

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

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49 **Abstract**

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51 High frequency, *in situ* observations from the Advanced Global Atmospheric Gases
52 Experiment (AGAGE), for the period 2003 to 2012, combined with archive flask
53 measurements dating back to 1977, have been used to capture the rapid growth of HFC-143a
54 (CH_3CF_3) and HFC-32 (CH_2F_2) mole fractions and emissions into the atmosphere. Here we
55 report the first *in situ* global measurements of these two gases. HFC-143a and HFC-32 are the
56 third and sixth most abundant HFCs respectively and they currently make an appreciable
57 contribution to the HFCs in terms of atmospheric radiative forcing (1.7 ± 0.04 and 0.7 ± 0.02
58 mWm^{-2} in 2012, respectively). In 2012 the global average mole fraction of HFC-143a was
59 13.4 ± 0.3 ppt (1-sigma) in the lower troposphere and its growth rate was 1.4 ± 0.04 ppt yr^{-1} ;
60 HFC-32 had a global mean mole fraction of 6.2 ± 0.2 ppt and a growth rate of 1.1 ± 0.04 ppt yr^{-1}
61 in 2012. The extensive observations presented in this work have been combined with an
62 atmospheric transport model to simulate global atmospheric abundances and derive global
63 emission estimates. It is estimated that 23 ± 3 Gg yr^{-1} of HFC-143a and 21 ± 11 Gg yr^{-1} of HFC-
64 32 were emitted globally in 2012, and the emission rates are estimated to be increasing $7 \pm 5\%$
65 yr^{-1} for HFC-143a and $14 \pm 11\%$ yr^{-1} for HFC-32.

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67 **1. Introduction**

68 Hydrofluorocarbons (HFCs) were developed as replacements for ozone depleting
69 chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) which have mainly been
70 used as working fluids in refrigerators and air conditioners, as blowing agents and active
71 insulating component in plastic foams, as aerosol propellants and as fire retardants. The
72 timescales over which HFC emissions to the atmosphere take place vary widely, depending
73 on the application. For example, HFCs used as aerosol propellants results in prompt release,

74 whereas when used as blowing agents for one-component foams (where the blowing agent is
75 not encapsulated into the foam), release occurs over a period on the order of 2 yr (McCulloch
76 et al., 2009). The predominant use of HFCs is in air conditioning and refrigeration. Here the
77 emissions are more complex and variable during the lifetime of the equipment and can be
78 characterised during three phases of their use: when the equipment is first filled (losses less
79 than 1%), during operation and servicing (0-30 % yr⁻¹ depending if hermetically sealed or not)
80 and finally when the equipment is scrapped (although recovery, re-use and destruction are
81 now more commonplace than in the 1990s when the remaining refrigerant would have been
82 released into the atmosphere upon disposal) (McCulloch et al., 2009).

83 HFCs are partially fluorinated hydrocarbons that have atmospheric lifetimes in the
84 range of 1-50 yr (with the exception of HFC-23 and HFC-236fa which have lifetimes of 222
85 and 242 yrs respectively) and are removed from the atmosphere through reaction with
86 tropospheric hydroxyl radicals (Ko et al., 2013; Forster et al., 2007). They are chlorine free,
87 and as such have effectively zero stratospheric ozone depletion potentials and therefore are
88 not yet included in the Montreal Protocol and its subsequent amendments. However, there is
89 concern about the accumulation of HFCs in the atmosphere, mainly because of their high
90 global warming potentials (GWPs). Most HFCs currently used have relatively long
91 atmospheric lifetimes and GWPs in excess of 1000, and are sometimes referred to as high-
92 GWP HFCs” (Velders et al., 2014). National HFC data are submitted to the United Nations
93 Framework Convention on Climate Change (UNFCCC) under the Rio Convention and Kyoto
94 Protocol, and countries that have ratified the Kyoto Protocol (Annex I parties or developed
95 countries and economies in transition) have committed over a short timescale (2008-2012) to
96 reduce their emissions of greenhouse gases. Signatories to the Protocol used emissions trading
97 to meet their emissions commitments. However, countries that did not ratify the Kyoto
98 Protocol (Non-Annex I or developing countries and the USA) were not required to submit

99 national HFC data, although some such as the USA do. It has been suggested that the total
100 GWP weighted HFC emissions for baseline scenarios in 2050 will be ~4 times larger than
101 those previously reported in the Intergovernmental Panel on Climate Change (IPCC) Special
102 Report on Emissions Scenarios (SRES, 2000). This discrepancy is thought to be primarily due
103 to sustained growth in demand for refrigeration, air-conditioning and insulating foam products
104 in non-reporting developing countries (Velders et al., 2009). In 2011 at the Durban climate
105 negotiations, it was decided that new climate commitments will come into effect from 2020
106 onwards leaving the years up to this date free from any legally binding global measures
107 (Velders et al., 2012). The 2012 Doha Amendment to the Kyoto Protocol included new
108 commitments for Article 5 countries, which agreed to take on commitments, in a second
109 period from 1 January 2013 to 31 December 2020. This amendment was adopted but has not
110 yet entered into force. A number of nations have also expressed interest in applying HFC
111 emissions control under an amended Montreal Protocol. However, these proposals have not
112 yet been adopted, resulting in a very uncertain outlook in terms of climate effects from
113 emissions of HFCs. The use of global atmospheric observations with atmospheric transport
114 models have been shown to provide an independent and effective method of assessing the
115 accuracy of globally and regionally aggregated reductions or increases in emissions of
116 individual greenhouse gases compiled from national reports to the UNFCCC (O'Doherty et
117 al., 2009; Montzka et al., 2010; Miller et al., 2011; Vollmer et al., 2011; Miller et al., 2012;
118 Rigby et al., 2013; Fang et al., 2014). These techniques have recently been applied to global
119 observations of HFCs in general (Rigby et al., 2014) but not used to explore the individual
120 global estimates of HFC-143a and HFC-32.

121 HFC-143a is mainly used as a working fluid component in refrigerant blends R404A
122 (52 % HFC-143a, 44 % HFC-125 and 4 % HFC-134a by weight) and R-507A (an azeotropic
123 blend of 50 % HFC-125 and 50 % HFC-143a) for low and medium temperature commercial

124 refrigeration systems, replacing R-502 (a blend containing HCFC-22 and CFC-115) (Velders
125 et al., 2009). Other minor uses are in R-408A, R-427A and R-428A as replacements for R-
126 502 and HCFC-22. The first reported atmospheric measurements of HFC-143a were made
127 using flask samples by Culbertson et al. (2000) from air samples collected in Montana, USA,
128 where they determined a mole fraction of HFC-143a of 3.2 ± 0.3 ppt. Measurement and
129 analysis of archived air samples collected at Cape Meares, Oregon from 1978 to 1997, at
130 Point Barrow, Alaska from 1995 to 1998 and at Palmer Station, Antarctica from 1991 to 1997
131 allowed the atmospheric accumulation of HFC-143a to be determined for the first time
132 (Culbertson et al., 2004). The Oregon samples showed an increase from about 0.2 ppt in 1978
133 to 2.0 ppt in 1997. Its growth rate increased to 0.04 ppt yr^{-1} between 1984 and 1992, then
134 between 1993 and 1997 the growth rate further increased to a level of 0.45 ppt yr^{-1} ($\sim 80 \% \text{ yr}^{-1}$)
135 ¹⁾ reaching a level of 1.9 ppt in the atmosphere by 1997. The rapid growth coupled with
136 significant differences in mole fraction measured at Alaska and Antarctica suggested rapidly
137 increasing emissions of this compound in the Northern Hemisphere. In situ measurements at
138 Mace Head, Ireland indicated an average mole fraction of 5.5 ppt in 2004, with a growth rate
139 of 0.9 ppt yr^{-1} ($16 \% \text{ yr}^{-1}$) (Greally et al., 2005). More recent measurements from the AGAGE
140 network show an increase to 8.5 ppt in 2008 with a growth rate of 1.0 ppt yr^{-1} ($13 \% \text{ yr}^{-1}$)
141 (Montzka, Reimann et al., 2011). Regional studies by Li et al., (2011) and Miller et al.,
142 (2012), have used observational data to investigate mole fraction and emission increases in E.
143 Asia and the US respectively.

144 HFC-143a has a significant radiative forcing value of 1.9 mWm^{-2} in 2008 (third
145 largest of all the HFCs) (Myhre et al., 2013) with a GWP of 4800 integrated over 100 years
146 (Myhre et al., 2013) and an estimated atmospheric lifetime of 51 yrs (Ko et al., 2013). It is
147 removed from the atmosphere predominantly by gas phase reaction with hydroxyl radicals
148 (OH), reaction rate $1.1 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$, (Sander et al., 2006). The degradation

149 products resulting from this reaction ($\text{CF}_3\text{C}(\text{O})\text{H}$, CF_3OH , $\text{C}(\text{O})\text{F}_2$ and CO_2) are all expected
150 to be removed from the atmosphere to varying degrees by incorporation into rain-sea cloud
151 water where hydrolysis will take place. It is also possible that photolysis of $\text{CF}_3\text{C}(\text{O})\text{H}$ in air
152 might produce CF_3H which is a potent greenhouse gas with an atmospheric lifetime of
153 approximately 10 times that of HFC-143a (Wallington et al., 1994). HFC-143a does not
154 absorb UV radiation in either the troposphere or the stratosphere and has no significant
155 oceanic or rainout loss (due to its low water solubility) (Orkin et al., 1996).

156 HFC-32 is used in air conditioning and refrigeration applications; R-410A is an
157 azeotropic mixture (50 % HFC-32, 50 % HFC-125 by weight) and R407C (23 % HFC-32, 52
158 % HFC-134a, 25 % HFC-125 by weight), replacing HCFC-22. As the phase-out of HCFC-22
159 gains momentum, it might be expected that demand for these refrigerant blends will increase.
160 The first reported measurements of this gas were by Greally et al. (2005), from in situ
161 AGAGE measurements at Mace Head, Ireland in 2004. The measurements indicated an
162 average mole fraction of about 0.7 ppt in 2004 with two periods of growth, 43 % yr^{-1} growth
163 in the first half of the year followed by accelerated growth of 86 % yr^{-1} in the latter half of the
164 year. More recent measurements from the AGAGE network show an average mole fraction of
165 2.7 ppt in 2008 with a growth rate of 0.6 ppt yr^{-1} (26 % yr^{-1}) (Montzka, Reimann et al., 2011).

166 HFC-32 has a GWP of 677 integrated over a 100-year time horizon, a value
167 appreciably lower than that of HFC-143a (Myhre *et al.*, 2013). The radiative forcing of HFC-
168 32 was estimated to be 0.5 mWm^{-2} (Myhre *et al.*, 2013). It has an estimated atmospheric
169 lifetime of 5.1 yr (Ko et al., 2013), and similar to HFC-143a, is removed from the atmosphere
170 by gas phase reaction with OH. The degradation product resulting from this reaction is
171 carbonyl fluoride (COF_2), reaction rate $1.7 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (Sander et al., 2006).

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

180 **2. Experimental Methods**

181 **2.1 Instrumentation and calibration**

182 High frequency, *in situ* measurements of HFC-143a and HFC-32 were obtained using gas
183 chromatography (GC, Agilent 6890) with quadrupole mass selective detection (MSD, Agilent
184 5973) coupled to the Medusa, an automated pre-concentration system (Miller et al., 2008;
185 Arnold et al., 2012). Medusa systems were installed at all AGAGE stations between 2003 and
186 2010, and routine ambient measurements of HFC-143a and HFC-32 commenced at each
187 station on a time frame detailed in Table 1.

188

189 Analysis of each 2 L sample of ambient air was alternated with analysis of a 2 L reference gas
190 to determine and correct for short term instrumental drift, resulting in 12 individually
191 calibrated air samples per day. The measurements at each AGAGE site are reported relative to
192 the SIO-2007 gravimetric calibration scale (as dry gas mole fractions in pmol mol^{-1}). The
193 SIO-2007 scale is based on five stable primary calibration standards in zero air with prepared
194 values of 5-6 ppt, each containing ~ 20 torr water vapour. Repeated measurements indicated
195 that the relative standard deviation of the scale was 0.56% (HFC-143a) and 0.49% (HFC-32).
196 The estimated absolute accuracy of the calibration scale for both compounds is ~ 2 -3%. A

197 more detailed discussion of the measurement technique and calibration procedure is reported
198 elsewhere (Mühle et al., 2010; O'Doherty et al., 2009; Miller et al., 2008).

199

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

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219 **2.2 Northern and Southern Archived Air Samples**

220 In order to extend the atmospheric history of HFC-143a and HFC-32 back before the
221 commencement of high frequency measurements, analysis of Northern Hemisphere (NH) and

222 Southern Hemispheric (SH) archived air samples was carried out using Medusa GC-MS
223 instruments at the Scripps Institution of Oceanography (SIO), La Jolla, California and at the
224 Commonwealth Scientific and Industrial Research Organisation (CSIRO), Aspendale,
225 Australia, respectively. The SH archive samples are part of the Cape Grim Air Archive
226 (CGAA: 1978-present, filled cryogenically into electropolished SS containers during
227 background conditions) (Langenfelds *et al.*, 1996; Krummel *et al.*, 2007), CGAA samples
228 dated between 1978-2006 were analysed for HFC-143a, and between 1997-2010 for HFC-32.
229 The NH samples were filled during background conditions using several sampling techniques
230 and provided by a variety of laboratories (Mühle *et al.*, 2010); these samples were filled
231 between 1977-2010 for HFC-143a and 1998-2009 for HFC-32. The archived samples were
232 analysed in replicate, typically 2-4 times each. Nonlinearity data were collected before, during
233 and after the analysis periods and frequent inclusion of blank runs allowed blank corrections
234 to be applied where needed. The resulting uncertainty due to the blank level variability was
235 negligible in comparison to the overall precision. Further, no significant blank levels
236 stemming from the used tanks (Essex Cryogenics) or the pressure regulators (Valin
237 Corporation) were observed.

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

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246

247 **3. Modelling studies**

248 To estimate global-average mole fractions, derive growth rates and infer emissions, a two-
249 dimensional model of atmospheric chemistry and transport was employed. The AGAGE 12-
250 box model simulates trace gas transport in four equal-mass latitudinal sections (divisions at
251 30°N, 0°N and 30°S) and at three heights (vertical divisions at 500hPa and 200hPa). The
252 model was originally developed by Cunnold et al. (1983) (9-box version), with subsequent
253 improvements by Cunnold et al. (1994) and Rigby et al. (2013). Model eddy diffusion
254 parameters and OH concentrations were prescribed, based on the values derived in the CFC
255 (for transport) and CH₃CCl₃ (for OH concentrations) inversions of Rigby et al. (2013).

256

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

270

271

272 4. Results and Discussion

273 4.1 Atmospheric Trends

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

278

279 A large increase in baseline mole fractions at all the AGAGE sites is evident. The results
280 indicate rapid growth of HFC-143a in the atmosphere. Furthermore, the observations show
281 that the growth rate has been increasing throughout this time period. The globally averaged
282 mole fraction in the lower troposphere in 2012 is estimated to be 13.4 ± 0.3 ppt. The growth
283 rate was calculated from the optimised model-derived global mean mole fractions. Monthly
284 global growth rates were smoothed using a Kolmogorov-Zurbenko filter with a 0.7 year
285 smoothing window and 4 filter passes, leading to an effective smoothing window of 1.4 years.
286 The main growth rate centred on July 2012 for HFC-143a was 1.4 ± 0.04 ppt yr^{-1} . The
287 atmospheric histories of both compounds have been extended back before high frequency
288 measurements became available, using analysis of NH and SH flask samples, as detailed in
289 Section 2.2. Figures 3 and 4 show the high-frequency baseline monthly means for
290 measurements averaged into latitude bands combined with flask measurements extending the
291 data record back to 1977 and 1997 for HFC-143a and HFC-32 respectively. The figures also
292 show the 12-box model fits to the atmospheric measurements illustrated by the solid lines and
293 show the growth rates in ppt yr^{-1} . The radiative forcing due to HFC-143a estimated using the
294 global average mole fraction obtained from the AGAGE 12-box model, was 1.7 ± 0.04 mWm^{-2}
295 in 2012.

296

297 For HFC-32, our observations also indicate rapid and accelerating growth. The calculated
298 global mean mole fractions have increased from 0.8 ± 0.02 ppt in 2004 (when high frequency
299 observations began) to 6.2 ± 0.2 ppt in 2012, the rate of increase in 2012 reached 1.1 ± 0.04 ppt
300 yr^{-1} ($17\% \text{ yr}^{-1}$), which likely reflects the increased usage of R410a, the preferred replacement
301 of HCFC-22 in many air conditioning applications. The radiative forcing due to HFC-32,
302 estimated using the AGAGE 12-box model global mole fractions, was $0.7 \pm 0.02 \text{ mWm}^{-2}$ in
303 2012. It is clear from the strong inter-hemispheric gradient for both compounds that emissions
304 are predominantly in the NH, as has been illustrated for many other purely anthropogenic
305 trace gases (O'Doherty et al., 2009; Mühle et al., 2010; Rigby et al., 2010; Laube et al., 2010;
306 Vollmer et al., 2011; Yao et al., 2012).

307

308 **4.2 Emission Estimates**

309 Estimated global emissions of HFC-143a from this work and a number of different sources
310 are shown in Figure 5 and Table 2. The blue solid line represents our model-derived
311 emissions with 1σ error bar shown by the shaded areas. Model derived emissions were
312 relatively constant between 1981 and 1993 (0.3 ± 11.8 in 1981 to $1.0 \pm 0.9 \text{ Gg yr}^{-1}$ in 1993) but
313 started to increase rapidly from a level of $1.4 \pm 0.6 \text{ Gg yr}^{-1}$ in 1994 to $23.3 \pm 3.2 \text{ Gg yr}^{-1}$ in 2012.
314 Global tropospheric average emissions calculated over five year periods were reported by
315 Culbertson et. al., (2004) as follows: 1977-1982, 0.2 Gg yr^{-1} ; 1982-1987, 0.6 Gg yr^{-1} ; 1987-
316 1992, 0.8 Gg yr^{-1} ; 1992-1997, 3.3 Gg yr^{-1} . These estimates are in reasonable agreement with
317 our estimates for the period 1981-1987, and exceed our estimate (if averaged over a 5 year
318 period to be comparable) by approximately 50% (1.6 Gg yr^{-1}) in 1987-1992. Estimated
319 emissions from EDGAR (v4.2) imply that there were no emissions of HFC-143a before 1993,
320 while there is reasonable agreement with our estimates from 1994 to 1998, but that since

321 1994, EDGAR (v4.2) emissions have grown at a faster rate, resulting in EDGAR emissions
322 being $\sim 13.9 \pm 7$ Gg yr⁻¹ higher than AGAGE emissions in 2008.

323 In contrast the AGAGE trend in global emissions is higher than the UNFCCC GHG emissions
324 reports (2012 submission), which contains nations annual estimates of HFC emissions
325 reported in the Common Reporting Format (CRF) files. It is not unreasonable that UNFCCC
326 reported emissions are lower than the AGAGE global emission estimates since developing
327 countries and regions in Asia (China, Indonesia, Korea, Malaysia, Philippines, Taiwan,
328 Vietnam etc.), the sub-continent (India, Pakistan, etc.), the Middle East, from Africa and Latin
329 America do not report to the UNFCCC, however Miller et al. (2012) report a EPA US GHG
330 inventory value of 4.4 Gg yr⁻¹ (average of 2005-2009) and a ¹⁴C-based US estimate of 5.2
331 (3.6-11.3) Gg yr⁻¹. The magnitude of these differences will vary over time according to the
332 expected usage of individual replacement compounds by Annex 1 countries on a country-by-
333 country basis.

334

335 Li et al. (2011) reported emission estimates for East Asia (China, S. Korea, Japan and
336 Taiwan) for the period between November 2007 and December 2008, where the emission
337 rates for each country were estimated using an interspecies correlation method (based on the
338 assumption that correlated compounds have co-located emission sources). For China,
339 emissions were estimated to be relatively low (HFC-143a, 0.6 ± 0.2 Gg yr⁻¹ and HFC-32, 4 ± 1.4
340 Gg yr⁻¹). They concluded that emission did not occur from consumption, but was more likely
341 as fugitive emissions from production sources, These findings were supported in Li et al.
342 (2014), where emission sources in East Asia were identified using high frequency
343 measurements analysed by positive matrix factorisation. Fugitive emissions from production
344 related sources in the Shandong and Jiangsu regions of eastern China dominated. Taiwan's
345 emissions were thought to be from refrigeration (HFC-143a, 0.04 ± 0.02 Gg yr⁻¹ and HFC-32,

346 $0.05 \pm 0.02 \text{ Gg yr}^{-1}$), as were S. Korea's (HFC-143a, $0.08 \pm 0.01 \text{ Gg yr}^{-1}$ and HFC-32, 0.21 ± 0.02
347 Gg yr^{-1}). Ratios of HFC measurements in S. Korea suggested an increasing use of R-410a and
348 R-507 as replacements for HCFC-22. Finally, emission estimates and ratios of HFC species
349 also indicated that Japan has moved some of its refrigeration to HFC blends (HFC-143a,
350 $0.4 \pm 0.1 \text{ Gg yr}^{-1}$ and HFC-32, $0.4 \pm 0.1 \text{ Gg yr}^{-1}$). These estimates, in comparison to our global
351 totals, suggest that HFC-143a is not yet widely used in E. Asia, and represents only ~6% of
352 2011 global emissions (Li et al., 2011).

353

354 In Figure 6 and Table 2 the estimates of global emissions of HFC-32 derived from our
355 measurements and a number of other sources are illustrated. For this compound the AGAGE a
356 posteriori results are higher than, but not statistically different from, the a priori UNFCCC and
357 EDGAR global emissions. The magnitude of this underestimate in 2008 was 4.5 ± 7 and 7.4 ± 7
358 Gg yr^{-1} respectively. Li et al. (2011) calculated that E. Asian total emissions of HFC-32 in
359 2008 represented 129% of the global total reported in the EDGAR database, and concluded
360 that EDGAR must underreport emissions. This conclusion concurs with the AGAGE global
361 estimates presented in Figure 6. Interestingly, if the UNFCCC reports of HFC-32 for Annex I
362 countries in 2008 is added to the Li et al. (2011) East Asia estimate, the total emission (9.8 Gg
363 yr^{-1}) closely matches the AGAGE derived global emission ($9.7 \pm 7 \text{ Gg yr}^{-1}$), adding weight to
364 the suggestion that EDGAR do not represent emissions in Asia adequately and that HFC-32 is
365 now increasingly released in E. Asia as fugitive emissions from halocarbon production
366 sources and from air conditioning and refrigeration applications (Li et al., 2014).

367

368 **5. Conclusions**

369 The first high frequency *in situ* global measurements of HFC-143a and HFC-32 have been
370 made at nine AGAGE stations between 2003 and 2012. These measurements indicate that, for

371 the entire time period, the atmospheric burden of both gases has been growing and that this
372 growth has been accelerating. The global mean growth rates in 2012 for HFC-143a and HFC-
373 32 were 1.4 ± 0.04 ppt yr⁻¹ and 1.1 ± 0.04 ppt yr⁻¹, respectively. The mole fractions in the global
374 lower troposphere in 2012 were estimated to be 13.4 ± 0.3 ppt for HFC-143a and 6.2 ± 0.2 ppt
375 for HFC-32. Moreover the continuous data record presented here was extended back in time
376 to 1977 and 1997 for HFC-143a and HFC-32 respectively, by analysis of NH and SH
377 archived air samples. These measurements suggest that emissions of HFC-143a started as
378 early as 1981 and HFC-32 by 1998.

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

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392

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417 **7. References**

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583

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

Station	Latitude °N	Longitude °E	Data* HFC-32	Data* HFC-143a
Zeppelin	78.5	11.5	Sep 10	Sep 10
Mace Head	53.3	-9.9	Jan 04	Nov 03
Jungfraujoch	46.5	8.0	May 04	Apr 08
Trinidad Head	41.0	-124.1	Mar 05	Mar 05
Shangdianzi	40.4	117.7	May 10	May 10
Gosan	33.3	126.2	Nov 07	Nov 07
Ragged Point	13.2	-59.4	May 05	May 05
Cape Matatula	-14.2	-170.6	May 06	May 06
Cape Grim	-40.7	144.7	Jan 04	Jan 04

586 *Start of data record for each compound
587

588 **Table 2.** Estimates of global emissions of HFC-143a (Gg yr⁻¹) based on AGAGE in situ
589 measurements and archived air samples (the NH flasks were collected primarily at Trinidad
590 Head and the SH flasks at Cape Grim) using the AGAGE 2-D 12-box model. Estimates of
591 total emissions prior to November 2003 are based only on archived air samples. Also shown
592 are 5-year averaged global emission estimates derived by Culbertson et al., (2004), global
593 emission estimates derived from UNFCCC National Inventory Reports (2012 submission),
594 and from the EDGAR (v4.2) database
595

Year	HFC-143a AGAGE (Gg yr ⁻¹)	HFC-143a Culbertson (Gg yr ⁻¹)	HFC-143a UNFCCC (Gg yr ⁻¹)	HFC-143a EDGAR (Gg yr ⁻¹)
1981	0.3 ± 11.8	0.2		
1982	0.3 ± 11.5	0.6		
1983	0.3 ± 10.3	0.6		
1984	0.4 ± 9.6	0.6		
1985	0.5 ± 9.5	0.6		
1986	0.5 ± 7.8	0.6		
1987	0.6 ± 7.0	0.8		
1988	0.8 ± 6.5	0.8		
1989	0.9 ± 5.7	0.8		
1990	0.9 ± 6.0	0.8	0.5	
1991	0.7 ± 4.6	0.8	0.5	
1992	0.7 ± 1.7	3.3	0.4	0.0
1993	1.0 ± 0.9	3.3	0.1	0.2
1994	1.4 ± 0.6	3.3	0.2	0.5
1995	2.1 ± 0.6	3.3	0.4	1.1
1996	3.3 ± 0.6	3.3	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 ± 1.4		2.1	6.6
2000	8.3 ± 1.7		2.7	9.1
2001	8.5 ± 1.8		3.3	11.9
2002	9.2 ± 1.9		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 ± 2.0		7.4	32.4

2009	18.6 ± 2.7		8.1	
2010	20.5 ± 2.8		9.1	
2011	21.6 ± 2.8		9.9	
2012	23.3 ± 3.2			

596

597

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

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

604

605

606 **Figure captions**

607

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

612

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

617

618 **Fig. 3.** Semi-hemispheric monthly average HFC-143a mole fractions (30°N-90°N: blue, 0°N-
619 30°N: green, 30°S-0°S: purple, 90°S-30°S: red). Averaged observations are shown as data
620 points with error bars. The more sparse circles represent NH and SH air archive samples, and
621 are highlighted in the inset box. The solid trend lines were calculated using a 12-box model
622 with emissions from the inversion as input. The lower plot shows the annual running mean
623 global mole fraction growth rate.

624

625 **Fig. 4.** Semi-hemispheric monthly average HFC-32 mole fractions (30°N-90°N: blue, 0°N-
626 30°N: green, 30°S-0°S: purple, 90°S-30°S: red). Averaged observations are shown as data
627 points with error bars. The more sparse circles represent NH and SH air archive samples, and
628 are highlighted in the inset box. The solid trend lines were calculated using a 12-box model
629 with emissions from the inversion as input. The lower plot shows the annual running mean
630 global mole fraction growth rate.

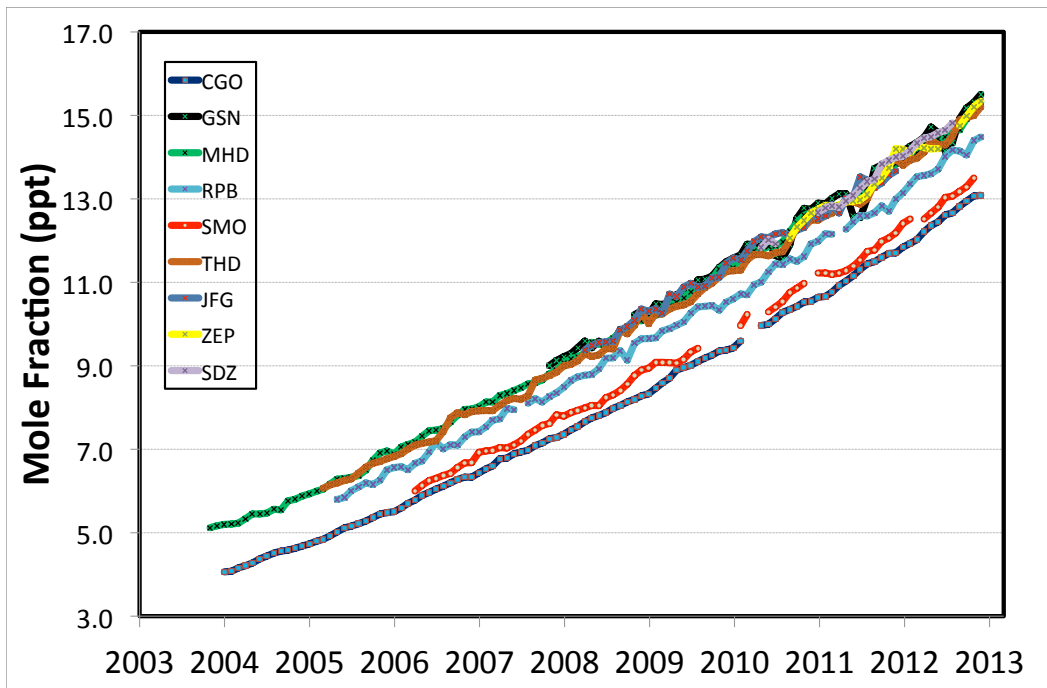
631 **Fig. 5.** HFC-143a emissions estimates derived from AGAGE observations (blue line and
632 shading, indicating 1-sigma uncertainty). The red line shows the global emissions estimates
633 from EDGAR v4.2 and the green line shows the emissions reported to the UNFCCC. The
634 purple point shows emissions estimated for East Asia by Li et al. (2011), and the orange
635 points represents the mid-point of 5 year average emissions estimated by Culbertson et al.
636 (2009).

637

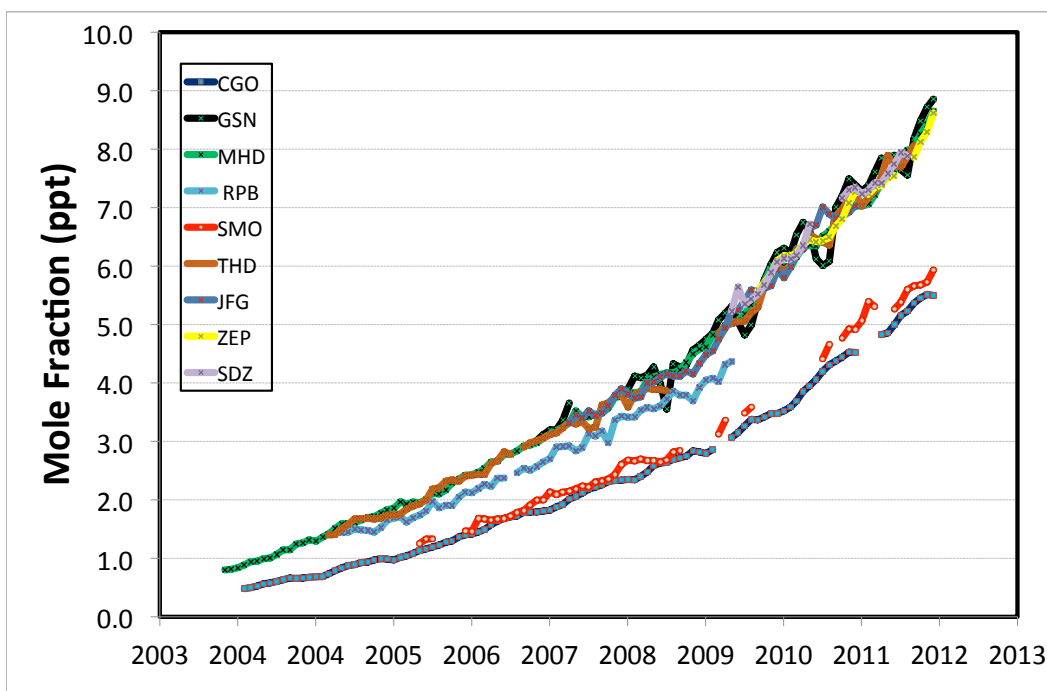
638 **Fig. 6.** HFC-32 emissions estimates derived from AGAGE observations (blue line and
639 shading, indicating 1-sigma uncertainty). The red line shows the global emissions estimates
640 from EDGAR v4.2 and the green line shows the emissions reported to the UNFCCC. The
641 purple point shows emissions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

642

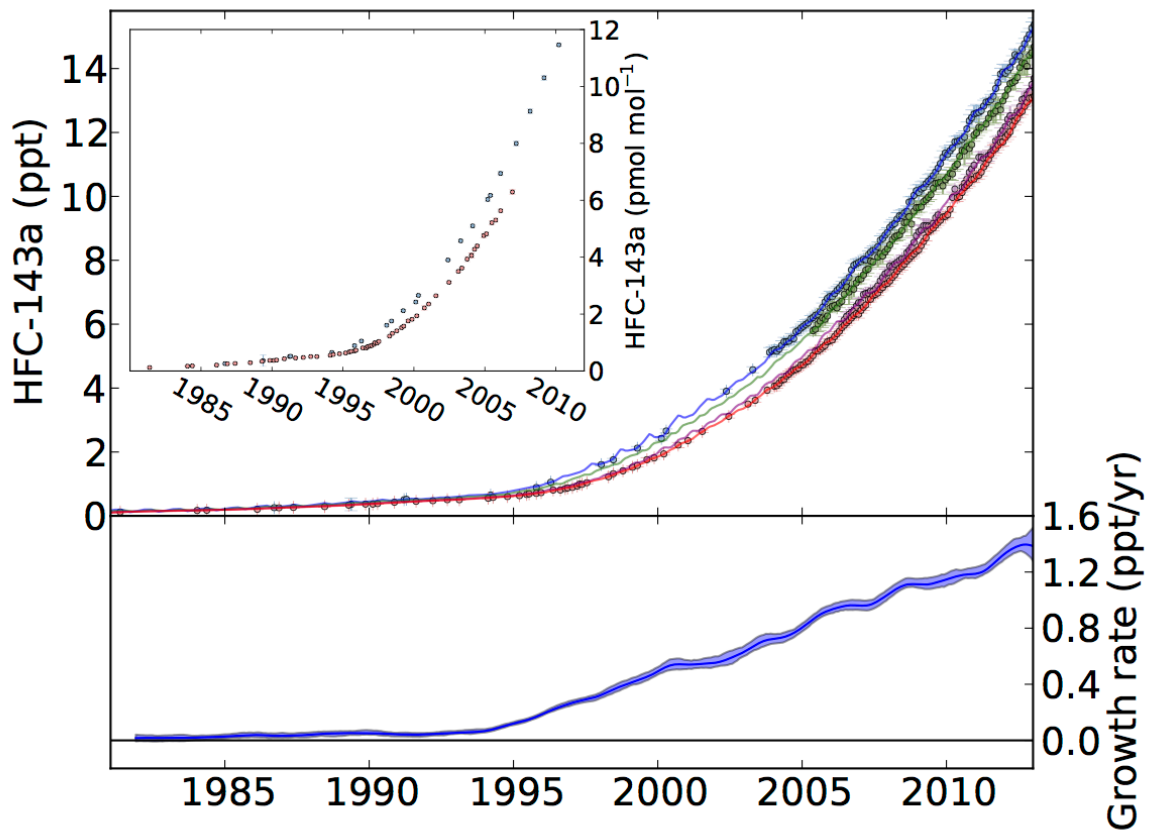
643 Figure 1



644 Figure 2
645

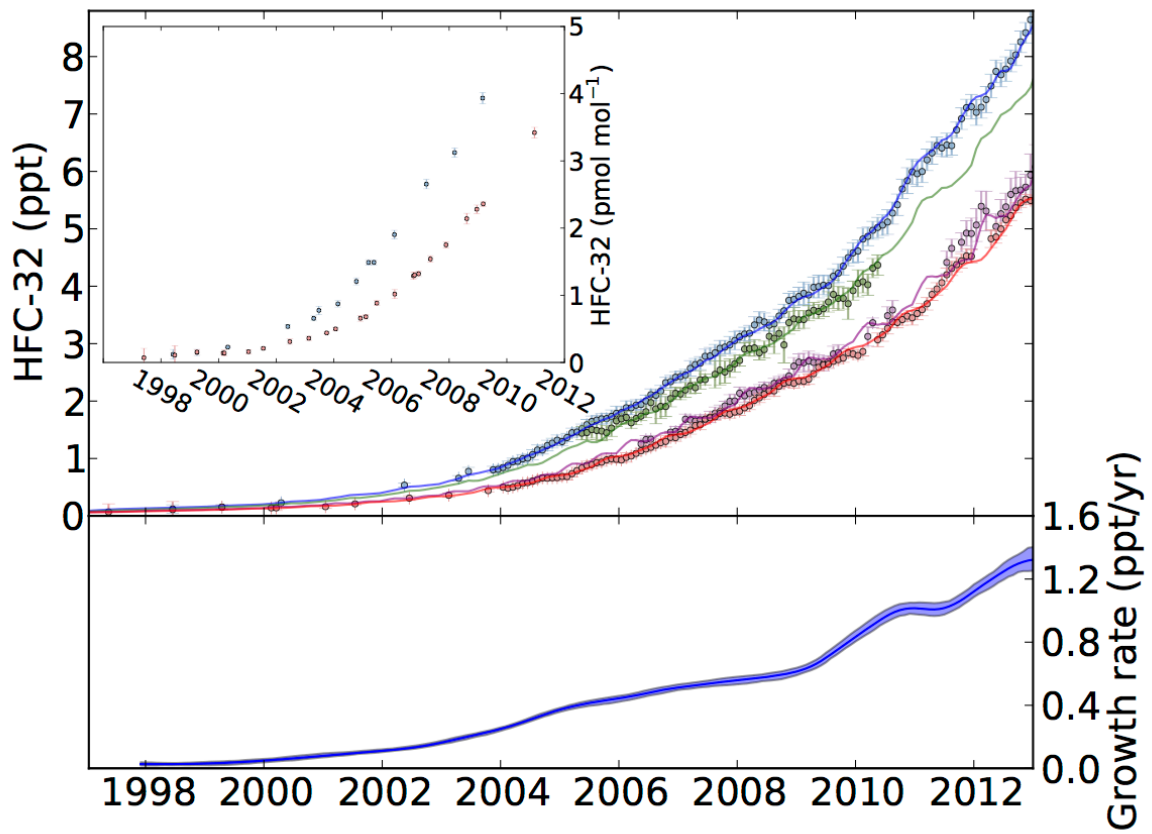


648 Figure 3

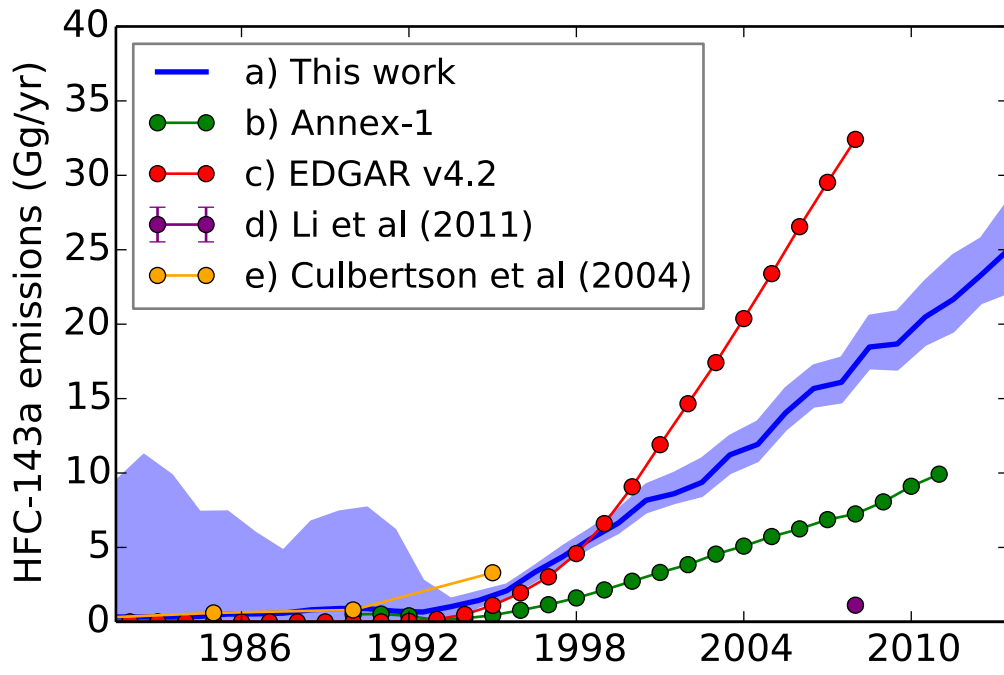


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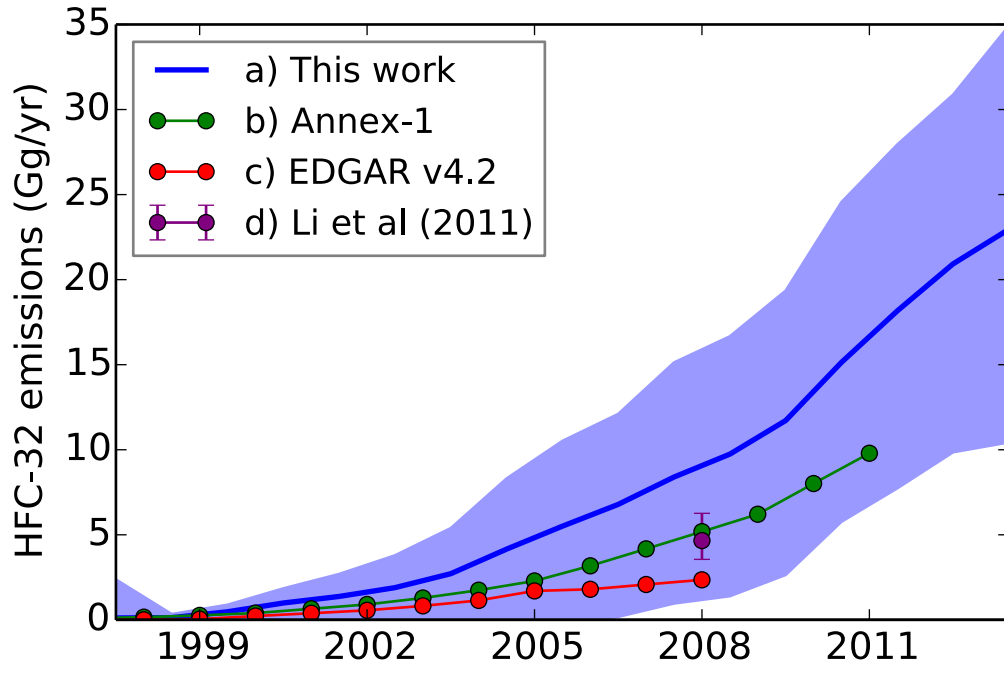
651 Figure 4



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653



656 Figure 6



657