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Global emissions of HFC-143a (CH₃CF₃) and HFC-32 (CH₂F₂) from in situ and air archive atmospheric observations

S. O'Doherty¹, M. Rigby¹, J. Mühle², D. J. Ivy³, B. R. Miller^{4,5}, D. Young¹, P. G. Simmonds¹, S. Reimann⁶, M. K. Vollmer⁶, P. B. Krummel⁷, P. J. Fraser⁷, L. P. Steele⁷, B. Dunse⁷, P. K. Salameh², C. M. Harth², T. Arnold², R. F. Weiss², J. Kim², S. Park⁸, S. Li⁹, C. Lunder¹⁰, O. Hermansen¹⁰, N. Schmidbauer¹⁰, L. X. Zhou¹¹, B. Yao¹¹, R. H. J. Wang¹², A. J. Manning¹³, and R. G. Prinn³

¹Atmospheric Chemistry Research Group, University of Bristol, Bristol BS8 1TS, UK

²Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California, USA

³Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA

⁴Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Colorado, USA

⁵Global Monitoring Division, ESRL, NOAA, Boulder, Colorado, USA

⁶Laboratory for Air Pollution and Environmental Technology, Swiss Federal Laboratories for Materials Testing and Research (Empa), Dübendorf, Switzerland

⁷Centre for Australian Weather and Climate Research, CSIRO Marine and Atmospheric Research, Aspendale, Victoria, Australia

⁸Department of Oceanography, Kungpook National University, Sangju, South Korea

⁹Research Institute of Oceanography, Seoul National University, Seoul, South Korea

¹⁰Norwegian Institute for Air Research (NILU), Kjeller, Norway

¹¹Chinese Academy of Meteorological Sciences (CAMS), Beijing, China

¹²School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA

¹³UK Meteorological Office, Exeter, UK

Correspondence to: S. O'Doherty (s.odoherty@bristol.co.uk)

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Abstract. High-frequency, in situ observations from the Advanced Global Atmospheric Gases Experiment (AGAGE), for the period 2003 to 2012, combined with archive flask measurements dating back to 1977, have been used to capture the rapid growth of HFC-143a (CH₃CF₃) and HFC-32 (CH₂F₂) mole fractions and emissions into the atmosphere. Here we report the first in situ global measurements of these two gases. HFC-143a and HFC-32 are the third and sixth most abundant hydrofluorocarbons (HFCs) respectively and they currently make an appreciable contribution to the HFCs in terms of atmospheric radiative forcing (1.7 ± 0.04 and 0.7 ± 0.02 mW m⁻² in 2012 respectively). In 2012 the global average mole fraction of HFC-143a was 13.4 ± 0.3 ppt (1σ) in the lower troposphere and its growth rate was 1.4 ± 0.04 ppt yr⁻¹; HFC-32 had a global

mean mole fraction of 6.2 ± 0.2 ppt and a growth rate of 1.1 ± 0.04 ppt yr⁻¹ in 2012. The extensive observations presented in this work have been combined with an atmospheric transport model to simulate global atmospheric abundances and derive global emission estimates. It is estimated that 23 ± 3 Gg yr⁻¹ of HFC-143a and 21 ± 11 Gg yr⁻¹ of HFC-32 were emitted globally in 2012, and the emission rates are estimated to be increasing by 7 ± 5 % yr⁻¹ for HFC-143a and 14 ± 11 % yr⁻¹ for HFC-32.

1 Introduction

Hydrofluorocarbons (HFCs) were developed as replacements for ozone-depleting chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), which have mainly been used as working fluids in refrigerators and air conditioners, as blowing agents and active insulating component in plastic foams, as aerosol propellants and as fire retardants. The timescales over which HFC emissions to the atmosphere take place vary widely, depending on the application. For example, HFCs used as aerosol propellants results in prompt release, whereas when used as blowing agents for one-component foams (where the blowing agent is not encapsulated into the foam), release occurs over a period of the order of 2 years (McCulloch et al., 2009). The predominant use of HFCs is in air conditioning and refrigeration. Here the emissions are more complex and variable during the lifetime of the equipment and can be characterised during three phases of their use: when the equipment is first filled (losses less than 1%), during operation and servicing (0–30% yr⁻¹ depending on whether hermetically sealed or not) and finally when the equipment is scrapped (although recovery, reuse and destruction are now more commonplace than in the 1990s, when the remaining refrigerant would have been released into the atmosphere upon disposal) (McCulloch et al., 2009).

HFCs are partially fluorinated hydrocarbons that have atmospheric lifetimes in the range of 1–50 years (with the exception of HFC-23 and HFC-236fa, which have lifetimes of 222 and 242 years respectively) and are removed from the atmosphere through reaction with tropospheric hydroxyl radicals (Ko et al., 2013; Forster et al., 2007). They are chlorine-free, and as such have effectively zero stratospheric ozone depletion potential and therefore are not yet included in the Montreal Protocol and its subsequent amendments. However, there is concern about the accumulation of HFCs in the atmosphere, mainly because of their high global warming potentials (GWPs). Most HFCs currently used have relatively long atmospheric lifetimes and GWPs in excess of 1000, and are sometimes referred to as “high-GWP HFCs” (Velders et al., 2014). National HFC data are submitted to the United Nations Framework Convention on Climate Change (UNFCCC) under the Rio Convention and Kyoto Protocol, and countries that have ratified the Kyoto Protocol (Annex I parties or developed countries and economies in transition) have committed over a short timescale (2008–2012) to reduce their emissions of greenhouse gases. Signatories to the Protocol used emissions trading to meet their emissions commitments. However, countries that did not ratify the Kyoto Protocol (non-Annex I or developing countries and the USA) were not required to submit national HFC data, although some such as the USA do. It has been suggested that the total GWP-weighted HFC emissions for baseline scenarios in 2050 will be ~4 times larger than those previously reported in the Intergovernmental Panel on Climate Change (IPCC) Special

Report on Emissions Scenarios (SRES, 2000). This discrepancy is thought to be primarily due to sustained growth in demand for refrigeration, air conditioning and insulating foam products in non-reporting developing countries (Velders et al., 2009). In 2011 at the Durban climate negotiations, it was decided that new climate commitments will come into effect from 2020 onwards, leaving the years up to this date free from any legally binding global measures (Velders et al., 2012). The 2012 Doha Amendment to the Kyoto Protocol included new commitments for Article 5 countries, which agreed to take on commitments, in a second period from 1 January 2013 to 31 December 2020. This amendment was adopted but has not yet entered into force. A number of nations have also expressed interest in applying HFC emissions control under an amended Montreal Protocol. However, these proposals have not yet been adopted, resulting in a very uncertain outlook in terms of climate effects from emissions of HFCs. The use of global atmospheric observations with atmospheric transport models has been shown to provide an independent and effective method of assessing the accuracy of globally and regionally aggregated reductions or increases in emissions of individual greenhouse gases compiled from national reports to the UNFCCC (O'Doherty et al., 2009; Montzka et al., 2010; Miller et al., 2011; Vollmer et al., 2011; Miller et al., 2012; Rigby et al., 2013; Fang et al., 2014). These techniques have recently been applied to global observations of HFCs in general (Rigby et al., 2014) but not used to explore the individual global estimates of HFC-143a (CH₃CF₃) and HFC-32 (CH₂F₂).

HFC-143a is mainly used as a working fluid component in refrigerant blends R404A (52% HFC-143a, 44% HFC-125 and 4% HFC-134a by weight) and R-507A (an azeotropic blend of 50% HFC-125 and 50% HFC-143a) for low- and medium-temperature commercial refrigeration systems, replacing R-502 (a blend containing HCFC-22 and CFC-115) (Velders et al., 2009). Other minor uses are in R-408A, R-427A and R-428A as replacements for R-502 and HCFC-22. The first reported atmospheric measurements of HFC-143a were made using flask samples by Culbertson et al. (2000) from air samples collected in Montana, USA, where they determined a mole fraction of HFC-143a of 3.2 ± 0.3 ppt. Measurement and analysis of archived air samples collected at Cape Meares, Oregon, from 1978 to 1997; at Point Barrow, Alaska, from 1995 to 1998; and at Palmer Station, Antarctica, from 1991 to 1997 allowed for the atmospheric accumulation of HFC-143a to be determined for the first time (Culbertson et al., 2004). The Oregon samples showed an increase from about 0.2 ppt in 1978 to 2.0 ppt in 1997. Its growth rate increased to 0.04 ppt yr⁻¹ between 1984 and 1992, then between 1993 and 1997 the growth rate further increased to a level of 0.45 ppt yr⁻¹ (~80% yr⁻¹), reaching a level of 1.9 ppt in the atmosphere by 1997. The rapid growth coupled with significant differences in mole fraction measured at Alaska and Antarctica suggested rapidly increasing emissions of this compound in the Northern Hemisphere. In

situ measurements at Mace Head, Ireland, indicated an average mole fraction of 5.5 ppt in 2004, with a growth rate of 0.9 ppt yr^{-1} ($16 \% \text{ yr}^{-1}$) (Greally et al., 2005). More recent measurements from the Advanced Global Atmospheric Gases Experiment (AGAGE) network show an increase to 8.5 ppt in 2008 with a growth rate of 1.0 ppt yr^{-1} ($13 \% \text{ yr}^{-1}$) (Montzka et al., 2011). Regional studies by Li et al. (2011) and Miller et al. (2012) have used observational data to investigate mole fraction and emission increases in East Asia and the US respectively.

HFC-143a has a significant radiative forcing value of 1.9 mW m^{-2} in 2008 (third largest of all the HFCs) (Myhre et al., 2013), with a GWP of 4800 integrated over 100 years (Myhre et al., 2013) and an estimated atmospheric lifetime of 51 years (Ko et al., 2013). It is removed from the atmosphere predominantly by gas-phase reaction with hydroxyl radicals (OH), reaction rate $1.1 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$, (Sander et al., 2006). The degradation products resulting from this reaction ($\text{CF}_3\text{C}(\text{O})\text{H}$, CF_3OH , $\text{C}(\text{O})\text{F}_2$ and CO_2) are all expected to be removed from the atmosphere to varying degrees by incorporation into rain–sea–cloud water, where hydrolysis will take place. It is also possible that photolysis of $\text{CF}_3\text{C}(\text{O})\text{H}$ in air might produce CF_3H , which is a potent greenhouse gas with an atmospheric lifetime of approximately 10 times that of HFC-143a (Wallington et al., 1994). HFC-143a does not absorb UV radiation in either the troposphere or the stratosphere and has no significant oceanic or rainout loss (due to its low water solubility) (Orkin et al., 1996).

HFC-32 is used in air conditioning and refrigeration applications; R-410A is an azeotropic mixture (50 % HFC-32, 50 % HFC-125 by weight) and R-407C (23 % HFC-32, 52 % HFC-134a, 25 % HFC-125 by weight), replacing HCFC-22. As the phase-out of HCFC-22 gains momentum, it might be expected that demand for these refrigerant blends will increase. The first reported measurements of this gas were by Greally et al. (2005), from in situ AGAGE measurements at Mace Head, Ireland, in 2004. The measurements indicated an average mole fraction of about 0.7 ppt in 2004, with two periods of growth, $43 \% \text{ yr}^{-1}$ growth in the first half of the year followed by accelerated growth of $86 \% \text{ yr}^{-1}$ in the latter half of the year. More recent measurements from the AGAGE network show an average mole fraction of 2.7 ppt in 2008 with a growth rate of 0.6 ppt yr^{-1} ($26 \% \text{ yr}^{-1}$) (Montzka et al., 2011).

HFC-32 has a GWP of 677 integrated over a 100-year time horizon, a value appreciably lower than that of HFC-143a (Myhre et al., 2013). The radiative forcing of HFC-32 was estimated to be 0.5 mW m^{-2} (Myhre et al., 2013). It has an estimated atmospheric lifetime of 5.1 years (Ko et al., 2013) and, similar to HFC-143a, is removed from the atmosphere by gas-phase reaction with OH. The degradation product resulting from this reaction is carbonyl fluoride (COF_2), with a reaction rate of $1.7 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (Sander et al., 2006).

Table 1. Overview of AGAGE measurement stations, their coordinates and periods for which data are available.

Station	Latitude	Longitude	Data* HFC-32	Data* HFC-143a
Zeppelin	78.5	11.5	Sep 2010	Sep 2010
Mace Head	53.3	−9.9	Jan 2004	Nov 2003
Jungfrauoch	46.5	8.0	May 2004	Apr 2008
Trinidad Head	41.0	−124.1	Mar 2005	Mar 2005
Shangdianzi	40.4	117.7	May 2010	May 2010
Gosan	33.3	126.2	Nov 2007	Nov 2007
Ragged Point	13.2	−59.4	May 2005	May 2005
Cape Matatula	−14.2	−170.6	May 2006	May 2006
Cape Grim	−40.7	144.7	Jan 2004	Jan 2004

*Start of data record for each compound.

In this paper we report HFC-32 and HFC-143a measurements of archived air samples collected at Cape Grim, Tasmania, and NH archived air samples mostly collected at Trinidad Head, California, along with modern ambient measurements from the Advanced Global Atmospheric Gases Experiment (AGAGE; Prinn et al., 2000). We then use these data and a two-dimensional chemical transport model to derive annual hemispheric and global emission rates for HFC-143a from 1981 to 2012 and HFC-32 from 1997 to 2012. The derived global emissions are compared to the Emissions Database for Global Atmospheric Research (EDGAR v4, JRC/PBL, 2009) and national submissions to the UN-FCCC.

2 Experimental methods

2.1 Instrumentation and calibration

High-frequency, in situ measurements of HFC-143a and HFC-32 were obtained using gas chromatography (GC, Agilent 6890) with quadrupole mass selective detection (MSD, Agilent 5973) coupled to the Medusa, an automated pre-concentration system (Miller et al., 2008; Arnold et al., 2012). Medusa systems were installed at all AGAGE stations between 2003 and 2010, and routine ambient measurements of HFC-143a and HFC-32 commenced at each station on a time frame detailed in Table 1.

Analysis of each 2 L sample of ambient air was alternated with analysis of a 2 L reference gas to determine and correct for short-term instrumental drift, resulting in 12 individually calibrated air samples per day. The measurements at each AGAGE site are reported relative to the SIO-2007 gravimetric calibration scale (as dry gas mole fractions in pmol mol^{-1}). The SIO-2007 scale is based on five stable primary calibration standards in zero air with prepared values of 5–6 ppt, each containing ~ 20 Torr water vapour. Repeated measurements indicated that the relative standard deviation of the scale was 0.56 % (HFC-143a) and 0.49 % (HFC-32).

The estimated absolute accuracy of the calibration scale for both compounds is $\sim 2\text{--}3\%$. A more detailed discussion of the measurement technique and calibration procedure is reported elsewhere (Mühle et al., 2010; O'Doherty et al., 2009; Miller et al., 2008).

HFC-143a was detected using the MSD in selected ion monitoring mode (SIM) with a target ion, CH_3CF_2^+ (m/z 65), and qualifier ion, CH_2CF_2^+ (m/z 64). HFC-32 was detected using a target ion, CH_2F^+ (m/z 33), and a qualifier ion, CHF_2^+ (m/z 51). The ratios of the target ion to qualifier ions were monitored to ensure that potential interferences from co-eluting species did not affect the analysis. Working standards were prepared for each AGAGE station by compressing ambient air into 34 L electropolished stainless steel canisters (Essex Cryogenics, Missouri, USA) using a modified oil-free compressor (SA-3, RIX, California, USA). An exception to this was the Cape Grim station, where the working standards were filled using a cryogenic filling technique. Working standards were filled to 50–60 bar and had a working life of approximately 2 months. Such a rapid turnaround of working standards resulted in minimal sampling and detector non-linearity issues since the ambient mole fractions and working standard mole fractions were very similar. Measurement precision (1σ) was determined as one standard deviation of the ratio of each standard response to the average of the closest in time preceding and subsequent standard responses. The typical daily precision for each standard varies with respect to mole fraction, at the 5–6 ppt level it was calculated to be 0.10 ppt. The daily precision value was used to estimate the precision of the in situ measurements. The analytical systems showed no sign of blanks and were determined to be linear over the 0.3–5 ppt and 0.2–7 ppt range for HFC-143a and HFC-32 respectively

2.2 Northern and southern archived air samples

In order to extend the atmospheric history of HFC-143a and HFC-32 back before the commencement of high-frequency measurements, analysis of Northern Hemisphere (NH) and Southern Hemispheric (SH) archived air samples was carried out using Medusa GC-MS instruments at the Scripps Institution of Oceanography (SIO), La Jolla, California, and at the Commonwealth Scientific and Industrial Research Organisation (CSIRO), Aspendale, Australia, respectively. The SH archive samples are part of the Cape Grim Air Archive (CGAA: 1978–present, filled cryogenically into electropolished stainless steel containers during background conditions) (Langenfelds et al., 1996; Krummel et al., 2007), CGAA samples dated between 1978 and 2006 were analysed for HFC-143a, and between 1997 and 2010 for HFC-32. The NH samples were filled during background conditions using several sampling techniques and provided by a variety of laboratories (Mühle et al., 2010); these samples were filled between 1977 and 2010 for HFC-143a and between 1998 and 2009 for HFC-32. The archived samples were analysed in

replicate, typically 2–4 times each. Non-linearity data were collected before, during and after the analysis periods, and frequent inclusion of blank runs allowed for blank corrections to be applied where needed. The resulting uncertainty due to the blank level variability was negligible in comparison to the overall precision. Further, no significant blank levels stemming from the tanks (Essex Cryogenics) or pressure regulators (Valin Corporation) were observed.

In addition, SH samples filled between 1995 and 2005, measured at SIO were all in good agreement with the SH samples of similar age measured at CSIRO (% mole fraction differences $\Delta\chi = 1\text{--}6\%$ for HFC-143a, $n = 7$; $\Delta\chi = 0.8\text{--}1.2\%$ for HFC-32, $n = 6$; and sample filling time differences $\Delta t = 3\text{--}45$ days). The good agreement for samples from 1995 to 2005 between SIO and CSIRO stored in different types of tanks (stainless steel tanks, Essex Cryogenics, and Silcosteel-treated tanks, Restek Corporation) serves both as confirmation of the good agreement of the two Medusa systems and the integrity of the archive tanks.

3 Modelling studies

To estimate global-average mole fractions, derive growth rates and infer emissions, 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°N , 0°N and 30°S) and at three heights (vertical divisions at 500 and 200 hPa). The model was originally developed by Cunnold et al. (1983) (nine-box version), with subsequent improvements by Cunnold et al. (1994) and Rigby et al. (2013). Model eddy diffusion parameters and OH concentrations were prescribed, based on the values derived in the CFC (for transport) and CH_3CCl_3 (for OH concentrations) inversions of Rigby et al. (2013).

Emissions were estimated using a Bayesian inverse method (Rigby et al., 2011, 2013, 2014), in which a priori estimates of the emissions growth rate was adjusted to bring the simulated mole fractions into agreement with the AGAGE observations. “Bottom-up” emissions estimates were taken from the Emissions Database for Global Atmospheric Research (EDGAR v4.2), a database that stores global emission inventories of anthropogenic GHGs on a country, region and grid basis. Based on the discrepancy between these estimates and the UNFCCC emissions reports, a 30 % uncertainty was assumed on the annual a priori emissions growth rates. Emissions were estimated seasonally for each year in each semi-hemisphere. The a priori latitudinal distribution of emissions was based on the EDGAR gridded global distribution, and we assumed a 100 % uncertainty on the latitudinal emissions gradient. Uncertainty in the a posteriori emissions estimates include contributions from the measurement and modelling uncertainty, as well as uncertainties in the atmospheric lifetimes and measurement calibration scale (Rigby et al., 2014).

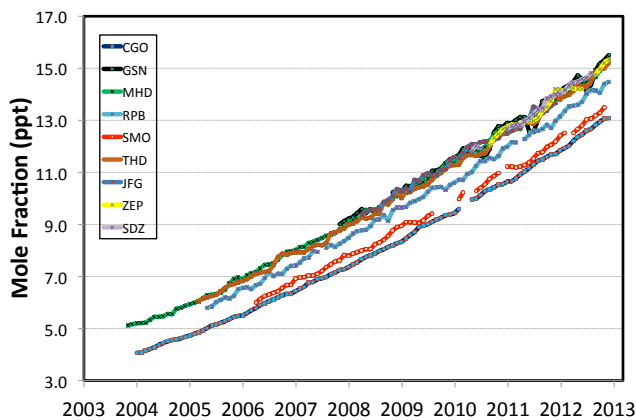


Figure 1. Baseline monthly mean HFC-143a mole fractions (ppt) from in situ Medusa GC-MS measurements at AGAGE stations: Cape Grim Observatory (CGO), Gosan (GSN), Mace Head (MHD), Ragged Point (RPB), Samoa (SMO), Trinidad Head (THD), Jungfraujoch (JFG), Zeppelin (ZEP) and Shangdianzi (SDZ).

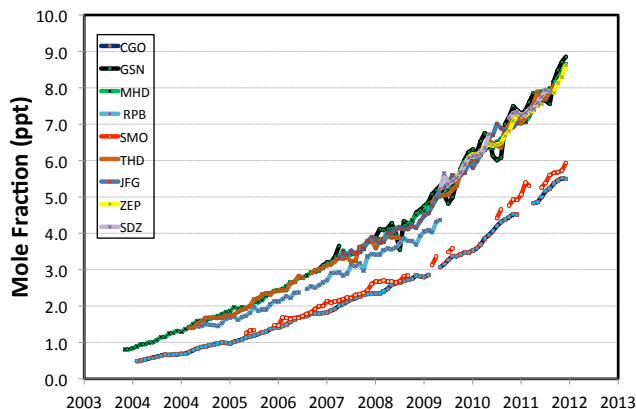


Figure 2. Baseline monthly mean HFC-32 mole fractions (ppt) from in situ Medusa GC-MS measurements at AGAGE stations: Cape Grim Observatory (CGO), Gosan (GSN), Mace Head (MHD), Ragged Point (RPB), Samoa (SMO), Trinidad Head (THD), Jungfraujoch (JFG), Zeppelin (ZEP) and Shangdianzi (SDZ).

4 Results and discussion

4.1 Atmospheric trends

The atmospheric records of HFC-143a and HFC-32, derived from the nine measurement sites are shown in Figs. 1 and 2. Baseline monthly mean values (expressed as dry gas mole fractions in ppt, or pmol mol^{-1}) were calculated by removing regional pollution effects using the AGAGE pollution identification algorithm, as described in Cunnold et al. (2002).

A large increase in baseline mole fractions at all the AGAGE sites is evident. The results indicate rapid growth of HFC-143a in the atmosphere. Furthermore, the observations show that the growth rate has been increasing throughout this time period. The globally averaged mole fraction in the

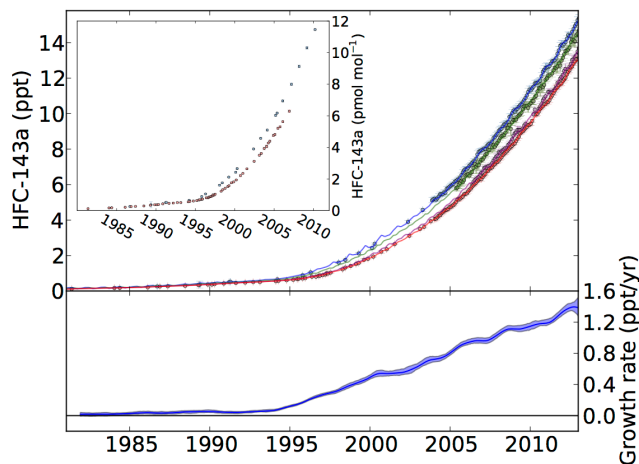


Figure 3. Semi-hemispheric monthly average HFC-143a mole fractions ($30\text{--}90^\circ\text{N}$: blue; $0\text{--}30^\circ\text{N}$: green; $30\text{--}0^\circ\text{S}$: purple; $90\text{--}30^\circ\text{S}$: red). Averaged observations are shown as data points with error bars. The more sparse circles represent NH and SH air archive samples, and are highlighted in the inset box. The solid trend lines were calculated using a 12-box model with emissions from the inversion as input. The lower plot shows the annual running mean global mole fraction growth rate.

lower troposphere in 2012 is estimated to be 13.4 ± 0.3 ppt. The growth rate was calculated from the optimised model-derived global mean mole fractions. Monthly global growth rates were smoothed using a Kolmogorov–Zurbenko filter with a 0.7-year smoothing window and four filter passes, leading to an effective smoothing window of 1.4 years. The main growth rate centred on July 2012 for HFC-143a was 1.4 ± 0.04 ppt yr^{-1} . The atmospheric histories of both compounds have been extended back before high-frequency measurements became available, using analysis of NH and SH flask samples, as detailed in Sect. 2.2. Figures 3 and 4 show the high-frequency baseline monthly means for measurements averaged into latitude bands combined with flask measurements extending the data record back to 1977 and 1997 for HFC-143a and HFC-32 respectively. The figures also show the 12-box model fits to the atmospheric measurements, illustrated by the solid lines, and show the growth rates in ppt yr^{-1} . The radiative forcing due to HFC-143a estimated using the global average mole fraction obtained from the AGAGE 12-box model was 1.7 ± 0.04 mW m^{-2} in 2012.

For HFC-32, our observations also indicate rapid and accelerating growth. The calculated global mean mole fractions have increased from 0.8 ± 0.02 ppt in 2004 (when high-frequency observations began) to 6.2 ± 0.2 ppt in 2012; the rate of increase in 2012 reached 1.1 ± 0.04 ppt yr^{-1} (17% yr^{-1}), which likely reflects the increased usage of R-410a, the preferred replacement for HCFC-22 in many air conditioning applications. The radiative forcing due to HFC-32, estimated using the AGAGE 12-box model global mole fractions, was 0.7 ± 0.02 mW m^{-2} in 2012. It is clear from

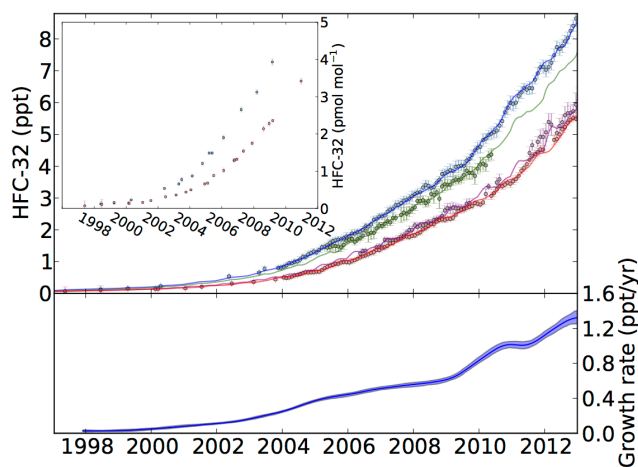


Figure 4. Semi-hemispheric monthly average HFC-32 mole fractions ($30\text{--}90^\circ\text{N}$: blue; $0\text{--}30^\circ\text{N}$: green; $30\text{--}0^\circ\text{S}$: purple; $90\text{--}30^\circ\text{S}$: red). Averaged observations are shown as data points with error bars. The more sparse circles represent NH and SH air archive samples, and are highlighted in the inset box. The solid trend lines were calculated using a 12-box model with emissions from the inversion as input. The lower plot shows the annual running mean global mole fraction growth rate.

the strong inter-hemispheric gradient for both compounds that emissions are predominantly in the NH, as has been illustrated for many other purely anthropogenic trace gases (O'Doherty et al., 2009; Mühle et al., 2010; Rigby et al., 2010; Laube et al., 2010; Vollmer et al., 2011; Yao et al., 2012).

4.2 Emission estimates

Estimated global emissions of HFC-143a from this work and a number of different sources are shown in Fig. 5 and Table 2. The blue solid line represents our model-derived emissions, with the 1σ error shown by the shaded areas. Model-derived emissions were relatively constant between 1981 and 1993 (0.3 ± 11.8 in 1981 to 1.0 ± 0.9 Gg yr^{-1} in 1993), but started to increase rapidly from a level of 1.4 ± 0.6 Gg yr^{-1} in 1994 to 23.3 ± 3.2 Gg yr^{-1} in 2012.

Global tropospheric average emissions calculated over 5-year periods were reported by Culbertson et al. (2004) as follows: 1977–1982, 0.2 Gg yr^{-1} ; 1982–1987, 0.6 Gg yr^{-1} ; 1987–1992, 0.8 Gg yr^{-1} ; 1992–1997, 3.3 Gg yr^{-1} . These estimates are in reasonable agreement with our estimates for the period 1981–1987, and exceed our estimate (if averaged over a 5-year period to be comparable) by approximately 50 % (1.6 Gg yr^{-1}) in 1987–1992. Estimated emissions from EDGAR (v4.2) imply that there were no emissions of HFC-143a before 1993, while there is reasonable agreement with our estimates from 1994 to 1998, but that EDGAR (v4.2) emissions have grown at a faster rate since 1994, resulting in EDGAR emissions being $\sim 13.9 \pm 7$ Gg yr^{-1} higher than

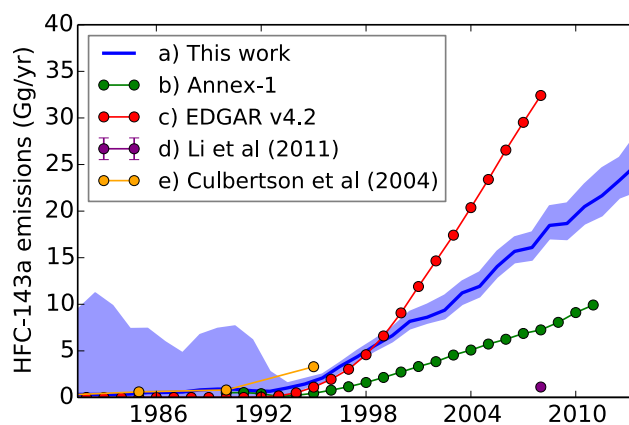


Figure 5. HFC-143a emissions estimates derived from AGAGE observations (blue line and shading, indicating 1σ uncertainty). The red line shows the global emissions estimates from EDGAR v4.2 and the green line shows the emissions reported to the UNFCCC. The purple point shows emissions estimated for East Asia by Li et al. (2011), and the orange points represents the mid-point of 5-year-average emissions estimated by Culbertson et al. (2009).

AGAGE emissions in 2008. In contrast the AGAGE trend in global emissions is higher than the UNFCCC GHG emissions reports (2012 submission), which contains nations' annual estimates of HFC emissions reported in the common reporting format (CRF) files. It is not unreasonable that UNFCCC-reported emissions are lower than the AGAGE global emission estimates, since developing countries and regions in Asia (e.g. China, Indonesia, Korea, Malaysia, the Philippines, Taiwan, Vietnam), the Indian sub-continent (e.g. India, Pakistan), the Middle East, Africa and Latin America do not report to the UNFCCC; however Miller et al. (2012) report a EPA US GHG inventory value of 4.4 Gg yr^{-1} (average of 2005–2009) and a ^{14}C -based US estimate of 5.2 ($3.6\text{--}11.3$) Gg yr^{-1} . The magnitude of these differences will vary over time according to the expected usage of individual replacement compounds by Annex 1 countries on a country-by-country basis.

Li et al. (2011) reported emission estimates for East Asia (China, South Korea, Japan and Taiwan) for the period between November 2007 and December 2008, where the emission rates for each country were estimated using an interspecies correlation method (based on the assumption that correlated compounds have co-located emission sources). For China, emissions were estimated to be relatively low (HFC-143a, 0.6 ± 0.2 Gg yr^{-1} , and HFC-32, 4 ± 1.4 Gg yr^{-1}). They concluded that emission did not occur from consumption, but was more likely to be fugitive emissions from production sources. These findings were supported in Li et al. (2014), where emission sources in East Asia were identified using high-frequency measurements analysed by positive matrix factorisation. Fugitive emissions from production-related sources in the Shandong

Table 2. Estimates of global emissions of HFC-143a (Gg yr^{-1}) based on AGAGE in situ measurements and archived air samples (the NH flasks were collected primarily at Trinidad Head and the SH flasks at Cape Grim) using the AGAGE 2-D 12-box model. Estimates of total emissions prior to November 2003 are based only on archived air samples. Also shown are 5-year averaged global emission estimates derived by Culbertson et al. (2004), global emission estimates derived from UNFCCC National Inventory Reports (2012 submission), and from the EDGAR (v4.2) database.

Year	HFC-143a AGAGE (Gg yr^{-1})	HFC-143a UNFCCC (Gg yr^{-1})	HFC-143a EDGAR (Gg yr^{-1})
1981	0.3 ± 11.7		
1982	0.3 ± 11.5		
1983	0.3 ± 10.2		
1984	0.4 ± 9.6		
1985	0.5 ± 9.4		
1986	0.5 ± 7.8		
1987	0.6 ± 6.9		
1988	0.8 ± 6.4		
1989	0.9 ± 5.7		
1990	0.9 ± 5.9	0.5	
1991	0.7 ± 4.5	0.5	
1992	0.7 ± 1.6	0.4	0.0
1993	1.0 ± 0.8	0.1	0.2
1994	1.4 ± 0.5	0.2	0.5
1995	2.1 ± 0.5	0.4	1.1
1996	3.3 ± 0.5	0.8	2.0
1997	4.4 ± 0.7	1.2	3.0
1998	5.6 ± 1.0	1.6	4.6
1999	6.5 ± 1.3	2.1	6.6
2000	8.3 ± 1.7	2.7	9.1
2001	8.5 ± 1.7	3.3	11.9
2002	9.2 ± 1.8	3.8	14.7
2003	11.5 ± 2.2	4.5	17.4
2004	11.9 ± 2.2	4.9	20.4
2005	14.1 ± 2.0	5.7	23.4
2006	15.7 ± 1.9	6.1	26.6
2007	16.1 ± 2.2	6.8	29.5
2008	18.5 ± 2	7.4	32.4
2009	18.6 ± 2.6	8.1	
2010	20.5 ± 2.7	9.1	
2011	21.6 ± 2.8	9.9	
2012	23.3 ± 3.2		

and Jiangsu regions of eastern China dominated. Taiwan's emissions were thought to be from refrigeration (HFC-143a, $0.04 \pm 0.02 \text{ Gg yr}^{-1}$, and HFC-32, $0.05 \pm 0.02 \text{ Gg yr}^{-1}$), as were South Korea's (HFC-143a, $0.08 \pm 0.01 \text{ Gg yr}^{-1}$, and HFC-32, $0.21 \pm 0.02 \text{ Gg yr}^{-1}$). Ratios of HFC measurements in South Korea suggested an increasing use of R-410a and R-507 as replacements for HCFC-22. Finally, emission estimates and ratios of HFC species also indicated that Japan has moved some of its refrigeration to HFC blends (HFC-143a, $0.4 \pm 0.1 \text{ Gg yr}^{-1}$, and HFC-32, $0.4 \pm 0.1 \text{ Gg yr}^{-1}$). These

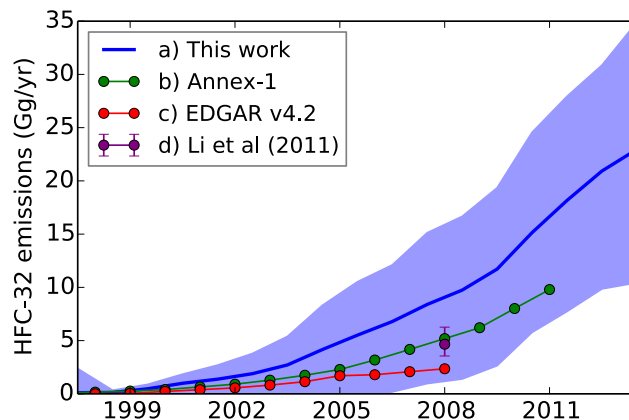


Figure 6. HFC-32 emissions estimates derived from AGAGE observations (blue line and shading, indicating 1σ uncertainty). The red line shows the global emissions estimates from EDGAR v4.2 and the green line shows the emissions reported to the UNFCCC. The purple point shows emissions estimated for East Asia by Li et al. (2011).

Table 3. Estimates of global emissions of HFC-32 (Gg yr^{-1}) based on AGAGE in situ measurements and archived air samples (the NH flasks were collected primarily at Trinidad Head and the SH flasks at Cape Grim) using the AGAGE 2-D 12-box model. Estimates of total emissions prior to January 2004 are based only on archived air samples. Also shown are global emission estimates derived from UNFCCC National Inventory Reports (2012 submission) and from the EDGAR (v4.2) database.

Year	HFC-32 AGAGE (Gg yr^{-1})	HFC-32 UNFCCC (Gg yr^{-1})	HFC-32 EDGAR (Gg yr^{-1})
1997	0.1 ± 2.2	0.1	
1998	0.1 ± 0.3	0.2	0.0
1999	0.5 ± 0.5	0.3	0.0
2000	1.0 ± 1.0	0.4	0.2
2001	1.4 ± 1.4	0.7	0.4
2002	1.9 ± 2.2	0.9	0.6
2003	2.7 ± 2.9	1.3	0.8
2004	4.1 ± 4.5	1.7	1.1
2005	5.5 ± 5.5	2.2	1.7
2006	6.8 ± 6.1	3.2	1.8
2007	8.4 ± 6.2	4.1	2.1
2008	9.7 ± 7.0	5.2	2.4
2009	11.7 ± 8.3	6.2	–
2010	15.1 ± 8.7	8.0	–
2011	18.0 ± 9.4	9.8	–
2012	20.5 ± 10.6	–	–

estimates, in comparison to our global totals, suggest that HFC-143a is not yet widely used in East Asia, and represents only $\sim 6\%$ of 2011 global emissions (Li et al., 2011).

In Fig. 6 and Table 2 the estimates of global emissions of HFC-32 derived from our measurements and a number of

other sources are illustrated. For this compound the AGAGE a posteriori results are higher than, but not statistically different from, the a priori UNFCCC and EDGAR global emissions. The magnitude of this underestimate in 2008 was 4.5 ± 7 and 7.4 ± 7 Gg yr⁻¹ respectively. Li et al. (2011) calculated that East Asian total emissions of HFC-32 in 2008 represented 129 % of the global total reported in the EDGAR database, and concluded that EDGAR must under-report emissions. This conclusion concurs with the AGAGE global estimates presented in Fig. 6. Interestingly, if the UNFCCC reports of HFC-32 for Annex I countries in 2008 is added to the Li et al. (2011) East Asia estimate, the total emission (9.8 Gg yr⁻¹) closely matches the AGAGE-derived global emission (9.7 ± 7 Gg yr⁻¹), adding weight to the suggestion that EDGAR does not represent emissions in Asia adequately and that HFC-32 is now increasingly released in East Asia as fugitive emissions from halocarbon production sources and from air conditioning and refrigeration applications (Li et al., 2014).

5 Conclusions

The first high-frequency in situ global measurements of HFC-143a and HFC-32 have been made at nine AGAGE stations between 2003 and 2012. These measurements indicate that, for the entire time period, the atmospheric burden of both gases has been growing and that this growth has been accelerating. The global mean growth rates in 2012 for HFC-143a and HFC-32 were 1.4 ± 0.04 and 1.1 ± 0.04 ppt yr⁻¹ respectively. The mole fractions in the global lower troposphere in 2012 were estimated to be 13.4 ± 0.3 ppt for HFC-143a and 6.2 ± 0.2 ppt for HFC-32. Moreover the continuous data record presented here was extended back in time to 1977 and 1997 for HFC-143a and HFC-32 respectively by analysis of NH and SH archived air samples. These measurements suggest that emissions of HFC-143a started as early as 1981, and HFC-32 by 1998.

The observations were combined with an atmospheric chemical transport model to simulate global atmospheric abundances and derive global emissions. We estimate that 23 ± 3 Gg yr⁻¹ of HFC-143a and 21 ± 11 Gg yr⁻¹ of HFC-32 were emitted globally in 2012, and that the emissions were increasing at a rate of 7 ± 5 % yr⁻¹ for HFC-143a and 14 ± 11 % yr⁻¹ for HFC-32 in 2012. Lastly, discrepancies were found between these emissions and those reported to the UNFCCC, reflecting the incomplete global reporting of these compounds and/or biases in the accounting methodology.

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