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Global and regional emissions estimates of 1,1-difluoroethane (HFC-152a, CH_3CHF_2) from in situ and air archive observations

P. G. Simmonds[1], M. Rigby[1], A. J. Manning[2], M. F. Lunt[1], S. O'Doherty[1], D. Young[1], A. McCulloch[1], P. J. Fraser[4], S. Henne[5], M. K. Vollmer[5], S. Reimann[5], A. Wenger[5], J. Mühle[3], C. M. Harth[3], P. K. Salameh[3], T. Arnold[2], R. F. Weiss[3], P. B. Krummel[4], L. P. Steele[4], B. L. Dunse[4], B. R. Miller[14], C. R. Lunder[6], O. Hermansen[6], N. Schmidbauer[6], T. Saito[7], Y. Yokouchi[7], S. Park[8], S. Li[9], B. Yao[10], L. X. Zhou[10], J. Arduini[11], M. Maione[11], R. H. J. Wang[12], and R. G. Prinn[13]

[1]Atmospheric Chemistry Research Group, University of Bristol, Bristol, BS8 1TS, UK
[2]Met Office Hadley Centre, Exeter, EX1 3PB, UK
[3]Scripps Institution of Oceanography, University of California San Diego, La Jolla, CA 92093, USA
[4]CSIRO Oceans and Atmosphere Flagship, Aspendale, VIC 3195, Australia

[5]Laboratory for Air Pollution and Environmental Technology, Swiss Federal Laboratories for Materials Science and Technology (Empa), Dubendorf, 8600, Switzerland
[6]Norwegian Institute for Air Research (NILU), 2027 Kjeller, Norway
[7]Centre for Environmental Measurement and Analysis, National Institute for Environmental Studies, Onogawa, Tsukuba, 305-8506, Japan
[8]Department of Oceanography, College of Natural Sciences, Kyungpook National University, Daegu, 702-701, Republic of Korea
[9]Kyungpook Institute of Oceanography, College of Natural Sciences, Kyungpook National University, Daegu, 702-701, Republic of Korea
[10]Chinese Academy of Meteorological Sciences (CAMS), Beijing, 10081, China
[11]Department of Basic Sciences and Foundations, University of Urbino, 61029 Urbino, Italy
[12]School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA
[13]Center for Global Change Science, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
[14]Global Monitoring Division, ESRL, NOAA, Boulder, Colorado, USA

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Correspondence to: P. G. Simmonds (petergsimmonds@aol.com)

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Abstract

High frequency, ground-based, in situ measurements from eleven globally-distributed sites covering 1994–2014, combined with measurements of archived air samples dating from 1978 onward and atmospheric transport models, have been used to estimate the growth of 1,1-difluoroethane (HFC-152a, CH_3CHF_2) mole fractions in the atmosphere and the global emissions required to derive the observed growth. HFC-152a is a significant greenhouse gas but since it does not contain chlorine or bromine, HFC-152a makes no direct contribution to the destruction of stratospheric ozone and is therefore used as a substitute for the ozone depleting chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). HFC-152a has exhibited substantial atmospheric growth since the first measurements reaching a maximum annualised global growth rate of 0.81 ± 0.05 ppt yr^{-1} in 2006, implying a substantial increase in emissions up to 2006. However, since 2007, the annualised rate of growth has slowed to 0.38 ± 0.04 ppt yr^{-1} in 2010 with a further decline to an average rate of change in 2013–2014 of -0.06 ± 0.05 ppt yr^{-1}. The average Northern Hemisphere (NH) mixing ratio in 1994 was 1.2 ppt rising to a mixing ratio of 10.2 ppt in December 2014. Average annual mixing ratios in the Southern Hemisphere (SH) in 1994 and 2014 were 0.34 and 4.4 ppt, respectively. We estimate global emissions of HFC-152a have risen from 7.3 ± 5.6 Gg yr^{-1} in 1994 to a maximum of 54.4 ± 17.1 Gg yr^{-1} in 2011, declining to 52.5 ± 20.1 Gg yr^{-1} in 2014 or 7.2 ± 2.8 Tg-CO_2 eq yr^{-1}. Analysis of mixing ratio enhancements above regional background atmospheric levels suggests substantial emissions from North America, Asia and Europe. Global HFC emissions (so called "bottom up" emissions) reported by the United Nations Framework Convention on Climate Change (UNFCCC) are based on cumulative national emission data reported to the UNFCCC, which in turn are based on national consumption data. There appears to be a significant underestimate of "bottom-up" global emissions of HFC-152a, possibly arising from largely underestimated USA emissions and undeclared Asian emissions.

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1 Introduction

HFC-152a (CH_3CHF_2) is primarily sold as an aerosol and foam-blowing agent, (Greally et al., 2007) and as a component of some refrigerant blends (Ashford et al., 2004). Emissions to the atmosphere show both temporal and regional variability depending on the specific application in which HFC-152a is used. Incorporation of HFC-152a into aerosol propellants results in prompt release, whereas when used as a single-component non-encapsulated blowing agent, release occurs over a period of about 2 years (McCulloch et al., 2009). Refrigerant use of HFC-152a results in release over longer periods, possibly up to 20 years. Reported emissions of HFC-152a are likely to be incomplete as a consequence of a limited number of producers and confidentiality considerations. Emissions of HFC-152a for some countries are aggregated with other HFCs in a category reported to the UNFCCC as "unspecified mix". For example, emissions reported by the USA to the UNFCCC for HFC-152a, 227ea, 245ca and 43-10mee are shown in the database as "commercially confidential" and they constitute the aggregated "unspecified" emissions. HFC-152a emissions from the USA are estimated to be the primary contributor to the total for this gas from Annex 1 countries (Lunt et al., 2015). Recent papers (Manning and Weiss, 2007; Millet et al., 2009; Stohl et al., 2009; Barletta et al., 2011; Miller et al., 2012; Simmonds et al., 2015) have reported major differences between USA HFC-152a emission estimates derived from atmospheric measurements (top down) and emissions calculated from US reports to the UNFCCC (bottom up). The apparent under-reporting of USA emissions to UNFCCC ranges from 20–60 Gg based on annual average estimates.

HFC-152a has the smallest 100-year global warming potential (GWP_{100}, 138) of all the major HFCs (Forster et al., 2007; Myhre et al., 2013), with a short atmospheric lifetime of 1.5 years, due to efficient reaction with tropospheric hydroxyl (OH) radicals (SPARC Report No. 6, 2013). Unlike hydrocarbons, HFC-152a does not participate in the reaction to form ozone in the troposphere. These desirable properties have made HFC-152a especially attractive as a replacement, not only for CFCs and HCFCs,

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but also increasingly for HFC-134a in technical aerosol applications and mobile air-conditioners (IPCC/TEAP, 2011).

Ryall et al. (2001), using observations from Mace Head, Ireland, reported the distribution of European HFC-152a emissions, centered on Germany, and estimated average European total emission of 0.48 $Gg\,yr^{-1}$ in 1995–1998. Reimann et al. (2004), used a 3-year data set (2000–2002) of HFC-152a observations at the Swiss Alpine station Jungfraujoch and trajectory modelling, also noting a predominantly German source for European HFC-152a emissions. This group estimated European emission strength of 0.8 $Gg\,yr^{-1}$ in 2000–2002, with a growth rate of 0.3 $ppt\,yr^{-1}$ (ppt – parts per trillion, 10^{-12} $mol\,mol^{-1}$, or $pmol\,mol^{-1}$) from 2000 to 2002, and a December 2002 mole fraction at the Jungfraujoch station of 3.2 ppt.

In the Southern Hemisphere HFC-152a monthly means, annual means and trends have been reported from observations at Cape Grim, Tasmania, for 1998–2004 (Sturrock et al., 2001; Fraser et al., 2014a; Krummel et al., 2014). The HFC-152a annual means have grown from 0.8 ppt (0.1 $ppt\,yr^{-1}$) in 1998 to 1.8 ppt (0.4 $ppt\,yr^{-1}$) in 2004. More recent estimates of SE Australian HFC-152a emissions (2005–2012) have been calculated by interspecies correlation and model inversions and by extrapolation based on population (Fraser et al., 2014a).

Here we further expand the HFC-152a record through 2014 using in situ observations from eleven globally-distributed monitoring stations (9 Advanced Global Atmospheric Gases Experiment (AGAGE) stations and 2 affiliated stations), together with atmospheric transport models to independently determine HFC-152a emission estimates on regional and global scales. We then compare these with HFC-152a emission estimates compiled from national reports to the UNFCCC and Emissions Database for Global Atmospheric Research (EDGAR v4.2; http://edgar.jrc.ec.europa.eu/), using the same techniques reported for other greenhouse gases (O'Doherty et al., 2009, 2014; Miller et al., 2010; Vollmer et al., 2011; Rigby et al., 2014).

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2 Experimental methods

2.1 Instrumentation and calibration

High frequency, in situ measurements of HFC-152a were determined by gas chromatography-mass spectrometry (GC-Agilent 6890) coupled with quadrupole mass selective detection (MSD-Agilent 5973/5975). Measurements commenced at Mace Head, Ireland in 1994 and Cape Grim, Tasmania in 1998, using a custom-built automated pre-concentration system to selectively and quantitatively retain halogenated compounds from 2 L air samples – the Adsorption Desorption System (ADS) based on a Peltier–cooled pre-concentration microtrap cooled to −50 °C during the adsorption phase, providing on site calibrated air samples every 4 h (Simmonds et al., 1995). In 2004 the ADS-GC-MS was replaced with a more advanced custom-built pre-concentration system (Medusa) with enhanced cooling to ∼ −180 °C and the relatively mild adsorbent HayeSep D (Miller et al., 2008; Arnold et al., 2012). Agilent 5973 MSDs (mass selective detector) were also upgraded to the Agilent 5975 MSDs over the course of the Medusa observations. Analysis of each 2 L sample of ambient air was alternated with analysis of a 2 L reference gas (designated as a working standard) to correct for short term instrumental drift, resulting in 12 (Medusa) individually calibrated air measurements per day. Working standards were prepared for each station by compressing ambient air into 34 L electropolished stainless steel canisters (Essex Industries, Inc, Missouri) using a modified oil-free compressor (SA-6, RIX, California). An exception to this was the Cape Grim and Zeppelin stations, where the working standards were filled using a cryogenic filling technique. Research-grade helium, which was used as a carrier gas in the Medusa systems, was further purified first by passage through an Agilent "Big Universal Trap", followed by a "getter" type purifier (Valco Instruments, Houston, Tx). The carrier gas was analysed for blanks on a regular basis and blank levels of HFC-152a were below the limit of detection at all field stations.

Table 1 lists the geographical location and the time frame when routine ambient measurements of HFC-152a commenced at each monitoring station. Stations with the

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longest observational records that deployed both ADS and Medusa GC-MS instruments include Mace Head (MHD), Jungfraujoch (JFJ), Ny-Ålesund (ZEP) and Cape Grim (CGO). Medusa GC-MS instruments were installed at five other AGAGE stations Trinidad Head (THD), Gosan (GSN), Ragged Point, (RPB), Shangdianzi (SDZ) and Cape Matatula (SMO) between 2003 and 2010. In addition two AGAGE affiliated stations Monte Cimone (CMN) and Hateruma (HAT), which use comparable GC-MS instruments, but a different pre-concentration design for sample enrichment, commenced HFC-152a measurements in 2001 and 2004, respectively. Importantly, all eleven stations listed in Table 1 report HFC-152a measurements relative to the Scripps Institution of Oceanography (SIO-2007) calibration scale (as dry gas mole fractions in pmol mol^{-1}).

The estimated accuracy of the calibration scale for HFC-152a is 4 % (1σ) and a more detailed discussion of the measurement technique and calibration procedure is reported elsewhere (Miller et al., 2008; O'Doherty et al., 2009; Mühle et al., 2010). HFC-152a was determined using the MS in selected ion monitoring mode (SIM) with a target ion $CH_3CF_2^+$ (m/z 65) and qualifier ion CH_3CF^+ (m/z 46). To ensure that potential interferences from co-eluting species did not compromise the analysis, the ratio of the target to qualifier ion was continuously monitored. Measurement precision was calculated as the daily standard deviation (1σ) of the ratios of each standard response to the average of the closest-in-time preceding and subsequent standard responses. Typical daily precisions vary from station to station with a range of 0.1–0.4 ppt. Individual station precisions were used to estimate the precision of each in situ measurement.

2.2 Northern and Southern Hemisphere archived air samples

In order to extend the HFC-152a data record back before the commencement of high-frequency measurements, analyses of Northern Hemisphere (NH) and Southern Hemisphere (SH) archived air samples were carried out using three similar Medusa GC-MS instruments at the Scripps Institution of Oceanography (SIO), La Jolla, California, the Commonwealth Scientific and Industrial Research Organisation (CSIRO), Aspendale,

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Australia and the Cape Grim Baseline Station, Tasmania. The SH samples are part of the Cape Grim Air Archive (CGAA) described in Langenfelds et al. (1996) and Krummel et al. (2007). The NH samples analysed for this paper were filled during background conditions mostly at Trinidad Head, but also at La Jolla, California; Cape Meares, Oregon and Point Barrow, Alaska, (courtesy of the National Oceanic and Atmospheric Administration).

In addition, eight SH samples were measured at SIO and compared with SH samples of similar age measured at CSIRO (February 1995, July 1995, November 1995, June 1998, July 2004, February 2006, August 2008, and December 2010, Δx = 0.01–0.07 ppt, Δt = 1–33 days) and three NH samples were measured at CSIRO and compared with NH samples of the same age measured at SIO (May 1989 and April 1999, Δx = 0.02–0.06 ppt, Δt = 1–11 days). The good agreement between SIO and CSIRO archived air stored in different types of tanks (Stainless steel tanks, Essex Industries, Inc and Silcosteel treated tanks, Restek Corporation) serves both as proof of the good consistency of the individual Medusa GC-MS instruments and the integrity of the tanks used. Samples were analysed in replicate typically 3–6 times each and several NH tanks were re-measured over a number of years.

2.3 Selection of baseline data

Baseline in situ monthly mean HFC-152a mixing ratios were calculated by removing above baseline enhancements, due to local and regional pollution influences, using the AGAGE pollution identification algorithm as described in O'Doherty et al. (2001) and Cunnold et al. (2002). For the core AGAGE stations, in situ baseline data and archive air data are then combined for each hemisphere, and outliers are rejected in an iterative filtering process.

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3 Modelling studies

We pursued several approaches to determine emissions at global, continental and regional scales. The methodologies have been published elsewhere and are summarised below. The global, continental and some regional estimates incorporate a priori estimates of emissions, which were subsequently adjusted using the observations.

There are several sources of information on production and emissions of HFC-152a; none of which, on their own, provides a complete database of global emissions. The more geographically comprehensive source of information 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 are reported in Table 2(II)s1 in the Common Reporting Format (CRF) available at http://unfccc.int/nationalreports/annex_i_ghg_inventories/national_inventories_submissions/items/8108.php. 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 greenhouse gases (GHGs) on a country, region and grid basis up to 2008.

To infer "top-down" emissions we select observations from the various observing sites listed in Table 1 and four chemical transport models. These eleven sites are sensitive to many areas of the world in which HFC-152a emissions are reported, however other areas of the globe are also likely to have significant emissions (such as South Asia, South Africa, and South America) that are not well monitored by this network.

3.1 Global emissions estimates using a 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 500 and 200 hPa). The model was originally developed by Cunnold et al. (1983)

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(nine-box version), with subsequent improvements by Cunnold et al. (1994) and Rigby et al. (2013, 2014). Emissions were estimated using a Bayesian method in which an a priori constraint (EDGAR v4.2) on the emissions growth rate was adjusted using the baseline-filtered AGAGE observations (Rigby et al., 2011a, 2014). Global emissions were derived that included estimates of the uncertainties due to the observations, the prior and the lifetime of HFC-152a. Note that historically and here the 12-box model only uses observations from the core AGAGE sites, MHD, THD, RPB, SMO, and CGO.

3.2 Global and continental emissions estimates using a combined Eulerian and Lagrangian model

We used the methodology outlined in Lunt et al. (2015) and Rigby et al., (2011b) to derive emissions of HFC-152a from continental regions. The high-resolution, regional UK Met Office Numerical Atmospheric dispersion Modelling Environment (NAME), Manning et al. (2011) was used to simulate atmospheric HFC transport close to a subset of AGAGE monitoring sites, which were strongly influenced by regional HFC sources (domains shown by red boxes in Fig. 1). Simultaneously, the influence of changes to the global emissions field on all measurement stations was simulated using the global Model for OZone and Related Tracers, MOZART (Emmons et al., 2010). We estimated annual emissions for the period 2007–2012 and aggregated the derived emissions fields into continental regions, separating countries that either do ("Annex-1"), or do not ("non-Annex-1") report detailed, annual emissions to the UNFCCC. Emissions were estimated using a hierarchical Bayesian inverse method (Ganesan et al., 2014) and observations from 10 of the 11 sites listed in Table 1, excluding Shangdianzi due to the short time series.

3.3 High-resolution regional emissions estimates using InTEM

A method for estimating emissions from observations and atmospheric transport modelling with NAME referred to as InTEM ("Inversion Technique for Emission Modelling")

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(Manning et al., 2011), uses a simulated annealing method (Press et al., 1992), to search for the emission distribution that produces a modelled times-series that has the best statistical match to the observations from certain AGAGE stations (e.g. Mace Head, Cape Grim). NAME was driven with output from the operational analysis of the UK Met Office Numerical Weather Prediction model, the Unified Model, at global horizontal resolution of 17–40 km (year dependent). InTEM estimates the spatial distribution of emissions across a defined geographical area, and can either start from a random emission distribution or be constrained by an inventory-defined distribution. Emission totals from specific geographical areas are calculated by summing the derived emissions from each grid (non-uniform) in that region.

3.4 High resolution European emission estimates using the FLEXPART model

A regional Bayesian inversion system using backward simulations of a Lagragian particle dispersion model FLEXPART (Stohl et al., 2005) was applied to the HFC-152a observations from Mace Head, Jungfraujoch and Mt. Cimone for the period 2006 to 2014. The inversion technique follows the description by Stohl et al. (2009) and was previously applied to regional halocarbon emissions from Europe (Keller et al., 2012; Maione et al., 2014) and China (Vollmer et al., 2009). The transport model FLEXPART was driven with output from the operational analysis of the Integrated Forecast System (IFS) of the European Centre for Medium Range Weather Forecast (ECMWF) using a spatial resolution of $0.2^{\circ} \times 0.2^{\circ}$ for a nested domain covering the larger area of the European Alps and a spatial resolution of $1^{\circ} \times 1^{\circ}$ elsewhere.

3.5 Regional emissions estimates using the inter-species correlation (ISC) methods

We also present regional emissions estimates using inter-species correlation (ISC) methods (Yokouchi et al., 2005). Emissions of a number of trace gases from the Melbourne/Port Phillip region (CFCs, HCFCs, HFCs, carbon tetrachloride: Dunse et al.,

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2001, 2002, 2005; O'Doherty et al., 2009; Fraser et al., 2014a, b), including HFC-152a (Greally et al., 2007), have been estimated utilising in situ high frequency measurements from Cape Grim and ISC with co-incident carbon monoxide (CO) measurements. Using HCFC-22 as the reference tracer, Li et al. (2011) reported that China is the dominant emitter of halocarbons in East Asia. North American HFC-152a emissions have been estimated from atmospheric data using interspecies correlation based techniques with CO (Millet et al., 2009; Barletta et al., 2011) and fossil fuel CO_2 (Miller et al., 2012) as the reference emissions.

4 Results and Discussion

4.1 In situ observations

The time series of HFC-152a in situ observations recorded at the various monitoring stations are shown in Fig. 2a–c. Data have been filtered into baseline (black) and above baseline (red) using the AGAGE pollution algorithm described above. Figure 2a shows the mole fractions in ppt for the four stations that deployed both ADS and Medusa GC-MS instruments (MHD, ZEP, JFJ, and CGO). Most notable are the substantial above baseline events at Mace Head (MHD) and Jungfraujoch (JFJ) that are influenced primarily by emissions from European sources. Conversely, the Zeppelin Arctic station (ZEP) and the SH station at Cape Grim (CGO) have relatively small above baseline events implying smaller emissions from local or regional sources.

Figure 2b shows measurements at the five other AGAGE stations (THD, GSN, RPB, SDZ, and SMO), which used only Medusa GC-MS instruments. The North American site at Trinidad Head (THD) and the Asian sites at Shangdianzi (SDZ) and Gosan (GSN) are the most strongly influenced by regional emissions. The tropical sites at Ragged Point, Barbados (RPB) and American Samoa (SMO) show very few enhancements above the baseline due mostly to local emissions occurring under night time inversion conditions and occasional influences from regional emission sources (note

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the different *Y* axis scales). Although the SDZ station was operational for only a short period, the enhancements above baseline are significant due to the sensitivity of this site to Chinese emissions, and comparable in magnitude to those at GSN.

Figure 2c illustrates the time series from the two AGAGE affiliated stations Monte Cimone (CMN) and Hateruma (HAT) that used comparable GC-MS instruments but with different methods of pre-concentration. Monte Cimone, like the Jungfraujoch, also has substantial emissions from sources in continental Europe. Hateruma (HAT) is influenced by sources in, China, Korea, Taiwan and Japan (Yokouchi et al., 2006).

4.2 Atmospheric trends and seasonal cycles

Figure 3 shows the in situ measurements of HFC-152a, as baseline monthly means, obtained from the two AGAGE stations Mace Head (MHD) and Cape Grim (CGO) with the longest time series that deployed both ADS and Medusa GC-MS instruments. Superimposed in Fig. 3 is the NH and SH archived flask data extending back to 1978. Annual average mole fractions at Mace Head increased from 1.2 ppt in 1994 to 10.0 ppt by 2014, Cape Grim annual average mole fractions increased from 0.85 ppt in 1998 when in situ measurements first began to 4.5 ppt in 2014. However, in the last few years the rates of growth at both sites have slowed to currently insignificant levels.

The NH archived samples are more variable than the SH archived samples. The SH archive is collected only under strict baseline conditions (Southern Ocean air) and is far removed from the major sources of HFC-152a. Conversely in the NH, where most major sources of emissions are located, sampling under strictly baseline conditions is more problematic.

Figure 4a illustrates HFC-152a baseline monthly means obtained from the five other AGAGE observing sites (RPB, GSN, SMO, THD, and SDZ) using only the more advanced Medusa GC-MS. There is a large seasonal cycle at Gosan (GSN) with a very deep minimum due to summertime transport from the Southern Hemisphere (Li et al., 2011).

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Figure 4b shows the baseline monthly mean mole fractions for the three mountain stations. Ny-Ålesund (ZEP) and Jungfraujoch (JFJ), using combined ADS and Medusa GC-MS measurements and Monte Cimone (CMN), which used a commercial pre-concentrator GC-MS. In most years Monte Cimone exhibits enhanced mixing ratios during the NH spring months (March–May).

The HFC-152a seasonal cycles at Mace Head and Cape Grim shown in Fig. 5a and b, are broadly representative of the Northern and Southern Hemispheres. The seasonal cycle at Mace Head shows a NH spring maximum (April–May) and late summer minimum (August–October), while the SH seasonal cycle at Cape Grim exhibits a broad SH spring maximum (July–November) and a late SH summer minimum (January–April). The summer minimum at both locations is attributed to enhanced summertime loss (OH) with possibly a contribution from seasonally varying emissions in the NH, that are possibly out-of-phase with the NH sink. At Cape Grim an additional source of seasonality is due to seasonally varying transport between the NH and SH, that is generally in phase with the sink induced seasonal cycle. This competition between OH summertime loss and seasonally varying transport has been observed at many other AGAGE locations (Prinn et al., 1992; Greally et al., 2007; O'Doherty et al., 2009, 2014; Li et al., 2011).

Figure 6 shows the NH and SH mole fractions (ppt) outputs from the AGAGE global 12-box model and the individual grid box average annual growth rate. Most notable is the positive growth rate from 1995 reaching a maximum of $\sim 0.84\,\mathrm{ppt\,yr^{-1}}$ in 2006, followed by a steady decline in the growth rate with a minimum in 2008–2009, possibly attributable to the economic recession. The positive growth rate then resumes increasing to $\sim 0.4\,\mathrm{ppt\,yr^{-1}}$ in 2010 followed by a subsequent decrease with an average negative growth rate in 2013–2014 of $0.06\,\mathrm{ppt\,yr^{-1}}$.

The globally averaged mole fraction in the lower troposphere in 2014 is estimated to be 6.8 ± 0.23 ppt and the annualised rate of increase is $-0.06\,\mathrm{ppt\,yr^{-1}}$. The radiative forcing due to HFC-152a estimated using the global average mole fraction obtained from the AGAGE 12-box model was $0.61\,\mathrm{mW\,m^{-2}}$ in 2014. The strong inter-

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hemispheric gradient demonstrates that emissions are predominantly in the NH, as has been illustrated for many other purely anthropogenic trace gases (Prinn et al., 2000).

5 Top-down emission estimates

5.1 Global estimates

Estimated global emissions of HFC-152a from this work and the UNFCCC and EDGAR inventory reports are shown in Fig. 7 and Table 2. The blue solid line represents our model-derived emissions, with the 1σ error band shown by the shaded areas. Model derived emissions grew steadily from 1995–2007 with a potential decrease in emissions in 2009 to $48 \pm 16.4\,\mathrm{Gg\,yr^{-1}}$, possibly as a result of the economic downturn in 2008–2009. The mean emission reached a maximum of $54.4 \pm 17.1\,\mathrm{Gg\,yr^{-1}}$ in 2011, followed by a period of relatively stable emissions, the mean showing a slight decline to $52.5 \pm 20.1\,\mathrm{Gg\,yr^{-1}}$ in 2014 ($7.3 \pm 2.8\,\mathrm{Tg\text{-}CO_2\,eq\,yr^{-1}}$).

The data shown in column 3 of Table 2 are the totals of submissions by the national governments to the UNFCCC (Rio Convention) as reported in Table 2(II) s1 in the Common Reporting Format (CRF), available on the UNFCCC website (http://unfccc.int/national_reports/annex_i_ghg_inventories/national_inventories_submissions/items/8108.php). The values were taken from the 2014 database and cover years 1995, the baseline year for submissions, to 2012. In addition to reporting calculated emissions of HFCs 23, 32, 125, 134a, 143a, 152a, 227ea, 236fa, 245ca and 43-10mee, individually, many countries also included "unspecified" emissions in this database (as the sum of their CO_2 equivalents). Where the unspecified component was small in relation to the national specified emissions, it was disaggregated by assuming that it had the same fractional contribution of each HFC as reported in the specified components (adjusted for their CO_2 equivalence). However, in the US, although values of emissions of several HFCs are calculated specifically for the individual substances, HFCs 152a,

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227ea, 245ca and 43-10mee are shown in the database as "commercially confidential" and their emissions apparently constitute the substantial aggregated "unspecified" emissions reported. Hence, for the US, these unspecified annual emissions were divided only between HFCs 152a, 227ea, 245ca and 43-10mee, assuming the same ratio as their reported global emissions, all expressed as CO_2 equivalents. The values shown in column 4 of Table 2 are the global totals of HFC-152a after adjusting in these ways for the quantities included in "unspecified" emissions.

The additional component of US emissions makes a substantial contribution to the very large difference between the UNFCCC data as reported and the adjusted values. This is partly due to the low global warming potential of HFC-152a (a factor of 10 lower than other HFCs) which magnifies its mass component in the 8200 Gg CO_2 equivalent of US "unspecified" emissions.

The AGAGE trend in global emissions is substantially higher than the emissions calculated from the UNFCCC GHG reports (2014 submission). 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, South Africa and Latin America do not report to the UNFCCC. Where we include the HFC-152a component of unspecified emissions (green line in Fig. 7) results are consistent within the error bars until 2005 when they diverge (UNFCCC + "unspecified" lower). From 1996–2002, estimated emissions from EDGAR (v4.2) are generally consistent with AGAGE emissions, but then begin to diverge with EDGAR emissions 22 Gg below 2008 AGAGE emissions, the last year in which EDGAR reports emissions.

5.2 Regional emissions of HFC-152a inferred for Europe, United States, Asia and Australia

Lunt et al. (2015) have reported global and regional emissions estimates for the most abundant HFCs, based on inversions of atmospheric mole fraction data, aggregated

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into two categories; those from Annex 1 countries and those from non-Annex 1 countries. The inversion methodology used the NAME model to simulate atmospheric transport close to the monitoring sites, and the Model for Ozone and Related chemical Tracers (MOZART, Emmons et al., 2010) to simultaneously calculate the effect of changes to the global emissions field on each measurement site. The model sensitivities were combined with a prior estimate of emissions (based on EDGAR) and the atmospheric measurements, in a hierarchical Bayesian inversion (Ganesan et al., 2014), to infer emissions.

Using this method we infer emissions estimates for the entire world, Europe, North America and East Asia. Table 3 lists our estimated regional emissions in $Gg\,yr^{-1}$ averaged across two time periods: 2007–2009 and 2010–2012, together with our global emission estimates averaged over the same time periods from the 12-box model. It is apparent that North American average annual emissions ($\sim 30\,Gg$) are the major contributor to the global total with Europe contributing annual average emissions from about 5–6 $Gg\,yr^{-1}$. East Asia and Europe contribute emissions of ~ 7 and $\sim 6\,Gg\,yr^{-1}$, respectively to the global total. The 2007–2009 North American emission estimate of $28\,Gg\,yr^{-1}$ agrees within the uncertainties of HFC-152a emission estimates reported in Barletta et al. (2011) and Simmonds et al. (2015). The North American estimate indicates one reason why the UNFCCC reported amount appears to be so low; more than half the global emissions appear to come from this continental region, yet the UNFCCC reports do not include specific HFC-152a emissions from the US.

5.2.1 InTEM North-West Europe (NWEU) estimated emissions from Mace Head observations

The HFC-152a perturbations above baseline, observed at Mace Head (MHD), are driven by emissions on regional scales that have yet to be fully mixed on the hemisphere scale. The MHD observations are coupled with the NAME model air history maps using the inversion system InTEM to estimate surface emissions across NWEU

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(Manning et al., 2011). NWEU is defined as United Kingdom, Ireland, Germany, France, Benelux and Denmark.

As shown in Fig. 8 the NWEU emission estimates for HFC-152a from both InTEM (rolling 3 yr averages) and the UNFCCC (2013 submission) inventory match very well and overlap within the uncertainties. The estimates of NWEU emissions grew steadily from 1995 reaching a maximum emission of $1.6 \pm 0.21\,\mathrm{Gg\,yr^{-1}}$ in 2003 with a subsequent decline to a level of $0.98 \pm 0.34\,\mathrm{Gg\,yr^{-1}}$ in 2013.

5.2.2 European estimated emissions from European observations at Mace Head, Jungfraujoch and Mt. Cimone

The FLEXPART model (see Sect. 3.4) was applied to the HFC-152a observations from Mace Head, Jungfraujoch and Mt. Cimone for the period 2006 to 2014. Prior to 2006, the model resolution of Integrated Forecast System (IFS) was not sufficiently fine to realistically simulate the transport to the two high altitude sites Jungfraujoch and Mt. Cimone. Therefore, no attempt was made here to apply the inversion system to years before 2006. As prior information of the HFC-152a emissions we used country totals as submitted to UNFCCC. These were spatially disaggregated following the HFC-152a distribution given in EDGAR (v4.2). For countries not reporting HFC-152a emissions to UNFCCC we used the original values given in EDGAR. The EDGAR inventory was only available up to the year 2008 beyond this year the EDGAR 2008 distribution was used. Where scaling with UNFCCC estimates was not possible the EDGAR estimates were used. The uncertainty of the prior emissions was set so that the region total uncertainty equalled 20 % of the region total emissions. The regional inversion grid covered a region similar to that shown in Fig. 1.

The temporal evolution of emission estimates for different European regions are given in Fig. 9. In contrast to the InTEM estimates the Bayesian inversion derived emissions in NWEU were slightly smaller than the UNFCCC estimate and showed a continued decrease until 2014. Total emissions in the inversion domain ranged from $4 \pm 0.5\,\mathrm{Gg\,yr^{-1}}$ (2σ confidence range) for 2006 to only $2.5 \pm 0.2\,\mathrm{Gg\,yr^{-1}}$ in 2014. This

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is considerably smaller than the European Annex I estimate given in Sect. 5.2, but covers a significantly smaller geographical region, the estimate given in Sect. 5.2 encompassed all countries in Europe extending beyond the bounds of the area indicated in Fig. 1. The steady decline in emissions was interrupted by a local maximum in the years 2011–2012, when emissions reached 3.6 ± 0.5 (Gg yr^{1-}). Previously, a minimum in the emissions was seen in 2009 and was most pronounced for the Iberian Peninsula, Italy, France and Germany, which could indicate the influence of the European recession in 2008–2009. For NWEU the emission estimate remains slightly below the UNFCCC estimates and those estimated by InTEM, but support the declining trend in European emissions. Despite the fact that Italy does not report HFC-152a emissions to the UNFCCC, the largest by country emissions were estimated for Italy (up to 1 Gg yr^{-1} in 2007). However, a strong decline in these emissions after 2011 was established here. Similar values for Italian HFC-152a emissions were reported by Brunner et al. (2012) using observations from Jungfraujoch and Mace Head (but not Mt. Cimone) in an extended Kalman Filter inversion.

5.2.3 US estimated emissions

Estimates of North American emissions have been reported by several groups. Millet et al. (2009) report average US emissions for 2004–2006 of 7.6 Gg (4.8–10 Gg) compared with the UNFCCC average 2005–2006 estimate of 12.3 Gg calculated from UNFCCC data. Miller et al. (2012) provided HFC-152a emissions estimates averaged from 2004–2009 of 25 Gg (11–50 Gg). Barletta et al. (2011) reported a 2008 HFC-152a emission estimate of 32 ± 4 Gg. In a recent investigation of the surface-to-surface transport of HFC-152a from North America to Mace Head, Ireland, an interspecies correlation method with HFC-125 as the reference gas was also used to estimate North American emissions primarily from the eastern seaboard region (Simmonds et al., 2015). The average 2008 HFC-152a emission estimate was 31.3 ± 5.9 Gg, in very close agreement with the estimate from Barletta et al. (2011). HFC-152a emission estimates

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for 2005 (10.1 Gg) and 2006 (12.5 Gg) reported by Stohl et al. (2009) are close to the (recalculated) UNFCCC estimates in those years.

If the sources of emission from the US were solely technical aerosols and construction foam, emissions would be expected to be far lower. These were the historic uses in Europe and Japan and resulted in emissions ten times less than those estimated for the US. However, in the US, do-it-yourself (DIY) refilling of car air conditioners is not only permitted but thriving (Zhan et al., 2014), with an estimated 24 million DIY refilling operations attempted each year. The practice is banned in Europe (OJ, 2014).

Furthermore, there is ample evidence online that HFC-152a is extensively used in DIY refilling on account of its lower cost. It is a technically suitable replacement for HFC-134a, although there are safety concerns of importance to vehicle manufacturers (Hill, 2003). If the quantities estimated by Zhan et al. (2014) were met using HFC-152a diverted from the retail trade in technical aerosols, some 10 to 20 $Gg\,yr^{-1}$ of HFC-152a could be released into the atmosphere from this source alone.

5.2.4 East Asian emissions

Emissions of HFC-152a from China were estimated to be $4.3 \pm 2.3\,Gg\,yr^{-1}$ in 2004–2005 (Yokouchi et al., 2006), $3.4 \pm 0.5\,Gg\,yr^{-1}$ in 2008 (Stohl et al., 2010) and 5.7 (4.3–7.6) $Gg\,yr^{1-}$ in 2008 (Kim et al., 2010). Li et al. (2011) also 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 5.4 (4–7.4) $Gg\,yr^{1-}$. In contrast the Taiwan region Korea and Japan had lower estimated emissions totalling $1.39\,Gg\,yr^{-1}$. These estimates are within the uncertainties of our East Asia emissions reported in Sect. 5.2.

Yao et al. (2012) using the interspecies correlation method with carbon monoxide as the reference tracer reported more recent Chinese emissions of $2 \pm 1.8\,Gg\,yr^{-1}$ in

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2010–2011. This would imply some reduction in Chinese emissions compared with earlier years.

5.2.5 Australian HFC-152a emissions from Cape Grim data

SE Australian emissions of HFC-152a are estimated using the positive enhancements above baseline or background concentrations. Figure 2a (CGO) shows an overall increase in the magnitude of HFC-152a pollution episodes, presumably due to increasing regional emissions. Detailed analysis of these pollution episodes using air mass back trajectories shows clearly that the HFC-152a pollution seen at Cape Grim originates largely from Melbourne and the surrounding Port Phillip region.

Australian HFC-152a emissions of 5–10 $Mg\,yr^{-1}$ via interspecies correlation (ISC) have been reported for the period 1998–2004, although it was noted that these emission estimates were near the detection limit of the ISC method (Greally et al., 2007). Recently, significant improvements have been made to this ISC method, including a revised (upward) CO emissions inventory for the Melbourne/Port Phillip region, exclusion of high CO events in the Cape Grim in situ CO record, resulting from CO emissions from biomass burning and coal combustion in the Latrobe Valley (east of Port Phillip) and a revised (upward) population-based scaling factor (5.4), used to convert Melbourne/Port Phillip emissions to Australian emissions (Fraser et al., 2014a, b). Each of these changes to the ISC method resulted in higher trace gas emission estimates. The revised (compared to Greally et al., 2007) Australian HFC-152a emission estimates from the ISC method are shown in the 2nd column of Table 4 and in Fig. 10 as 3-year running averages.

The InTEM model (Manning et al., 2003, 2011) has been used to derive HFC-152a emissions from Victoria/Tasmania, (Fraser et al., 2014a). Annual Australian emissions are calculated from Victoria/Tasmania emissions using a population based scale factor of 3.7 and are shown in Fig. 10 and the 3rd column of Table 4, interpolated from rolling 3-year emission estimates. Over the period 2002–2011, the average Australian HFC-152a emissions from ISC and InTEM agree to within 2 %.

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Australian HFC-152a emissions have increased steadily from 25 Mg yr^{-1} in the late-1990s to over 60 Mg yr^{-1} in the late-2000s. The 2012 and 2013 emissions have been estimated from Cape Grim data by ISC at 77 and 69 Mg, respectively. Australian HFC-152a emissions (1998–2004) are 25–30 Mg, significantly higher than estimated (5–10 Mg yr^{-1}) in Greally et al. (2007), resulting from improvements in the ISC method (see above).

Compared to the global values derived above, Australian emissions are 0.1 % of global emissions based on ISC/InTEM data. It is unusual for Australian emissions of an industrial chemical to be as low as 0.1 % of global emissions (Fraser et al., 2014b). The possible reasons for the low Australian HFC-152a emissions (relatively low use in Australia compared to rest of world) are being investigated. One suggestion (M. Bennett, Refrigerant Reclaim Australia, personal communication, 2013) is that a significant major-volume use in other parts of the world for HFC-152a is as an aerosol propellant, a use not taken up to any significant degree in Australia.

6 Conclusions

Atmospheric abundances and temporal trends of HFC-152a have been estimated from data collected at the network of eleven globally-distributed monitoring sites. The longest continuous in situ record at Mace Head, Ireland covers a 20-year period from 1994–2014. Other stations within the network have observational records from 9–16 years, with only a short record (2010–2012) at Shangdianzi, China. From selected baseline in situ measurements and measurements of archived air samples dating back to 1978 the long-term growth rate of HFC-152a has been deduced. Analysing the enhancements above baseline coupled with atmospheric transport models permitted us to estimate both regional and global HFC-152a emissions. However, it should be noted that the various models use different domains to obtain regional emissions estimates.

The average NH baseline mixing ratio in 1994 was 1.2 ppt increasing to 8.5 ppt in 2004 and reaching an average mixing ratio of 10.2 ppt in December 2014. In the SH

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the mixing ratio increased from 0.34 ppt in 1994 to 4.4 ppt in 2014. Using the global average mole fraction obtained from the AGAGE 12-box model we estimate that the HFC-152a contribution to radiative forcing was 0.61 mW m^{-2} in 2014. The global annualised growth rate of HFC-152a from 1996–2006 averaged 0.38 ppt yr^{-1}, with a maximum annual growth rate in 2006 of 0.81 ± 0.05 ppt yr^{-1}. More recently the average annual growth rate has slowed to 0.38 ± 0.04 ppt yr^{-1} in 2010, reaching a negative growth rate in 2013–2014 of 0.06 ± 0.05 ppt yr^{-1}.

Global HFC-152a emissions increased from 7.3 ± 5.6 Gg yr^{-1} in 1994 to 52.5 ± 20.15 Gg yr^{-1} in 2014. Global emissions are dominated by emissions from North America with this region being responsible for ~ 67 % of global emissions in our estimates. Estimates of North-West European emissions of ~ 0.9 Gg yr^{-1} (2010–2012 average) agree within the uncertainties for the two regional models (see Sects. 3.3 and 3.4) and overlap with the UNFCCC inventory. For the combined Eulerian and Lagrangian models (see 3.2), that encompass all European countries, we derive a 2010–2012 average emission of 5.2 Gg yr^{-1}. East Asia countries contribute 1 Gg yr^{-1} (Annex 1) and 6 Gg yr^{-1} (Non-Annex 1) to the global total (2010–2012 averages). All of the model studies indicate a current declining trend in European and Asian emissions.

Substantial differences in emission estimates of HFC-152a were found between this study and those reported to the UNFCCC which we suggest arises from underestimated North American emissions and undeclared Asian emissions; reflecting the incomplete global reporting of GHG emissions to the UNFCCC and/or biases in the accounting methodology. Ongoing, continuous, globally-distributed and accurate measurements of GHGs, such as HFC-152a, are required to enable so-called "top-down" verification (or otherwise) of global and regional emissions derived from national inventories, or "bottom-up" data collected and reported to the UNFCCC (Weiss and Prinn, 2011).

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Data availability

The entire ALE/GAGE/AGAGE data base comprising every calibrated measurement including pollution events from June 1978 to current is archived on the Carbon Dioxide Information and Analysis Center (CDIAC) at the U.S. Department of Energy, Oak Ridge National Laboratory.

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Table 1. Overview of the eleven measurement stations used in this study, their coordinates and periods for which data are available.

Station	Latitude	Longitude	ADS Data[4]	Medusa Data[5]
Ny-Ålesund, Norway[1]	78.9° N	11.9° E	2001–2010	September 2010–present
Mace Head, Ireland[1]	53.3° N	9.9° W	1994–2004	June 2003–present
Jungfraujoch, Switzerland[1]	46.5° N	8.0° E	2000–2008	May 2008–present
(Monte Cimone, Italy[2])	44.2° N	10.7° E		(June 2001–present[2])
Trinidad Head, California[1]	41.0° N	124.1° W		March 2005–present
Shangdianzi, China[1,3]	40.4° N	117.7° E		May 2010–August 2012
Gosan, Jeju Island, Korea[1]	33.2° N	126.2° E		November 2007–present
(Hateruma, Japan[2])	21.1° N	123.8° E		(May 2004–present[2])
Ragged Point, Barbados[1]	13.2° N	59.4° W		May 2005–present
Cape Matatula, Samoa[1]	14.2° S	170.6° W		May 2006–present
Cape Grim, Tasmania[1]	40.7° S	144.7° E	1998–2004	Jan 2004–present

[1] AGAGE stations.
[2] (Affiliated stations) use a different pre-concentration system (non-Medusa) than the AGAGE stations, but comparable GC-MS analytical instruments (see Yokouchi et al., 2006; Maione et al., 2014).
[3] Shangdianzi was only operational for a short period and not included in the modelling studies.
[4] Period of HFC-152a data record using ADS-GC-MS.
[5] Period of HFC-152a data record using and Medusa-GC-MS.

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Table 2. Estimates of global emissions of HFC-152a ($Gg\,yr^{1-}$ ± standard deviation) based on AGAGE in situ measurements using the AGAGE 2-D 12-box model. Global emission inventories as reported in UNFCCC National Inventory Reports (2014 submission) and recalculated from the UNFCCC data as described in the text, and from the EDGAR (v4.2) database.

Year	AGAGE ($Gg\,yr^{1-}$)	As reported ($Gg\,yr^{1-}$)	EDGAR (4.2) ($Gg\,yr^{1-}$)	Including "unspecified" contribution ($Gg\,yr^{1-}$)
1994	7.3 ± 5.6			
1995	7.9 ± 7.4	1.0	7.3	8.8
1996	9.1 ± 8.4	1.1	8.9	13.3
1997	11.3 ± 8.6	1.3	10.3	15.4
1998	12.5 ± 10.9	1.2	11.7	13.3
1999	14.4 ± 11.2	1.4	13.2	14.0
2000	16.6 ± 12.2	2.2	15.2	13.0
2001	18.4 ± 13.4	3.5	15.9	15.4
2002	22.5 ± 14.7	4.5	18.6	17.6
2003	26.3 ± 15.3	4.7	20.6	17.7
2004	29.2 ± 15.6	4.8	21.7	18.1
2005	35.8 ± 14.7	4.3	23.0	16.5
2006	43.3 ± 14.9	4.4	24.9	16.7
2007	48.1 ± 17.6	4.4	26.4	16.8
2008	48.9 ± 16.7	4.3	28.0	16.4
2009	48.0 ± 16.4	4.6		17.6
2010	53.4 ± 17.5	4.9		18.6
2011	54.4 ± 17.1	5.0		19.3
2012	53.2 ± 18.5	5.2		20.5
2013	52.5 ± 17.8			
2014	52.5 ± 20.1			

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Table 3. Annex 1 and non-Annex 1 global and regional emissions in Gg yr^{1-} averaged over two 3-year periods. The global estimates from the 12-box model are not in exact agreement with the combined Annex I and non-Annex I emissions from CELS. However, this is not unexpected, given the vastly different transport and inversion models used to estimate these terms. We note that the uncertainty range of the combined Annex I and non-Annex I estimates from CELS does overlap with the uncertainty range from the 12-box model, and a similar growth in emissions is seen across the two averaging periods.

3-year Averages	Europe Annex 1	North America Annex 1	East Asia Annex 1	East Asia Non-Annex 1	GLOBAL Annex 1	GLOBAL Non-Annex 1	GLOBAL 12-Box model
2007–2009	6.4 (5.2–7.5)	28.0 (22.5–33.4)	0.4 (0.2–1.2)	5.8 (4.5–7.5)	35.2 (27.7–42.6)	6.6 (4.3–9.2)	48.5 (37.0–60.6)
2010–2012	5.2 (4.1–6.4)	31.6 (24.5–38.6)	1.0 (0.5–1.6)	6.0 (4.3–8.2)	40.2 (31.3–49.3)	6.6 (3.9–9.8)	53.9 (43.0–67.3)

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Table 4. Australian HFC-152a emissions (Mg, 3-year running averages) calculated from Cape Grim in situ observations via ISC (ADS and Medusa data, uncertainty: ±1 standard deviation) and inverse modelling using InTEM (Medusa data, range: 25th–75th percentiles); ISC, NAME averages weighted by uncertainties, ISC InTEM average for 2004 is based on only InTEM data.

YEAR	ISC	InTEM	ISC and InTEM average	ISC/InTEM ratio
1999	24 ± 7			
2000	25 ± 8			
2001	27 ± 9			
2002	28 ± 10	32 (31–34)	31 ± 2	
2003	28 ± 10	32 (29–33)	31 ± 4	0.88
2004	29 ± 10	31 (29–33)	31 ± 2	0.94
2005	32 ± 10	31(30–33)	31 ± 4	1.03
2006	38 ± 10	35 (32–38)	35 ± 6	1.09
2007	51 ± 15	41 (37–43)	42 ± 6	1.24
2008	49 ± 15	43 (41–47)	44 ± 5	1.14
2009	52 ± 15	68 (64–72)	65 ± 8	0.76
2010	59 ± 20	69 (64–74)	67 ± 10	0.86
2011	56 ± 15	72 (68–76)	69 ± 7	0.78
2012	77 ± 25			
2013	69 ± 24			

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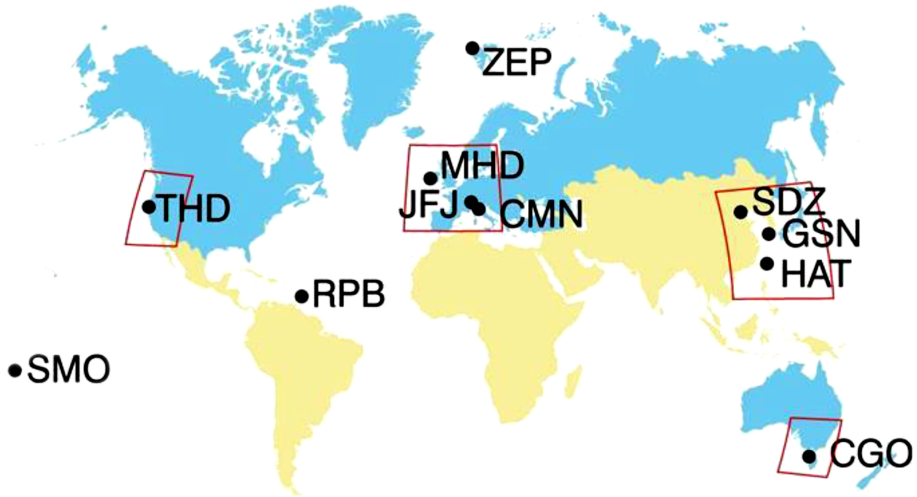

Figure 1. Location of AGAGE and affiliated stations. Ny-Ålesund, Zeppelin, Norway (ZEP); Mace Head, Ireland (MHD); Jungfraujoch, Switzerland (JFJ); Monte Cimone, Italy (CMN); Trinidad Head, USA (THD); Shangdianzi, China (SDZ); Gosan, South Korea (GSN); Hateruma, Japan (HAT); Ragged Point, Barbados (RPB); Cape Matatula, American Samoa (SMO); and Cape Grim, Tasmania (GCO). Red boxes indicate "local regions" where the NAME model was used with increased resolution compared to the global MOZART model, Annex 1 countries are shaded blue and non-Annex 1 countries in yellow. Note: [1] SDZ was not used in any of the modelling studies due to the relatively short time series.

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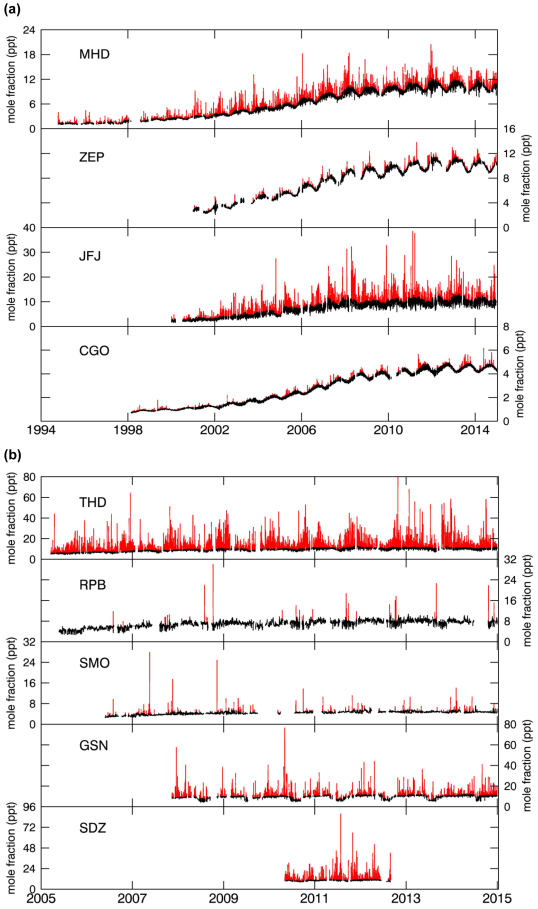

Figure 2.

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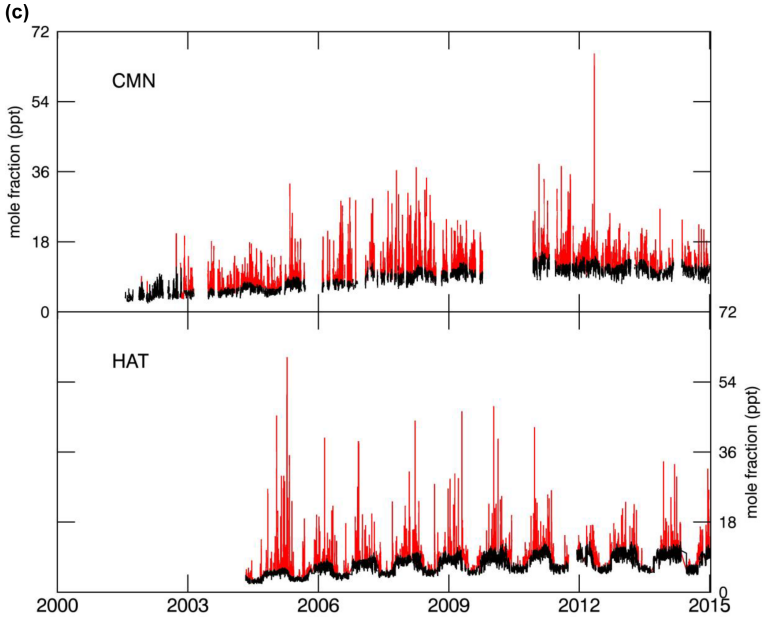

Figure 2. (a) Time series of HFC-152a mole fractions (ppt) recorded at the four monitoring stations with combined ADS and Medusa data. (MHD) Mace Head, (ZEP) Ny-Ålesund, (JFJ) Jungfraujoch and (CGO) Cape Grim, (note the different *Y* axis scales). Data have been assigned as baseline (black) and non-baseline (red) using the AGAGE pollution identification algorithm. **(b)** Time series of HFC-152a mole fractions (ppt), recorded with the Medusa GC-MS instruments at the five AGAGE monitoring stations Trinidad Head (THD), Ragged Point (RPB), Gosan (GSN), American Samoa (SMO) and Shangdianzi (SDZ). Data have been assigned as baseline (black) and non-baseline (red) using the AGAGE pollution identification algorithm. **(c)** Time series of HFC-152a mole fractions (ppt) recorded with the GC-MS instruments at the two affiliated AGAGE stations Monte Cimone (CMN) and Hateruma (HAT). Data have been assigned as baseline (black) and non-baseline (red) using the AGAGE pollution identification algorithm.

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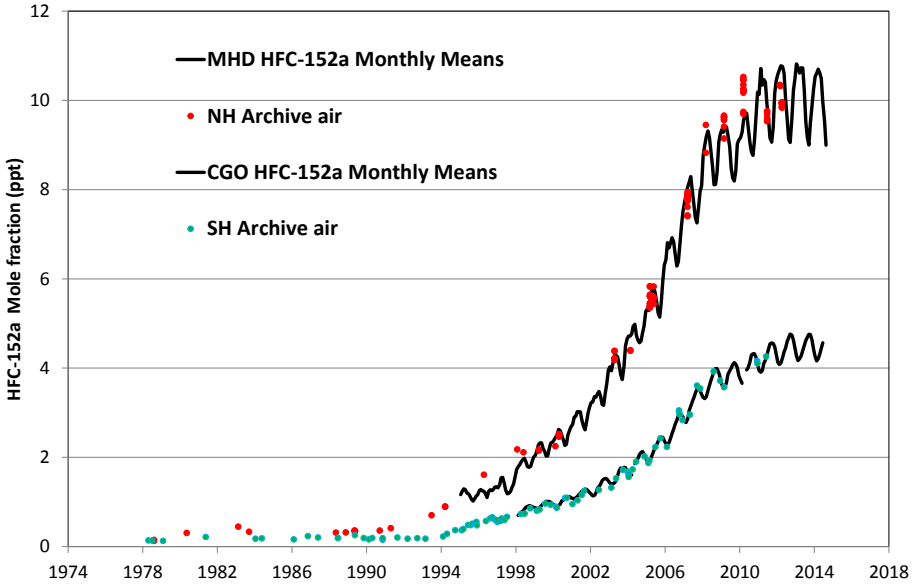

Figure 3. HFC-152a baseline monthly mean mole fraction (ppt) recorded at Mace Head-MHD (ADS GC-MS, 1994–2003; Medusa GC-MS, 2004–2014) and at Cape Grim-CGO (ADS GC-MS, 1998–2003; Medusa GC-MS, 2004–2014) and from analysis of archived NH and SH air samples extending back to 1975: in situ (black), air archive NH (red) and SH (blue).

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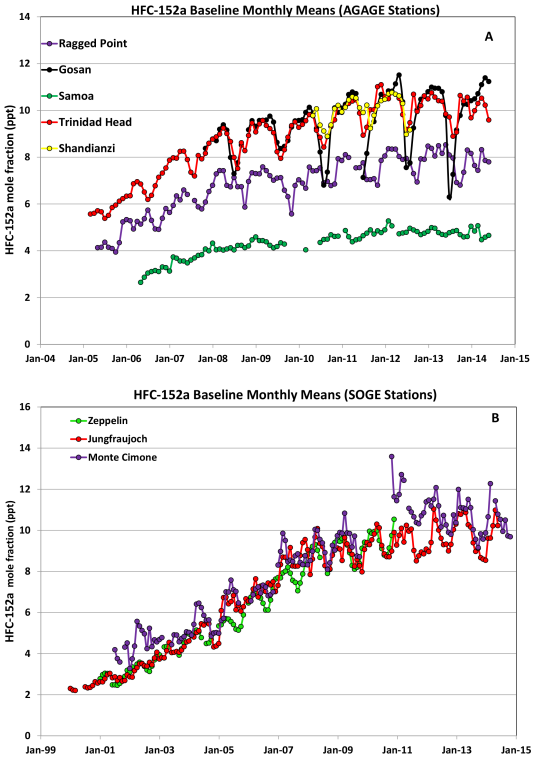

Figure 4. (a) Medusa GC-MS baseline monthly means (ppt) recorded at Trinidad Head, USA (THD); Ragged Point, Barbados (RPB); Gosan, Jeju Island, Korea (GSN); Cape Matatula, American Samoa (SMO); and Shangdianzi, China (SDZ). Observations at Shangdianzi were discontinued in August 2012. **(b)** Combined ADS and Medusa GC-MS baseline monthly means recorded at Ny-Ålesund (ZEP), Jungfraujoch (JFJ) and Monte Cimone (CMN).

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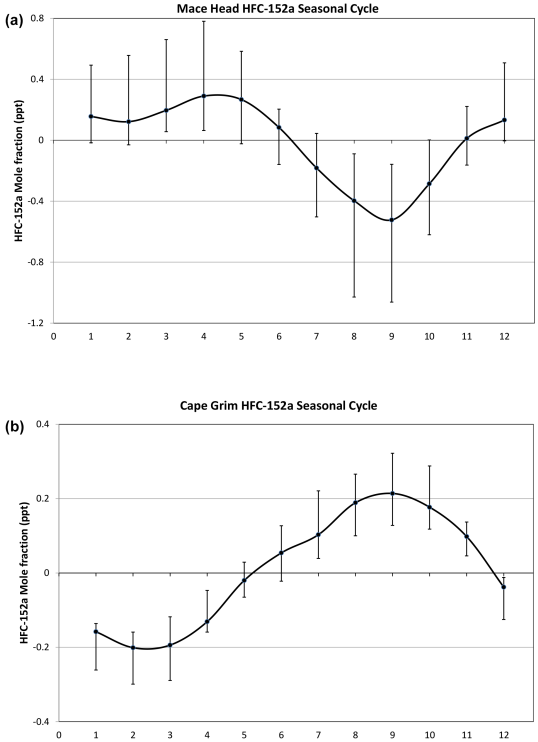

Figure 5. (a) Average seasonal cycle at Mace Head, Ireland (MHD, 2004–2014). **(b)** Average seasonal cycle at (CGO) Cape Grim, Tasmania (2004–2014).

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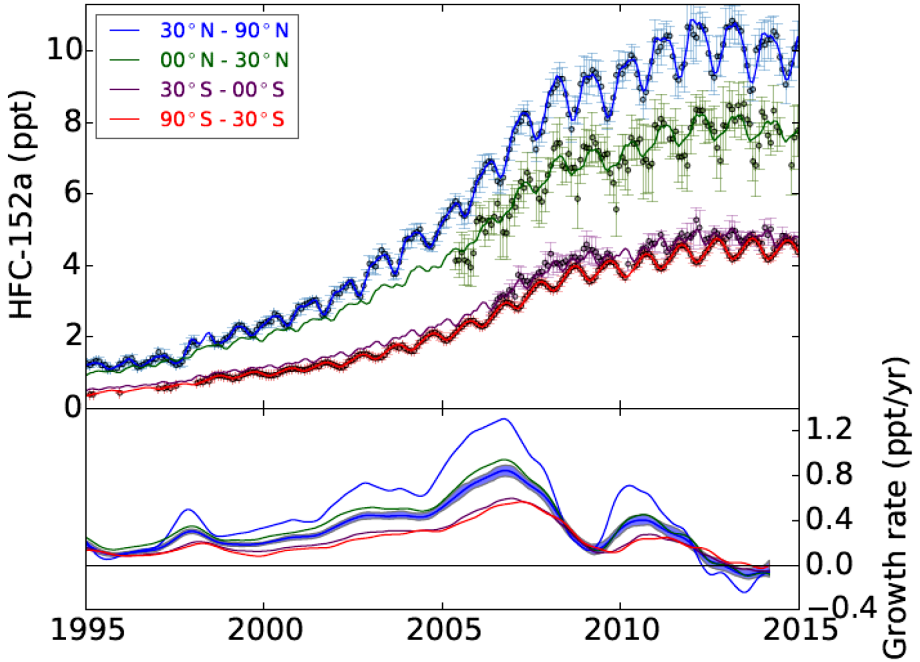

Figure 6. AGAGE 12-box model mole fraction (ppt) outputs for the two NH and two SH latitudinal bands. Lower box shows the HFC-152a annualised growth rate (ppt yr^{-1}), with the heavy blue line showing the global average.

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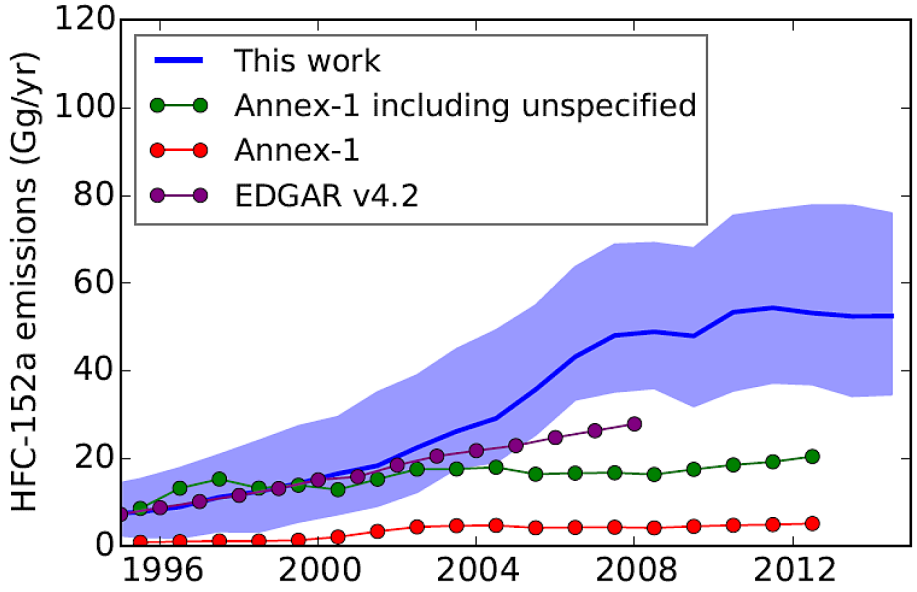

Figure 7. HFC-152a emissions estimates derived from observations (blue line and shading, 1σ uncertainty). The purple line shows the global emissions estimates from EDGAR (v4.2), the red line shows the emissions reported to the UNFCCC and the green line shows emissions calculated from all data reported to UNFCCC, including allowance for the HFC-152a component of unspecified emissions.

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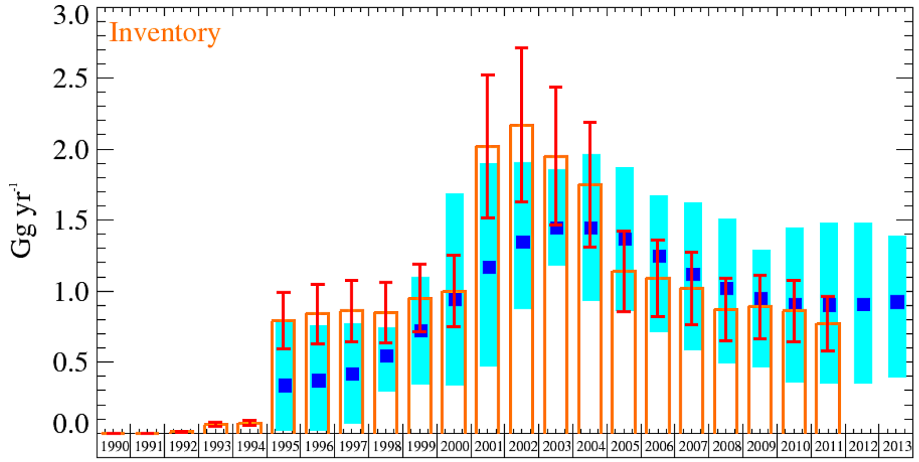

Figure 8. Emission (Gg yr^{1-}) estimates for HFC-152a from NWEU. The blue uncertainty bars represent the 5th and 95th percentiles of the InTEM estimates (rolling 3 yr averages). The UNFCCC uncertainty is set as 25 %.

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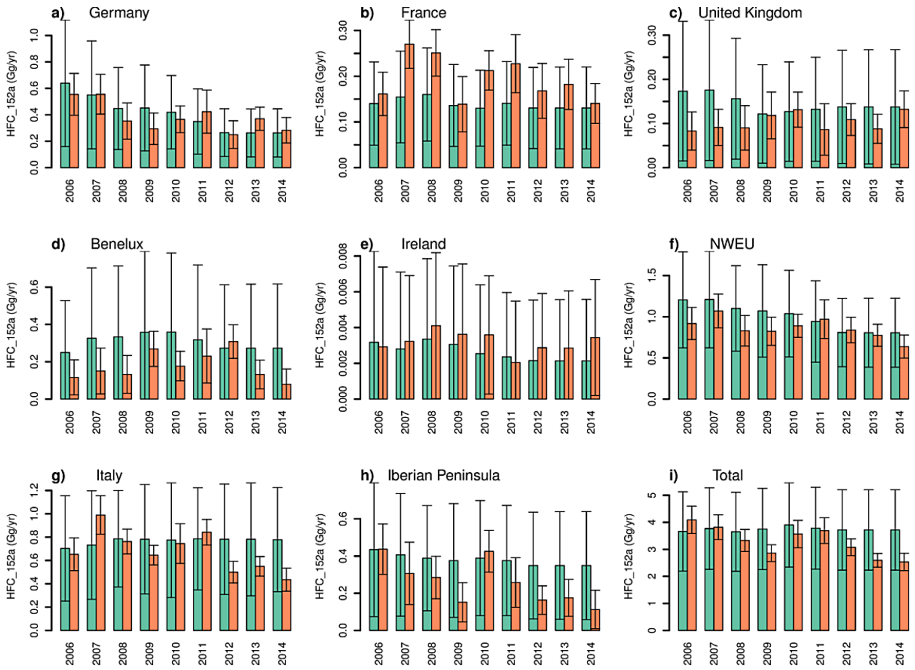

Figure 9. Time line of HFC-152a emission estimates for different European regions using the Bayesian regional inversion (orange bars) and prior estimates as reported to UNFCCC (green bars). Error bars indicate 2σ confidence levels. Total prior uncertainties were set to 20 % of the total domain emissions, which may result in different levels of relative uncertainty for each country/region. Note that prior estimates for Italy were taken from EDGAR instead. Prior values for 2012 were repeated for each region after 2012.

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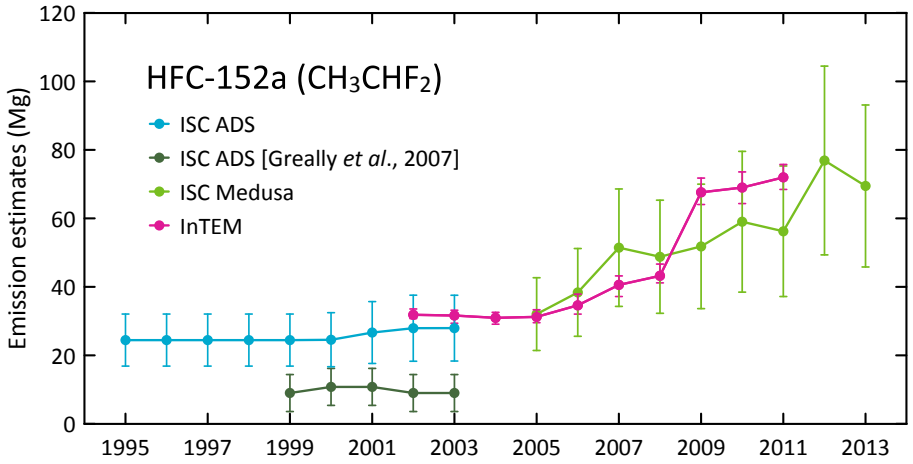

Figure 10. Australian HFC-152a emissions (Mg) calculated from Cape Grim in situ observations via ISC, using ADS and Medusa data, and inverse modelling using InTEM (Medusa data). Australian emissions are derived from SE Australian emissions, scaled by population (see text). Uncertainties are 25th-75th percentiles (InTEM) and 1 standard deviation (ISC).

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