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

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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±28.0 Tg-CO_2-eq·yr^{-1} against the 95.1 Tg-CO_2-eq·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)

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

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

In addition, HFCs were regulated under the United Nations Framework Convention on Climate Change (UNFCCC) Kyoto Protocol and their production and use were subject only to voluntary regulation (UNFCCC, 1997). Parties included in Annex I to the UNFCCC (Annex I Parties) have been required to submit annual national GHG inventories, covering emissions and removals of the six direct GHGs included in the so-called Kyoto basket: carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), the F-gases (hydrofluorocarbons, HFCs and perfluorocarbons, PFCs) and sulfur hexafluoride (SF_6). Each gas is weighted by its 100-year global warming potential (GWP) and aggregated to give total GHG emissions in CO_2 equivalents (UNFCCC, 2006). The reliability of the emission data reported by the parties to UNFCCC is crucial in assessing the Parties compliance with the Kyoto Protocol and therefore in determining the Protocol's effectiveness. Following the IPCC guidelines (IPCC, 2006), the UNFCCC requires only bottom-up reporting, which relies on declared anthropogenic activities, that for F-gases are industrial processes and product use, and on emission factors for the release into the atmosphere. However, the combination of atmospheric measurements of GHGs and atmospheric modelling, the so-called 'top-down approach', can be efficiently used for estimating emissions from the global to the country level (e.g. Bergamaschi et al., 2004; Nisbet and Weiss, 2010; Manning et al., 2011; Weiss and Prinn, 2011; Graziosi et al., 2015; Henne et al., 2016).

Among the Kyoto gases HFCs are considered particularly suitable for estimating emissions using inverse modelling as they are solely of anthropogenic origin and sufficiently long-lived. This approach could be used in support of the quality assurance of the inventories, whose uncertainty is only loosely constrained among different countries (IPCC, 2006). In the past decade, the increased capability of producing high-quality atmospheric data of HFCs in combination with rapidly developing inverse modelling techniques has allowed the realisation of a number of studies 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.

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).

Industrial Name	Chemical formula	Lifetime (Years)	Radiative Efficiency (W m^{-2} ppb^{-1})	GWP 20 Years	GWP 100 Years	Main use
HFC-32	CH_2F_2	5.2	0.11	2430	677	Refrigerant
HFC-125	CHF_2CF_3	28.2	0.23	6090	3170	Refrigerant
HFC-134a	CH_2FCF_3	13.4	0.19	3710	1300	Refrigerant
HFC-143a	CH_3CF_3	47.1	0.16	6940	4800	Refrigerant
HFC-152a	CH_3CHF_2	1.5	0.10	506	138	Foam blowing
HFC-227ea	CF_3CHFCF_3	38.9	0.26	5360	3350	Fire retardant
HFC-236fa	$CF_3CH_2CF_3$	242	0.24	6940	8060	Fire retardant, Refrigerant
HFC-245fa	$CHF_2CH_2CF_3$	7.7	0.24	2920	858	Foam blowing
HFC-365mfc	$CH_3CF_2CH_2CF_3$	8.6	0.22	2660	804	Foam blowing

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

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

2.2 Inverse Modelling

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

3. Results and Discussion

3.1 European emissions

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

Since not all stations started to monitor the HFCs considered in this study at the same time, the inversions have been performed for those years in which data from at least two stations were available. Detailed annual emissions for each compound and the associated percent error from the EGD and from the twelve macro-areas considered in this study are reported in Table 2S in the SM. UNFCCC estimates up to 2014 (blue dots) are reported for each compound and the comparison with the inversion results is discussed. For the sake of completeness EDGAR estimates up to 2010 (grey dots) are also given. In many instances large differences between the two bottom-up data sets are observed. Such differences in the annual emissions can be due to inconsistencies in the base year estimates for each country, which in EDGAR are based on AFEAS (Alternative Fluorocarbons Environmental Acceptability Study) data. Differences in emission trends can be due to the use of different proxies, like e.g. the use of a relatively strong growth curve (often linearly increasing from 1990 onwards), as in the case of the use of air conditioning in European cars, or of fire retardants.

In the following we provide, for each compound, details on emission fluxes and their temporal trends. It should be noted that we found that only three out of nine HFCs (namely, HFC-125, 152a and 227ea) exhibit a significant (significance level $\alpha = 0.01$) linear trend. UNFCCC emission data exhibit, during the period in common with the inversion, a significant ($\alpha = 0.01$) linear trend for all the compounds considered, with the exception of HFC-152a. We did not evaluate trends of EDGAR emissions, since the overlapping with our estimates is for the majority of the compounds limited to three years.

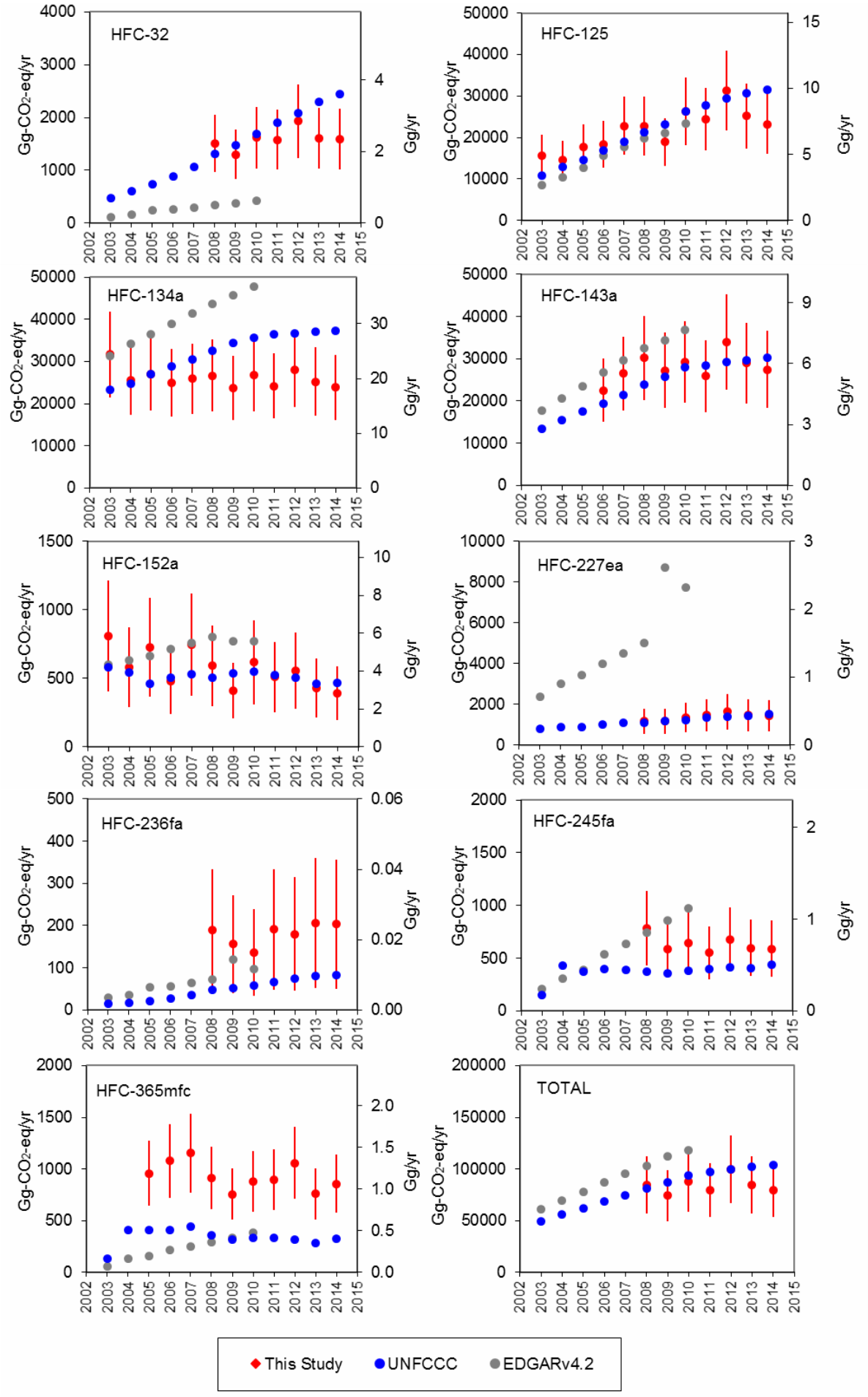
HFC-32
HFC-125
HFC-134a
HFC-143a
HFC-152a
HFC-227ea
HFC-236fa
HFC-245fa
HFC-365mfc
TOTAL
Gg-CO2-eq/yr
Gg/yr
This Study
UNFCCC
EDGARv4.2

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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-CO_2-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% yr^{-1}, R^2=0.24) do not show any statistically significant trend. The trend exhibited by UNFCCC data is 4.2% 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.

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 CO_2-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% yr^{-1}, R^2=0.38) slower with respect to the quasi-linear trends of UNFCCC (5.1% 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).

HFC-152a

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

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

HFC-227ea

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

HFC-236fa

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

HFC-245fa

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

HFC-365mfc

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

Aggregated emissions of nine HFCs

The last panel in Figure 1 (TOTAL), reports the aggregated emissions for the nine HFCs expressed in Gg-CO_2-eq·yr^{-1}. Considering the time period in which the inversion results are available for nine

HFCs (2008-2014), average emissions are 84.2 (±28.0) Tg-CO_2-eq·yr^{-1} compared with the average emission fluxes in the UNFCCC database of 95.1 Tg-CO_2-eq·yr^{-1}, resulting in a difference of 13% between the two datasets.

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

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

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

We also calculated the percentage contribution of the single HFCs to the total EGD emissions, reported both as percentage of the total mass emitted in Gg yr^{-1} and percentage of Gg-CO_2-eq·yr^{-1}. Pie charts in Figure 2 show the percent contribution of each of the nine compounds here considered to EGD HFC aggregated emissions. Percentages are given for the period 2008-2014, when top-down estimates for all the nine HFCs are available. Since the relative share is not changing

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

When reporting emissions in Gg-CO_2-eq·yr^{-1} (Fig.2B), the relative contribution of the single HFCs is completely different with respect to the mass emitted (Fig. 2A), because of the "weighting" with different GWP values associated to the various compounds (see Table 1). Using this metric HFC-143a becomes the compound that contributes more than one third over the total, going from the 14.5% of the total Gg yr^{-1} to the 34.4% of the total Gg-CO_2-eq·yr^{-1}, while the HFC-134a contribution drops from 47.1% of the total Gg yr^{-1} to 30.3% of the total Gg-CO_2-eq·yr^{-1}. Analogously, the HFC-125 relative share increases from 18.6 to 29.2%, while HFC-32 relative share drops from 5.6 to 1.9%. Overall, these four HFCs that are used in refrigerant blends account for 95.8% of the total EGD Gg-CO_2-eq emissions.

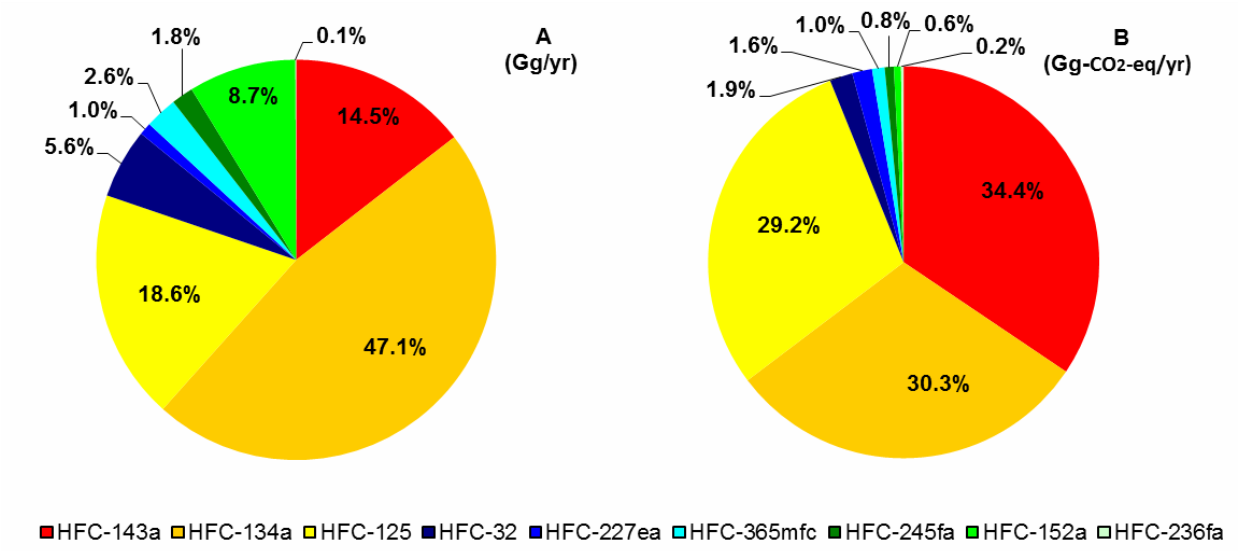

Figure 2. Averaged relative share of each compound considered in this study to overall HFC emissions from Europe over 2008-2014. A) percentage of the total emissions in Gg·yr^{-1}; B) percentage of the total emissions in Gg-CO_2-eq·yr^{-1}.

A comparison of percent contribution to Gg-CO_2-eq·yr^{-1} of emissions derived from the inversion and those reported by UNFCCC and EDGAR is given in Figure 3. Note that for the inversion results and UNFCCC data we refer to 2008-2014, whereas for EDGAR we refer to the period 2008-2010. A reasonable agreement is found for the three most emitted HFCs, whose aggregated emissions are 95.8 %, 97.2% and 91.6% as from the inversion, UNFCCC and EDGAR,

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

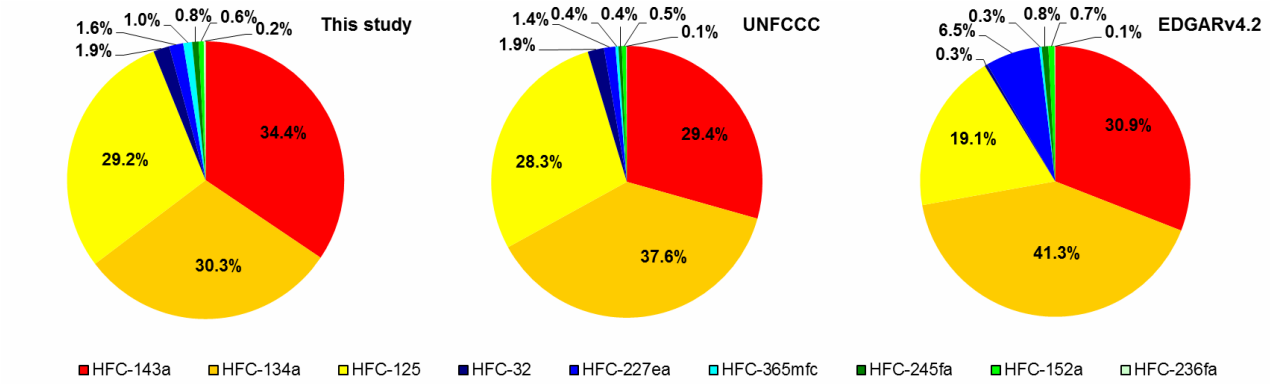

Figure 3. Relative share, in Gg-CO_2-eq·yr^{-1}, of nine HFCs to the total European HFC emissions: comparison among inversion estimates (2008-2014), UNFCCC (2008-2014) and EDGARv4.2FT2010 (2008-2010).

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

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

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

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

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

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

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

The main emitting macro-areas of HFC-143a in our study are FR, ES-PT, IT, UK, NEE and DE. These six macro-areas account for more than 80% of total EGD emissions. The agreement with UNFCCC is very good, with DE and NEE report values slightly outside the uncertainty of the inversion. The agreement between the inversion and EDGAR is generally good with the exception of DE, for which EDGAR reports emissions that are more than double than the inversion. The agreement between the top-down and bottom-up estimates is particularly relevant, given the high GWP value of HFC-143a, which is the major HFC emitted in terms of CO_2-eq.

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

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

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

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

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

Despite some large discrepancies in selected macro-areas and/or compounds, when converting emissions in CO_2-eq again the aggregated HFC estimated emissions from the twelve macro-areas show a fair agreement with the bottom-up inventories. In particular UNFCCC data are within the error bar of the inversion for most of the macro-areas, whereas in the comparison with EDGAR some discrepancies are observed with DE, BE-NE-LU and SEE inventory exceeding the inversion results.

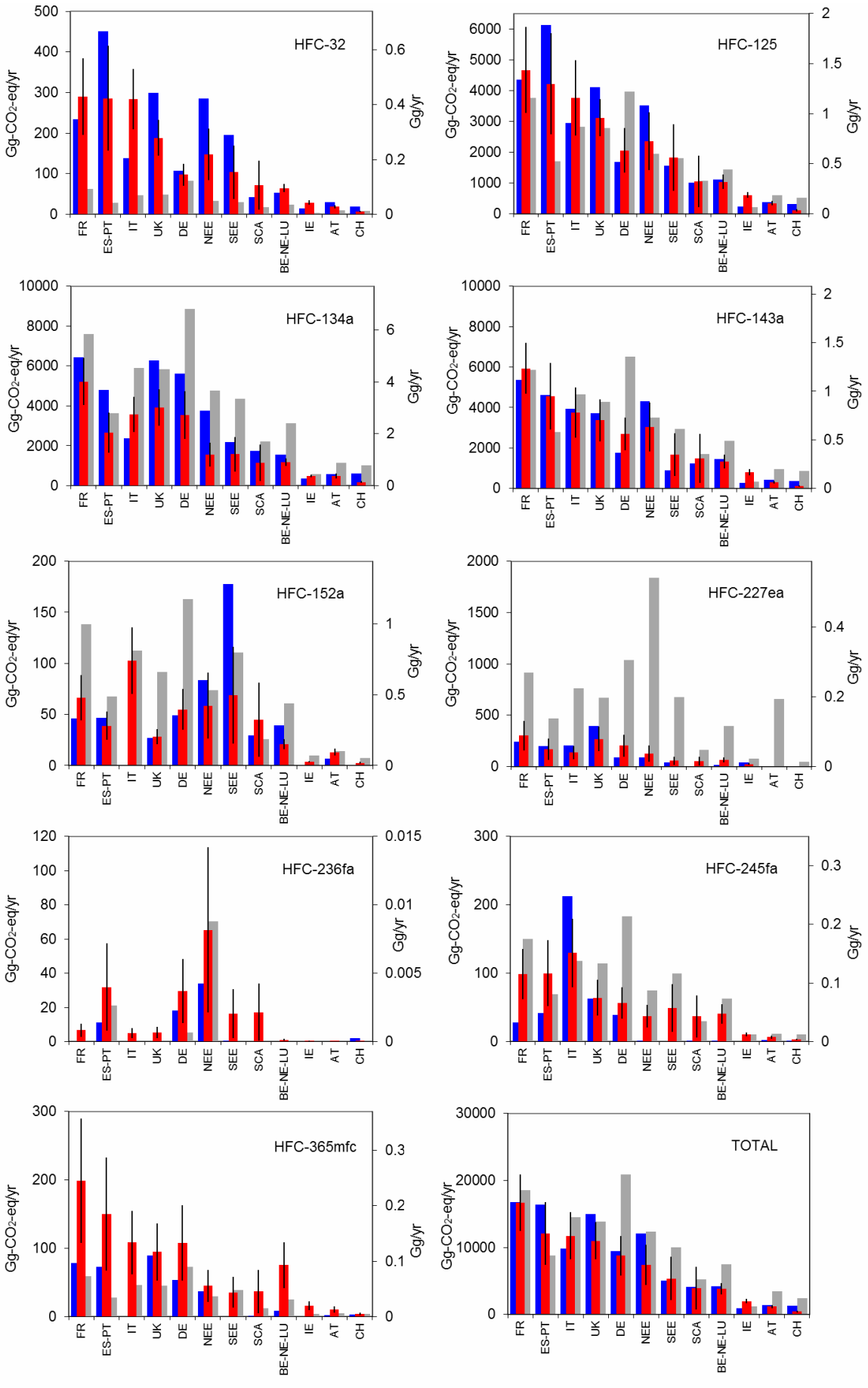
HFC-32
HFC-125
HFC-134a
HFC-143a
HFC-152a
HFC-227ea
HFC-236fa
HFC-245fa
HFC-365mfc
TOTAL
Gg-CO2-eq/yr
Gg/yr
FR
ES-PT
IT
UK
DE
NEE
SEE
SCA
BE-NE-LU
IE
AT
CH
This Study
UNFCCC
EDGARv4.2

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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).

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 kg-CO_2-eq·yr^{-1} ·$inhabitants^{-1}$, 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 kg-CO_2-eq·yr^{-1} ·$inhabitants^{-1}$ is that referred to Ireland (IE), where we estimated a much higher value of 427 kg-CO_2-eq·yr^{-1} ·$inhabitants^{-1}$. 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 208-272 kg-CO_2-eq·yr^{-1}·$inhabitants^{-1}$, 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 kg-CO_2-eq·yr^{-1} ·$inhabitants^{-1}$.

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

circa one thirtieth of the inversion estimates. Unfortunately, the European Regulation CE/166/2006 requires this inventory to include HFC aggregated emissions reported not in CO_2-eq but in weight mass, a metric that does not allow a comparison with the inversion results, nor does it allow an assessment of the actual impact of industrial emissions to the total radiative forcing due to HFCs.

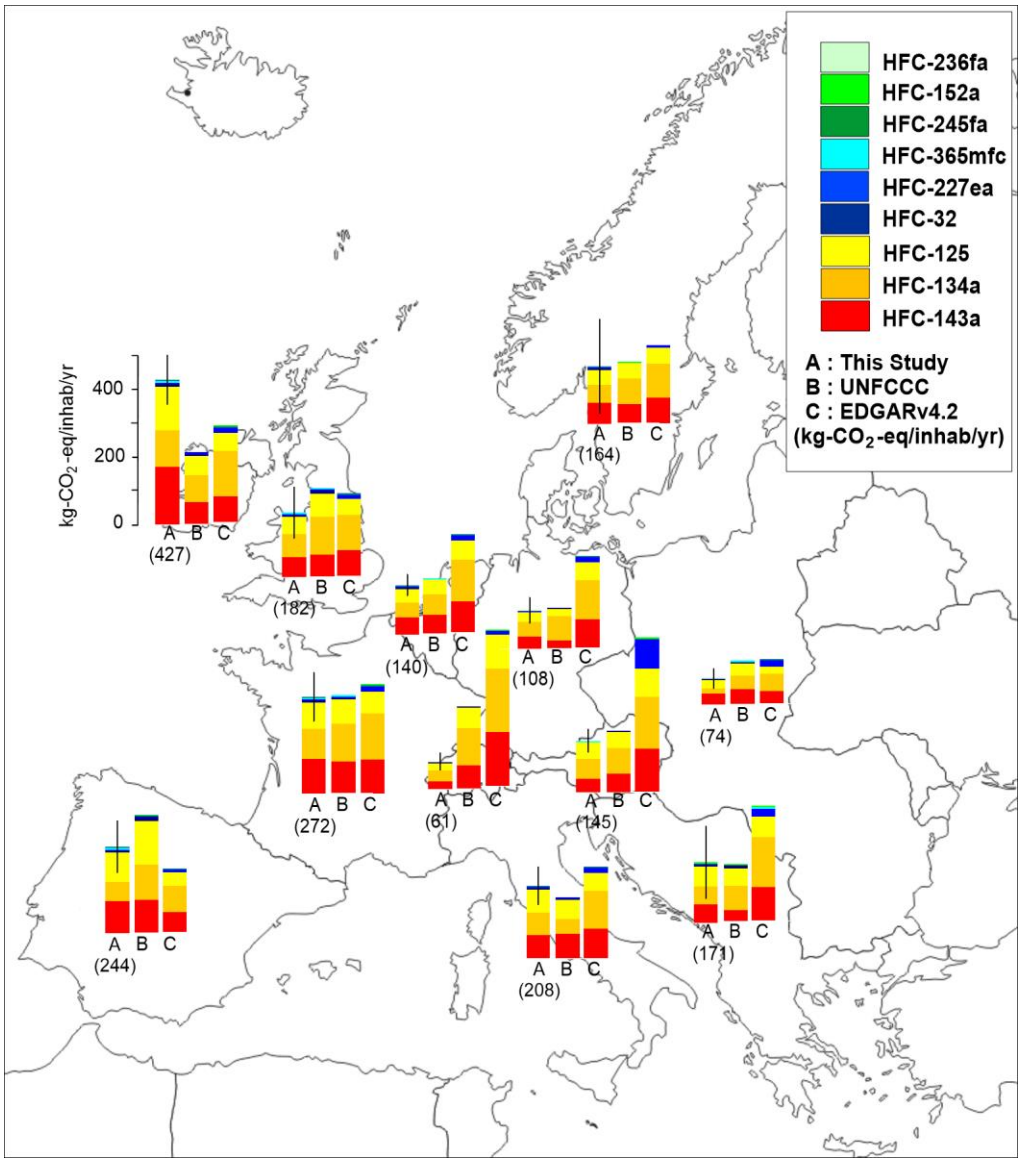

Figure 5: Per-capita emissions from twelve macro-areas in the European Geographic Domain. Emissions, given in kg-CO_2-eq·y^{-1} ·inhabitants^{-1}, are averaged over 2008-2014 for the inversion results (columns A) and the IPCCC country reports (columns B). EDGAR data (columns C) are averaged over 2008-2010.

The average EGD per-capita CO_2 equivalent emissions derived through the inversion resulted to be up to four times larger than the average global ones, calculated from top-down estimates reported by Rigby et al. (2014) and higher than Chinese per-capita emissions based on Fang et al. (2016), but lower than those estimated by Lunt et al. (2015) from the West USA, (representing the 21 % of U.S. 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 kg-CO_2-eq·y^{-1}·$inhabitants^{-1}$.

kg-CO2-eq·y^{-1} ·$inhabitants^{-1}$	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±28.0 Tg-CO_2-eq·yr^{-1} against the 95.1 Tg-CO_2-eq·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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831

Supplementary Material

1. The observing network

We used HFC atmospheric data from four European stations embedded in the global AGAGE network and classified as WMO GAW (World Meteorological Organisation-Global Atmosphere Watch) global. Two stations are mountain continental: Monte Cimone (CMN), located on the highest peak of the Northern Apennines in Italy (at 2165 m above sea level) at the border between continental Europe and the Mediterranean Basin and Jungfraujoch (JFJ), 3580 m above sea level, located on a mountain saddle in the central Swiss Alps. Both stations are well suited for long-term monitoring of trace gas concentration trends in the free troposphere. In addition, the proximity to important anthropogenic source regions in central Europe, like e.g. the Po basin, makes them appropriate for regional source allocation studies. Mace Head (MHD), located on the west coast of Ireland, is exposed to the North Atlantic Ocean and is therefore the ideal location to study both natural and man-made trace constituents in marine and continental air masses. Zeppelin (ZEP) is located in the Arctic on Zeppelin Mountain, 474 meters a.s.l, close to the town of Ny-Ålesund (Svalbard Islands, Norway), one of the world's northernmost human settlements. The site is well suited for the monitoring of global atmospheric change and long-range pollution transport.

2. Analytical methods

Long term, high-frequency, high-precision measurements of HFCs are performed with gas chromatographic-mass spectrometric (GC-MS) instruments equipped with pre-concentration systems. At JFJ, MHD and ZEP the equipment currently used is an Agilent 5975 mass spectrometer coupled to a Medusa pre-concentration system that allows cooling to ~-165^{0}C and trapping compounds in a micro-trap filled with relatively mild adsorbent (Miller et al., 2008). 2 L samples of ambient air are analysed every two hours, alternated with 2 L reference gas (working standard). CMN uses the same MS instrument but with a different pre-concentration unit that allows trapping

858 compounds at -30°C in a multi-bed trap filled with adsorbents of increasing adsorption capacity
859 (Markes International, UNITY2-Air Server2); the higher trapping temperature limits the total
860 volume sampled to 1 L. Also in this case, ambient air samples analyses are alternated with 1 L
861 working standard analyses (Maione et al., 2013). In spite of the differences in the analytical
862 methodologies, measurements at the four stations are fully inter-comparable, because the same
863 calibration protocol is used: the working standards are air samples pumped at the stations during
864 relatively clean-background conditions into 35 L electro-polished stainless steel canisters (Essex
865 Cryogenics, Missouri) using a modified oil-free compressor (SA-3, RIX California) up to ~60 bar.
866 The tanks are humidified with purified water during the pumping process in order to improve the
867 stability of the compounds (Miller et al., 2008). The working standards are calibrated weekly
868 against a tertiary standard prepared at MHD and in turn calibrated against the SIO-2005 (Scripps
869 Institution for Oceanography) scale, where primary gravimetric standard are prepared.
870
871 **3. Inversion method**
872 3.1 Bayesian Inversion
873 In order to derive the emissions of nine HFCs from the European domain, high-frequency trace gas
874 atmospheric data have been combined with high-resolution atmospheric transport simulations. For
875 this aim we run the FLEXPART stochastic model that has a detailed treatment of turbulence and
876 convection (Stohl et al., 1998; 2005; Seibert and Frank, 2004) and employs meteorological analyses
877 from the European Centre for Medium-Range Weather Forecasts (ECMWF). We used the ECMWF
878 analyses at 1° of latitude × 1° longitude resolution. FLEXPART was run backward in time from the
879 measurement stations at 3-hourly intervals, using 40000 particles for each backward run. The
880 particles were followed for 20 days with the aim of establishing the so-called source–receptor
881 relationship (SRR) between the potential HFC emission sources and the changes in mixing ratios
882 observed at each measurement station. Due to the HFC low reactivity, no loss process has been
883 considered. SRR (in units of s kg^{-1}) in a particular grid cell is proportional to the particle residence

884 time in that cell and measures the simulated mixing ratio at the receptor that a source of unit
885 strength (1 kg s^{-1}) in the cell would produce (Stohl et al., 2009). The SRR is also called "footprint"
886 or "emission sensitivity".
887 Figure 1S shows the SRR obtained from two years of FLEXPART backward calculations using the
888 entire network of stations. There is not a homogenous sensitivity over the domain, this hinders the
889 ability of the inversion to determine emission source strengths over the entire domain with the same
890 accuracy. Therefore, there are areas, like e.g. the Scandinavia region and Eastern Europe, with a
891 lower sensitivity with respect to the rest of the domain.
892 For HFC-152a, the species with the shortest atmospheric lifetime (567 d), 3.5% in mass would be
893 lost after the maximum transport time of 20 d, which introduces a systematic under-prediction of
894 the emissions in the inversion not higher than 3.5%, whatever is the compound considered.
895 The contribution of each grid cell to the mixing ratios at the receptor is obtained by multiplying the
896 SRR values by the emission flux densities (in units of kg m^{-2} s^{-1}) in that cell. The spatial
897 integration of each cell contributions gives the simulated mixing ratios at the receptor.
898 The inversion procedure used in this paper for estimating both emission strength and distribution
899 over the domain influencing the measurement sites is based on the analytical inversion method of
900 Seibert (2000, 2001), improved by Eckhardt et al. (2008). The inversion algorithm models the
901 emission field with the aim of optimizing the agreement between the measured and model
902 simulated concentration, considering at the same time *a priori* emissions and the uncertainties in
903 emissions, observations and model simulations.
904 Stohl et al. (2009) further improved the method considering a baseline in the observations that is
905 adjusted as part of the inversion process and adding a more detailed quantification of errors. All the
906 mathematical details of the method used in this study are described by Stohl et al. (2009).
907 The cost function *J* to be minimized is:
908
909 $$J = (M\tilde{x} - \tilde{y})^T diag(\sigma_0^{-2})(M\tilde{x} - \tilde{y}) + \tilde{x}^T diag(\sigma_x^{-2})\tilde{x} \quad \text{(Eq.1)}$$

910 This function is composed of two terms: the first term on the right hand side measures the model-
911 observation misfit while the second term measures the deviation from the *a priori* values. In the
912 equation M represents the SRR matrix elements determined by model simulations; $\tilde{x}$ is the
913 difference between the *a posteriori* and *a priori* emission vector and $\tilde{y}$ is the difference between the
914 observed and the simulated *a priori* mixing ratio vector, respectively; σ_0 and σ_x are the error vector
915 in the observations and the vector of errors of the *a priori* values, respectively. The diag (a) yields a
916 diagonal matrix with the elements of *a* in the diagonal.
917 The inversions have been performed with a variable resolution grid. The grid resolution was related
918 to the sensitivity: in the vicinity of the receptor a maximum resolution of 0.5° x 0.5° was used
919 whereas further away the resolution becomes lower, down to 2° x 2°.
920
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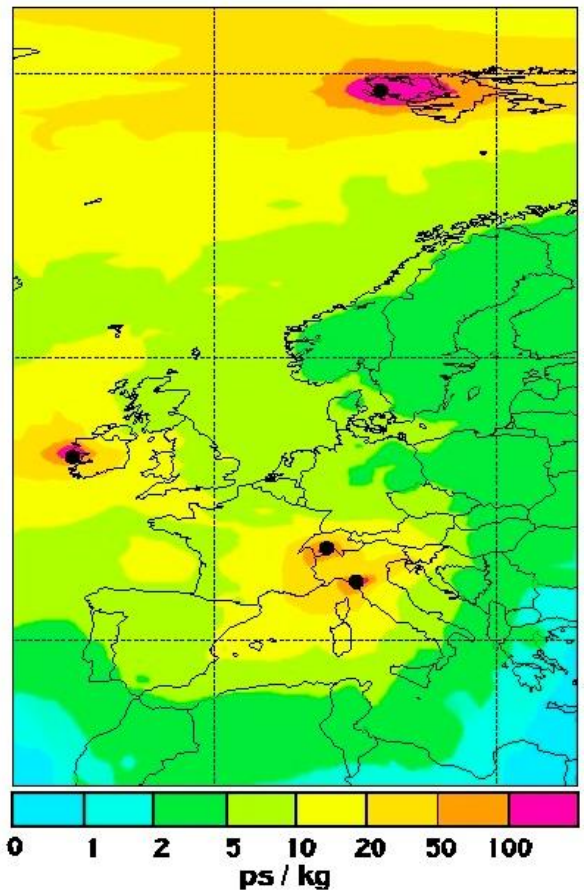

Figure 1S. Footprint emission sensitivity in picoseconds per kilogram (ps kg^{-1}) obtained from FLEXPART 20 d backward calculations averaged over all model calculations, over two years (Jan 2008- Dec 2009). Measurement sites are marked with black dots.

3.1.1 *A priori* emission field

For creating the most suitable *a priori* emission field to be adopted in the inversion, hereinafter called reference *a priori* field (RPF), we evaluated the best agreement between the observation data and the *a priori* simulated mixing ratios (modelled time series) produced using two different data bases. The simulated mixing ratios at each receptor point were obtained from the gridded *a priori* emissions multiplied by the gridded FLEXPART emission sensitivities. The reference emissions (REs) are those obtained using the RPF. We tested two different *a priori* emission fields. The first one is based on the annual national emissions as reported to the UNFCCC disaggregated within each country borders according to a gridded population density data set (CIESIN, Center for International Earth Science Information Network, www.ciesin.org). The second data base tested is the EDGARv4.2FT2010 (Emission Database for Global Atmospheric Research, version 4.2,

942 hereinafter EDGAR) inventory, which provides details on the emission distribution over the
943 domain, in a grid map with 0.1° x 0.1° resolution. The most recent EDGAR data are for 2010 and a
944 linear extrapolation based on eleven-year emission trends (1998-2010) was used to extract the
945 emission values from 2011 to 2014.
946
947 In Figure 2S are reported the Pearson correlation coefficients r_a^2 between observations and the *a*
948 *priori* time series of both databases, obtained for each station and for each compound for 2012,
949 being the year in which the complete time series for all gases at all the four stations are available.
950 On the base of this criterion, UNFCCC emerged as the *a priori* emission field better correlated with
951 the observations of the HFCs considered. This is particularly evident for compounds like HFC-152a
952 and HFC-227ea, as shown in Figure 2S.
953

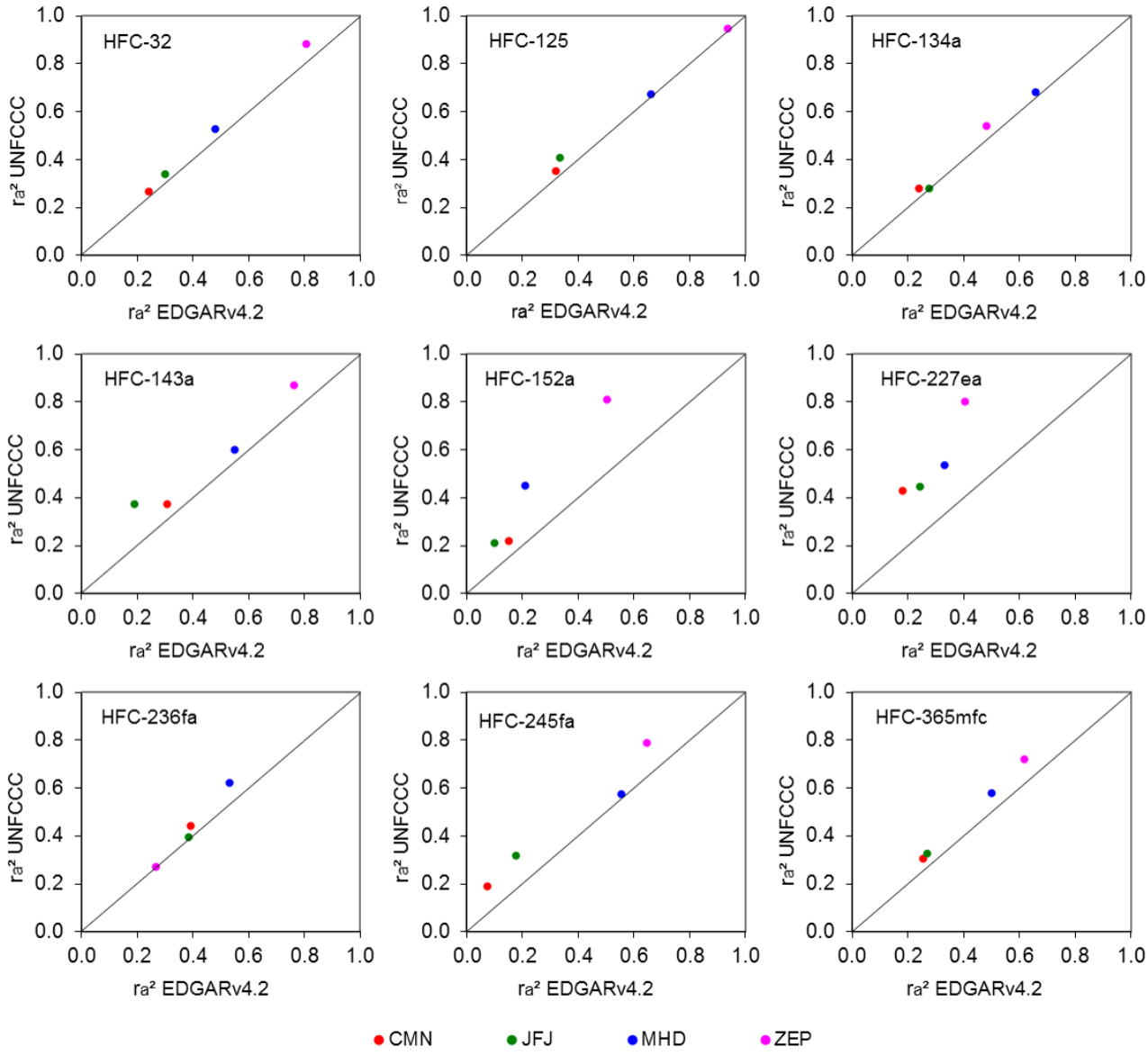

Figure 2S. r_a^2 Pearson correlation coefficients between the observations and the *a priori* time series of UNFCCC vs EDGARv4.2FT2010, obtained for each station and for each compound.

As no information is available on the uncertainty of emissions (σ_x) for both databases, we have to specify this uncertainty for every grid cell. For this purpose we have used $\sigma_j = p \max(1.2\ x_j, 1.0\ x_{surf})$, where p is the uncertainty emission scale factor, x_j is the *a priori* emission flux in the inversion box j and x_{surf} is the average emission flux over the domain. We chose p = 2 after testing several alternative values. p =2 appears to be the most appropriate because for higher values of p the obtained emission maps showed increasing levels of noise whereas lower values forced the

964 results close to the *a priori* field. Details on the parameterisation used here are described in Graziosi
965 et al., 2015.
966 Another source of information is the *European Pollutant Release and Transfer Register (E-PRTR)*,
967 where European member states must report the HFCs aggregated emission values for each industry
968 together with the geographical coordinates. However, since the information contained in the E-
969 PRTR is not available for the single HFCs, we increased by two the σ_j in the grid cells where the
970 HFC industries are located.
971
972 3.2 Sensitivity tests
973 With the purpose of estimating the influence of different uncertainty factors on the inversion results
974 we ran several sensitivity tests for each gas, obtaining a set of *a posteriori* emission fluxes. We ran
975 the sensitivity tests for 2012. The reduction of sigma values $\sigma^{j}_{x\_priori}$ for each inverted grid cell to
976 an uncertainty value $\sigma^{j}_{x\_posteriori}$ is due to the minimisation of the cost function J (Eq.1). After the
977 inversion we obtained an average uncertainty $\sigma^{j}_{x_posteriori}\cong$35% over the study domain. As the
978 reduction of uncertainty in each grid box is linked to the sensitivity of the grid itself, larger
979 reductions are obtained in regions well covered by the simulations, whereas low sensitivity regions
980 show a lower uncertainty reduction.
981 For characterising the test results we used the *Pd* parameter, defined as
982
983 $$Pd = \frac{RE - Test}{RE} * 100$$
984
985 where *RE* is, as defined above, the reference emission and *Test* is the emission obtained in the
986 single tests described below.
987
988

3.3 A Priori field tests

3.3.1 *A priori* field modulation

With the aim of testing the influence of the *a priori* emission flux on the inversion results we repeated the reference inversion, using three different *a priori* emission scaling factors: 0.5, 1 and 2. We performed this test for each compound and the obtained *Pd* values are given in Fig. 3S. Results obtained showed how the inversions, using the three different scaling factors of the *a priori* emission field, are able to give rather constant *a posteriori* emission fluxes, with a *Pd* of 7% (average of nine HFCs). When fewer receptors are available, the sensitivity of the domain decreases, reducing the inversion capability to "correct" the *a priori* emission field. As a consequence, when repeating the same analysis for a year in which the observations were available for a lower number of receptors (2008, not shown), the average *Pd* value rose to 12%.

The *Pd* value is inversely proportional to the sensitivity of the emitting area, highlighting that areas with higher sensitivity are more independent from the *a priori* field. On the whole, the average *Pd* values obtained suggest a good reliability of our emission estimates for all the gases considered in this study.

3.3.2 Testing EDGAR as *a priori* emission field

In order to assess to what extent the *a posteriori* emission fluxes obtained are affected by the *a priori* emission field used, we ran the inversions using as *a priori* emissions those given in the EDGAR database. In so doing, we test the capability of the inversion to converge to the same *a posteriori* flux starting from *a priori* emission fields different both in intensity and spatial distribution. In the plot in Figure 3S the *Pd* values obtained using the two different *a priori* fields are reported, showing that the difference between the REs obtained is always within the error bar associated with our estimates. The compounds exhibiting higher *Pd* values are HFC-32 and l'HFC-227ea, which starting from a ratio in the *a priori* emissions ((UNFCCC-EDGAR)/UNFCCC*100) of 76% and -590% converge to a ratio of 29% and -30%, respectively). This test confirmed the

1014 robustness of the method, highlighting how the emission fluxes calculated through the inversion are
1015 not greatly affected by the database used to create the *a priori* emission field.
1016
1017 3.4 Numbers of stations included in the inversion
1018 With this test we investigated how sensitive the inversion results are to the number of stations used
1019 for the inversion itself. In order to do that, we compared the inversion results obtained with a full
1020 data set (data from four stations) with those obtained using three or two stations at a time.
1021
1022 3.4.1 Removing one station
1023 The *Pd* values are shown in Figure 3S. For all the nine HFCs considered the average of *Pd* values
1024 were 7%, 10%, 13% and 9% removing CMN (no_CMN), JFJ (no_JFJ), MHD (no_MHD) and ZEP
1025 (no_ZEP), respectively. These results suggest that the data sets from the different stations are quite
1026 consistent with each other in constraining the European total emissions, and show the robustness of
1027 the inversion method even when using a sub set of concentration data.
1028
1029 3.4.2 Removing station pairs
1030 The aim of this test was to evaluate to what extent the obtained emissions are affected by the
1031 removal of station pairs. We tested i) the removal of the mountain stations CMN and JFJ
1032 (no_MOUNT), both characterised by a complex topography, both affected by air mass trajectories
1033 not well reproduced and by close-by polluted regions; ii) the removal of MHD and ZEP
1034 (no_REMOTE), both scarcely affected by anthropogenic emissions; iii) the removal of JFJ and ZEP
1035 (no_JFJ ZEP), i.e. two stations with different characteristics.
1036 The obtained *Pd* values are summarized in Figure 3S, showing that the removal of two stations at a
1037 time produced a significant spread of the emissions values, with an *Pd* value over the EGD of 22%
1038 (average of nine HFCs), where the maximum variations are registered for HFC-134a (+32%
1039 NO_REMOTE) and HFC-227ea (-32% NO_MOUNT), respectivetly. It is noteworthy that the

removal of the two mountain continental stations produced the highest variability, suggesting the importance of including receptors affected by the strongest source areas. This test produced the highest deviation from the inversion results.

Figure 3S shows the *Pd* values obtained from all the sensitivity tests and for all the compounds considered.

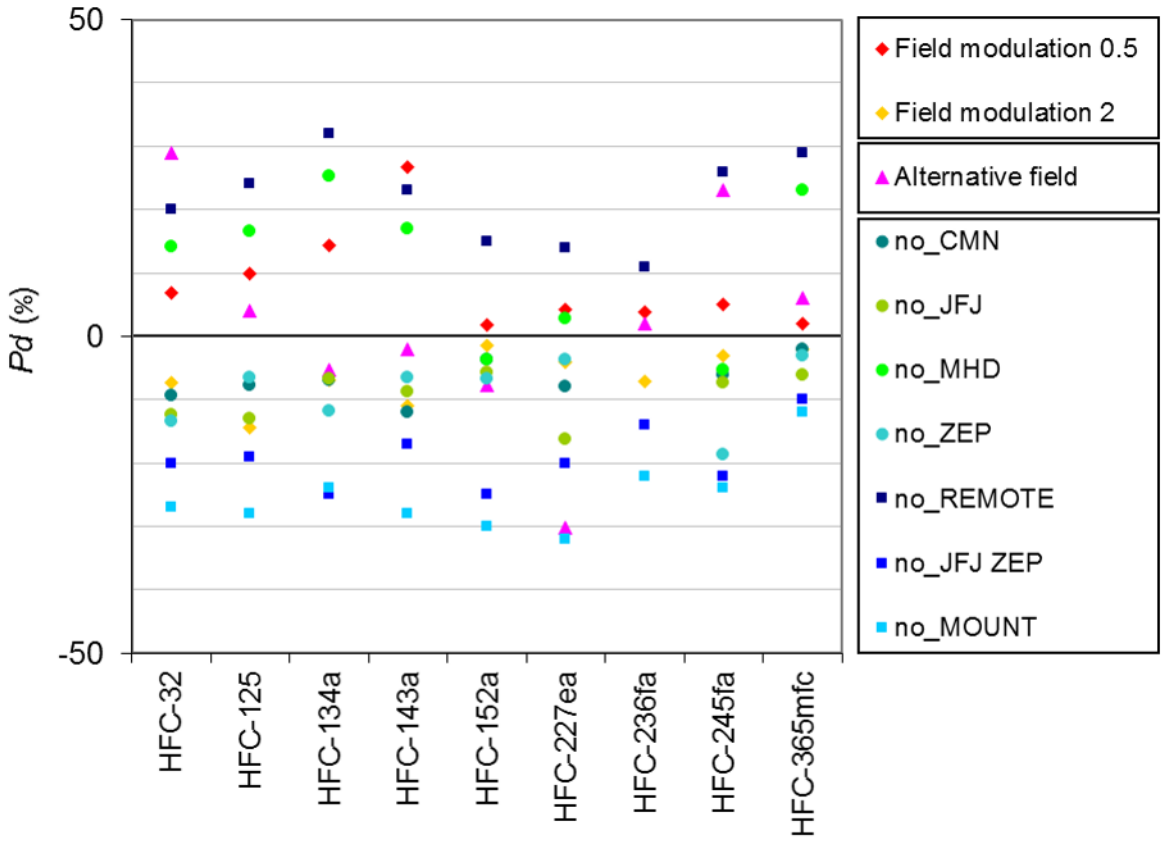

Figure 3S. *Pd* values obtained for nine HFCs through the sensitivity tests.

3.5 Station model performance

For assessing the inversion performance and evaluating the time series at the four stations, we show HFC-134a statistical parameter values. Similar results, not shown, were obtained with the other HFCs.

The station-specific error statistics for 2012 were evaluated by comparing the *a posteriori* and *a priori* errors at the four stations, using several different statistical parameters. The relative error reduction $1-E_b/E_a$ %, where E_a and E_b are the *a priori* and *a posteriori* Root Mean Square (RMS) errors was 14.2%, 20.1%, 33.1%, and 14.3% at CIMN, JFJ, MHD and ZEP, respectively (see also Table 1S). On the time scale of 20 days, also for a remote station like ZEP scarcely affected by source regions, the relative error reduction is similar as in the other sites. The two mountain stations, CMN and JFJ that are even closer to the source regions, show the highest observed values as well as the highest standard deviation (SD on table 1S). Nevertheless, we obtained lower, but still significant error reduction. The reason of this behaviour is due to the model problem linked to the complex topography of mountain stations. Generally, the model shows the best performance in areas with simple topography, where the meteorology is well described by the ECMWF data; this aspect is largely discussed in previous papers (Stohl et al., 2009, Maione et al., 2014 and Graziosi et al., 2015). As a consequence, for the two mountain stations r_a^2 and r_b^2 values lower than those at the others stations are observed.

The squared Pearson correlation coefficient r_{ba}^2 (and r_{bb}^2) between the *a priori* (and *a posteriori*) baseline and the observed concentrations describes the baseline variability and trend. The *a priori* signal for CMN, JFJ, MHD, and ZEP are 22%, 11%, 40% and 60% respectively. The higher values obtained for the remote stations are due to the lower occurrence of pollution events.

A comparison between the modelled time series and the observations at the receptors is used to evaluate the proximity of the modelled emission field to the actual one. The ability of the model to reproduce the values above the baseline is described by the correlation analysis of the polluted events with the simulated emission contributions, described by the *a priori* (r_{ea}^2) and the *a posteriori* (r_{eb}^2) values (Table 1S).

Table 1S: Station parameters. Mean, mean HFC-134a mixing ratios; SD, standard deviation of the observed mixing ratios; N, number of observations; E_a, RMS *a priori* error; E_b, RMS *a posteriori* error; $1-E_a/E_b$, relative error reduction; r^2_a and r^2_b, squared Pearson correlation coefficients between the observations and the *a priori* (r^2_a) and *a posteriori* (r^2_b) simulated time series; r^2_{ba} (and r^2_{bb}) is the squared Pearson correlation coefficients between the *a priori* (and *a posteriori*) baseline and the measured concentrations; r^2_{ea} (and r^2_{eb}) is the squared Pearson correlation coefficients between the *a priori* (and *a posteriori*) enhancements above the baseline and the measured concentrations.

Station	**Mean (ppt)**	**SD (ppt)**	**N**	**E_a (ppt)**	**E_b (ppt)**	**1-E_b/E_a %**	**r^2_a**	**r^2_b**	**r^2_{ba}**	**r^2_{bb}**	**r^2_{ea}**	**r^2_{eb}**
CMN	80.58	7.40	2030	6.7	5.8	14.2	0.28	0.39	0.22	0.26	0.16	0.22
JFJ	76.44	4.74	2112	4.4	3.5	20.1	0.28	0.46	0.11	0.17	0.20	0.36
MHD	74.82	3.98	2483	2.8	1.9	33.1	0.66	0.79	0.40	0.44	0.45	0.56
ZEP	73.73	2.63	1716	1.8	1.6	14.3	0.54	0.65	0.60	0.62	0.31	0.38

European annual emissions

In the following tables (Tables 2Sa-i) we report for each compound annual emissions and the associated percent error from the EGD and from the twelve macro-areas considered in this study.

Table 2S: Annual estimated emissions (Mg y^{-1}) and associated percent uncertainty, from the European Geographic Domain (EGD) and from twelve macro-areas in Europe for nine HFCs: a) HFC-32; b) HFC-125; c) HFC-134a; d) HFC-143a; e) HFC-152a; f) HFC-227ea; g) HFC-236fa; h) HFC-245fa; i) HFC-365mfc.

a)

HFC-32	<err %>	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	<>
EGD							2229	1920	2393	2330	2852	2370	2352	2350
AT	22%						57	6	13	19	50	11	38	28
BE-NE-LU	15%						13	104	74	146	166	84	80	95
CH	24%						5	13	4	24	13	7	8	11
DE	28%						150	118	99	77	229	170	165	144
ES-PT	45%						412	284	537	475	373	423	456	423
FR	32%						388	385	395	444	689	371	331	429
IE	18%						34	30	41	39	39	69	52	43
IT	26%						316	322	524	484	479	447	365	419
NEE	43%						330	172	112	166	267	240	241	218
SCA	83%						89	164	124	109	108	88	64	106
SEE	63%						219	42	170	163	213	141	127	153
UK	23%						217	282	299	184	226	319	426	279

b)

HFC-125	<err %>	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	<>
EGD		4950	4608	5590	5795	7192	7174	5948	8313	7666	9864	7937	7324	7746
AT	20%	31	74	326	23	107	201	46	33	54	147	73	193	107
BE-NE-LU	22%	295	153	46	149	468	100	164	330	590	466	267	323	320
CH	36%	53	67	57	83	46	16	30	16	86	34	33	32	35
DE	35%	353	670	324	403	558	754	310	514	614	867	752	629	634
ES-PT	39%	882	517	665	813	717	900	842	1855	1303	1406	1514	1262	1297
FR	30%	816	786	1134	1192	881	1285	1044	1462	1398	2133	1652	1080	1436
IE	16%	75	115	99	128	118	174	158	215	180	175	211	206	188
IT	32%	982	799	1189	801	2162	717	872	1351	1254	1567	1455	887	1158
NEE	40%	475	117	595	795	607	870	861	424	755	761	654	762	727
SCA	80%	182	297	413	295	293	328	367	374	156	346	276	409	322
SEE	60%	238	228	121	249	236	899	99	501	702	1106	240	386	562
UK	19%	567	785	621	866	999	931	1155	1238	574	855	810	1155	960

c)

HFC-134a	<err %>	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	<>
EGD		24376	19690	20745	19232	19972	20478	18222	20608	18623	21611	19405	18347	19614
AT	26%	128	338	1416	267	640	724	325	222	226	279	222	566	366
BE-NE-LU	16%	1388	1127	633	924	885	542	626	714	1541	1377	719	886	915
CH	29%	153	512	238	280	130	123	159	102	175	155	127	122	137
DE	34%	3756	4347	1509	2465	4005	3218	1831	2482	2533	3845	2540	2600	2721
ES-PT	38%	6851	707	2115	1768	1599	1952	1768	2843	2013	1546	1540	2652	2045
FR	23%	3358	2104	4875	3819	3007	4060	3348	4346	3676	5304	4635	2714	4012
IE	12%	173	260	206	244	238	302	426	358	328	406	330	471	374
IT	25%	3456	3342	3039	2483	3859	2406	2458	3496	2410	2503	4285	1640	2743
NEE	38%	1828	791	1344	2364	1016	1496	1481	820	898	1020	1034	1587	1191
SCA	80%	375	1327	980	896	721	801	1531	915	532	974	605	843	886
SEE	56%	456	1393	1901	686	509	1505	913	795	1707	1576	922	1055	1210
UK	23%	2454	3441	2489	3036	3364	3349	3356	3516	2584	2626	2445	3211	3013

d)

HFC-143a	<err %>	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	<>
EGD					4698	5529	6287	5679	6084	5398	7075	6030	5725	6040
AT	20%				34	65	128	22	46	28	62	52	89	61
BE-NE-LU	27%				129	277	72	292	217	419	398	256	276	276
CH	31%				11	27	11	26	8	61	21	27	23	25
DE	30%				377	288	758	400	462	631	560	625	488	561
ES-PT	36%				365	954	803	803	1206	1016	779	1229	802	948
FR	21%				1534	1051	1180	1066	1219	1056	1922	1257	949	1235
IE	19%				127	121	165	158	196	162	141	166	173	166
IT	33%				372	475	538	553	802	869	985	858	856	780
NEE	40%				658	787	1008	750	388	262	631	662	733	633
SCA	82%				228	232	372	557	326	276	241	189	197	308
SEE	64%				147	302	528	75	352	204	661	157	444	346
UK	31%				717	950	724	977	862	415	674	552	696	700

e)

HFC-152a	<err %>	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	<>
EGD		5873	4220	5257	3454	5406	4287	2963	4469	3684	4016	3115	2839	3625
AT	25%	143	129	297	16	126	139	25	219	29	57	118	74	94
BE-NE-LU	23%	208	189	128	115	187	121	149	105	228	254	97	110	152
CH	33%	81	24	92	16	16	10	20	13	41	28	19	7	20
DE	37%	1046	1076	425	381	643	336	238	356	444	550	367	469	394
ES-PT	36%	765	250	901	545	467	349	131	864	153	130	177	153	280
FR	33%	758	491	743	490	404	585	372	539	449	567	550	281	478
IE	19%	26	16	11	19	10	17	27	32	15	26	24	33	25
IT	32%	620	576	885	590	1553	947	660	978	866	636	597	479	738
NEE	55%	366	166	379	360	805	442	595	388	408	488	327	309	422
SCA	80%	390	476	611	456	608	504	141	423	152	348	296	400	323
SEE	69%	1243	587	576	310	353	635	376	373	696	712	345	333	496
UK	26%	227	239	210	157	234	201	228	179	202	220	197	191	203

f)

HFC-227ea	<err %>	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	<>
EGD							348	348	408	435	489	435	432	414
AT	41%						0,0	0,0	0,0	0,4	0,0	0,3	2,1	0,4
BE-NE-LU	40%						5	16	23	53	8	15	14	19
CH	48%						1,0	1,2	0,2	1,2	1,2	0,4	0,3	0,8
DE	52%						59	53	63	54	103	64	24	60
ES-PT	62%						40	41	53	69	21	67	54	49
FR	48%						66	85	82	62	155	92	81	89
IE	41%						5	6	6	5	7	10	8	7
IT	47%						40	40	40	38	48	39	38	40
NEE	64%						31	28	40	45	29	35	48	37
SCA	81%						10	16	10	28	16	5	25	16
SEE	74%						25	5	12	5	35	13	22	17
UK	45%						67	56	79	75	66	95	117	79

g)

HFC-236fa	<err %>	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	<>
EGD							24	19	17	24	22	26	25	22
AT	57%						0,0	0,0	0,1	0,0	0,0	0,0	0,0	0,0
BE-NE-LU	56%						0,2	0,2	0,2	0,1	0,1	0,1	0,0	0,1
CH	52%						0,0	0,0	0,0	0,1	0,0	0,0	0,0	0,0
DE	64%						2,9	3,9	2,4	5,1	4,6	3,2	3,7	3,7
ES-PT	80%						6,5	3,7	1,8	4,4	4,7	3,2	3,7	4,0
FR	59%						1,1	0,8	0,8	0,7	0,7	1,1	0,8	0,8
IE	52%						0,0	0,0	0,1	0,0	0,1	0,0	0,1	0,0
IT	60%						0,9	0,8	0,4	0,3	0,6	0,7	0,6	0,6
NEE	74%						7,7	6,6	6,7	8,0	9,5	3,8	15,0	8,2
SCA	98%						1,9	2,2	3,5	3,9	1,5	1,7	0,5	2,2
SEE	87%						1,8	0,1	0,3	0,8	0,2	11,2	0,0	2,0
UK	60%						0,6	1,2	0,7	0,5	0,4	0,4	0,9	0,7

h)

HFC-245fa	<err %>	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	<>
EGD							917	686	751	641	788	694	688	738
AT	35%						2	3	8	3	11	18	11	8
BE-NE-LU	35%						38	59	39	48	51	39	58	47
CH	34%						2	2	2	6	4	4	4	3
DE	40%						35	66	64	53	106	74	61	66
ES-PT	48%						216	112	214	103	44	46	80	116
FR	37%						81	98	88	93	176	150	121	115
IE	27%						19	11	10	10	15	8	12	12
IT	38%						184	131	143	143	159	168	131	151
NEE	45%						89	45	28	27	34	30	47	43
SCA	83%						70	61	42	23	19	45	40	43
SEE	71%						68	29	29	60	123	52	42	58
UK	41%						113	70	82	73	46	59	79	75

i)

HFC-365mfc	<err %>	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	<>
EGD				1188	1340	1433	1135	941	1093	1114	1316	943	1067	1087
AT	45%			9	5	10	11	2	7	6	29	3	28	12
BE-NE-LU	45%			50	70	76	50	50	68	184	139	73	85	93
CH	47%			7	17	4	4	3	1	9	7	4	3	5
DE	51%			75	48	198	112	65	140	113	219	168	113	133
ES-PT	55%			220	203	311	315	233	191	222	135	103	99	185
FR	46%			276	321	195	213	216	227	221	364	245	231	245
IE	41%			36	80	37	26	14	18	15	19	18	25	19
IT	43%			95	196	254	147	96	176	131	136	142	108	134
NEE	52%			47	62	34	31	56	55	30	55	45	117	55
SCA	87%			56	48	34	64	37	35	47	56	25	52	45
SEE	64%			58	29	24	21	48	43	56	76	17	45	44
UK	44%			260	262	256	141	121	132	79	81	101	162	116

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