European emissions of the powerful greenhouse gases hydrofluorocarbons inferred from atmospheric measurements and their comparison with annual national reports to UNFCCC.

F. Graziosi^{1,2}, J. Arduini^{1,3}, F. Furlani^{1,2}, U. Giostra^{1,2}, P. Cristofanelli³, X. Fang⁴, O. Hermanssen⁵, C. Lunder⁵, G. Maenhout⁶, S. O'Doherty⁷, S. Reimann⁸, N. Schmidbauer⁵, M.K. Vollmer⁸, D. Young⁷ and M. Maione^{1,2,3}

¹ Department of Pure and Applied Sciences, University of Urbino, Urbino, Italy

² CINFAI (National Inter-University Consortium for Physics of the Atmosphere and Hydrosphere), Rome, Italy

³ Institute of Atmospheric Sciences and Climate, National Research Council, Bologna, Italy

⁴ Centre for Global Change Science, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA

⁵ Norwegian Institute for Air Research, Kjeller, Norway

⁶ Joint Research Centre of the European Commission, Ispra (VA), Italy

⁷ Atmospheric Chemistry Research Group, School of Chemistry, University of Bristol, Bristol, UK

⁸ Laboratory for Air Pollution and Environmental Technology, Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland

Corresponding author: michela.maione@uniurb.it

Abstract

Hydrofluorocarbons are powerful greenhouse gases developed by industry after the phase-out of the ozone depleting chlorofluorocarbons and hydrochlorofluorocarbons required by the Montreal Protocol. The climate benefit of reducing the emissions of hydrofluorocarbons has been widely recognised, leading to an amendment of the Montreal Protocol (Kigali Amendment) calling for developed countries to start to phase-down hydrofluorocarbons by 2019 and in developing countries to follow with a freeze between 2024 and 2028. In this way, nearly half a degree Celsius of warming would be avoided by the end of the century. Hydrofluorocarbons are also included in the basket of gases controlled under the Kyoto Protocol of the United Nations Framework Convention on Climate Change. Annex I parties to the Convention submit annual national greenhouse gas

inventories based on a bottom-up approach, which relies on declared anthropogenic activities. Top-down methodologies, based on atmospheric measurements and modelling, can be used in support to the inventory compilation. In this study we used atmospheric data from four European sites combined with the FLEXPART dispersion model and a Bayesian inversion method, in order to derive emissions of nine individual hydrofluorocarbons from the whole European Geographic Domain and from twelve regions within it, then comparing our results with the annual emissions that the European countries submit every year to the United Nations Framework Convention on Climate Change, as well as with the bottom-up Emissions Database for Global Atmospheric Research. We found several discrepancies when considering the specific compounds and on the country level. However, an overall agreement is found when comparing European aggregated data, which between 2008 and 2014 are on average $84.2 \pm 28.0 \text{ Tg-CO}_2\text{-eq}\cdot\text{yr}^{-1}$ against the $95.1 \text{ Tg-CO}_2\text{-eq}\cdot\text{yr}^{-1}$ reported by UNFCCC in the same period. Therefore, in agreement with other studies, the gap on the global level between bottom-up estimates of Annex I countries and total global top-down emissions should be essentially due to emissions from non-reporting countries (non-Annex I).

1.Introduction

The increase of hydrofluorocarbon (HFC) concentrations in the atmosphere has been recognised as a major driver for climate change (IPCC, 1990; 2013). HFCs have been produced by industry for a variety of uses (refrigerants, foam blowing agents, propellants, solvents, fire retardants, besides the non-reported military uses) as a replacement of the ozone-depleting chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), whose emissive uses were phased-out under the Montreal Protocol (MP) on Substances that Deplete the Ozone Layer (UNEP, 1987). The MP, through the phase-out of production and consumption of ozone depleting substances, led to a significant decline in CFC and HCFC atmospheric concentrations. Originally HFCs, having only an indirect impact on the ozone layer (Hurwitz et al., 2015), were not under the MP regulatory framework. Yet the potential climate benefits of reducing HFC emissions has been recognised by the UNEP-CCAC (Climate and Clean Air Coalition), an international initiative aiming at catalysing rapid reductions in short-lived climate pollutants (SLCPs), based on the assumption that a timely reduction of SLCPs can slow the rate of climate change within the first half of this century, i.e. before the long lived CO_2 reduction measures will take effect (Velders et al., 2009; UNEP, 2011; Shindell et al., 2012; Xu et al., 2013). In addition, it has been estimated that, due to the high GWPs of the HFCs, without direct regulation the HFC atmospheric increase could lead to 14 to 27% of the increase in CO_2 radiative forcing (RF) under the range of IPCC (Intergovernmental Panel on Climate Change)

65 business-as usual scenarios from 2010 to 2050 (Velders et al., 2012 and 2015; Montzka and
66 Reimann, 2011).

67 Consequently, in 2015 several formal proposals were issued (UNEP 2015a, b, c, d) to amend the
68 Montreal Protocol to phase down the production and consumption of HFCs. This resulted in the
69 Kigali Amendment to the MP agreed during the 28th meeting of the parties (MOP28) in October
70 2016, calling for developed countries to start to phase-down HFCs by 2019 and in developing
71 countries to follow with a freeze of HFC consumption levels between 2024 and 2028
72 (www.unep.org). This legally binding agreement would avoid nearly half a degree Celsius of
73 warming by the end of the century.

74 In addition, HFCs were regulated under the United Nations Framework Convention on Climate
75 Change (UNFCCC) Kyoto Protocol and their production and use were subject only to voluntary
76 regulation (UNFCCC, 1997). Parties included in Annex I to the UNFCCC (Annex I Parties) have
77 been required to submit annual national GHG inventories, covering emissions and removals of the
78 six direct GHGs included in the so-called Kyoto basket: carbon dioxide (CO₂), methane (CH₄),
79 nitrous oxide (N₂O), the F-gases (hydrofluorocarbons, HFCs and perfluorocarbons, PFCs) and
80 sulfur hexafluoride (SF₆). Each gas is weighted by its 100-year global warming potential (GWP)
81 and aggregated to give total GHG emissions in CO₂ equivalents (UNFCCC, 2006). The reliability
82 of the emission data reported by the parties to UNFCCC is crucial in assessing the Parties
83 compliance with the Kyoto Protocol and therefore in determining the Protocol's effectiveness.
84 Following the IPCC guidelines (IPCC, 2006), the UNFCCC requires only bottom-up reporting,
85 which relies on declared anthropogenic activities, that for F-gases are industrial processes and
86 product use, and on emission factors for the release into the atmosphere. However, the combination
87 of atmospheric measurements of GHGs and atmospheric modelling, the so-called 'top-down
88 approach', can be efficiently used for estimating emissions from the global to the country level (e.g.
89 Bergamaschi et al., 2004; Nisbet and Weiss, 2010; Manning et al., 2011; Weiss and Prinn, 2011;
90 Graziosi et al., 2015; Henne et al., 2016).

91 Among the Kyoto gases HFCs are considered particularly suitable for estimating emissions using
92 inverse modelling as they are solely of anthropogenic origin and sufficiently long-lived. This
93 approach could be used in support of the quality assurance of the inventories, whose uncertainty is
94 only loosely constrained among different countries (IPCC, 2006). In the past decade, the increased
95 capability of producing high-quality atmospheric data of HFCs in combination with rapidly
96 developing inverse modelling techniques has allowed the realisation of a number of studies
97 reporting top-down HFC emission estimates from the global to the regional scale (Yokouchi et al.,

2006; Greally et al., 2007; Stemmler et al., 2007; Stohl et al., 2009; Miller et al., 2010; Montzka et al., 2010; Li et al., 2010; Stohl et al., 2010; Vollmer et al., 2011; Brunner et al., 2012; Keller et al., 2012; Yao et al., 2012; O’ Doherty et al. 2014; Rigby et al., 2014; Fang et al., 2016; Hu et al., 2015; Lunt et al., 2015; Simmonds et al., 2016). The inversion results have shown different degrees of disagreement with HFC bottom-up emissions as reported to the UNFCCC, especially when the individual species are considered rather than the aggregated numbers (Lunt et al., 2015). In addition, for those HFCs whose commercial production has started only in recent years and whose annual reports are lacking or whose obligations for publicly reporting of data are lifted because of industrial confidentiality, the use of the top-down approach can serve to monitor the emission trends and to raise early warning in case of inconsistencies or incompleteness.

Since emissions control legislation is based on national or regional numbers, it would be important to assess the annual reports through the use of top-down methods at these same geographic scales. In Europe the reference regulations on fluorinated greenhouse gases are the EU mobile air conditioning (MAC) directive (EU, 2006), which bans the use of HFC-134a in motor vehicle AC from 2017, and the revised F-gas regulation (EU, 2014) which bans the use of high-GWP HFCs in other sectors starting in 2015 and also contains a phase down of HFC consumption from a base level. This Regulation also states “Effective monitoring of fluorinated greenhouse gas emissions is critical for tracking progress towards the achievement of emission reduction targets and for assessing the impact of this Regulation”.

Using atmospheric data from four European sites combined with the Lagrangian 3-D particle dispersion model FLEXPART and a Bayesian inversion method, we estimated the emissions of nine individual HFCs from the whole European Geographic Domain (EGD) and from twelve regions (representing individual countries or group of countries) within the EGD. These numbers were then compared with the annual emissions that the European countries submit to the UNFCCC. The observed discrepancies are then discussed. The list of the HFCs considered in this study is reported in Table 1, where their main characteristics in relation to their impact on climate (i.e. Radiative Efficiency and GWP) are given. The study period is from January 2003 to December 2014, although for some compounds shorter time series are available. In addition, we compared our results with the bottom-up Emissions Database for Global Atmospheric Research (EDGARv4.2FT2010, hereinafter EDGAR), a database that estimates global emission inventories of anthropogenic GHGs on a country, region and grid basis up to 2010.

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Table 1: List of the compounds considered in this study. Lifetime, radiative efficiency and GWP values are from Myhre et al. (2013) for all the compounds, excluding HFC-365mfc for which values are as in UNEP-TEAP (2010).

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Industrial Name	Chemical formula	Lifetime (Years)	Radiative Efficiency (W m ⁻² ppb ⁻¹)	GWP 20 Years	GWP 100 Years	Main use
HFC-32	CH ₂ F ₂	5.2	0.11	2430	677	Refrigerant
HFC-125	CHF ₂ CF ₃	28.2	0.23	6090	3170	Refrigerant
HFC-134a	CH ₂ FCF ₃	13.4	0.19	3710	1300	Refrigerant
HFC-143a	CH ₃ CF ₃	47.1	0.16	6940	4800	Refrigerant
HFC-152a	CH ₃ CHF ₂	1.5	0.10	506	138	Foam blowing
HFC-227ea	CF ₃ CHFCF ₃	38.9	0.26	5360	3350	Fire retardant
HFC-236fa	CF ₃ CH ₂ CF ₃	242	0.24	6940	8060	Fire retardant, Refrigerant
HFC-245fa	CHF ₂ CH ₂ CF ₃	7.7	0.24	2920	858	Foam blowing
HFC-365mfc	CH ₃ CF ₂ CH ₂ CF ₃	8.6	0.22	2660	804	Foam blowing

134

2. Method

2.1 Observations

In Europe, atmospheric measurement data for a wide range of HFCs are available at four sites: Jungfraujoch (JFJ), Switzerland (CH), Mace Head (MHD), Ireland (IE), Monte Cimone (CMN), Italy (IT), and Zeppelin (ZEP), Norway, Spitzbergen (NO). Through the use of gas chromatographic-mass spectrometric instrumentation (Miller et al., 2008; Maione et al., 2013), these stations are providing long-term, high-frequency and high-precision measurements of several halogenated gases. This is the result of a coordination effort that started in 2001 under the European SOGE (System for Observations of Halogenated Greenhouse Gases in Europe) Project. The four European stations are embedded in the AGAGE (Advanced Global Atmospheric Gases Experiment) programme (Prinn et al., 2000), which, together with the NOAA/GMD (National Oceanic and

146 Atmospheric Administration/Global Monitoring Division) (Montzka et al., 1994) and the NIES
147 (National Institute for Environmental Studies, Japan) (Yokouchi et al., 2006) monitoring networks,
148 represents the most important observation system for a wide range of ozone depleting and climate
149 altering species. Details of the monitoring network and on the analytical methods are given in the
150 Supplementary Material (SM) section.

151 2.2 Inverse Modelling

152 The approach that we used for this study combines the high-frequency trace gas observations with
153 an atmospheric particle dispersion model and a Bayesian inversion. To simulate transport to the
154 receptor sites, we used trajectories obtained with the 3-D FLEXPART v-9.02 dispersion model
155 (Stohl et al., 1998; 2005; Seibert and Frank, 2004) run every three hours for 20 days backward,
156 driven by operational three-hourly meteorological data at $1^\circ \times 1^\circ$ resolution from the European
157 Centre for Medium-Range Weather Forecasts (ECMWF). This allowed us to obtain the sensitivity
158 of the receptor to the source, also defined as the source receptor relationship (SRR) which in a
159 particular grid cell is proportional to the particle residence time in that cell and measures the
160 simulated mixing ratio that a source of unit strength (1 kg s^{-1}) in the cell would produce at the
161 receptor (Stohl et al., 2009). Multiplying the SRR by the emission flux taken from an appropriate
162 emission inventory (the *a priori* emission field), the simulated mixing ratio at the receptor to be
163 compared with the observations is obtained. After having tested two different *a priori* emission
164 fields (see paragraph 3 in the SM), we selected as *a priori* the UNFCCC inventory that gives the
165 best correlation coefficient between the simulated times series and the observations. Finally, the *a*
166 *posteriori* emission field was obtained through the Bayesian inversion method developed by Seibert
167 (2000; 2001), improved by Eckhardt et al. (2008) and Stohl et al. (2009; 2010) and recently applied
168 by Maione et al. (2014) and Graziosi et al. (2015). The uncertainty associated with the obtained
169 EGD emission values resulted to be 35%, averaged over time and compound. Details of the inverse
170 modelling method are given in the SM (paragraph 3).

171

172

173 3. Results and Discussion

174

175 3.1 European emissions

176

177 In Figure 1 EGD yearly emissions estimated through the proposed method are reported for nine
178 HFCs (red dots). The uncertainty in the estimates is derived from the model (see SM, paragraph 3).

179 Since not all stations started to monitor the HFCs considered in this study at the same time, the
180 inversions have been performed for those years in which data from at least two stations were
181 available. Detailed annual emissions for each compound and the associated percent error from the
182 EGD and from the twelve macro-areas considered in this study are reported in Table 2S in the SM.
183 UNFCCC estimates up to 2014 (blue dots) are reported for each compound and the comparison
184 with the inversion results is discussed. For the sake of completeness EDGAR estimates up to 2010
185 (grey dots) are also given. In many instances large differences between the two bottom-up data sets
186 are observed. Such differences in the annual emissions can be due to inconsistencies in the base
187 year estimates for each country, which in EDGAR are based on AFEAS (Alternative Fluorocarbons
188 Environmental Acceptability Study) data. Differences in emission trends can be due to the use of
189 different proxies, like e.g. the use of a relatively strong growth curve (often linearly increasing from
190 1990 onwards), as in the case of the use of air conditioning in European cars, or of fire retardants.
191 In the following we provide, for each compound, details on emission fluxes and their temporal
192 trends. It should be noted that we found that only three out of nine HFCs (namely, HFC-125, 152a
193 and 227ea) exhibit a significant (significance level $\alpha = 0.01$) linear trend. UNFCCC emission data
194 exhibit, during the period in common with the inversion, a significant ($\alpha = 0.01$) linear trend for all
195 the compounds considered, with the exception of HFC-152a. We did not evaluate trends of EDGAR
196 emissions, since the overlapping with our estimates is for the majority of the compounds limited to
197 three years.

Figure 1. Emissions of nine HFCs from the European Geographic Domain from January 2003 to December 2014. Emissions are given in Gg yr⁻¹ (right axis) and in Gg-CO₂-eq yr⁻¹ (left axis). TOTAL = aggregated emissions of nine HFCs. Red: this study; Blue: UNFCCC; Grey: EDGARv4.2FT2010.

HFC-32

HFC-32 is, in association with HFC-125, a component of the refrigerant mix used in stationary air conditioning in substitution of the ozone depleting HCFC-22. Due to the availability of observation data from at least two stations starting from 2008, the inversion covers a 7-year period (2008-2014), during which we estimated a yearly average emission from the EGD of 2.3 (± 0.8) Gg yr⁻¹ with a not significant increasing trend of 2.6% yr⁻¹ ($R^2=0.23$). During the common period 2008-2014 our average emission flux is in a fair agreement with the one given by UNFCCC (2.1 Gg yr⁻¹). On the contrary, the analysis of the emission trend highlights an important discrepancy between the inversion (2.6% yr⁻¹) and the UNFCCC database (13.3% yr⁻¹, $R^2=1.0$). EDGAR reported much lower emission fluxes (0.5 Gg yr⁻¹ on average), suggesting incompleteness in the activity data for the inventory compilation. As a further comparison, our estimates of HFC-32 for 2012 represent 13.6% of the global emissions calculated by O'Doherty et al. (2014) for the same year. Since the population of the EGD represents about the 7% of global population, this result implies that EGD per-capita emissions are about two times larger than the global average for 2012 given by O'Doherty et al. (2014).

HFC-125

For the cooling agent (stationary air conditioning) and fire extinguisher HFC-125 inversion results are available over 2003-2014. We estimated yearly average emission of 6.9 (± 2.4) Gg yr⁻¹ and an increasing trend of 5.0% yr⁻¹ ($R^2=0.65$). Our estimates are on average ca. 20% higher than UNFCCC and EDGAR, even if both inventories report emissions within the uncertainty of the inversion. Larger differences are observed in the trend comparison. Once again, the emission trend derived by the inversion is slower than that observed for UNFCCC (9.1%, $R^2=0.99$). EDGAR data show a good agreement with UNFCCC. Brunner et al. (2012), considering a smaller domain including twelve European countries (corresponding to our EGD with NEE, SCA and SEE subtracted), obtained for the same compound emissions of 3.9 (± 0.2) and 4.5 (± 0.2) Gg yr⁻¹, in 2006 and 2009, respectively, using a different modelling approach and a different station geometry. Such values compare with our estimates, for the same years and domain of Brunner et al. (2012), of 4.5 (± 1.3) and 4.6 (± 1.3) Gg yr⁻¹.

HFC-134a

For HFC-134a we estimated emissions over the period 2003-2014 that are on average 20.1 (± 6.3) Gg yr⁻¹, making HFC-134a the most emitted HFC in Europe. This value is 25% lower than UNFCCC. Emissions reported by European countries to UNFCCC are likely to be affected by an overestimate of the emission factors (EFs) used in some countries in order to compile the emission inventories (Lunt et al., 2015). It is interesting to note how annual emissions of the three databases are essentially coincident in the first part of the record, and then diverge rapidly after 2006. In Europe, HFC-134a is mainly (48-59% in 2010) used as refrigerant fluid in Mobile Air Conditioning (MAC) systems. Our results suggest, in agreement with Say et al. (2016), an overestimation of HFC-134a EFs. The European MAC directive 2006/40/EC, entered into force in 2008, implies the rejection of new type of vehicles fitted with MACs containing i) gases with a GWP higher than 150 or ii) leaking more than 40 or 60 grams of the refrigerant per year in the one or dual evaporator systems, respectively. Since car manufacturers were not ready to substitute HFC-134a with lower GWP fluids, it is reasonable to assume that the compliance with the MAC directive has been pursued through the reduction of leaking, not followed by a consistent adjustment of the EFs. Annual emissions derived by the inversion ($-1.1\% \text{ yr}^{-1}$, $R^2=0.24$) do not show any statistically significant trend. The trend exhibited by UNFCCC data is $4.2\% \text{ yr}^{-1}$ ($R^2=0.94$). EDGAR, which used the growth trend 1995-2005 of the car manufacturing as proxy for HFC-134a trend for the air conditioning of cars, shows even higher emission fluxes and trends.

252

253 *HFC-143a*

The high GWP value of HFC-143a makes reliable estimates of its emissions particularly relevant, since it represents the main single contributor to CO₂-eq normalized emissions in Europe. HFC-143a is mainly used as a working fluid component in refrigerant blends for low- and medium-temperature commercial refrigeration systems (O'Doherty et al. 2014). The inversion estimated HFC-143a average emission of 5.8 (± 2.0) Gg yr⁻¹ over 2006-2014. These figures are on average 7% higher than UNFCCC data, which are anyway within the error bar of the top-down estimates. The annual inversion estimates exhibit a trend ($3.0\% \text{ yr}^{-1}$, $R^2=0.38$) slower with respect to the quasi-linear trends of UNFCCC ($5.1\% \text{ yr}^{-1}$, $R^2=0.92$). Also in this case the EDGAR data exhibit a higher average emission flux and a faster emission trend. As a further comparison, analogously to HFC-32, we put our EGD estimates in a global perspective, comparing the HFC-143a inversion estimates for 2012 (7.1 Gg yr^{-1}) with the global ones (23.3 Gg yr^{-1}) given by O'Doherty et al. (2014). As stated above, considering that the population of the EGD represents about the 7% of global population, this result implies that EGD per-capita emissions are more than four times larger than the global average for 2012 (O'Doherty et al., 2014).

268

269 *HFC-152a*

270 In 2003-2014 yearly EGD emissions of the blowing agent HFC-152a are on average 4.1 (± 1.8) Gg
271 yr^{-1} , with a decreasing trend of $-4.6\% \text{ yr}^{-1}$ ($R^2=0.49$). Our estimates are in reasonable agreement
272 with UNFCCC national reports (3.7 Gg yr^{-1}) that always fall within the uncertainty of the inversion.
273 UNFCCC emissions do not show any significant trend ($-1\% \text{ yr}^{-1}$, $R^2=0.25$). In contrast, EDGAR
274 data tend to estimate higher emission fluxes and an increasing trend.

275 HFC-152a top-down emission estimates from similar studies, obtained following different
276 approaches, show an overall fair agreement with our results. Brunner et al. (2012) estimated
277 emissions of 2.0 (± 0.2) and 1.9 (± 0.2) Gg yr^{-1} for 2006 and 2009, respectively. Such emissions refer
278 to the twelve European countries domain corresponding to our EGD with NEE, SCA and SEE
279 subtracted. When considering the same geographic domain our estimates are 2.3 ± 0.8 and 1.8 ± 0.6
280 Gg yr^{-1} , respectively. Simmonds et al. (2016) estimated European emissions of 6.4 (5.2–7.5) and
281 5.2 (4.1–6.4) Gg yr^{-1} in 2010–2012 and 2007–2009, respectively to be compared with 4.2 ± 1.8 and
282 4.0 ± 1.8 obtained through our method in the same three-years for an approximately coincident
283 domain.

284

285 *HFC-227ea*

286 Yearly emissions of HFC-227ea, a fire retardant and a propellant in metered-dose inhalers, have
287 been estimated from 2008 to 2014 at an average value of 0.41 (± 0.22) Gg yr^{-1} , with a positive trend
288 of $4.4\% \text{ yr}^{-1}$ ($R^2=0.59$). It should be noted that, in this case, annual average emissions estimated
289 through the inversion are affected by an uncertainty of 45% (higher than the 35% uncertainty
290 resulting from the model), because of the high uncertainty in the measurement due to the very low
291 atmospheric mixing ratios of HFC-227ea. Our EGD inversion results are in a very good agreement
292 with the UNFCCC annual emission values (average 0.39 Gg yr^{-1}). Analogously, we found a fair
293 agreement also in the emission trend (5.6% , $R^2=0.99$) of UNFCCC. EDGAR reports a steep
294 increasing trend not confirmed by the inversions, with emission values one order of magnitude
295 larger than the top-down estimates. Moreover an outlier in 2009 indicates an error (related to the
296 Austria macro-area). The good agreement of our inversion results with the UNFCCC records
297 suggests that the large underestimation of global UNFCCC reports found by Vollmer et al. (2011)
298 based on a global inversion, is probably due to regions other than Europe, where many countries do
299 not report to the UNFCCC.

300

301 *HFC-236fa*

302 HFC-236fa is a fire retardant and a coolant in specialized applications. Average estimated
303 emissions over 2008-2014 are $0.02 (\pm 0.01) \text{ Gg yr}^{-1}$, with a trend of $3.6\% \text{ yr}^{-1}$ ($R^2=0.30$). As for HFC-
304 227ea, for this compound the average annual emission is affected by a high uncertainty (54%) due to
305 the measurement uncertainty. Our results exceed both UNFCCC and EDGAR by about 50%. This
306 suggests that there could be a deficit in the UNFCCC and EDGAR inventories, with very few
307 countries reporting their emissions. Our inversion values are significantly larger than projections
308 given by the IPCC (2005) that estimated for 2015 global emissions of 0.05 Gg yr^{-1} , corresponding
309 to about twice the total emissions from EGD, suggesting an important gap in the reported global
310 emissions. Such an underestimation is also reported in Vollmer et al. (2011), which estimated
311 global HFC- 236fa emissions of 0.018 Gg yr^{-1} in the 2008–2010 period.

312

313 *HFC-245fa*

314 The main market for HFC-245fa is in North America, where it is used for polyurethane structural
315 foam blowing (UNEP-TEAP, 2010). We estimated average EGD HFC-245fa emissions over the
316 period 2008-2014 of $0.74 \pm 0.33 \text{ Gg yr}^{-1}$ and a trend of $-3.0\% \text{ yr}^{-1}$ ($R^2=0.28$). The UNFCCC
317 database is in a very good agreement over the common period 2008-2014. On the contrary, EDGAR
318 exhibits a positive trend of 18.9% ($R^2=1.0$).

319

320 *HFC-365mfc*

321 HFC-365mfc is mainly used for polyurethane structural foam blowing and, to a minor extent, as a
322 blend component for solvents. According to the inversion results, HFC-365mfc emissions from the
323 EGD over 2005-2014 are on average $1.2 \text{ Gg yr}^{-1} (\pm 0.6)$ a value that is three times that given by the
324 UNFCCC (0.4 Gg yr^{-1}). Emissions estimated by the inversion, affected by an uncertainty of 50%
325 because of the low atmospheric mixing ratios of HFC-365mfc, do not show any significant trend ($-$
326 $2.3\% \text{ yr}^{-1}$, $R^2=0.24$), whereas UNFCCC data exhibit a decreasing trend of $-4.0\% \text{ yr}^{-1}$ ($R^2=0.7$).
327 EDGAR emission fluxes are closer to UNFCCC reports but with a positive emission trend. As
328 HFC-365mfc is predominantly released in Europe (Stemmler et al., 2007) with negligible emissions
329 from USA and East Asia (Vollmer et al., 2011), and the bottom-up estimates seem to significantly
330 underestimate emissions, it is important to constrain the intensity and distribution of emissions of
331 this growing compound from the EGD.

332

333 *Aggregated emissions of nine HFCs*

334 The last panel in Figure 1 (TOTAL), reports the aggregated emissions for the nine HFCs expressed
335 in $\text{Gg-CO}_2\text{-eq}\cdot\text{yr}^{-1}$. Considering the time period in which the inversion results are available for nine

336 HFCs (2008-2014), average emissions are $84.2 (\pm 28.0) \text{ Tg-CO}_2\text{-eq}\cdot\text{yr}^{-1}$ compared with the average
337 emission fluxes in the UNFCCC database of $95.1 \text{ Tg-CO}_2\text{-eq}\cdot\text{yr}^{-1}$, resulting in a difference of 13%
338 between the two datasets.

339 This is in agreement with what reported for Annex I countries in a recent study by Lunt et al.
340 (2015), who used AGAGE and NIES observations combined with a hierarchical Bayesian
341 framework to derive global emissions of five HFCs (HFC-32, HFC-125, HFC-134a, HFC-143a,
342 HFC-152a) during 2010-2012. The authors found that, as in our European study, discrepancies
343 between the top-down and bottom-up estimates of the single compounds were balanced when
344 considering the aggregated emissions.

345 However, it is important to underline how, despite the agreement obtained on a yearly basis
346 between the aggregated inversion results and the aggregated UNFCCC national reports, the
347 temporal pattern is different. Whereas the UNFCCC reports show a smooth (monotonic) behaviour,
348 our results exhibit annual variations matching the sales records as reported by UNFCCC, that show
349 for the main HFCs a slight sales increase in 2007-2008 and a 10% sharp decline in 2009, due to the
350 economic crisis, followed by a new increase in 2010, the last year for which sales data are available
351 (Schwartz et al., 2011). Consequently, our results do not show any statistically significant trend in
352 the emissions ($0.7\% \text{ yr}^{-1}$, $R^2=0.04$), whereas according to UNFCCC, European HFC emissions are
353 significantly ($\alpha=0.01$) increasing by $4.0\% \text{ yr}^{-1}$ ($R^2=0.94$) over the period 2008-2014. This finding is
354 particularly relevant for the elaboration of projection scenarios for future HFC emissions. The
355 comparison with EDGAR shows a disagreement both in average emissions, which are 35% higher
356 than the inversion, and in the trend, with EDGAR reporting a significant ($\alpha=0.01$) emission trend of
357 $7.3\% \text{ yr}^{-1}$ ($R^2=0.99$).

358
359 To summarise, we observed that based on the inversion results only three (HFC-125, HFC-152a and
360 HFC-227ea) out of the nine HFCs considered exhibit a significant ($\alpha = 0.01$) trend over the studied
361 period. In particular, despite the good agreement between the estimated annual aggregated
362 emissions and the UNFCCC aggregated reports, the former do not exhibit any significant trend,
363 differently than UNFCCC and EDGAR time series, which show a marked increasing trend.

364
365 We also calculated the percentage contribution of the single HFCs to the total EGD emissions,
366 reported both as percentage of the total mass emitted in Gg yr^{-1} and percentage of $\text{Gg-CO}_2\text{-eq}\cdot\text{yr}^{-1}$.
367 Pie charts in Figure 2 show the percent contribution of each of the nine compounds here considered
368 to EGD HFC aggregated emissions. Percentages are given for the period 2008-2014, when top-
369 down estimates for all the nine HFCs are available. Since the relative share is not changing

370 significantly from year to year, average values can be considered representative for the entire
 371 period.

372
 373 When reporting emissions in $\text{Gg-CO}_2\text{-eq}\cdot\text{yr}^{-1}$ (Fig.2B), the relative contribution of the single HFCs
 374 is completely different with respect to the mass emitted (Fig. 2A), because of the “weighting” with
 375 different GWP values associated to the various compounds (see Table 1). Using this metric HFC-
 376 143a becomes the compound that contributes more than one third over the total, going from the
 377 14.5% of the total Gg yr^{-1} to the 34.4% of the total $\text{Gg-CO}_2\text{-eq}\cdot\text{yr}^{-1}$, while the HFC-134a
 378 contribution drops from 47.1% of the total Gg yr^{-1} to 30.3% of the total $\text{Gg-CO}_2\text{-eq}\cdot\text{yr}^{-1}$.
 379 Analogously, the HFC-125 relative share increases from 18.6 to 29.2%, while HFC-32 relative
 380 share drops from 5.6 to 1.9%. Overall, these four HFCs that are used in refrigerant blends account
 381 for 95.8% of the total EGD $\text{Gg-CO}_2\text{-eq}$ emissions.

382

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384

385 Figure 2. Averaged relative share of each compound considered in this study to overall HFC emissions from
 386 Europe over 2008-2014. A) percentage of the total emissions in $\text{Gg}\cdot\text{yr}^{-1}$; B) percentage of the total emissions
 387 in $\text{Gg-CO}_2\text{-eq}\cdot\text{yr}^{-1}$.
 388

389 A comparison of percent contribution to $\text{Gg-CO}_2\text{-eq}\cdot\text{yr}^{-1}$ of emissions derived from the inversion
 390 and those reported by UNFCCC and EDGAR is given in Figure 3. Note that for the inversion
 391 results and UNFCCC data we refer to 2008-2014, whereas for EDGAR we refer to the period 2008-
 392 2010. A reasonable agreement is found for the three most emitted HFCs, whose aggregated
 393 emissions are 95.8 %, 97.2% and 91.6% as from the inversion, UNFCCC and EDGAR,

394 respectively. Differences are mainly due to the under-estimation of HFC-143a and over-estimation
 395 of HFC-134a in the bottom-up inventories with respect to the inversion results. A major
 396 discrepancy is found in relation to EDGAR estimates of HFC-227ea that are five times larger than
 397 the other two data-sets.

398

399

400 Figure 3. Relative share, in Gg-CO₂-eq·yr⁻¹, of nine HFCs to the total European HFC emissions: comparison among
 401 inversion estimates (2008-2014), UNFCCC (2008-2014) and EDGARv4.2FT2010 (2008-2010).

402

403 3.2 Spatial distribution of HFC emissions from the European Geographic Domain.

404 As noted in previous studies (Lunt et al., 2015), it is important to derive emission estimates at
 405 national scales in order to better understand the discrepancies in the UNFCCC reports, evaluate the
 406 reliability of EFs used by various countries and monitor the effectiveness of climate policy
 407 directives.

408 In this section we analyse the spatial distribution of emissions of the nine HFCs considered within
 409 twelve macro-areas in the EGD. In order to allow a comparison with the bottom-up inventories
 410 available, such analysis concerns the average emissions during period 2008-2014, when emissions
 411 for the nine HFCs have been estimated. Emissions from twelve macro-areas of nine HFCs are
 412 reported in Figure 4. Macro-areas acronyms are reported in Figure 4 caption.

413 For HFC-32, according to this study, the main emitters in the EGD are FR, ES-PT and IT, followed
 414 by UK and NEE that together account for the 75% of the EGD emissions. Despite a difference of
 415 only 10% between the total estimated amount of emitted HFC-32 from twelve macro-areas and the
 416 corresponding UNFCCC country reports, going to the single macro-area level significant
 417 discrepancies are found. We estimate for ES-PT, UK, NEE and SEE emissions that are only about
 418 half of the UNFCCC ones, whereas the UNFCCC number of IT accounts only ca. 50% of the
 419 inversion estimates. As already shown by the previous analysis, EDGAR reports HFC-32 emissions

420 that are ca. 25% of the inversion estimates for all macro-areas except DE, where a very good
421 agreement is found.

422 For HFC-125 the main emitters in our study are FR, ES-PT, IT, UK, and NEE, accounting for 72%
423 of total EGD emissions. The agreement with UNFCCC is within the error bars of the inversion for
424 most of the macro-areas, except ES-PT, UK and NEE reporting higher emissions with respect to our
425 estimates. A fair agreement is observed with EDGAR, with the exception of DE and BE-NE-LU,
426 for which the EDGAR estimated emissions are approximately double the inversion results, and ES-
427 PT that according to the inventory emits less than half the inversion estimates.

428 74% of HFC-134a EGD emissions in our study are attributed to FR, UK, IT, DE and ES-PT. As
429 discussed in the previous section, in general UNFCCC reports higher emissions than our results for
430 all the macro-areas, and especially in NEE, UK and DE. The only exception is Italy that reports
431 emissions that are two thirds of the estimated ones. Indeed, the HFC-134a EFs used by the Italian
432 National Institute for Environmental Protection (Istituto Superiore per la Protezione e la Ricerca
433 Ambientale, ISPRA) have been regularly updated after confrontation with the motor manufacturers'
434 association and are lower than those suggested in the IPCC guidelines (ISPRA, personal
435 communication, 2016). As for the EDGAR inventory, we observe a general overestimation,
436 especially in DE, NEE and SEE.

437 The main emitting macro-areas of HFC-143a in our study are FR, ES-PT, IT, UK, NEE and DE.
438 These six macro-areas account for more than 80% of total EGD emissions. The agreement with
439 UNFCCC is very good, with DE and NEE report values slightly outside the uncertainty of the
440 inversion. The agreement between the inversion and EDGAR is generally good with the exception
441 of DE, for which EDGAR reports emissions that are more than double than the inversion. The
442 agreement between the top-down and bottom-up estimates is particularly relevant, given the high
443 GWP value of HFC-143a, which is the major HFC emitted in terms of CO₂-eq.

444 The main emitter of HFC-152a in our study is IT, accounting alone for 20% of total EGD
445 emissions, followed by SEE, FR, NEE, and DE (total contribution 70%). The agreement with
446 UNFCCC is generally fair for all macro-areas, with two major exceptions: IT does not report any
447 emission to UNFCCC whereas SEE reports emissions 2.5 times larger than the inversion. The
448 discrepancy with UNFCCC is likely to be due to the incompleteness of reported emissions as a
449 consequence of a limited number of producers and confidentiality considerations. For this reason,
450 some countries report to UNFCCC HFC-152a emissions aggregated with other HFCs in the
451 "unspecified mix" category (Simmonds et al., 2015). The emission overestimates in EDGAR are
452 essentially due to FR, DE and UK.

453 In our study HFC-227ea is mainly emitted by FR, UK, DE, ES-PT and IT (overall contribution
454 77%). We observe good agreement with UNFCCC country reports, while EDGAR data for all
455 macro-areas are at least three times larger than the inversion results.

456 Major emitters of HFC-236fa in our study are NEE, ES-PT and DE (contributing the 71% of the
457 EGD emissions) that are also the only macro-areas in the EGD for which UNFCCC and EDGAR
458 data are available. The agreement between our estimates and the bottom-up inventories is
459 satisfactory only for the NEE macro-area.

460 In our study IT, ES-PT, FR, UK and DE account for 71% of HFC-245fa EGD emissions. The very
461 good agreement between the inversion estimates and UNFCCC at the EGD scale does not apply at
462 the single country scale, where UNFCCC reports larger emissions from IT and lower emissions
463 from ES-PT and UK. In addition, UNFCCC reports for seven macro-areas in the EGD are lacking.
464 The EDGAR inventory on average reports emissions larger than the inversion, in particular, for DE
465 and ES-PT.

466 In our study HFC-365mfc is mainly emitted by FR and ES-PT that, together with IT, DE and UK,
467 emit 75% of the total EGD. UNFCCC reports emissions that are only one third of the inversion
468 estimates at the EGD scale. This discrepancy is due to the lack of reporting of five macro-areas and
469 the remaining ones are greatly underestimated with the exception of UK and NEE. The EDGAR
470 database reports for this compound emissions which are significantly lower than the inversion,
471 especially for ES-PT, FR, IT, UK.

472 Despite some large discrepancies in selected macro-areas and/or compounds, when converting
473 emissions in CO₂-eq again the aggregated HFC estimated emissions from the twelve macro-areas
474 show a fair agreement with the bottom-up inventories. In particular UNFCCC data are within the
475 error bar of the inversion for most of the macro-areas, whereas in the comparison with EDGAR
476 some discrepancies are observed with DE, BE-NE-LU and SEE inventory exceeding the inversion
477 results.

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479

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Figure 4. Average emissions during 2008-2014 of nine HFCs from twelve macro-areas in the European Geographic Domain. Red, this study; Blue, UNFCCC; Grey, EDGARv4.2FT2010. Macro-areas, listed according to their aggregated (TOTAL) emission intensity are: FR (France); UK (United Kingdom); ES-PT (Spain, Portugal); IT (Italy); DE (Germany); NEE (Poland, Czech Republic, Slovakia, Lithuania, Latvia, Estonia, Hungary, Romania, Bulgaria); SCA (Norway, Sweden, Finland, Denmark); SEE (Slovenia, Croatia, Serbia, Bosnia-Herzegovina, Montenegro, Albania, Greece); BE-NE-LU (Belgium, The Netherlands, Luxembourg), IE (Ireland); AT (Austria); CH (Switzerland).

488

3.3 Per-capita emissions from the European Geographic Domain.

Considering the strong inhomogeneity in terms both of area, population and HFC production facilities of the twelve macro-areas under investigation, per-capita emissions have been calculated. They are representative of the sum of emissions due to industrial processes (point source emissions) and individual consumption (diffusive emissions).

Figure 5 shows the geographic distribution of per-capita emissions, given in $\text{kg-CO}_2\text{-eq}\cdot\text{yr}^{-1}\cdot\text{inhabitants}^{-1}$, from twelve macro-areas in the EGD. Columns A, B and C refer to the inversion estimates (averaged over 2008-2014), UNFCCC (averaged over 2008-2014) and EDGAR (averaged over 2008-2010), respectively.

The per-capita value for which we found the largest deviation from the EGD average emission of $183 \text{ kg-CO}_2\text{-eq}\cdot\text{yr}^{-1}\cdot\text{inhabitants}^{-1}$ is that referred to Ireland (IE), where we estimated a much higher value of $427 \text{ kg-CO}_2\text{-eq}\cdot\text{yr}^{-1}\cdot\text{inhabitants}^{-1}$. Emissions from IE larger than the average are also reported in the bottom-up inventories. Such deviation from the average value is likely to be due to the weight of industrial emissions that become more relevant in a low-populated area.

Further emissions above the European average, in the range $208\text{-}272 \text{ kg-CO}_2\text{-eq}\cdot\text{yr}^{-1}\cdot\text{inhabitants}^{-1}$, have been estimated for FR, ES-PT and IT whereas for UK, SEE, SCA, AT, BE-NE-LU, DE and NEE we estimated below average emissions ranging from 74 to $183 \text{ kg-CO}_2\text{-eq}\cdot\text{yr}^{-1}\cdot\text{inhabitants}^{-1}$.

Finally, for the CH area we estimated per-capita emissions significantly lower than the European average and lower than the bottom-up inventories. However, it must be underlined that the model allocation of emissions from a relatively small area is affected by the so-called border problem, and is therefore less reliable.

In order to assess the contribution of industrial emissions to per-capita ones, it might be useful to analyse fluxes reported to the European Pollutant Release and Transfer Register (E-PRTR). The E-PRTR is a Europe-wide register that provides environmental data from 30,000 industrial facilities covering 65 economic activities within 9 industrial sectors in EU member states, as well as in Iceland, Liechtenstein, Norway, Serbia and Switzerland and reports HFC atmospheric emissions higher than 100 kg yr^{-1} . Based on E-PRTR data, aggregated HFC emissions in mass correspond to

516 circa one thirtieth of the inversion estimates. Unfortunately, the European Regulation CE/166/2006
 517 requires this inventory to include HFC aggregated emissions reported not in CO₂-eq but in weight
 518 mass, a metric that does not allow a comparison with the inversion results, nor does it allow an
 519 assessment of the actual impact of industrial emissions to the total radiative forcing due to HFCs.

520
 521 Figure 5: Per-capita emissions from twelve macro-areas in the European Geographic Domain. Emissions, given in kg-
 522 CO₂-eq·y⁻¹·inhabitants⁻¹, are averaged over 2008-2014 for the inversion results (columns A) and the IPCC country
 523 reports (columns B). EDGAR data (columns C) are averaged over 2008-2010.

524
 525 The average EGD per-capita CO₂ equivalent emissions derived through the inversion resulted to be
 526 up to four times larger than the average global ones, calculated from top-down estimates reported
 527 by Rigby et al. (2014) and higher than Chinese per-capita emissions based on Fang et al. (2016), but
 528 lower than those estimated by Lunt et al. (2015) from the West USA, (representing the 21 % of U.S.
 529 population). A summary of such comparison is reported in Table 2.

Table 2. Per-capita average HFC emissions in 2010-2012 derived through top-down methods across different world areas. Emissions are given in $\text{kg-CO}_2\text{-eq}\cdot\text{y}^{-1}\cdot\text{inhabitants}^{-1}$.

$\text{kg-CO}_2\text{-eq}\cdot\text{y}^{-1}\cdot\text{inhabitants}^{-1}$	EGD (this study)	China (Fang et al. 2016)	West USA (Lunt et al. 2015)	Global (Rigby et al. 2014)
HFC-32	3.4 ± 1.2	4.0	3.4	1.5
HFC-125	55 ± 19	15	88	15
HFC-134a	53 ± 18	22	140	31
HFC-143a	59 ± 21	8.7	83	14
HFC-152a	1.1 ± 0.4	1.6	9.0	1.0
HFC-227ea	3 ± 1	NA	NA	1.3
HFC-236fa	0.3 ± 0.1	NA	NA	0.2
HFC-245fa	1.2 ± 0.4	NA	NA	0.9
HFC-365mfc	1.9 ± 0.7	NA	NA	0.4

4. Conclusions

This study captures the current status of HFC emissions at the European scale at a time immediately preceding their phase-down, as agreed during the 28th Meeting of the Parties to the Montreal Protocol (Kigali, October 2016). The top-down approach used in this study allowed us to derive emission fluxes of nine HFCs based on long-term, high-frequency observations. It is a very powerful tool for integrating and supporting existing emission data available in the bottom-up inventories that are prone to be affected by the use of different emission factors or absences in the national reports. The sensitivity analyses have shown that the inversion results are robust and produce stable results despite the high variability of input data and inversion settings.

Spatial distribution: The analysis of the spatial distribution of HFC emissions within the European geographic domain allowed us to identify four macro-areas, FR, UK, ES-PT and IT, as the main emitting areas responsible for the 61% of aggregated emissions from 2008 to 2014. According to UNFCCC and EDGAR the four macro-areas represent the 60% (2008-2014) and 47% (2008-2010) of total emissions, respectively. Important discrepancies are highlighted when considering the spatial distribution, for example the IT macro-area being the main emitter of HFC-152a, whereas in the UNFCCC database no emissions are reported.

Single compound emissions: The comparison with the UNFCCC database was done over 2003-2014 or shorter periods, according to the considered compounds. Our results are in fair agreement for most of the compounds. Percent variations, calculated as (inversion results –

UNFCCC)/inversion results, for HFC-125, HFC-143a, HFC-152a and HFC-227ea are lower than 10%. HFC-32 and HFC-134a are estimated by the inversion are lower than UNFCCC by -19% and 23%, respectively. Such values are always within the inversion uncertainty. A larger discrepancy was found for HFC-236fa, HFC-245fa and HFC-365mfc (65%, 39% and 62%, respectively). The comparison with EDGAR (2003-2008 or shorter periods according to the different compounds) reveals that this inventory underestimates emission data for HFC-32 and HFC-365mfc but overestimates emission data for HFC-227ea. Inversion estimates for the compound with the highest emissions, HFC-134a, are 50% lower than the inventory and with a markedly different trend, suggesting a shortcoming in the activity data as non-representative proxy for the emission trends for this compound affecting bottom-up estimates.

Aggregated emissions: Despite the several discrepancies when considering the single compounds, an overall agreement is found when comparing aggregated data. We estimated that European aggregated emissions from 2008 to 2014, the period in which the inversions have been run for all the nine HFCs, and considering their 100-yr GWP, are on average $84.2 \pm 28.0 \text{ Tg-CO}_2\text{-eq}\cdot\text{yr}^{-1}$ against the $95.1 \text{ Tg-CO}_2\text{-eq}\cdot\text{yr}^{-1}$ reported by UNFCCC in the same period. These results support, as far as Europe is concerned, the findings by Lunt et al. (2015). These authors observed a substantial agreement between emissions from Annex I countries inferred by atmospheric observations and those reported to UNFCCC, suggesting that the existing gap between global top-down and bottom-up estimates (Rigby et al., 2014) should be essentially due to non-reporting countries. However, the discrepancies between the UNFCCC country reports and the inversion results evidenced by this study when considering the single countries and the single compounds confirm that the agreement is more due to a cancellation of errors rather than to the accuracy in compiling the emission inventories. Thus, our results could help in identifying which compounds and macro-areas would need more robust estimates of emission fluxes.

Further regional studies from other Annex I countries are necessary in order to better constrain the HFC global budget. In addition, the differences found when comparing the emission trends as derived by the inversion with those reported to UNFCCC could affect the effectiveness of the adopted climate policies.

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602

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