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Changing trends and emissions of hydrochlorofluorocarbons (HCFCs) and their hydrofluorocarbon (HFCs) replacements

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Abstract. High-frequency, in situ global observations of HCFC-22 ($CHClF_2$), HCFC-141b (CH_3CCl_2F), HCFC-142b (CH_3CClF_2) and HCFC-124 ($CHClFCF_3$) and their main HFC replacements, HFC-134a (CH_2FCF_3), HFC-125 (CHF_2CF_3), HFC-143a (CH_3CF_3) and HFC-32 (CH_2F_2), have been used to determine their changing global growth rates and emissions in response to the Montreal Protocol and its recent amendments. Global mean mole fractions of HCFC-22, -141b, and -142b have increased throughout the observation period, reaching 234, 24.3 and 22.4 pmol mol^{-1}, respectively, in 2015. HCFC-124 reached a maximum global mean mole fraction of 1.48 pmol mol^{-1} in 2007 and has since declined by 23 % to 1.14 pmol mol^{-1} in 2015. The HFCs all show increasing global mean mole fractions. In 2015 the global mean mole fractions (pmol mol^{-1}) were 83.3 (HFC-134a), 18.4 (HFC-125), 17.7 (HFC-143a) and 10.5 (HFC-32).

The 2007 adjustment to the Montreal Protocol required the accelerated phase-out of emissive uses of HCFCs with global production and consumption capped in 2013 to mitigate their environmental impact as both ozone-depleting substances and important greenhouse gases. We find that this change has coincided with a stabilisation, or moderate reduction, in global emissions of the four HCFCs with aggregated global emissions in 2015 of 449 ± 75 Gg yr^{-1}, in CO$_2$ equivalent units (CO$_2$ eq.) 0.76 ± 0.1 Gt yr^{-1}, compared with 483 ± 70 Gg yr^{-1} (0.82 ± 0.1 Gt yr^{-1} CO$_2$ eq.) in 2010 (uncertainties are 1σ throughout this paper). About 79 % of the total HCFC atmospheric burden in 2015 is HCFC-22, where global emissions appear to have been relatively similar since 2011, in spite of the 2013 cap on emissive uses. We attribute this to a probable increase in production and consumption of HCFC-22 in Montreal Protocol Article 5 (developing) countries and the continuing release of HCFC-22 from the large banks which dominate HCFC global emissions. Conversely, the four HFCs all show increasing mole fraction growth rates with aggregated global HFC emissions of 327 ± 70 Gg yr^{-1} (0.65 ± 0.12 Gt yr^{-1} CO$_2$ eq.) in 2015 compared to 240 ± 50 Gg yr^{-1} (0.47 ± 0.08 Gt yr^{-1} CO$_2$ eq.) in 2010. We also note that emissions of HFC-125 and HFC-32 appear to have increased more rapidly averaged over the 5-year period 2011–2015, compared to 2006–2010. As noted by Lunt et al. (2015) this may reflect a change to refrigerant blends, such as R-410A, which contain HFC-32 and -125 as a 50 : 50 blend.

1 Introduction

Hydrochlorofluorocarbons (HCFCs) were first used in the 1940s and, in the 1980s, adopted as alternatives to chlorofluorocarbons (CFCs) in some refrigeration and air conditioning applications. Production and consumption grew rapidly in developed countries until the mid-1990s (AFEAS, 2016). However, because they are ozone-depleting substances (ODSs), HCFCs were included in the 1992 Montreal Protocol amendment, with a view to eventual phase-out of production and consumption. Subsequently the 2007 adjustments to the Montreal Protocol required an accelerated phase-out of emissive uses of HCFCs in both "non-Article 5" developed and "Article 5" developing countries, with a 2004 cap on production and consumption for non-Article 5 countries and a 2013 global cap on production and consumption (UNEP, 2016a). Historically, HCFC-22, -141b and -142b account for > 90 % of the total consumption of all HCFCs in non-Article 5 countries (AFEAS, 2016).

A more rapid phase-out of the HCFCs should result in a marginally faster (0.1–0.2 %, 2015–2050; Harris et al., 2014) recovery of the depleted stratospheric ozone layer, with the additional benefit of mitigating climate change, since these compounds are also potent greenhouse gases (GHGs). The ozone depletion potential (ODP), global warming potential (GWP) and atmospheric lifetimes of these eight compounds are listed in Table 1.

Detailed studies of the rates of atmospheric accumulation of the HCFCs indicate periods of rapid growth, temporary slowing followed by accelerated growth (Oram et al., 1995; Simmonds et al., 1998; O'Doherty et al., 2004; Reimann et al., 2004; Derwent et al., 2007; Montzka et al., 2009; Miller et al., 2010; Saikawa et al., 2012; Fortems-Cheiney et al., 2013; Carpenter et al., 2014; Krummel et al., 2014; Rigby et al., 2014; Graziosi et al., 2015). More recently the global growth rates of HCFC-22 and HCFC-142b have slowed significantly and Montzka et al. (2015) reported that the 2007 adjustments to the Montreal Protocol had limited HCFC emissions significantly prior to the 2013 cap on global production, although the atmospheric growth rate of HCFC-141b had almost doubled between 2007 and 2012.

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

In this study we focus on high-frequency atmospheric measurements (6–12 per day) of HCFC-22, HCFC-141b, HCFC-142b and HCFC-124 and their main replacements HFC-134a, HFC-125, HFC-143a, and HFC-32 from the five core globally distributed Advanced Global Atmospheric Gases Experiment (AGAGE) sites, listed in Table 2, with 10–

Table 1. Steady-state atmospheric lifetimes (year), ozone depletion and global warming potentials (100-year time horizon) for the HCFCs and HFCs discussed in this study.

Compound	[a]ODP	[b]GWPs	[c]GWPs	[d]Lifetime
HCFC-22	0.055	1810	1760	12
HCFC-141b	0.11	725	782	9.4
HCFC-142b	0.065	2310	1980	18
HCFC-124	0.02	609	527	6
HFC-134a	0*	1430	1300	14
HFC-143a	0*	4470	4800	51
HFC-125	0*	3500	3170	31
HFC-32	0*	675	677	5.4

* Hurwitz et al. (2015) calculated small, non-zero effects on stratospheric ozone due to the influence of these substances on stratospheric temperature (an effect not confined to HFCs). Notes: [a] ODPs from the Montreal Protocol; [b] GWPs (100-year) from Forster et al. (2007); [c] GWPs from Myhre and Shindell (2013); [d] atmospheric lifetimes, from SPARC (2013).

20-year records (Prinn et al., 2000). We have previously estimated global emissions of HFC-152a (CH_3CHF_2) using the same modelling methods discussed in this paper (Simmonds et al., 2016) and global emissions of minor HFCs, including HFC-245fa and HFC-365mfc, have been reported in Vollmer et al. (2011).

We combine these observations with a two-dimensional (12-box) atmospheric chemical transport model whose circulations are based on meteorological climatology, which has been adjusted in inverse modelling studies to provide improved agreements with global distributions of reactive and stable trace gases (Cunnold et al., 1983; Rigby et al., 2011). We then estimate global emissions which we relate to the global phase-out and adoption schedules of HCFCs and HFCs, respectively. We compare these estimated global emissions with the quantities of HCFCs emitted based on consumption data (see Supplement) compiled from national reports to the United Nations Environment Programme (UNEP) for HCFCs and the United Nations Framework Convention on Climate Change (UNFCCC) for HFCs and the Emissions Database for Global Atmospheric Research (EDGAR v4.2; http://edgar.jrc.ec.europa.eu/ for HFCs, using the same techniques reported earlier for these HCFCs and HFCs (O'Doherty et al., 2009, 2014; Rigby et al., 2014; Lunt et al., 2015). We recognise that due to the historic range of use of these substances (refrigeration, foam blowing, and fire-fighting equipment), the derivation of emissions from production and consumption data is difficult given the uncertainties of the distribution of consumption among the various emissions sources, the uncertainty of the bank emission factors and the applicability of time-invariant emission factors.

We examine the evolution of the changing growth rates of the HCFCs with a view to determining whether the 2013 cap on their production and consumption has been reflected in an accelerated reduction in HCFC emissions. Furthermore, we examine the rapid growth rates of the HFCs and whether

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

Site	Latitude	Longitude	ADS data[a]	Medusa data[b]
Mace Head, Ireland	53.3° N	9.9° W	1994–2004	Jun 2003–present
Trinidad Head, California, USA	41.0° N	124.1° W		Mar 2005–present
Ragged Point, Barbados	13.2° N	59.4° W		May 2005–present
Cape Matatula, American Samoa	14.2° S	170.6° W		May 2006–present
Cape Grim, Tasmania, Australia	40.7° S	144.7° E	1998–2004	Jan 2004–present

For instrumental description see Sect. 2.2. [a] Period of HCFC and HFC data records using GC-MS-ADS. [b] Period of HCFC and HFC data records using GC-MS-Medusa.

these reflect manufacturers of air conditioning and refrigeration equipment switching to HFC refrigerant blends with lower GWPs, as suggested by Montzka et al. (2015). For example HFC-143a with a high GWP (4800, 100-year) is a major component of refrigerant blends R-404A and R-507A. Lower-GWP blends such as R-407C and R-410A (with equal GWPs of 1923, 100-year) have been progressively introduced into existing and new refrigeration equipment (Lunt et al., 2015; Montzka et al., 2015). However, there are a significant number of other blends where there is no specific information on their usage and when they were introduced. In the Supplement we attempt to reconcile the quantities of individual HFCs released with the composition of the refrigerant blends.

HCFC-22 is used in commercial and domestic refrigeration, air conditioning, extruded polystyrene foams and as a feedstock in the manufacture of fluoropolymers. We also note the linkage between HCFC-22 and HFC-23, also a potent GHG, which is emitted during the production of HCFC-22 and has been demonstrated to be avoidable (Miller et al., 2010; Rigby et al., 2014). Therefore, further reductions in HCFC-22 production and consumption will benefit the efforts of the UNFCCC Clean Development Mechanism (CDM) to mitigate HFC-23 emissions by voluntary incineration.

HCFC-141b and HCFC-142b are primarily used as foam blowing agents; in addition, HCFC-141b is used as a solvent in electronics and precision cleaning applications; HCFC-142b is also used as an aerosol propellant and as a refrigerant. HCFC-124 has uses in specialised air conditioning equipment, refrigerant mixtures, and fire extinguishers and as a component of sterilant mixtures (Midgley and McCulloch, 1999).

HFC-134a has been used since the early 1990s in vehicle air conditioning systems and other refrigeration and air conditioning largely to replace CFC-12. Other uses include plastic foam blowing, as a cleaning solvent and as a propellant. HFC-125 and HFC-32 have been used as a 50 : 50 blend (R-410A) in residential air conditioning systems as well as in three-component blends with HFC-134a. HFC-125 has also found application as a fire suppressant agent. HFC-143a is predominantly a component of refrigerant blends used in commercial refrigeration and in some air conditioning applications (Ashford et al., 2004).

Although the HFCs make no contribution to the destruction of stratospheric ozone, as GHGs the HFC-143a, -125, -134a and -32 have global warming potentials (GWP 100-year horizon) of 4800, 3170, 1300, and 677, respectively (Myhre and Shindell, 2013). The HCFCs, in addition to their ozone depletion potentials (ODPs), listed in Table 1, are also GHGs with GWPs comparable to the HFCs. This combination of ozone depletion and climate forcing has provided the impetus for the accelerated phase-out of the HCFCs.

2 Materials and methods

2.1 AGAGE sites

The data used here are compiled from in situ measurements at the five core AGAGE sites. Table 2 lists the coordinates and the time frame when the measurements of individual HCFCs and HFCs are available at each AGAGE site.

2.2 AGAGE instrumentation and measurement techniques

Two similar measurement technologies have been used at AGAGE stations over time, both based on gas chromatography coupled with mass spectrometry (GC-MS) and cryogenic sample pre-concentration techniques. The earlier instrument, referred to as the GC-MS-ADS, incorporated an adsorption–desorption system (ADS) based on a Peltier-cooled microtrap maintained at $-50\,°C$ during the adsorption phase (Simmonds et al., 1995; Prinn et al., 2000) and was used for several years at the Mace Head and Cape Grim sites. These were replaced by another GC-MS instrument, the GC-MS-Medusa with doubled sampling frequency and enhanced cooling to $\sim -180\,°C$. Compared to the ADS, the Medusa uses the milder trap adsorbent HayeSep D to extend compound selection and improve measurement precisions (Miller et al., 2008; Arnold et al., 2012).

The GC-MS-Medusa system is currently deployed at all AGAGE sites used in this study (Table 2). Typically for each measurement the analytes from 2 L of air are collected on the sample traps, and after various steps of fractionated dis-

tillation, purifications and transfers, desorbed onto a single main capillary chromatography column (CP-PoraBOND Q, 0.32 mm ID × 25 m, 5 µm, Agilent Varian Chrompack, batch-made for AGAGE applications) purged with helium (grade 6.0) that is further purified using a heated getter helium purifier (HP2, VICI, USA). The separation and detection of the compounds are achieved using Agilent Technology GCs (model 6890N) and quadrupole mass spectrometers in selected ion mode (initially model 5973 series, progressively converted to 5975C over the later years). For the field GC-MS-Medusa instruments, ambient air samples are analysed approximately every 2 h (cf. 4 h for the GC-MS-ADS) and are bracketed by measurements of quaternary standards to detect and correct for short-term drift in instrument response. The quaternary standards are whole-air pressurised into 34 L internally electropolished stainless steel canisters (Essex Industries, USA). They are filled by the groups who are in charge of the respective AGAGE stations using modified oil-free diving compressors (SA-3 and SA-6, RIX Industries, USA) to ∼ 60 bar (older tanks to ∼ 30 bar). Cape Grim is an exception, where the canisters used for quaternary standard purposes are typically filled cryogenically. This method of cryogenically collecting large volumes of ambient air is the same as that used for collecting air for the Cape Grim Air Archive (Langenfelds et al., 1996). Briefly, the evacuated cylinder is partially (about 75 %) immersed in a bath of liquid nitrogen, and ambient air flow into the cylinder is assisted by a small, clean, metal bellows pump (Metal Bellows Corp, MB-118E, P/N 31185). The flow rate of the air and the elapsed time determine the volume of air collected. Measurements of many atmospheric trace species in air samples collected in this manner show that the trace gas composition of the air is well preserved (Langenfelds et al., 1996).

The on-site quaternary standards are compared weekly to tertiary standards from the central calibration facility at the Scripps Institution of Oceanography (SIO) in order to propagate the primary calibration scales and to characterise any potential long-term drift of the measured compounds in the quaternary standards. Importantly, all of the stations report HCFC and HFC measurements relative to the SIO (SIO-05, SIO-07 and SIO-14) and University of Bristol (UB-98) calibration scales.

The GC-MS-Medusa measurement precisions for the four HCFCs and four HFCs are determined as the precisions of replicate measurements of the quaternary standards over twice the time interval as for sample-standard comparisons (Miller et al., 2008). Accordingly, they are upper-limit estimates of the precisions of the sample-standard comparisons. Typical daily precisions for each compound vary with abundance and individual instrument performance over time. Typical ranges for each compound measured between 2004 and 2016 are 0.5–1.0 ppt for HCFC-22; 0.05–0.1 ppt for HCFC-141b; 0.05–0.1 ppt for HCFC-142b; 0.03–0.06 ppt for HCFC-124; 0.15–0.3 ppt for HFC-134a; 0.03–0.06 ppt for

HFC-125; 0.07–0.15 ppt for HFC-143a; and 0.04–0.2 ppt for HFC-32.

2.3　Calibration scales

The estimated accuracies of the calibration scales for the various HCFCs and HFCs are reported below, and more detailed discussion of the measurement techniques and calibration procedures are reported elsewhere (Miller et al., 2008; O'Doherty et al., 2009; Mühle et al., 2010). As noted in the preceding section, these AGAGE HCFC and HFC measurements are reported relative to SIO and UB primary calibration scales: SIO-05 (HCFC-22, -141b, -142b, and HFC-134a), UB98 (HCFC-124), SIO-07 (HFC-143a, and -32), and SIO-14 (HFC-125). SIO calibration scales are defined by suites of standard gases prepared by diluting gravimetrically prepared analyte mixtures in N_2O to near-ambient levels in synthetic air (Prinn et al., 2000; Miller et al., 2008) and UB calibration scales are defined by similar dilutions of commercially prepared (Linde Gases, UK) analyte mixtures (O'Doherty et al., 2004). Results are reported as dry gas mole fractions in pmol mol^{-1} (or parts per trillion – ppt).

The absolute accuracies of these primary standard scales are difficult to assess because they are vulnerable to systematic effects that are difficult to quantify or may not even be identified. This is why the use of traceable calibration scales that are tied to a maintained set of specific calibration mixtures is of paramount importance in the measurement of atmospheric composition change. Combining known uncertainties such as measurement and propagation errors and quoted reagent purities generally yields lower uncertainties than are supported by comparisons among independent calibration scales (Hall et al., 2014). Furthermore, some systematic uncertainties may be normally distributed, while others like reagent purity are skewed in only one direction. Estimates of absolute accuracy are nevertheless needed for interpretive modelling applications, and in this work they are liberally estimated at 2 % for HCFC-22, -141b, and -142b; 10 % for HCFC-124; 1.5 % for HFC-134a; and 3 % for HFC-125, -143a, and -32.

2.4　Selection of baseline data

Baseline in situ monthly mean HCFC and HFC mole fractions were calculated by excluding values enhanced by local and regional pollution influences, as identified by the iterative AGAGE pollution identification algorithm (for details see Appendix in O'Doherty et al., 2001). Briefly, baseline measurements are assumed to have Gaussian distributions around the local baseline value, and an iterative process is used to filter out the points that do not conform to this distribution. A second-order polynomial is fitted to the subset of daily minima in any 121-day period to provide a first estimate of the baseline and seasonal cycle. After subtracting this polynomial from all the observations a standard devia-

tion and median are calculated for the residual values over the 121-day period. Values exceeding three standard deviations above the baseline are thus identified as non-baseline (polluted) and removed from further consideration. The process is repeated iteratively to identify and remove additional non-baseline values until the new and previous calculated median values agree within 0.1 %.

3 Modelling studies

There are several sources of information on production and emissions of HCFCs and HFCs, none of which, on their own, provide a complete database of global emissions. The more geographically comprehensive source of information for HFC emissions is provided by the parties to the UNFCCC, but only includes Annex 1 countries (developed countries). The 2014 database covers years 1990 to 2012 and emissions are reported in Table 2(II) s1 in the Common Reporting Format (CRF) available at http://unfccc.int/national-reports/annexighginventories/ nationalinventoriessubmissions/items/8108.php. We note that most countries report emissions for financial years which may be calendar years or may not be calendar years (e.g., Australia, Japan). An alternative inventory estimate was also obtained from the Emissions Database for Global Atmospheric Research (EDGAR v4.2; http://edgar.jrc.ec.europa.eu/), a database that estimates global emission inventories of anthropogenic GHGs, including HFCs on a country, regional and gridded basis up to 2008.

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

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

Global emissions estimates using the AGAGE two-dimensional 12-box model

To estimate global-average mole fractions and derive growth rates, a two-dimensional model of atmospheric chemistry and transport was employed. The AGAGE 12-box model simulates trace gas transport in four equal mass latitudinal sections (divisions at 30–90° N, 0–30° N, 30–0° S and 90–30° S) and at three heights (vertical divisions at 200, 500 and 1000 hPa). The model was originally developed by Cunnold et al. (1983) (nine-box version), with subsequent improve-

ments by Cunnold et al. (1994) and Rigby et al. (2013, 2014). Emissions were estimated between 1998 and 2015 using a Bayesian method in which an a priori constraint (EDGAR v4.2) on the emissions growth rate was adjusted using the baseline-filtered monthly mean AGAGE observations. Our methodology calculates uncertainties in each derived quantity such as global emissions, mole fractions or growth rates as described in Rigby et al. (2014). Briefly, uncertainties in each quantity comprise contributions from the measurement uncertainty and an estimate of the model representation error (which was taken to be equal to the monthly baseline variability), which are propagated through the inversion to each derived parameter. Since these uncertainties only represent "unbiased" or random sources of error, we then add the influence of potential biases due to the calibration scale and uncertain lifetime estimates. The uncertainty on global mean mole fractions includes the contribution of errors in the calibration scale, and uncertainties in derived emissions include contributions from the calibration scale and the lifetime uncertainty. The total uncertainty is calculated from these random and bias terms from a Monte Carlo ensemble in which each member has a perturbed value of each type of uncertainty.

4 Results and discussion

4.1 Atmospheric mole fractions

Based on the output from the 12-box model, into which AGAGE observations had been assimilated, Fig. 1 illustrates the global mean mole fractions for the four HCFCs and the four HFCs (the model output was used for "gap-filling" purposes). To compare AGAGE HCFCs results with the recent measurements reported by NOAA (Montzka et al., 2015), we list NOAA 2012 global mean mole fractions (pmol mol^{-1}) and in parentheses the corresponding AGAGE 2012 global mixing ratios: HCFC-22, 218.2 (219.4); HCFC-141b, 22.3 (22.5); and HCFC-142b, 21.5 (21.9). In addition, the Supplement includes a section on comparison of NOAA flask and AGAGE in situ HCFC measurements at common sites, which is summarised here as percentage differences (NOAA/AGAGE-1) × 100: HCFC-22, -0.3 ± 0.3 %; HCFC-141b, -0.6 ± 0.5 %; and HCFC-142b, -2.6 ± 0.5 %. These comparisons between the two independent observing networks are generally in good agreement. We also include in the Supplement the percentage difference between the model calculated mole fractions and the actual observations.

Although global mean mole fractions of HCFC-22, -141b, and -142b have increased throughout the observation period reaching 234, 24.3 and 22.4 pmol mol^{-1}, respectively in 2015, their rate of increase, shown in Fig. 2, has slowed with HCFC-22 and -142b beginning to decline in 2007–2008. HCFC-141b reached a minimum in 2005 and then increased until 2008, before starting a steep decline. HCFC-
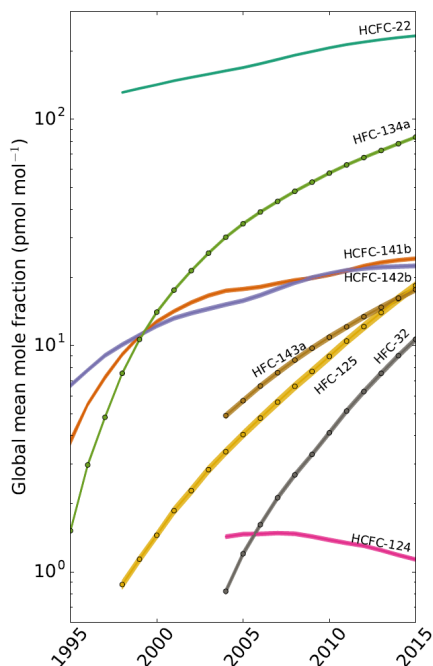
Figure 1. Illustrates the global mean mole fractions for the four HCFCs and the four HFCs discussed here (the model output was used for "gap-filling" purposes). Shading in the figure reflects the uncertainty on the mole fractions derived in the inversion and includes a contribution from random and scale-related measurement errors and modelling uncertainties (further details are provided in Rigby et al., 2014). Note that for HCFC-124, HFC-143a and HFC-32 we only use GC-MS-Medusa data for these calculations; for all others we use combined GC-MS-ADS and GC-MS-Medusa data.

124 reached a maximum global mean mole fraction of $1.48 \, \mathrm{pmol \, mol^{-1}}$ in 2007 and has since declined by 23 % to $1.14 \, \mathrm{pmol \, mol^{-1}}$ in 2015.

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

The HFCs all show increasing global mean mole fractions and growth rates over the entire period of observations. The global mean mole fractions ($\mathrm{pmol \, mol^{-1}}$) observed in 2015, in descending order of abundance, are HFC-134a (83.3), HFC-125 (18.4), HFC-143a (17.7) and HFC-32 (10.5) with
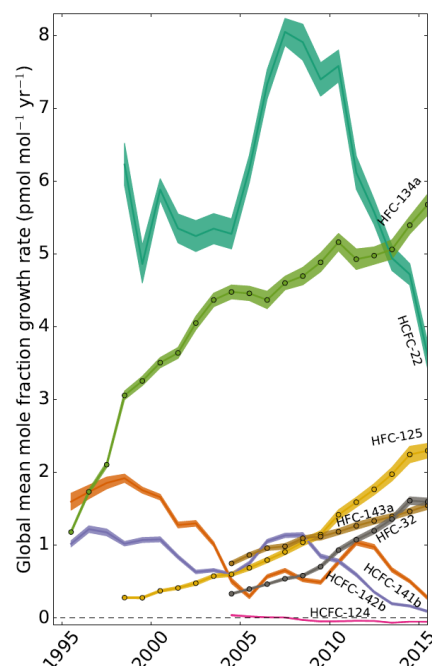

Figure 2. Average global mean mole fraction growth rates ($\mathrm{pmol \, mol^{-1} \, yr^{-1}}$) determined from the 12-box model for the HCFCs and HFCs. Note that for HCFC-124, HFC-143a and HFC-32 we only use Medusa data for these calculations; for all others we use combined GC-MS-ADS and GC-MS-Medusa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

growth rates ($\mathrm{pmol \, mol^{-1} \, yr^{-1}}$) for HFC-134a (5.6), HFC-125 (2.3), HFC-143a (1.5) and HFC-32 (1.6).

Montzka et al. (2015) reported 2012 HFC mean mole fractions ($\mathrm{pmol \, mol^{-1}}$), which we compare with our 2012 global mixing ratios in parentheses: HFC-134a, 67.5 (67.7); HFC-143a, 12.3 (13.4); HFC-125, 11.4 (12.1); and HFC-32, 5.1 (6.3). The Supplement also includes a section on comparisons of NOAA flask and AGAGE in situ HFC measurements at common sites, which is summarised here as percentage differences (NOAA/AGAGE-1) × 100: HFC-134a, 0.1 ± 0.5 %; HFC-143a, -7.7 ± 0.8 %; HFC-125, -5.4 ± 0.8 %; and HFC-32, -9 ± 2 %.

4.2　Top-down emission estimates

4.2.1　Global estimates of HCFCs

Estimated global emissions flux ($\mathrm{Gg \, yr^{-1}}$) of the HCFCs using the 12-box model (emissions listed in Supplement), the emissions calculated from consumption data reported to UNEP (2016b) (see Supplement) and EDGAR emission inventories are shown in Fig. 3a–d. The blue solid line represents our model-derived emissions, with the uncertainties shown by the shaded areas. The following HCFC global emissions estimates are updates for HCFC emissions reported in Rigby et al. (2014).
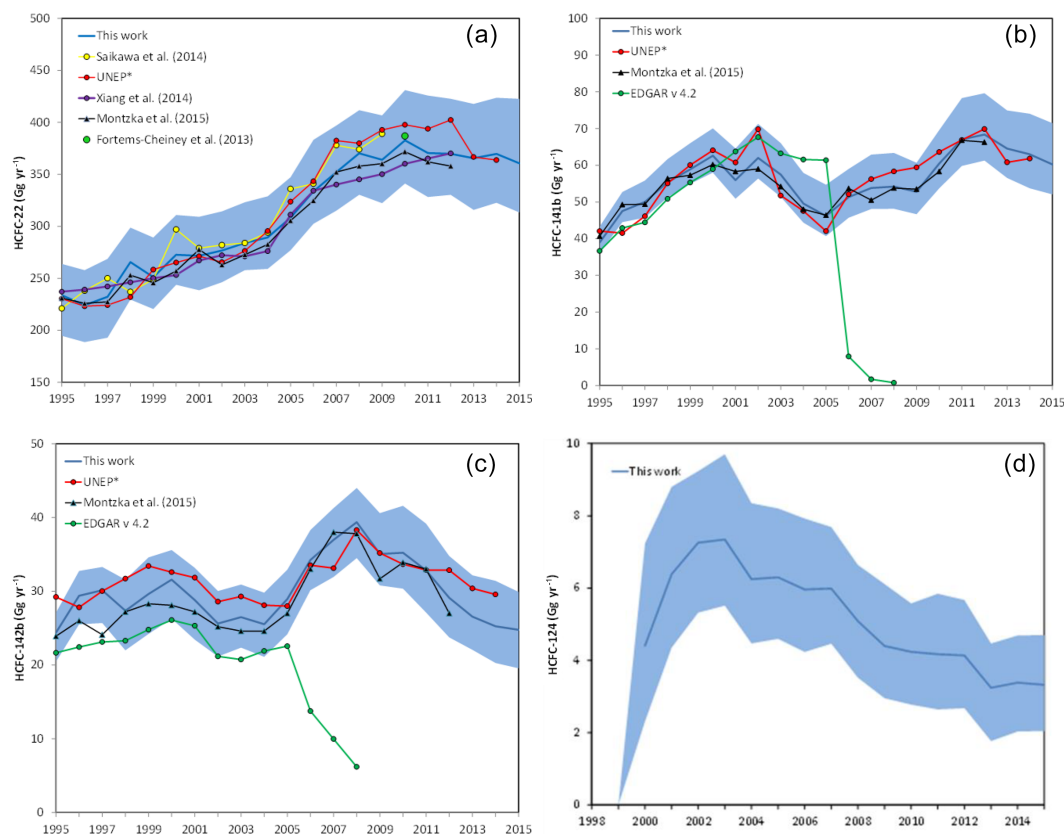
Figure 3. Global HCFC emissions ($Gg\,yr^{-1}$) from the 12-box model (solid blue line); shading represents 1σ uncertainties. Emissions calculated from UNEP data (see Supplement). EDGAR v4.2 and other works are also shown. Note that for HCFC-124 we only use GC-MS-Medusa data for these calculations; for all others we use combined GC-MS-ADS and GC-MS-Medusa data.

HCFC-22

AGAGE box-model-derived global emissions (based on atmospheric data) of HCFC-22 increased from $234 \pm 35\,Gg\,yr^{-1}$ in 1995 to a maximum of $383 \pm 45\,Gg\,yr^{-1}$ in 2010, increasing by $\sim 10\,Gg\,yr^{-1}$. Since 2010 global HCFC-22 emissions have declined by 6.6 % to $361 \pm 55\,Gg\,yr^{-1}$ in 2015. Figure 3a includes estimated emissions from UNEP consumption data (for method see Supplement) and other reported global HCFC-22 emissions estimates (Saikawa et al., 2012; Fortems-Cheiney et al., 2013; Xiang et al., 2014; Montzka et al., 2015) which all agree within the uncertainties of our estimates. It should be noted that Montzka used a three-box model with NOAA data, while Saikawa and Xiang used independent 3-D atmospheric chemistry-transport models with NOAA and AGAGE + NOAA data, respectively. Fortems-Cheiney et al. (2013), using observations from multiple networks, an inversion and a new gridded bottom-up inventory, estimated global emissions of $387 \pm 9\,Gg\,yr^{-1}$ in 2010, very close to the estimated HCFC-22 emissions derived in this study.

HCFC-141b and HCFC-142b

These two HCFCs have exhibited several fluctuations in emissions with maxima around 2000 of $63 \pm 6\,Gg\,yr^{-1}$ (HCFC-141b) and $32 \pm 5\,Gg\,yr^{-1}$ (HCFC-142b) followed by minima of $46 \pm 7\,Gg\,yr^{-1}$ (HCFC-141b) and $29 \pm 4\,Gg\,yr^{-1}$ (HCFC-142b) in 2003–2005. HCFC-141b and HCFC-142b emissions then grew rapidly to new maxima of $68 \pm 8\,Gg\,yr^{-1}$ (2012) and $39 \pm 5\,Gg\,yr^{-1}$ (2008), respectively. These trends were again reversed with subsequent declines to $60 \pm 10\,Gg\,yr^{-1}$ (HCFC-141b) and $25 \pm 5\,Gg\,yr^{-1}$ (HCFC-142b) in 2015. Montzka et al. (2015), using an independent sampling network, also provided emissions estimates for HCFC-141b and -142b, which are included in Fig. 3b and c and agree within the uncertainties with our estimates with similar fluctuations. Inventory emissions estimates reported from EDGAR v4.2 are considerably lower than all other reported emissions post-2005. Global emissions of HCFC-141b and HCFC-142b from AGAGE data have declined by 0.5 and 30 %, respectively, from 2010 to 2015. Emission calculated from UNEP consumption data are consistent, within uncertainties, with emissions calculated from atmospheric data.
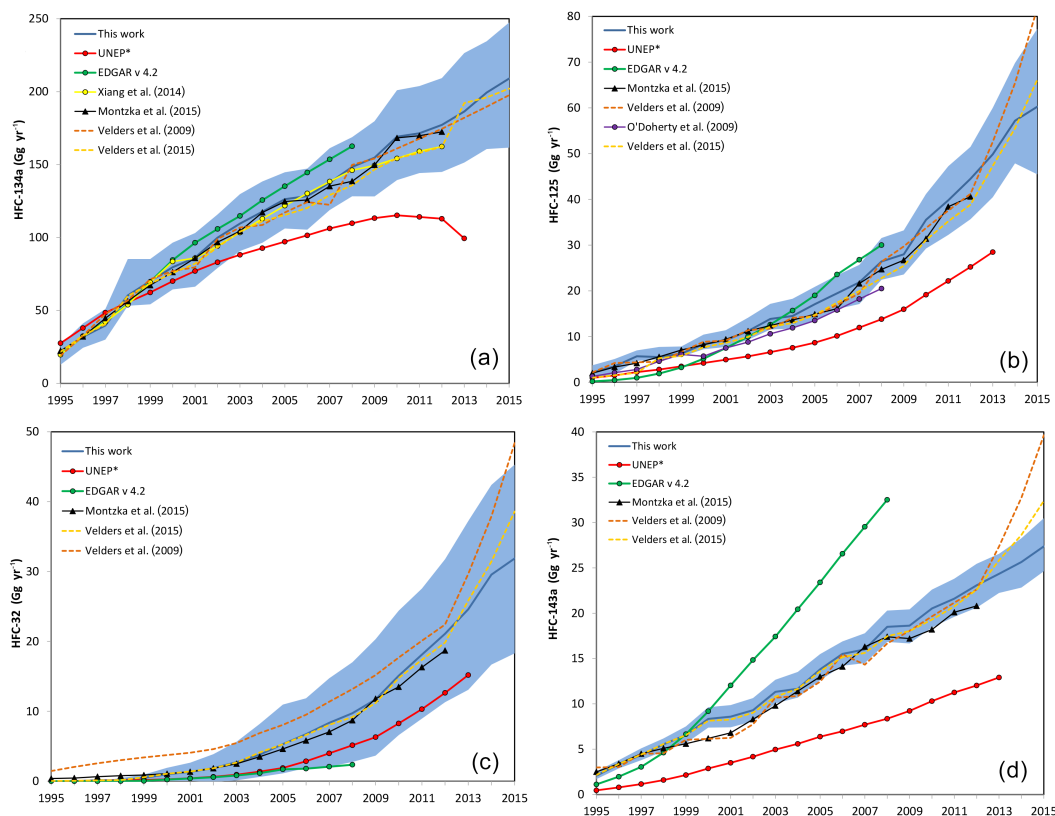
Figure 4. Global HFC emissions ($\mathrm{Gg\,yr^{-1}}$) from the 12-box model (solid blue line); shading represents 1σ uncertainties. UNFCCC* values are the aggregates of national data reported to UNFCCC (2016). Note that for HFC-143a and HFC-32 we only use Medusa data for these calculations; for all others we use combined GC-MS-ADS and GC-MS-Medusa data.

HCFC-124

Global emissions of this less abundant HCFC had a maximum in 2003 of $7.3 \pm 2.1\,\mathrm{Gg\,yr^{-1}}$, followed by a steady decline to $3.3 \pm 1.3\,\mathrm{Gg\,yr^{-1}}$ in 2015, a decrease in emissions over this 12-year time frame of 45 %. There are no bottom-up estimates of HCFC-124 emissions or top-down global estimates to compare with our results. However, we note that HCFC-124 emissions make only a minor contribution to climate change of $0.002\,\mathrm{Gt\,yr^{-1}}$ in CO_2 equivalent emissions (CO_2 eq.) in 2015.

The combined model-derived aggregated global emissions of these four HCFCs in 2015 were $449 \pm 75\,\mathrm{Gg\,yr^{-1}}$ ($0.76 \pm 0.1\,\mathrm{Gt\,yr^{-1}}\,CO_2$ eq.). We estimate that these four HCFCs contribute $55 \pm 1\,\mathrm{mW\,m^{-2}}$ to climate forcing in 2015 with HCFC-22 accounting for 79 % of this forcing.

4.2.2 Global estimates of HFCs

In contrast to the HCFCs, estimates of HFC emissions fluxes shown in Fig. 4a–d (see Supplement for actual values) have increased over the entire observational record, reaching maxima in 2015 of $209 \pm 43\,\mathrm{Gg\,yr^{-1}}$ (HFC-134a), $60 \pm 10\,\mathrm{Gg\,yr^{-1}}$ (HFC-125), $31 \pm 14\,\mathrm{Gg\,yr^{-1}}$ (HFC-32) and

$27 \pm 3.0\,\mathrm{Gg\,yr^{-1}}$ (HFC-143a). These estimates are updates for HFC-32 and HFC-143a emissions reported in O'Doherty et al. (2014) and updates for HFC emissions reported in Rigby et al. (2014). The most recent HFC emissions estimated from NOAA data (Montzka et al., 2015) are in most cases in close agreement with our emission estimates from AGAGE data and generally within our uncertainties. We include in Fig. 4b previously published HFC-125 global emissions (O'Doherty et al., 2009) increasing from $6.1\,\mathrm{Gg\,yr^{-1}}$ (1998) to $20.5\,\mathrm{Gg\,yr^{-1}}$ (2007). This compares well with our current emission estimates of 5.5 to $21.8\,\mathrm{Gg\,yr^{-1}}$ (1998–2007).

UNFCCC emission estimates (UNFCCC, 2016) which are compiled only from Annex 1 countries are consistently lower than our HFC emission estimates. This same discrepancy was noted in Lunt at al. (2015) due to the fact that many developing nations are not required to report HFC emissions and reporting methods for individual HFCs are subject to substantial inaccuracies. EDGAR v4.2 inventory emissions of HFC-143a post-2000 are substantially larger than our estimates, but the other three HFCs are in reasonable agreement (within the uncertainties of our estimates). Published HFC-134a emissions estimates by Velders et al. (2009) are in close

agreement with the results from this work. For HFC-32 the Velders et al. (2009) results agree within the uncertainties of our estimates with the exception of the early period from 1995–2002. Post-2012, Velders et al. (2009) HFC-125 and HFC-143a projections begin to diverge substantially from our emission estimates.

The combined AGAGE model-derived aggregated emissions from atmospheric observations of these four HFCs in 2015 were $327 \pm 70\,\mathrm{Gg\,yr^{-1}}$ ($0.65 \pm 0.14\,\mathrm{Gt\,yr^{-1}}\,CO_2$ eq.). We estimate that these four HFCs contribute $21.0 \pm 0.5\,\mathrm{mW\,m^{-2}}$ to radiative forcing in 2015, less than half of the combined forcing of the four HCFCs treated in this study.

4.3 Overall emissions trends

In Fig. 5, we plot individual HCFCs and HFCs in terms of CO_2 eq. emissions, noting that HCFC-22 is the largest contributor to these emissions and they have declined relatively slowly since 2010.

HCFC-141b and HCFC-142b exhibit declines in CO_2 eq. emissions after 2010, in agreement with substantial changes in emissions over time and dramatic declines in their global mean mole fraction growth rates (see Fig. 2). All of the HFCs have increasing CO_2 eq. emissions over time with HFC-125 and HFC-32 increasing most rapidly in relative terms.

Figure 6 shows the trends in CO_2 eq. emissions from 2005 to 2015 for aggregated HCFCs and HFCs, with an increase in aggregated HCFC emissions until around 2010, and subsequent reduction in CO_2 eq. emissions through 2015. HFC emissions were observed to increase throughout this period. Using 2010 as a "reference" year, we compare the relative trends in HCFC and HFC emissions and determine broadly whether the decline in HCFC emissions was being matched by the increase in HFC emissions. In order to determine a potential "business as usual" trajectory for HCFC and HFC emissions post-2010, we first assumed that emissions would continue to follow the 2005–2010 growth rates (dashed line). We also examined the potential change in emissions according to the projections of Velders et al. (2009) and Montzka and Reimann (2010). Because the studies of Velders et al. (2009, 2015) are similar over the 1995 to 2015 time frame we opted to make the comparison with the most widely quoted 2009 paper, also noting that the 2015 paper includes an assimilation of atmospheric observed abundances (Velders et al., 2015).

Each of these projections suggests a growth in HCFC emissions during this period, whereas our observation-derived HCFC estimates show a decline. Over this 5-year period, the accumulated difference between the top-down and projected emissions is -0.67, -0.71 and $-0.66\,\mathrm{Gt\,yr^{-1}}\,CO_2$ eq. (with a 1σ uncertainty 0.25 Gt for each) for the three linear projections Velders et al. (2009) and Montzka and Reimann (2010), respectively. For the HFCs, the linear projection shows lower growth than we de-
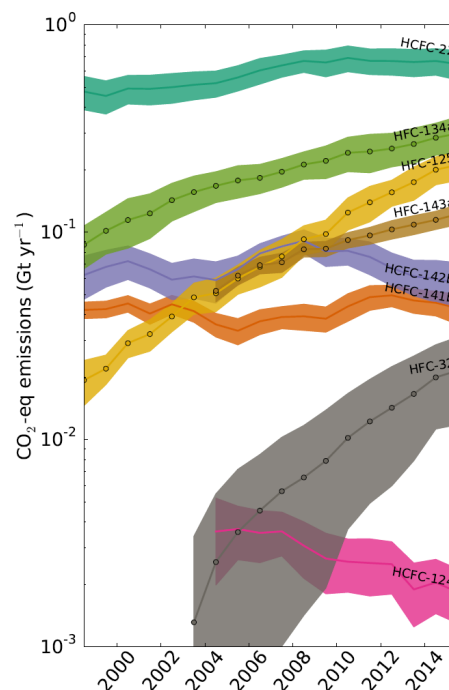

Figure 5. Individual HCFC and HFC carbon dioxide equivalent (CO_2 eq.) emissions ($\mathrm{Gt\,yr^{-1}}$) derived from the 12-box model. Shading, representing 1σ uncertainties. Note that for HCFC-124, HFC-143a and HFC-32 we only use GC-MS-Medusa data for these calculations; for all others we use combined GC-MS-ADS and GC-MS-Medusa data.
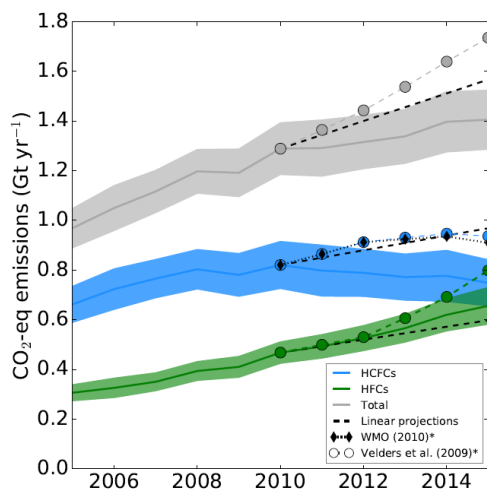
rive from AGAGE data, with an accumulated 5-year difference of $0.12 \pm 0.15\,\mathrm{Gt\,yr^{-1}}\,CO_2$ eq. However, the Velders et al. (2009) emissions projection exhibits more rapid growth than the AGAGE estimates, leading to a difference of $-0.27 \pm 0.15\,\mathrm{Gt\,yr^{-1}}\,CO_2$ eq. When considered together, we find that the growth in HFC and HCFC emissions has been slower than these post-2010 projections by an accumulated total of -0.55 ± 0.29 and $-0.97 \pm 0.29\,\mathrm{Gt\,yr^{-1}}\,CO_2$ eq. for the linear projection and Velders et al. (2009), respectively.

In Table 3, we compare the cumulative emissions of the four HCFCs and the four HFCs over two 5-year periods, 2006–2010 and 2011–2015. From the percentage change in emissions between the two periods we note that HCFC-141b emissions have increased by 18 % and HCFC-22 by 1.7 %. In comparison HCFC-142b and -124 emissions have decreased by 23 and 30 %, respectively. Aggregating the four HCFCs we observe that there is an equal contribution of $3.9\,\mathrm{Gt}\,CO_2$ eq. over the two 5-year periods, implying a stabilisation of the cumulative emissions.

Conversely, global emissions of the HFCs have grown continuously throughout the period of observations with substantial increases between the two 5-year periods. The largest increases in relative terms were observed for HFC-32 (143 %) and HFC-125 (92 %) with smaller increases for HFC-143a (37 %) and HFC-134a (28 %). In terms of the

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

HCFCs	2015 Emissions (Gg yr^{-1})	2006–2010 HCFCs Cumulative emissions (Gg) and CO$_2$ eq. emissions (Gt CO$_2$ eq.)	2011–2015 HCFCs Cumulative emissions (Gg) and CO$_2$ eq. emissions (Gt CO$_2$ eq.)	% Change in cumulative emissions between 2006–2010 and 2011–2015
22	360.6 ± 58.1	1802.0 (3.26)	1833.2 (3.32)	1.7
141b	60.2 ± 9.8	272.5 (0.20)	322.4 (0.23)	18.3
142b	24.8 ± 6.3	180.8 (0.42)	138.9 (0.32)	-23.2
124	3.3 ± 0.89	25.4 (0.02)	17.8 (0.01)	-29.9
Total	448.8	2281 (3.9)	2312 (3.9)	1.4
HFCs	2015 Emissions (Gg yr^{-1})	2006–2010 HFCs Cumulative emissions (Gg) and CO$_2$ eq. emissions (Gt CO$_2$ eq.)	2011–2015 HFCs Cumulative emissions (Gg) and CO$_2$ eq. emissions (Gt CO$_2$ eq.)	% Change in cumulative emissions between 2006–2010 and 2011–2015
125	59.7 ± 9.5	131.3 (0.46)	251.2 (0.88)	91.7
134a	209.0 ± 42.9	736.6 (1.05)	943.8 (1.35)	28.1
143a	27.4 ± 3.0	89.2 (0.4)	122.0 (0.55)	36.9
32	31.2 ± 14.4	51.6 (0.04)	125.2 (0.09)	142.7
Total	327.3	1009 (1.9)	1442 (2.9)	43

Figure 6. Aggregated HCFC and HFC emissions as CO$_2$ eq. (Gt yr^{-1}) solid blue and green lines, respectively; shading represents 1σ uncertainties. The grey line and shading represents the total HCFC and HFC CO$_2$ eq. emissions. The thick black dashed line is a linear projection from 2010 to 2015, based on the 2005–2010 emissions growth rate. * The thin dashed lines with the circular data points are the Velders et al. (2009) projection and the dashed line with the diamonds show the same but for HCFC emissions projections (Montzka and Reimann, 2010). We have adjusted the start date of the Velders et al. (2009) emission trends to 2010 in alignment with the observationally derived value.

aggregated HFC emissions we see a 43 % increase representing a rise from 1.95 to 2.87 Gt CO$_2$ eq., or an additional 0.92 Gt CO$_2$ eq. between the two periods.

It is also apparent that emissions of HCFC-22 represent ∼ 79 % of the global cumulative HCFC burden during 2011–2015 and HCFC-22 alone contributes 0.45 Gt CO$_2$ eq. (13.5 %), more than all HFC cumulative emissions during 2011–2015.

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 fully until 2040. As noted in Fig. 2, the HCFCs show decreasing rates of growth with HCFC-142b declining by ∼ 93 % from 2007–2015, HCFC-141b by 53 % and HCFC-22 by 54 %, in agreement with the 2004 production and consumption cap and reduction targets of 75 % by 2010 and 90 % by 2015 for non-Article 5 countries. This is reflected in the aggregated HCFC global CO$_2$ eq. emissions (shown as in Fig. 6) exhibiting a small but steady decline from 2010 to 2015. In spite of the 2013 cap on emissive uses and a reduction target of 10 % by 2015 for Article 5 countries, the pace of decline driven by the phase-out in non-Article 5 countries has to some extent been moderated by the increased emissions of HCFC-22 and HCFC-141b in Article 5 countries (Carpenter et al., 2014). 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

are replacing HCFCs, their aggregated emissions in 2015 of 327 Gg yr^{-1} have not yet reached the total HCFC aggregated emissions of 449 Gg yr^{-1} (see Table 3).

Although there has been a shift in developed countries (non-Article 5) from HCFCs to 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 (Wan et al., 2009; Li et al., 2011, 2014; Fang et al., 2012, 2016; Yao et al., 2012; Zhang and Wang, 2014; Su et al., 2015; Velders et al., 2015). There has been a trend in recent years to move to refrigerant blends with lower GWPs, and in Japan in 2014 residential air conditioners were switched to using HFC-32 (UNEP, 2016c).

HFC-134a, -125, -143a and -32 are the principal components of all alternative substitutes for HCFCs. In the Supplement we examine the composition of the main refrigerant blends to determine whether there is evidence for a significant use of single-component refrigerants. In general, we find that the atmospheric mole fractions of HFC-32, -125, and -143a are consistent with their release predominantly from blends.

5　Conclusions

This study confirms that the Montreal Protocol and its amendments have been effective in slowing the atmospheric accumulation of the HCFCs. If there had been no change in the emissions growth rate post-2010, we find that, based on a linear projection of emissions pre-2010, there would have been an additional 0.67 ± 0.24 Gt CO_2 eq. of aggregated HCFCs (-22, -141b, -142b) emitted to the atmosphere from 2010 to 2015. This compares favourably with the forward projections of "business as usual" scenarios in the Velders et al. (2009) and Montzka and Reimann (2010) of an additional 0.71 ± 0.25 and 0.66 ± 0.24 Gt CO_2 eq., respectively, of total HCFCs that would have been emitted during this same period.

We calculate that the aggregated cumulative emissions of HCFC-22, -141b, -142b, and -124 during the most recent 5-year period (2011–2015) are only slightly larger than in the previous 5 years (2006–2010). This modest increase has most likely been driven by the emissions of HCFC-22 and -141b in Article 5 countries, offsetting the emission declines in non-Article 5 countries, suggesting that cumulative HCFCs emissions have recently stabilised. As shown in Fig. 2, the HCFC-22 growth rate has steadily declined since the introduction of the 2007 adjustment to the Montreal Protocol, yet global emissions have tended to remain approximately constant with only a modest decline in emissions post-2007 (see Fig. 5). Since we are only 2 years beyond the 2013 cap on emissive uses of HCFCs for non-Article 5 countries, it is probably too early for our current observations through 2015 to show an accelerating phase-out for all

HCFCs, although HCFC-142b and -124 have both recently undergone substantial declines in global emissions.

Although global emissions of HFCs have increased throughout the course of this study, Montzka et al. (2015) suggested that there may have been a shift to lower GWP refrigerant blends which can account for the observed emissions. It is also noteworthy that the two HFCs with the largest percentage changes in emissions in recent years are HFC-125 and -32 (see Table 3), which implies a trend towards blends containing these two refrigerants. However, we are unable to confirm the extent to which other lower-GWP blends (e.g., R-410A) have been substituted for R-404A and R-507A with the possibility that there has simply been a switch from one blend to another with similar GWPs. In terms of CO_2 eq., HCFC-22 emissions alone contribute 0.45 Gt CO_2 eq., about 14 % more to climate change than the four aggregated HFCs during 2011–2015. This could potentially be attributed to the continuing use of HCFC-22 in existing refrigeration equipment with the consequence of large slowly leaking banks. HCFC-22 represents about 79 % of total global HCFC emissions.

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

We find that the increase in HFC emissions from 2010 to 2015 has been more rapid than the linear projection of growth, shown in Fig. 6, would imply. This may provide some insight into the relative phase-in of HFCs and phase-out of HCFCs. Compared to this linear trend, the cumulative excess of HFCs emissions during this period is 0.12 ± 0.15 Gt CO_2 eq., which is smaller than the deficit of $(-0.67 \pm 0.24$ Gt CO_2 eq.) in HCFCs over the same time frame. This suggests that the phase-out in HCFCs post-2010 has not coincided with an equivalent increase in HFC emissions in CO_2 eq. terms. Compared to alternative projections by Velders et al. (2009, 2015), our top-down estimates show a much more rapid decline in emissions of HCFCs and a slower increase in HFC emissions. Therefore, similarly to our linear projection, where Velders et al. (2009) predicted a relatively steady growth in CO_2 eq. emissions due to HCFCs and HFCs from 2005 to 2015, we find an overall slowing of emissions post-2010.

Finally we note that national regulations to limit HFC use are already in place in the European Union, Japan and the

USA, and recently there has been an agreement to amend the Montreal Protocol to further restrict HFC use beginning in 2019 (28th meeting of the Parties to the Montreal Protocol, Kigali, Rwanda, October 2016). By including HFCs, which do not deplete ozone, into the Montreal Protocol, this has the benefit of regulating production and consumption rather than emissions as by the Kyoto Protocol.

The Supplement related to this article is available online at doi:10.5194/acp-17-4641-2017-supplement.

Competing interests. The authors declare that they have no conflict of interest.

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