-23, also a potent GHG, which  
624 is an unavoidable by-product of HCFC-22 production, (Miller et al., 2010; Rigby et al., 2014). Therefore  
625 further reductions in HCFC-22 production and consumption will benefit the efforts of the UNFCCC  
626 Clean Development Mechanism (CDM) that mitigates HFC-23 emissions by voluntary incineration.  
627 Since we are only two years beyond the 2013 cap on global production and consumption of HCFCs, it is  
628 probably too early for our current observations through 2015 to show an accelerating phase-out for all  
629 HCFCs, although HCFCs-142b and -124 have both recently undergone substantial declines in global  
630 emissions.

631 Although global emissions of HFCs have increased throughout the course of this study,  
632 Montzka et al., (2014) suggested that there may have been a shift to lower GWP refrigerant blends which  
633 can account for the observed emissions. It is also noteworthy that the two HFCs with the largest  
634 percentage changes in emissions in recent years are HFCs-125 and -32 (see Table 3), which implies a



635 trend towards blends containing these two refrigerants. However, we are unable to confirm the extent to  
636 which other lower GWP blends (e.g. R404A and R507A) have been substituted with the possibility that  
637 there has simply been a switch from one blend to another with similar GWPs. In terms of CO<sub>2</sub>-e,  
638 surprisingly HCFC-22 emissions alone contribute 0.45 Gt CO<sub>2</sub>-e, about 14% more to climate change than  
639 the four aggregated HFCs during 2011-2015. This could potentially be attributed to the continuing use of  
640 HCFC-22 in existing refrigeration equipment with the consequence of large slowly leaking banks.

641 With regard to inventory-based HFC emissions estimates it is important to acknowledge that  
642 attempting to quantify the release of individual HFCs to the atmosphere is complicated by the continuous  
643 introduction of new blends many of which contain hydrocarbons and lower GWP refrigerants and their  
644 substitution into older existing refrigeration equipment. This problem is further compounded by the lack  
645 of information on the actual usage of the various blends in commercial and residential refrigeration,  
646 coupled with the difficulty of quantifying emission magnitudes from the many banks and immediate  
647 release as solvents and in foam blowing applications. Nevertheless, the atmospheric mole fractions  
648 observed are consistent with emissions of HFCs in refrigerant blends, rather than substantial emissions  
649 from single component refrigerants.

650 We find that the increase in HFC emissions from 2010 to 2015 has been more rapid than a linear  
651 growth would imply. However, compared to this linear trend, the cumulative excess of emissions during  
652 this period is 0.12±0.15 Gt CO<sub>2</sub>-e, which is smaller than the deficit in HCFCs during the same time  
653 frame. This suggests that the phase-down in HCFCs post-2010 has not coincided with an equivalent  
654 increase in HFC emissions in CO<sub>2</sub>-e terms. Compared to alternative projections by Velders et al. (2009),  
655 our top-down estimates show a much more rapid decline in emissions of HCFCs, and slower increase in  
656 HFC emissions. Therefore, similarly to our linear projection, where Velders et al. (2009) predicted a  
657 relatively steady growth in CO<sub>2</sub>-e emissions due to HCFCs and HFCs from 2005 – 2015, we find an  
658 overall slowing of emissions post-2010.

659 Finally we note that national regulations to limit HFC use are already in place in the European  
660 Union, Japan and the USA, and recently there has been an agreement to amend the Montreal Protocol to  
661 further restrict HFC use beginning in 2019, (28<sup>th</sup> meeting of the parties to the Montreal Protocol, Kigali,  
662 Rwanda, October 2016). By including HFCs, which have been shown to have a small, but non-zero  
663 ozone-depletion potential (Hurwitz et al., 2015) into the Montreal Protocol, this has the benefit of further  
664 regulating production and sales.

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683

## 684 Data availability

685

686 The entire ALE/GAGE/AGAGE data base comprising every calibrated measurement  
687 including pollution events is archived on the Carbon Dioxide Information and Analysis  
688 Center (CDIAC) at the U.S. Department of Energy, Oak Ridge National Laboratory.

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## 690 References

- 691 | Arnold, T., Mühle, J., Salameh, P. K., Harth, C. M., Ivy, D. J., Weiss, R. F., 2012. Automated  
692 measurement of nitrogen trifluoride in ambient air, *Anal. Chem.*, 84, 4798–4804.
- 693 Carpenter, L. & S. Reimann (Lead Authors), J. Burkholder, C. Clerbaux, B. Hall, R. Hossaini, J. Laube &  
694 S. Yvon-Lewis (Co-authors), D. Blake, M. Dorf, G. Dutton, P. Fraser, L. Froidevaux, F. Hendrick, J. Hu,  
695 A. Jones, P. Krummel, L. Kuijpers, M. Kurylo, Q. Laing, E. Mahieu, J. Muhle, S. O'Doherty, K. Ohnishi,  
696 V. Orkin, K. Pfeilsticker, M. Rigby, I. Simpson & Y. Yokouchi (Contributing Authors), Update on  
697 Ozone-Depleting Substances (ODSs) and Other Gases of Interest to the Montreal Protocol, Chapter 1 in  
698 Scientific Assessment of Ozone Depletion: 2014, Global Ozone Research and Monitoring Project –  
699 Report No. 55, 1.1-1.101, World Meteorological Organization, Geneva, Switzerland, 2014.
- 700 Cunnold, D. M., Prinn, R.G., Rasmussen, R., Simmonds, P.G., Alyea, F.N., Cardlino, C., Crawford, A.J.,  
701 Fraser, P.J., Rosen, R., 1983. The lifetime atmospheric experiment, III: lifetime methodology and  
702 application to three years of CFC<sub>13</sub> data, *J. Geophys. Res.*, 88, 8379-8400.



- 703 Cunnold, D. M., Fraser, P.J., Weiss, R.F., Prinn, R.G., Simmonds, P.G., Miller, B.R., Alyea, F.N.,  
704 Crawford, A.J., Rosen, R., 1994. Global trends and annual releases of CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub> estimated from  
705 ALE/GAGE and other measurements from July 1978 to June 1991, *J. Geophys. Res.*, 99, 1107-1126.
- 706 Derwent, R.G., Simmonds, P.G., Grealley, B.R., O'Doherty, S., McCulloch, A., Manning, A., Reimann,  
707 S., Folini, D., Vollmer, M.K., 2007. The phase-in and phase-out of European emissions of HCFC-141b  
708 and HCFC-142b under the Montreal Protocol: Evidence from observations at Mace Head, Ireland and  
709 Jungfraujoch, Switzerland from 1994 to 2004. *Atmos Environ.* 41 757-767.
- 710 Fang, X., Wu, J., Su, S., Han, J., Wu, Y., Shi, Y., Wan, D., Sun, X., Zhang, J., Hu, J., 2012. Estimates of  
711 major anthropogenic halocarbon emissions from China based on interspecies correlations, *Atmos.*  
712 *Environ.*, 62, 26-33, doi: 10.1016/j.atmosenv.2012.08.010.
- 713  
714 X. Fang., G. J. M. Velders, A. R. Ravishankara, M. J. Molina, J. Hu and R. G. Prinn. Hydrofluorocarbon  
715 (HFC) Emissions in China: An Inventory for 2005–2013 and Projections to 2050. *Environ. Sci.*  
716 *Technol.*, 2016, 50 (4), pp 2027–2034. DOI: 10.1021/acs.est.5b04376.
- 717  
718 Fortems-Cheiney, A., Chevallier, F., Saunois, M., Pison, I., Bousquet, P., Cressot, C., Wang, H.L.,  
719 Yokouchi, Y., Artuso, F., 2013. HCFC-22 emissions at global and regional scales between 1995 and  
720 2010: Trends and variability. *J. Geophys. Res.*, 118, 7379-7388.
- 721  
722 Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D. W., Haywood, J., Lean, J.,  
723 Lowe, D. C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., Van Dorland, R., 2007. Changes in  
724 atmospheric constituents and in radiative forcing, in: *Climate Change 2007: The Physical Science Basis.*  
725 *Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on*  
726 *Climate Change*, edited by: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B.,  
727 Tignor, M., and Miller, H. L., Cambridge University Press, Cambridge, UK, New York, NY, USA, 131–  
728 234.
- 729 Grazioli, F., Arduini, J., Furlani, F., Giostra, U., Kuijpers, L.J.M., Montzka, S.A., Miller, B.R.,  
730 O'Doherty, S.J., Stohl, A., Bonasoni, P., Maione, M., 2015. European emissions of HCFC-22 based on  
731 eleven years of high frequency atmospheric measurements and a Bayesian inversion. *Atmos. Environ.*,  
732 112, 196-207.
- 733  
734 Hurwitz, M.M., Fleming, E.L., Newman, P.A., Li, F., Mlawer, E., Cady-Pereira, K., Bailey, R., 2015.  
735 Ozone depletion by hydrofluorocarbons. *Geophys. Res. Lett.*, DOI. 10.1002/2015GL065856.
- 736  
737 Intergovernmental Panel on Climate Change/Technology and  
738 Economic Assessment Panel, Safeguarding the Ozone Layer and Global  
739 Climate System: Issues Related to Hydrofluorocarbons and Perfluorocarbons;  
740 Metz, B., Kuijpers, L., Solomon, S., Andersen, S. O., Davidson, O., Pons, J., deJager, D., Kestin, T.,  
741 Manning, M., Meyer, L., Eds.; Cambridge University Press: N.Y., 2005; p 478.
- 742  
743 IPCC (Intergovernmental Panel on Climate Change), *Climate Change 2013: The Physical Science Basis:*  
744 *Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on*  
745 *Climate Change*, edited by Stocker, T.F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S.K., Boschung, J.,  
746 Nauels, A., Xia, Y., Bex, V., Midgley, P.M., 1535 pp., Cambridge University Press, Cambridge, UK and  
747 New York, NY, USA, 2013.





- 748 IPCC/TEAP (Intergovernmental Panel on Climate Change/Technology and Economic Assessment  
749 Panel), *IPCC/TEAP Special Report on Safeguarding the Ozone Layer and the Global Climate System:  
750 Issues Related to Hydrofluorocarbons and Perfluorocarbons*, prepared by Working Groups I and III of  
751 the Intergovernmental Panel on Climate Change, and the Technical and Economic Assessment Panel,  
752 Cambridge University Press, Cambridge, U.K. and New York, NY, U.S.A., 2005.  
753
- 754 Krummel, P. B., Fraser, P. Steele, P., Derek, N., Rickard, C., Ward, J., Somerville, N., Cleland, S.,  
755 Dunse, B., Langenfelds, R., Baly S., and Leist, M., 2014. The AGAGE *in situ* program for non-CO<sub>2</sub>  
756 greenhouse gases at Cape Grim, 2009-2010, *Baseline Atmospheric Program (Australia) 2009-2010*, N.  
757 Derek P. Krummel & S. Cleland (eds.), Australian Bureau of Meteorology and CSIRO Marine and  
758 Atmospheric Research, Melbourne, Australia, 55-70.
- 759
- 760 Li, S.; Kim, J.; Kim, K. R.; Mühle, J.; Kim, S. K.; Park, M. K.; Stohl, A.; Kang, D. J.; Arnold, T.; Harth,  
761 C. M.; Salameh, P. K.; Weiss, R. F., 2011. Emissions of Halogenated Compounds in East Asia  
762 Determined from Measurements at Jeju Island, Korea. *Environ. Sci. Technol.*, 45 (13), 5668–5675.  
763
- 764 Li, L., Fang, X., Jia, S., Hu, J., 2014. Estimated HFCF-142b emissions in China 2000-2050. *Chinese  
765 Science Bulletin*, Doi:10.1007/s11434-014-0337-z.  
766
- 767 Lunt, M.F., Rigby, M., Ganesan, A. L., Manning, A.J., Prinn, R.G., O’Doherty, S., Mühle, J.,  
768 Harth, C.M., Salameh, P.K., Arnold, T., Weiss, R.F., Saito, T., Yokouchi. Y., Krummel, P.B., Steele,  
769 L.P., Fraser, P.J., Li, S., Park, S., Reimann, S., Vollmer, M.K., Lunder, C., Hermansen, O., Schmidbauer,  
770 N., Maione, M., Young, D., Simmonds, P.G., 2015. Reconciling reported and unreported HFC emissions  
771 with atmospheric observations, *PNAS*, 112, 5927-5931, doi/10.1073/pnas.1420247112.  
772
- 773 Miller, B. R., Weiss, R. F., Salameh, P. K., Tanhua, T., Grealley, B. R., Mühle, J., Simmonds, P. G., 2008.  
774 Medusa: a sample pre-concentration and GC-MS detector system for *in situ* measurements of  
775 atmospheric trace halocarbons, hydrocarbons and sulphur compounds, *Anal. Chem.*, 80, 1536-1545.  
776
- 777 Miller, B. R., Rigby, M., Kuijpers, L.J.M., Krummel, P.B., Steele, L.P., Leist, M., Fraser, P.J., McCulloch, A.,  
778 Harth, C. Salameh, P.K., Mühle, J., Weiss, R.F., Prinn, R.G., Wang, R.H.J., O’Doherty, S., Grealley, B.R.,  
779 Simmonds, P.G., 2010. HFC-23 (CHF<sub>3</sub>) Emission Trend Response to HCFC-22 (CHClF<sub>2</sub>) Production and Recent  
780 HFC-23 Emission Abatement Measures. *Atmos. Chem. Phys.* 10, 7875–7890.  
781
- 782 Montzka, S. A., Myers, R.C., Butler, J. H., Elkins, J.W., Lock, L., Clarke, A., Goldstein, A.H., 1996.  
783 Observations of HFC-134a in the Remote Troposphere. *Geophys. Res. Lett.*, 23, 169–172.  
784
- 785 Montzka, S. A., Hall, B.D., Elkins, J.W., 2009. Accelerated Increases Observed for  
786 Hydrochlorofluorocarbons Since 2004 in the Global Atmosphere. *Geophys. Res. Lett.*, 36, L03804.  
787
- 788 Montzka, S. A., McFarland, M., Andersen, S.O., Miller, B.R., Fahey, D.W., Hall, B.D., Hu, L., Ciso, C.,  
789 Elkins, J.W., Recent Trends in Global Emissions of Hydrochlorofluorocarbons and Hydrofluorocarbons;  
790 2015. Reflecting on the 2007 Adjustments to the Montreal Protocol. *J. Phys. Chem. A.* 2015, 119, 4439-  
791 4449. Doi:10.1021/jp50973761.  
792
- 793 Mühle, J., Ganesan, A. L., Miller, B. R., Salameh, P. K., Harth, C. M., Grealley, B. R., Rigby, M., Porter,  
794 L. W., Steele, L. P., Trudinger, C. M., Krummel, P. B., O’Doherty, S., Fraser, P. J., Simmonds, P. G.,  
795 Prinn, R. G., Weiss, R. F., 2010. Perfluorocarbons in the global atmosphere: tetrafluoromethane,  
796 hexafluoroethane, and octafluoropropane, *Atmos. Chem. Phys.*, 10, 5145–5164, doi:10.5194/acp-10-  
797 5145.



798

799 O'Doherty, S., Cunnold, D., Sturrock, G.A., Ryall, D., Derwent, R.G., Wang, R.H.J., Simmonds, P.G.,  
800 Fraser, P.J., Weiss, R.F., Salameh, P., Miller, B.R., Prinn, R.G., 2001. In-Situ Chloroform Measurements  
801 at AGAGE Atmospheric Research Stations from 1994 –1998, *J. Geophys. Res.*, 106, No. D17, 20,429-  
802 20,444, ISSN: 0747-7309.

803 O'Doherty, S., Cunnold, D. M., Manning, A.J. Miller, B.R., Wang, H.J., Krummel, P. B., Fraser, P.J., Simmonds,  
804 P.G., McCulloch, A., Weiss, R.F., Salameh, P.K., Porter, L.W., Prinn, R.G., Huang, J., Sturrock, G., Ryall, D.,  
805 Derwent, R.G., Montzka, S.A., 2004. Rapid growth of hydrofluorocarbon 134a and hydrochlorofluorocarbons,  
806 141b, 142b, and 22 from Advanced Global Atmospheric Gases Experiment (AGAGE) observations at Cape Grim,  
807 Tasmania, and Mace Head, Ireland. *J. of Geophys. Res.*, 109, D06310, doi:10.1029/2003JD004277.

808

809 O'Doherty, S., Cunnold, D.M., Miller, B.R., Mühle, J., McCulloch, A., Simmonds, P.G., Manning, A.J.,  
810 Reimann, S., Vollmer, M.K., Grealley, B.R., Prinn, R.G., Fraser, P.J., Steele, P., Krummel, P.B., Dunse, B.L.,  
811 Porter, L.W., Lunder, C.R., Schmidbauer, N., Hermansen, O., Salameh, P.K., Harth, C.M., Wang, R.H. J.,  
812 Weiss, R. F., 2009. Global and Regional Emissions of HFC-125 (CHF<sub>2</sub>CF<sub>3</sub>) from In Situ and Air Archive  
813 Atmospheric Observations at AGAGE and SOGE Observatories. *J. Geophys. Res.*, 114, D23304.

814

815 O'Doherty, S., Rigby, M., Mühle, J., Ivy, D., Miller, B.R., Young, D., Simmonds, P.G., Reimann, S., Vollmer,  
816 M.K., Krummel, P. B., Fraser, P.J., Steele, L.P., Dunse, B., Salameh, P.K., Harth, C.M., Arnold, T., Weiss, R.F.,  
817 Kim, J., Park, S., Li, S., Lunder, C., Hermansen, O., Schmidbauer, N., Zhou, L. X., Yao, B., Wang, R.H.L.,  
818 Manning, A.J., Prinn, R.G., 2014. Global Emissions of HFC-143a (CH<sub>3</sub>CF<sub>3</sub>) and HFC-32 (CH<sub>2</sub>F<sub>2</sub>) from In Situ  
819 and Air Archive Atmospheric Observations. *Atmos. Chem. Phys.*, 14, 6471–6500.

820

821 Oram, D., Reeves, C., Penkett, S., Fraser, P., 1995. Measurements of HCFC-142b and HCFC-141b in the  
822 Cape Grim air archive: 1978-1993, *Geophys. Res. Letts*, 22, 2741-2744.

823

824 Oram, D.E; Reeves, C.E., Sturges, W.T., Penkett, S.A., Fraser, P.J., Lanngensfelds, R.L., 1996. Recent  
825 tropospheric growth rate and distribution of HFC-134a (CF<sub>3</sub>CH<sub>2</sub>F). *Geophys. Res. Letts*, DOI:  
826 10.1029/96GL01862.

827

828 Prinn, R.G., Weiss, R.F., Fraser, P.J., Simmonds, P.G., Cunnold, D.M., Alyea, F.N., O'Doherty, S.,  
829 Salameh, P.K., Miller, B.R., Huang, J., Wang, R.H.J., Hartley, D.E., Harth, C., Steele, L.P., Sturrock, G.,  
830 Midgley, P.M., McCulloch, A., 2000. A history of chemically and radiatively important gases in air  
831 deduced from ALE/GAGE/AGAGE, *J. Geophys. Res.*, 105 (D14), 17751-17792, doi:  
832 10.1029/2000JD900141.

833

834 Rigby, M., Ganesan, A.L., Prinn, R.G., 2011. Deriving emissions time series from sparse atmospheric  
835 mole fractions, *J. Geophys. Res.*, 116, D08306, doi:10.1029/2010JD015401.

836

837 Rigby, M., Prinn, R.G., O'Doherty, S., Miller, B.R., Ivy, D., Mühle, J., Harth, C., Salameh, P.K.,  
838 Arnold, T., Weiss, R.F., Krummel, P.B., Steele, P., Fraser, P.J., Young, D., Simmonds, P.G., 2014.  
839 Recent and Future Trends in Synthetic Greenhouse Gas Radiative Forcing. *Geophys. Res. Lett.*, 41,  
840 2623–2630.

841

842 Saikawa, E., Rigby, M., Prinn, R.G., Montzka, S.A., Miller, B.R., Kuijpers, L.J.M., Fraser, P.J., Vollmer,  
843 M.K., Saito, T., Yokouchi, Y., Harth, C.M., Mühle, J., Weiss, R.F., Salameh, P.K., Kim, J., Li, S., Park,  
844 S., Kim, K.-R., Young, D., O'Doherty, S., Simmonds, P.G., McCulloch, A., Krummel, P.B., Steele, L.P.,  
845 Lunder, C., Hermansen, O., Maione, M., Arduini, J., Yao, B., Zhou, L.X., Wang, R.H.J., Elkins, J.W.,



- 846 Hall, B., 2012. Global and Regional Emission Estimates for HCFC-22. *Atmos. Chem. Phys.*, 12,  
847 10033–10050.
- 848
- 849 Simmonds, P. G., O’Doherty, S., Nickless, G., Sturrock, G.A., Swaby, R., Knight, P., Ricketts, J.,  
850 Woffenden, G., and Smith, R., 1995. Automated gas chromatographic/mass spectrometer for routine  
851 atmospheric field measurements of the CFC replacement compounds, the hydrofluorocarbons and  
852 hydrochlorofluorocarbons, *Anal. Chem.*, 67, 717– 723.
- 853 Simmonds, P.G., O’Doherty, S., Huang, J., Prinn, R.G., Derwent, R.G., Ryall, D., Nickless, G., and  
854 Cunnold, D.M., 1998. Calculated trends and atmospheric abundance of 1,1,1,2-tetrafluoroethane, 1,1-  
855 dichloro-1-fluoroethane, and 1-dichloro-1,1-difluoroethane using automated in-situ gas chromatography-  
856 mass spectrometry recorded at Mace Head, Ireland from October 1994 to March 1997. *J. Geophys Res.*, 103,  
857 16029-16037.
- 858
- 859 Simmonds, P. G., Rigby, M., Manning, A. J., Lunt, M. F., O’Doherty, S., Young, D., McCulloch, A.,  
860 Fraser, P. J., Henne, S., Vollmer, M. K., Reimann, S., Wenger, A., Mühle, J., Harth, C. M.,  
861 Salameh, P. K., Arnold, T., Weiss, R. F., Krummel, P. B., Steele, L. P., Dunse, B. L., Miller, B. R.,  
862 Lunder, C. R., Hermansen, O., Schmidbauer, N., Saito, T., Yokouchi, Y., Park, S., Li, S., Yao, B.,  
863 Zhou, L. X., Arduini, J., Maione, M., Wang, R. H. J., and Prinn, R. G., 2015. Global and regional  
864 emissions estimates of 1,1-difluoroethane (HFC-152a, CH<sub>3</sub>CHF<sub>2</sub>) from in situ and air archive  
865 observations, *Atmos. Chem. Phys. Discuss.*, 15, 21335-21381, doi:10.5194/acpd-15-21335-2015.
- 866 SPARC (2013) *SPARC Report on the Lifetimes of Stratospheric Ozone-Depleting Substances, Their*  
867 *Replacements, and Related Species*, edited by Ko, M., Newman, P., Reimann, S., Strahan, S., 2013.  
868 SPARC Report No. 6, WCRP-15/2013.
- 869
- 870 Su, S.; Fang, X.; Li, L.; Wu, J.; Zhang, J.; Xu, W.; Hu, J., 2015. HFC-134a emissions from mobile air  
871 conditioning in China from 1995 to 2030. *Atmos. Environ.*, 102 (0), 122–129.
- 872
- 873 UNEP (United Nations Environment Programme), 2016a, Data Centre of the Montreal Protocol  
874 Secretariat on <http://ozone.unep.org/en/data-reporting/data-centre>, accessed May 2016.
- 875 UNEP, 2016b, Refrigeration, Air Conditioning and Heat Pump Technical Options Committee in Report  
876 of the UNEP Technical and Economic Assessment Panel, June 2016, available at:  
877 <http://ozone.unep.org/en/assessment-panels/technology-and-economic-assessment-panel>.
- 878 UNFCCC (United Nations Framework Convention on Climate Change), 2016, Reported greenhouse  
879 gas emissions inventories in  
880 [unfccc.int/national\\_reports/annex\\_1\\_ghg\\_inventories/national\\_inventories\\_submissions/items/9492.php](http://unfccc.int/national_reports/annex_1_ghg_inventories/national_inventories_submissions/items/9492.php)  
881 accessed October 2016.
- 882
- 883 Velders, G. J. M., Fahey, D.W., Daniel, J.S., McFarland, M., Andersen, S.O., 2009. The Large  
884 Contribution of Projected HFC Emissions to Future Climate Forcing. *Proc. Natl. Acad. Sci. U.S.A.* 106,  
885 10949–10954.
- 886
- 887 Velders, G. J. M., Fahey, D.W., Daniel, J.S., Andersen, S.O., McFarland, M., 2015. Future atmospheric  
888 abundances and climate forcings from scenarios of global and regional hydrofluorocarbon (HFC)  
889 emissions. *Atmos. Environ.* 123, 200-209.
- 890



891 WMO (2010). World Meteorological Organization, *Scientific Assessment of Ozone Depletion: Report*  
892 No. 52; Global Ozone Research and Monitoring Project: Geneva, Switzerland, 2010. (Chapter 1. Lead  
893 authors: S. A. Montzka and S. Reimann)  
894  
895 Xiang, B, Prabir, B., Patra, K., Montzka, S.A., Miller, S.M., Elkins, J.W., Moore, F.L., Atlas, E.L.,  
896 Miller, B.R., Weiss, R. F., Prinn, R.G., Wofsy, S.C., 2014. Global emissions of refrigerants HCFC-22  
897 and HFC-134a: Unforeseen seasonal contributions. PNAS, doi/10.1073/pnas.1417372111.  
898  
899 Zhang, J., Wang, C., 2014. China's hydrofluorocarbon challenge. Nat.Clim.Change, 4, 943-945.  
900  
901  
902  
903  
904  
905  
906  
907  
908  
909  
910  
911  
912  
913  
914  
915  
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