Atmos. Chem. Phys. Discuss., 14, 6471–6500, 2014
www.atmos-chem-phys-discuss.net/14/6471/2014/
doi:10.5194/acpd-14-6471-2014

Atmospheric Chemistry and Physics Discussions
Open Access

Global emissions of HFC-143a (CH_3CF_3) and HFC-32 (CH_2F_2) from in situ and air archive atmospheric observations

S. O'Doherty[1], M. Rigby[1], J. Mühle[2], D. J. Ivy[3], B. R. Miller[4,5], D. Young[1], P. G. Simmonds[1], S. Reimann[6], M. K. Vollmer[6], P. B. Krummel[7], P. J. Fraser[7], L. P. Steele[7], B. Dunse[7], P. K. Salameh[2], C. M. Harth[2], T. Arnold[2], R. F. Weiss[2], J. Kim[2], S. Park[8], S. Li[9], C. Lunder[10], O. Hermansen[10], N. Schmidbauer[10], L. X. Zhou[11], B. Yao[11], R. H. J. Wang[12], A. Manning[13], and R. G. Prinn[3]

[1]Atmospheric Chemistry Research Group, University of Bristol, Bristol, BS8 1TS, UK
[2]Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California, USA
[3]Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA
[4]Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Colorado, USA
[5]Global Monitoring Division, ESRL, NOAA, Boulder, Colorado, USA
[6]Laboratory for Air Pollution and Environmental Technology, Swiss Federal Laboratories for Materials Testing and Research (Empa), Dübendorf, Switzerland

[7]Centre for Australian Weather and Climate Research, CSIRO Marine and Atmospheric Research, Aspendale, Victoria, Australia
[8]Departement of Oceanography, Kungpook National University, Sangju, Republic of Korea
[9]Research Institute of Oceanography, Seoul National University, Seoul, South Korea
[10]Norwegian Institute for Air Research (NILU), Kjeller, Norway
[11]Chinese Academy of Meteorological Sciences (CAMS), Beijing, China
[12]School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA
[13]UK Meteorological Office, Exeter, UK

Received: 13 February 2014 – Accepted: 24 February 2014 – Published: 11 March 2014

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

Published by Copernicus Publications on behalf of the European Geosciences Union.

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 (CH_3CF_3) and HFC-32 (CH_2F_2) 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 HFCs respectively and they currently make an appreciable contribution to the HFCs in terms of atmospheric radiative forcing (1.7 and 0.7 $\mathrm{mW\,m^2}$ in 2012, respectively). In 2012 the global average mole fraction of HFC-143a was 13.4 ± 0.3 ppt (1-sigma) in the lower troposphere and its growth rate was 1.4 ± 0.04 $\mathrm{ppt\,yr^{-1}}$; HFC-32 had a global mean mole fraction of 6.2 ± 0.2 ppt and a growth rate of 1.1 ± 0.04 $\mathrm{ppt\,yr^{-1}}$ 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 $\mathrm{Gg\,yr^{-1}}$ of HFC-143a and 21 ± 11 $\mathrm{Gg\,yr^{-1}}$ of HFC-32 were emitted globally in 2012, and the emission rates are estimated to be increasing 7 ± 5 $\%\,\mathrm{yr^{-1}}$ for HFC-143a and 14 ± 11 $\%\,\mathrm{yr^{-1}}$ for HFC-32.

1 Introduction

Hydrofluorocarbons (HFCs) were developed as replacements for ozone depleting chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) which have 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 on the order of 2 yr (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 if hermetically sealed or not) and finally when the equipment is scrapped (although recovery, re-use 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 yr and are removed from the atmosphere through reaction with tropospheric hydroxyl radicals (Forster et al., 2007). They are chlorine free, and as such have effectively zero stratospheric ozone depletion potentials 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). 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 mostly developing countries) were not required to submit national HFC data. It has been suggested that projected baseline HFC emissions are ∼ 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 have 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; Miller et al., 2010; Vollmer et al., 2011; Rigby et al., 2013); however to date these techniques have not been applied to global observations of HFC-143a and HFC-32.

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 the atmospheric accumulation of HFC-143a to be determined for the first time (Culberson 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} ($\sim 80\,\%\,\mathrm{yr}^{-1}$) 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. Global tropospheric average emissions calculated over five year periods were reported 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} (Culberson et al., 2004). 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 % yr^{-1}) (Greally et al., 2005). More recent measurements from the AGAGE network show an increase to 8.5 ppt in 2008 with a growth rate of 1.0 ppt yr^{-1} (13 % yr^{-1}) (Montzka and Reimann et al., 2011).

HFC-143a has a significant radiative forcing value of 1 mW m^{-2} in 2008 (third largest of all the HFCs) (Montzka and Reimann, 2011) with a GWP of 4470 integrated over 100 yr (Forster et al., 2007) and an estimated atmospheric lifetime of 47 yr (Montzka and Reimann, 2011). It is removed from the atmosphere predominantly by gas phase reaction with hydroxyl radicals (OH), reaction rate 1.1×10^{-12} cm^3 molecules^{-1} s^{-1}, (Sander et al., 2011). The degradation products resulting from this reaction ($CF_3C(O)H$, CF_3OH, $C(O)F_2$ 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 $CF_3C(O)H$ 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 R407C (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 % yr^{-1} growth in the first half of the year followed by accelerated growth of 86 % 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 % yr^{-1}) (Montzka and Reimann, 2011).

HFC-32 has a GWP of 675 integrated over a 100 yr time horizon, a value appreciably lower than that of HFC-143a (Forster et al., 2007). The radiative forcing of HFC-32 was estimated by Orkin et al. (2003) to be 0.44 $mW\,m^{-2}$. It has an estimated atmospheric lifetime of 5.2 yr (Montzka and Reimann, 2011), 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), reaction rate $1.7 \times 10^{-12}\,cm^3\,molecules^{-1}\,s^{-1}$ (Sander et al., 2011).

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 1981–2012 and HFC-32 from 1997–2012. The derived global emissions are compared to the Emissions Database for Global Atmospheric Research (EDGAR v4, JRC/PBL, 2009) and national submissions to the UNFCCC.

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 calibration scale (as dry gas mole fractions in pmol mol^{-1}). The estimated accuracy of the calibration scale is 1–2 %. 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/qualifier ions were monitored to ensure that potential interferences from co-eluting species did not affect the analysis. Measurement precision was determined as one standard deviation (1σ) of the ratio of each standard response to the average of the closest-in-time preceding and subsequent standard responses. The typically daily precision for each standard was calculated as 0.10 ppt, this value was used to estimate the precision of each in situ measurement.

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 SS containers during background conditions) (Langenfelds et al., 1996; Krummel et al., 2007), CGAA samples dated between 1978–2006 were analysed for HFC-143a, and between 1997–2010 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 1977–2010 for HFC-143a and 1998–2009 for HFC-32. The archived samples were analysed in replicate, typically 2–4 times each. Nonlinearity data were collected before, during and after the analysis periods and frequent inclusion of blank runs allowed 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 used tanks (Essex Cryogenics) or the 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 $\Delta\chi = 1$–$6\,\%$ for HFC-143a, $n = 7$, $\Delta\chi = 0.8$–$1.2\,\%$ for HFC-32, $n = 6$ and sample filling time differences $\Delta t = 3$–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 hPa and 200 hPa). The model was originally developed by Cunnold et al. (1983) (9-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), in which a priori estimates of the emissions growth rate were adjusted to bring the simulated mole fractions into agreement with the AGAGE observations and the a posteriori emissions estimates with the a priori estimates, both within their prescribed uncertainties. “Bottom-up” emissions estimates were taken from UNEP reports and used as a priori constraints. An alternative inventory estimate was also obtained 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 two estimates, a 30 % uncertainty was assumed on the annual a priori emissions growth rates. Emissions were estimated annually 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).

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 $\mathrm{pmol\,mol^{-1}}$) 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 lower troposphere in 2012 is estimated to be 13.4 ± 0.3 ppt, and the rate of increase is 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. The radiative forcing of HFC-143a in 2012 estimated using the AGAGE 12-box model is 1.7 ± 0.04 mW m^{-2} (excluding uncertainties in radiative efficiency estimates, which are estimated to be approximately 10 %, Forster et al., 2007).

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 R410a, the preferred replacement of HCFC-22 in many air conditioning applications. The radiative forcing of HFC-32 estimated using the AGAGE 12-box model is 0.7 ± 0.02 mW m^{-2} in 2012 (excluding uncertainties in radiative efficiency estimates, which are estimated to be ~ 10 %, Forster et al., 2007).

It is clear from 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; Vollmer et al., 2011; Yao et al., 2012). It is also clear from the change in the inter-hemispheric fractional gradients with time, as determined from the ratio of the average annual baseline mole fraction at Mace Head and Cape Grim that the pattern of emissions is changing. For HFC-143a the ratio (NH/SH) changed from 1.25 in 2004 to 1.16 in 2012, whereas HFC-32 changed from 1.83 to 1.53, which (assuming the OH sink is not changing) implies decreasing emissions of the NH and/or increasing emissions in the SH. Australian emission estimates derived from pollution episodes at Cape Grim and emissions reported in the National Greenhouse Gas Inventory (NGGI: ageis.climatechange.gov.au) (DIICCSRTE 2013) indicate rapidly increasing Australian emissions (Table 2). However, in contrast to the global picture, the NGGI estimates indicate the ratio of emissions from the two compounds is opposite from the ratio derived by atmospheric measurements, i.e., HFC-32 shows substantially higher emissions than HFC-143a in the NGGI, whereas the Cape Grim data suggest the reverse, with HFC-143a emissions from Australia being substantially higher than HFC-32 emissions. This contrasts with current global emissions of these two HFCs which are approximately the same (20–25 Gg in 2012). However, historically, global HFC-32 emissions have been lower than HFC-143a emissions – which is consistent with emissions calculated from Cape Grim data but not the emissions reported in the Australian NGGI. There have been significant inconsistencies in the NGGI emission estimates for these two HFCs in recent years (DCCEE, 2012; DIICCSRTE, 2013) and these are currently under investigation.

4.2 Emission estimates

Estimated of global emissions of HFC-143a from this work and a number of different sources are shown in Fig. 5 and Table 3. The blue solid line represents our model-derived emissions with 1σ error bar shown by the shaded areas. Model derived emissions were relatively constant between 1978 and 1993 (0.3 ± 11.8 in 1978 to $1 \pm 0.9\,\mathrm{Gg\,yr^{-1}}$ in 1993) but started to increase rapidly from a level of $1.4 \pm 0.6\,\mathrm{Gg\,yr^{-1}}$ in 1994 to $23.2 \pm 3\,\mathrm{Gg\,yr^{-1}}$ in 2012. In contrast, 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 since 1994, EDGAR (v4.2) emissions have grown at a faster rate, resulting in EDGAR emissions being ~ 13.9 ± 7 Gg yr^{-1} higher than 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 (China, Indonesia, Korea, Malaysia, Philippines, Taiwan, Vietnam etc.), the sub-continent (India, Pakistan, etc.), the Middle East, from Africa and Latin America do not report to the UNFCCC. 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. A United Nation Development Program (UNDP) presentation in Bangkok, February 2013 reported that the market for air-conditioners is growing rapidly in developing countries (~ 20 % yr^{-1}), perhaps explaining part of the growing discrepancy between reported UNFCCC and global top-down emissions estimates.

Li et al. (2011) reported emission estimates for East Asia (China, S. Korea, Japan and Taiwan) where the emission rates for each country were estimated using an inter-species 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 as 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 and Jiangsu regions of eastern China dominated. Taiwan's emissions were thought to be from refrigeration (HFC-143a, 0.04 ± 0.02 Gg yr^{-1} and HFC-32, 0.05 ± 0.02 Gg yr^{-1}), as were S. Korea's (HFC-143a, 0.08 ± 0.01 Gg yr^{-1} and HFC-32, 0.21 ± 0.02 Gg yr^{-1}). Ratios of HFC measurements in S. 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±0.1 Gg yr^{-1} and HFC-32, 0.4±0.1 Gg yr^{-1}). These estimates, in comparison to our global totals, suggest that HFC-143a is not yet widely used in E. Asia, and represents only ~ 6 % of 2011 global emissions (Li et al., 2011).

In Fig. 6 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 E. Asian total emissions of HFC-32 in 2008 represented 129 % of the global total reported in the EDGAR database, and concluded that EDGAR must underreport 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 do not represent emissions in Asia adequately and that HFC-32 is now increasingly released in E. 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 ppt yr^{-1} 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 $\mathrm{Gg\,yr^{-1}}$ of HFC-143a and 21 ± 11 $\mathrm{Gg\,yr^{-1}}$ of HFC-32 were emitted globally in 2012, and that the emissions were increasing at a rate of 7 ± 5 $\%\,\mathrm{yr^{-1}}$ for HFC-143a and 14 ± 11 $\%\,\mathrm{yr^{-1}}$ 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.

Supplementary material related to this article is available online at http://www.atmos-chem-phys-discuss.net/14/6471/2014/acpd-14-6471-2014-supplement.pdf.

Acknowledgements. We specifically acknowledge the cooperation and efforts of the station operators and support staff at all AGAGE and SOGE and the NOAA American Samoa monitoring stations. We also particularly thank NOAA for supplying some of the archived air samples shown allowing us to fill important gaps. We thank the Physics Department, National University of Ireland, Galway, for making the research facilities at Mace Head available. The operation of the AGAGE stations was supported by the National Aeronautic and Space Administration (NASA, USA) (grants NNX07AE89G and NNX11AF17G to MIT; grants NAGW-2034, NAG5-4023 to SIO); the Department of the Energy and Climate Change (DECC, UK) (contracts GA0201 to the University of Bristol); the National Oceanic and Atmospheric Administration (NOAA, USA) (contract RA133R09CN0062 in addition to the operations of American Samoa station); and the Commonwealth Scientific and Industrial Research Organization (CSIRO, Australia), Bureau of Meteorology (Australia). The measurements at Jungfraujoch are part of the Swiss National HALCLIM-project and are supported by the Swiss Federal Office for the Environment (FOEN). We also acknowledge the International Foundation “High Altitude Research Stations Jungfraujoch and Gornergrat" for providing an excellent infrastructure. Support of the Jungfraujoch station was provided by International Foundation High Altitude Research Stations Jungfraujoch and Gornergrat (HFSJG). The measurements at Gosan, South Korea are supported by the Korean Meteorological Administration Research and Development Program under Grant CATER 2012–3010. Financial support for the Zeppelin measurements are acknowledged from the Norwegian Environment Agency. Financial support for the Shangdianzi measurements are acknowledged from the National Nature Science Foundation of China (41030107, 41205094). M. Rigby is supported by a NERC Advanced Fellowship NE/I021365/1.

References

Arnold, T., Mühle, J., Salameh, P. K., Harth, C. M., Ivy, D. J., and Weiss, R. F.: Automated measurement of nitrogen trifluoride in ambient air, Anal. Chem., 84, 4798–4804, 2012.

Culbertson, J. A., Prins, J. M., and Grimsrud, E. P.:. Improvements in the detection and analysis of CF3-containing compounds in the background atmosphere by gas chromatography-high-resolution mass spectrometry, J. Chromatogr. A, 903, 261–265, 2000.

Culbertson, J. A., Prins, J. M., Grimsrud, E. P., Rasmussen, R. A., Khalil, M. A. K., and Shearer, M. J.: Observed trends for CF3-containing compounds in background air at Cape Meares, Oregon, Point Barrow, Alaska, and Palmer Station, Antarctica, Chemosphere, 55, 1109–1119, doi:10.1016/j.chemosphere.2003.11.002, 2004.

Cunnold, D. M., Prinn, R. G., Rasmussen, R., Simmonds, P. G., Alyea, F. N., Cardelino, C., Crawford, A., Fraser, P. J., and Rosen, R.: The atmospheric lifetime experiment, III: lifetime methodology and application to three years of CFCl3 data, J. Geophys. Res., 88, 8379–8400, 1983.

Cunnold, D. M., Fraser, P. J., Weiss, R. F., Prinn, R. G., Simmonds, P. G., Miller, B. R., Alyea, F. N., and Crawford, A. J.: Global trends and annual releases of CCl3F and CCl2F2 estimated from ALE/GAGE and other measurements from July 1978 to June 1991, J. Geophys. Res., 99, 1107–1126, 1994.

Cunnold, D. M., Steele, L. P., Fraser, P. J., Simmonds, P. G., Prinn, R. G., Weiss, R. F., Porter, L. W., O'Doherty, S., Langenfelds, R. L., Krummel, P. B., Wang, H. J., Emmons, L., Tie, X. X., and Dlugokencky, E. J.: In situ measurements of atmospheric methane at

GAGE/AGAGE sites during 1985–2000 and resulting source inferences, J. Geophys. Res., 107, ACH 20-1–ACH20-18, doi:10.1029/2001JD001226, 2002.

DCCEE: Australian National Greenhouse Accounts, National Inventory Report 2010, vol. 1, Department of Climate Change and Energy Efficiency, Commonwealth of Australia, 292 pp., 2012.

DIICCSRTE: Australian National Greenhouse Accounts, National Inventory Report 2011, vol. 1, Department of Industry, Innovation, Climate Change, Science, Research and Tertiary Education, 299 pp., Commonwealth of Australia, 2013.

Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D. W., Haywood, J., Lean, J., Lowe, D. C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., and Van Dorland, R.: Changes in atmospheric constituents and in radiative forcing, in: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L., Cambridge University Press, Cambridge, UK, New York, NY, USA, 131–234, 2007.

Greally, B. R., Simmonds, P. G., O'Doherty, S., McCulloch, A., Miller, B. R., Salameh, P. K., Mühle, J., Tanhua, T., Harth, C. M., Weiss, R. F., Fraser, P. J., Krummel, P. B., Dunse, B. L., Porter, L. W., and Prinn, R. G.: Improved continuous in situ measurements of C1–C3 PFCs, HFCs, HCFCs, CFCs and SF6 in Europe and Australia, Environm. Sci., 2, 253–261, doi:10.1080/15693430500402614, 2005.

IPCC/SRES: Special Report on Emissions Scenarios, Intergovernmental Panel on Climate Change, edited by: Nakicenovic, N. and Swart, R., Geneva, Switzerland, 2000.

Krummel, P. B., Langenfelds, R. L., Fraser, P. J., Steele, L. P., and Porter, L. W.: Archiving of Cape Grim air, in: Baseline Atmospheric Program Australia 2005–2006, edited by: Cainey, J. M., Derek, N., and Krummel, P. B., Australian Bureau of Meteorology and CSIRO Marine and Atmospheric Research, Melbourne, Australia, 55–57, 2007.

Langenfelds, R. L., Fraser, P. J., Francey, R. J., Steele, L. P., Porter, L. W., and Allison, C. E.: The Cape Grim Air Archive: the first seventeen years, 1978–1995, in: Baseline Atmospheric Program Australia 1994–1995, edited by: Francey, R. J., Dick, A. L., and Derek, N., Bureau of Meteorology and CSIRO Division of Atmospheric Research, Melbourne, 53–70, 1996.

Li, S., Kim, J., Kim, K.-R., Mühle, J., Kim, S.-K., Park, M.-K., Stohl, A., Kang, D.-J., Arnold, T., Harth, C. M., Salameh, P. K., and Weiss, R. F.: Emissions of halogenated compounds in

East Asia determined from measurements at Jeju Island, Korea, Environ. Sci. Technol., 45, 5668–5675, doi:10.1021/es104124k, 2011.

Li, S., Kim, J., Park, S., Kim, S.-K., Park, M.-K., Mühle, J., Lee, G., Jo, C. O., and Kim, K.-R.: Source identification and apportionment of halogenated compounds observed at a remote site in East Asia, Environ. Sci. Technol., 48, 491–498, doi:10.1021/es402776w, 2014.

McCulloch, A.: Evidence for improvements in containment of fluorinated hydrocarbons during use: an analysis of reported European emissions, Environ. Sci. Policy, 12, 149–156, doi:10.1016/j.envsci.2008.12.003, 2009.

Miller, B. R., Weiss, R. F., Salameh, P. K., Tanhua, T., Greally, B. R., Muhle, J., and Simmonds, P. G.: Medusa: a sample preconcentration and GC/MS detector system for in situ measurements of atmospheric trace halocarbons, hydrocarbons, and sulfur compounds, Anal. Chem., 80, 1536–1545, doi:10.1021/ac702084k, 2008.

Miller, B. R., Rigby, M., Kuijpers, L. J. M., Krummel, P. B., Steele, L. P., Leist, M., Fraser, P. J., McCulloch, A., Harth, C., Salameh, P., Mühle, J., Weiss, R. F., Prinn, R. G., Wang, R. H. J., O'Doherty, S., Greally, B. R., and Simmonds, P. G.: HFC-23 (CHF_3) emission trend response to HCFC-22 ($CHClF_2$) production and recent HFC-23 emission abatement measures, Atmos. Chem. Phys., 10, 7875–7890, doi:10.5194/acp-10-7875-2010, 2010.

Montzka S. A., Reimann, S., Engel, A., Krueger, K., O'Doherty, S., Sturges, W. T., Blake, D., Dorf, M., Fraser, P. J., Froidevaux, L., Jucks, K., Kreher, K., Kurylo, M. J., Mellouki, A., Miller, J., Nielsen, O.-J., Orkin, V. L., Prinn, R. G., Rhew, R., Santee, M. L., and Verdonik, D.: Ozone-Depleting Substances (ODSs) and Related Chemicals. Chapter 1 in Scientific Assessment of Ozone Depletion: 2010, Global Ozone Research and Monitoring Project-Report No. 52, 516 pp., World Meteorological Organization, Geneva, Switzerland, 2011.

Mühle, J., Ganesan, A. L., Miller, B. R., Salameh, P. K., Harth, C. M., Greally, B. R., Rigby, M., Porter, L. W., Steele, L. P., Trudinger, C. M., Krummel, P. B., O'Doherty, S., Fraser, P. J., Simmonds, P. G., Prinn, R. G., and Weiss, R. F.: Perfluorocarbons in the global atmosphere: tetrafluoromethane, hexafluoroethane, and octafluoropropane, Atmos. Chem. Phys., 10, 5145–5164, doi:10.5194/acp-10-5145-2010, 2010.

O'Doherty, S., Cunnold, D. M., Miller, B. R., Muhle, J., McCulloch, A., Simmonds, P. G., Mühle, J., McCulloch, A., Simmonds, P. G., Manning, A. J., Reimann, S., Vollmer, M. K., Greally, B. R., Prinn, R. G., Fraser, P. J., Steele, L. P., Krummel, P. B., Dunse, B. L., Porter, L. W., Lunder, C. R., Schmidbauer, N., Hermansen, O., Salameh, P. K., Harth, C. M., Wang, R. H. J., and Weiss, R. F.: Global and regional emissions of HFC-125 (CHF2CF3) from in situ and air archive atmospheric observations at AGAGE and SOGE observatories, J. Geophys. Res., 114, D23304, doi:10.1029/2009jd012184, 2009.

Orkin, V. L., Huie, R. E., and Kurylo, M. J.:. Atmospheric lifetimes of HFC-143a and HFC-245fa: flash photolysis resonance fluorescence measurements of the oh reaction rate constants, 2, 8907–8912, 1996.

Orkin, V. L., Guschin, A. G., Larin, I. K., Huie, R. E., and Kurylo, M. J.: Measurements of the infrared absorption cross-sections of haloalkanes and their use in a simplified calculational approach for estimating direct global warming potentials, J. Photoch. Photobio. A, 157, 211–222, doi:10.1016/S1010-6030(03)00057-1, 2003.

Prinn, R. G., Weiss, R. F., Fraser, P. J., Simmonds, P. G., Cunnold, D. M., Alyea, F. N., O'Doherty, S., Salameh, P., Miller, B. R., Huang, J., Wang, R. H. J., Hartley, D. E., Harth, C., Steele, L. P., Sturrock, G. A., Midgley, P. M., and McCulloch, A.: A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE, J. Geophys. Res.-Atmos., 105, 17751–17792, 2000.

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

Rigby, M., Prinn, R. G., O'Doherty, S., Montzka, S. A., McCulloch, A., Harth, C. M., Mühle, J., Salameh, P. K., Weiss, R. F., Young, D., Simmonds, P. G., Hall, B. D., Dutton, G. S., Nance, D., Mondeel, D. J., Elkins, J. W., Krummel, P. B., Steele, L. P., and Fraser, P. J.: Re-evaluation of the lifetimes of the major CFCs and CH_3CCl_3 using atmospheric trends, Atmos. Chem. Phys., 13, 2691–2702, doi:10.5194/acp-13-2691-2013, 2013.

Rigby, M., Prinn , R. G., O'Doherty, S., Miller, B. R., Ivy, D. J., Muhle, J., Harth, C. M., Salameh, P. K., Arnold, T., Weiss, R. F., Krummel, P. B., Steele, L. P., Fraser, P. J., Young, D., and Simmonds, P. G.: Recent and future trends in synthetic greenhouse gas radiative forcing, Geophys. Res. Lett., 41, doi:10.1002/2013GL059099, 2014.

Sander, S. P., Abbatt, J., Barker, J. R., Burkholder, J. B., Friedl, R. R., Golden, D. M., Huie, R. E., Kolb, C. E., Kurylo, M. J., Moortgat, G. K., Orkin, V. L., and Wine, P. H.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17, JPL Publication 10-6, Jet Propulsion Laboratory, Pasadena, http://jpldataeval.jpl.nasa.gov (last access: 10 June 2011), 2011.

Velders, G. J. M., Fahey, D. W., Daniel, J. S., McFarland, M., and Andersen, S. O.: The large contribution of projected HFC emissions to future climate forcing, P. Natl. Acad. Sci. USA, 106, 10949–10954, doi:10.1073/pnas.0902817106, 2009.

Vollmer, M. K., Miller, B. R., Rigby, M., Reimann, S., Muhle, J., Krummel, P. B., O'Doherty, S., Jim, J., Rhee, T. S., Weiss, R. F., Fraser, P. J., Simmonds, P. G., Salameh, P. K., Harth, C. M., Wang, R. H. J., Steele, L. P., Young, D., Lunder, C. R., Hermansen, O., Ivy, D., Arnold, T., Schmidbauer, N., Kim, K.-R., Greally, B. G., Hill, M., Leist, M., Wenger, A., and Prinn, R. G.: Atmospheric histories and global emissions of the anthropogenic hydrofluorocarbons HFC-365mfc, HFC-245fa, HFC-227ea, and HFC-236fa, J. Geophys. Res, 116, D08304, doi:10.1029/2010jd015309, 2011.

Wallington, T. J., Schneider, W. F., Worsnop, D. R., Nielsen, O. J., Sehested, J., Debruyn, W. J., and Shorter, J. A.:. The environmental impact of CFC replacements – HFCs and HCFCs, Environ. Sci. Technol., 28, 320–326, 1994.

Yao, B., Vollmer, M. K., Zhou, L. X., Henne, S., Reimann, S., Li, P. C., Wenger, A., and Hill, M.: In-situ measurements of atmospheric hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) at the Shangdianzi regional background station, China, Atmos. Chem. Phys., 12, 10181–10193, doi:10.5194/acp-12-10181-2012, 2012.

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

Station	Latitude °N	Longitude °E	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
Jungfraujoch	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

Table 2. Estimated emissions of HFC-143a and HFC-32 reported in the Australian National Greenhouse Gases Inventory (NGGI), and from atmospheric measurements by interspecies correlation (ISC), and from the UK MetOffice NAME model using the InTEM inversion (DIICC-SRTE, 2013).

Date	Estimate Type	HFC-143a ($\mathrm{Gg\,yr^{-1}}$)	HFC-32 ($\mathrm{Gg\,yr^{-1}}$)
1995	NGGI	2	5
2005	NGGI	126	335
	ISC	383 ± 135	29 ± 10
	NAME	337 ± 20	34 ± 5
2011	NGGI	232	951
	ISC	725 ± 230	251 ± 75
	NAME	771 ± 35	172 ± 10

Table 3. Estimates of global emissions of HFC-143a (Gg yr^{-1}) based on AGAGE in situ measurements and archived air samples collected primarily at Trinidad Head and 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 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 ± 0.8	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		

Table 4. Estimates of global emissions of HFC-32 ($\mathrm{Gg\,yr^{-1}}$) based on AGAGE in situ measurements and archived air samples collected primarily at Trinidad Head and 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 ($\mathrm{Gg\,yr^{-1}}$)	HFC-32 UNFCCC ($\mathrm{Gg\,yr^{-1}}$)	HFC-32 EDGAR ($\mathrm{Gg\,yr^{-1}}$)
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	–	–

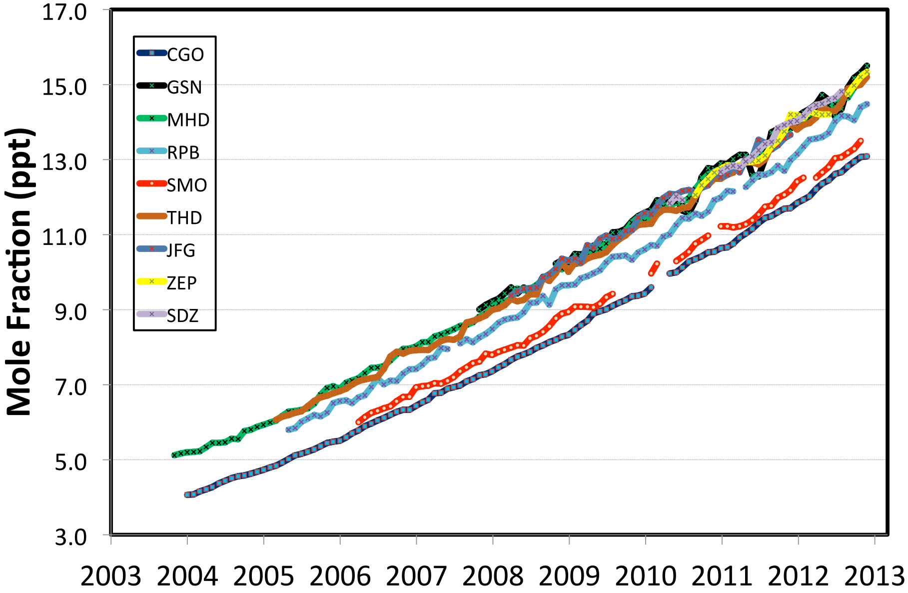

Fig. 1. Baseline monthly mean HFC-143a mole fractions (ppt) fromin situ Medusa-GCMS measurements at AGAGE stations. Cape Grim Observatory (CGO); Gosan (GSN); Mace Head (MHD); Ragged Point (RPB); Samoa (SMO); Trinidad Head (THD); Jungfraujoch (JFG); Zeppelin (ZEP) and Shangdianzi (SDZ).

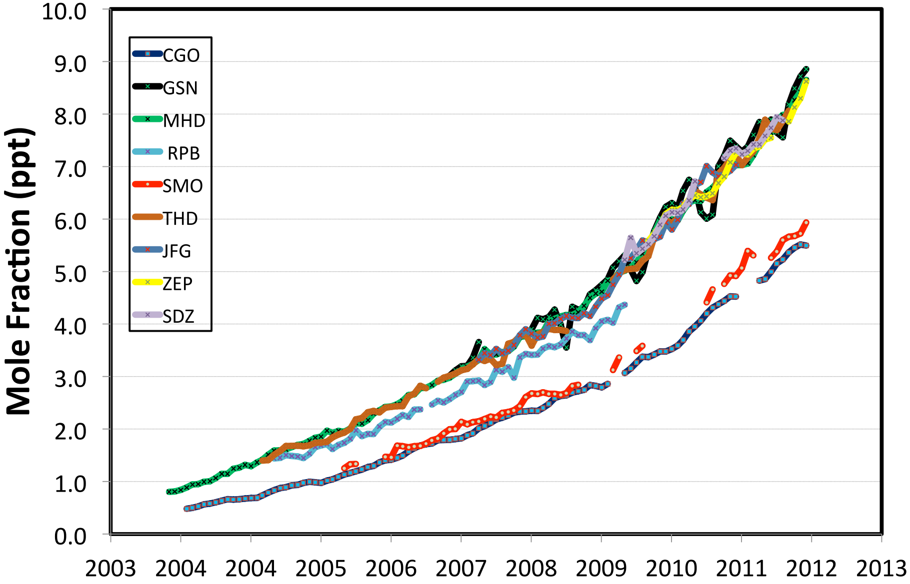

Fig. 2. Baseline monthly mean HFC-32 mole fractions (ppt) fromin situ Medusa-GCMS measurements at AGAGE stations. Cape Grim Observatory (CGO); Gosan (GSN); Mace Head (MHD); Ragged Point (RPB); Samoa (SMO); Trinidad Head (THD); Jungfraujoch (JFG); Zeppelin (ZEP) and Shangdianzi (SDZ).

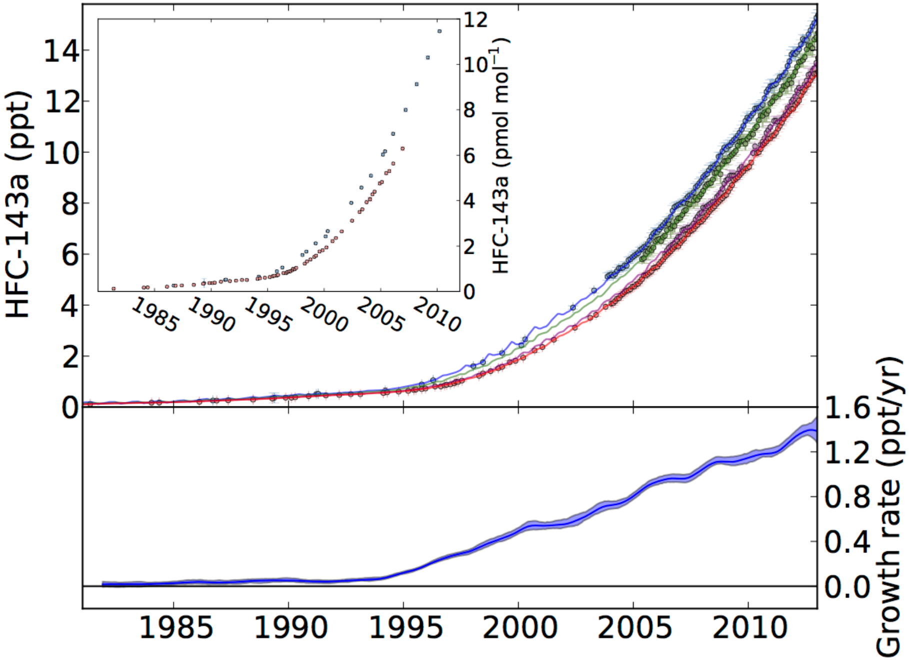

Fig. 3. HFC-143a monthly mean dry air mole fraction (ppt) measured at a selection of in situ AGAGE sampling sites are indicated by different coloured circles with respective error bars. The more sparse circles represent NH and SH air archive samples, and are highlighted in the inset box. The solid trend lines were calculated using a 12-box model with emissions from the inversion as input. The lower plot shows the annual running mean global growth rate.

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

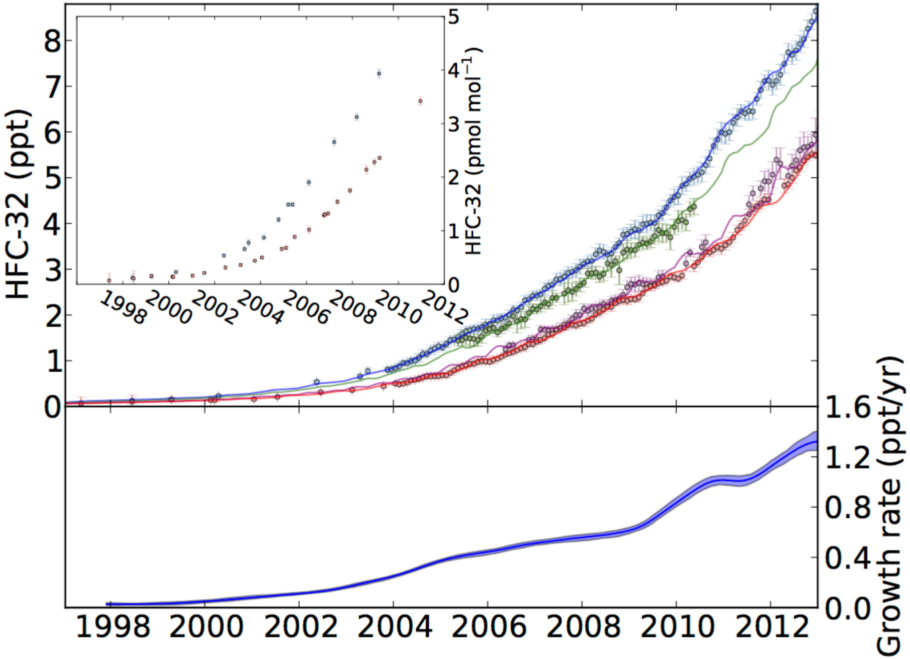

Fig. 4. HFC-32 monthly mean dry air mole fraction (ppt) measured at a selection of in situ AGAGE sampling sites are indicated by different coloured circles with respective error bars. The more sparse circles represent NH and SH air archive samples, and are highlighted in the inset box. The solid trend lines were calculated using a 12-box model with emissions from the inversion as input. The lower plot shows the annual running mean global growth rate.

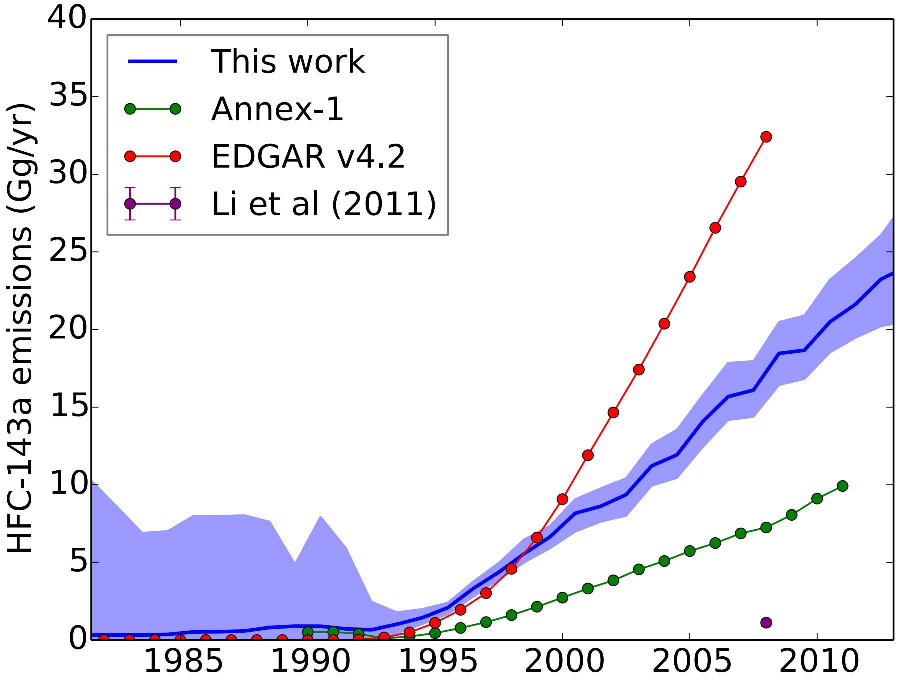

Fig. 5. HFC-143a emissions estimates derived from AGAGE observations (blue line and shading, indicating 1-sigma uncertainty). The red line shows the global emissions estimates from EDGAR v4.2 and the green line shows the emissions reported to the UNFCCC. The purple point shows emissions estimated for East Asia by Li et al. (2011).

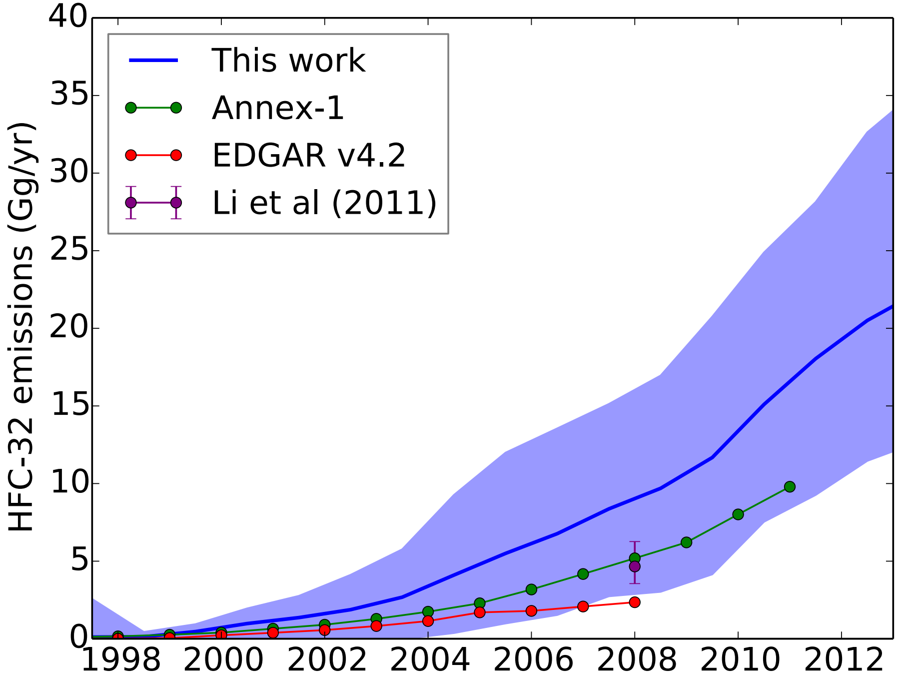

Fig. 6. HFC-32 emissions estimates derived from AGAGE observations (blue line and shading, indicating 1-sigma uncertainty). The red line shows the global emissions estimates from EDGAR v4.2 and the green line shows the emissions reported to the UNFCCC. The purple point shows emissions estimated for East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