European emissions of HCFC-22 based on eleven years of high frequency atmospheric measurements and a Bayesian inversion method

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HIGHLIGHTS

- We found a reduction in HCFC-22 global atmospheric increasing trends.
- European emissions of HCFC-22 decreased significantly in the last decade.
- The efficacy of inverse modelling as an emission inventories verification tool is shown.
- European emissions of HCFC-22 will approach zero starting from 2025.

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ABSTRACT

HCFC-22 ($CHClF_2$), a stratospheric ozone depleting substance and a powerful greenhouse gas, is the third most abundant anthropogenic halocarbon in the atmosphere. Primarily used in refrigeration and air conditioning systems, its global production and consumption have increased during the last 60 years, with the global increases in the last decade mainly attributable to developing countries. In 2007, an adjustment to the Montreal Protocol for Substances that Deplete the Ozone Layer called for an accelerated phase out of HCFCs, implying a 75% reduction (base year 1989) of HCFC production and consumption by 2010 in developed countries against the previous 65% reduction. In Europe HCFC-22 is continuously monitored at the two sites Mace Head (Ireland) and Monte Cimone (Italy). Combining atmospheric observations with a Bayesian inversion technique, we estimated fluxes of HCFC-22 from Europe and from eight macro-areas within it, over an 11-year period from January 2002 to December 2012, during which the accelerated restrictions on HCFCs production and consumption have entered into force. According to our study, the maximum emissions over the entire domain was in 2003 (38.2 ± 4.7 Gg yr^{-1}), and the minimum in 2012 (12.1 ± 2.0 Gg yr^{-1}); emissions continuously decreased between these years, except for secondary maxima in the 2008 and 2010. Despite such a decrease in regional emissions, background values of HCFC-22 measured at the two European stations over 2002 −2012 are still increasing as a consequence of global emissions, in part from developing countries, with an average trend of ca 7.0 ppt yr^{-1}. However, the observations at the two European stations show also that since 2008 a decrease in the global growth rate has occurred. In general, our European emission estimates are in good agreement with those reported by previous studies that used different techniques. Since the currently dominant emission source of HCFC-22 is from banks, we assess the banks' size and their contribution to the total European emissions up to 2030, and we project a fast decrease approaching negligible emissions in the last five years of the considered period. Finally, inversions

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conducted over three month periods showed evidence for a seasonal cycle in emissions in regions in the Mediterranean basin but not outside it. Emissions derived from regions in the Mediterranean basin were ca. 25% higher in warmer months than in colder months.

1. Introduction

HCFC-22 (CHClF$_2$) is a man-made stratospheric ozone depleting substance with an ozone depletion potential (ODP) of 0.04 (Daniel et al., 2011) and a powerful greenhouse gas with a Global Warming Potential (GWP) over 100 yr of 1760 (Myhre et al., 2013). Its relatively short lifetime of ca. 11.9 yr (SPARC, 2013) is mainly due to the reaction with OH radical. HCFC-22 is used primarily in refrigeration and air conditioning systems as the working fluid. Releases into the atmosphere occur partly when these systems are first filled, but mostly during maintenance, or as the result of accidental damage or when the equipment is finally removed from service, unless provisions are made to capture and destroy the material still in equipment (McCulloch et al., 2003). It is also used in foam blowing and as feedstock for the manufacture of fluoropolymers, but in this last use HCFC-22 is mostly destroyed during the process.

HCFC-22 was firstly introduced in the 1950s but its production and consumption have increased over time as it has been used as an interim replacement for several chlorofluorocarbons (CFCs), making it the third most abundant anthropogenic halocarbon, after CFC-12 and CFC-11, with a current atmospheric mixing ratio of about 220 ppt. A substantial growth of HCFC-22 global mixing ratio has been reported by O'Doherty et al. (2004) and Montzka et al. (2009), based on long term measurements conducted at remote sites across the globe in the frame of the AGAGE (Advanced Global Atmospheric Gases Experiment) and NOAA/ESRL (National Oceanic Atmospheric Administration/Earth System Research Laboratory) programmes, respectively. The acceleration in the growth rate observed in the last decade in the global atmosphere (Montzka et al., 2009) is consistent with the UNEP (United Nations Environmental Programme) data on production and consumption of the HCFCs. Such data also indicate that by 2004 the HCFCs production and consumption in developed countries exceeded the values reported from developed countries (UNEP, 2013). This reflects provisions within the Montreal Protocol for Substances that Deplete the Ozone Layer reported in Table 1, calling for an HCFCs phase-out with different schedules in Article 5 (A-5; or developing) countries and non A-5 (developed) countries (UNEP, 2009). In the European Union, the phase-out of HCFCs is covered by the European Regulation (EC) No 2037/2000 on substances that deplete the ozone layer that, among other things, declared illegal the use of virgin HCFCs to service refrigeration and air conditioning (RAC) equipment as of 1st January 2010.

Estimating emissions of HCFC-22 from atmospheric observations is important in order to ascertain the effectiveness of the Montreal Protocol in the protection of the ozone layer as well as of the climate (Velders et al., 2007). HCFC-22 is used in refrigerators and air conditioners (AC) and also as blowing agent. Therefore it released into the atmosphere over years to decades after production. The amount of HFCF-22 in equipment and foam represents a bank of produced but not yet emitted chemical. Currently, the dominant emission for HCFC-22 is from these banks (Montzka et al., 2011). The primary HCFC-22 banks are in existing refrigeration and air conditioning (AC) applications, from which it is released on a timescale of years to more than a decade (medium timescale). However, HCFC-22 has been also used for open-cell foam blowing having a short banking time (<1 years) and for closed-cell foam blowing, implying a long banking time (up to 20 years) (Midgley and Fisher, 1993; Velders et al., 2014). Relating emissions to the banks of non-released material is crucial for predicting future trends in stratospheric chlorine. In addition, reliable estimates of future trends imply a good understanding of production magnitudes, particularly from the past, in order to enable an accurate estimate of the size of the bank.

The main source of information on the production and consumption of HCFC-22 is from UNEP (United Nation Environmental Programme, Ozone Secretariat http://ozone.unep.org/new_site/en/ozone_data_tools_access.php) that makes available the aggregated HCFCs consumption and production data, expressed in ODP tons. In the UNEP database, data pertinent to the European Union Member States (EUMSs) are given in a grouped form.

The AFEAS (Alternative Fluorocarbons Environmental Acceptability Study, http://www.afeas.org/data.php) provides production and sales magnitudes of HCFC-22, expressed in metric tons. The sales data are split into three regions (Northern Hemisphere 0°−30° degrees north; 30°−90° degrees north; and Southern Hemisphere 0−90° degrees south) and into three categories corresponding to end uses with short, medium and long time scales ("banking time") before the substance is emitted. Several studies (Midgley and Fisher, 1993; Fisher and Midgley 1993, McCulloch

Table 1
HCFCs phase out schedule as decided during the 19th Meeting of the Parties to the Montreal Protocol, Montreal, Canada, 2007.

Non A-5 consumption		A-5 consumption		Non A-5 production		A-5 production	
Base level: 1989[a]		Base level: Average 2009−10		Base level: 1989[b]		Base level: Average 2009−10	
Freeze: 1996		Freeze: Jan 2013		Freeze: Jan 2004		Freeze: Jan 2013	
% reduction	Year	% reduction	Year	% reduction	Year	% reduction	Year
35	Jan 2004	10	Jan 2015	75	Jan 2010	10	Jan 2015
75	Jan 2010	35	Jan 2020			35	Jan 2020
90	Jan 2015	67.5	Jan 2025	90	Jan 2015	67.5	Jan 2025
99.5	Jan 2020[c]	97.5	Jan 2030[c]	99.5	Jan 2020[c]	97.5	Jan 2030[c]
100	Jan 2030	100	Jan 2040	100	Jan 2030	100	Jan 2040

[a] Average HCFC consumption +2.8% of 1989 CFC consumption.
[b] Average HCFC production +2.8% of 1989 CFC production.
[c] Thereafter, consumption restricted to the servicing of refrigeration and air conditioning equipment existing at that date.

et al., 2006) provided parameterisations useful in order to derive emissions starting from sales and consumption data.

Bottom up emission estimates are provided by the E-PRTR (European Pollutant Release and Transfer Register) inventory reporting HCFCs emissions values and location of industrial facilities in the European Union Member States and other countries in the Geographic Europe, like Iceland, Liechtenstein, Norway, Serbia and Switzerland. The E-PRTR registry provides data representing the total annual emission releases during normal operations and accident, submitted by industrial facilities.

In addition to bottom-up estimates, in recent years several studies have provided HCFC-22 emission estimates for Europe using top-down approaches, based on long term high-frequency observations combined with various inversion modelling techniques. O'Doherty et al. (2004), based on measurements conducted at Mace Head (MHD, Ireland) combined with the NAME Lagrangian dispersion model (Ryall et al., 2001), estimated the UK emissions at 2.4 and 2.2 Gg per year in 1999–2001 and 2000–2002, respectively and European emissions at 19, 17 and 15 Gg per year in 1998–2000, 1999–2001 and 2000–2002, respectively. The NAME approach does not make use of any *a priori* information. More recently, Stohl et al. (2009), in order to derive regional and global emission magnitudes, used observations from the AGAGE network (MHD and Mt. Cimone, Italy, CMN, included), the FLEXPART dispersion model, and a Bayesian inversion method, taking as *a priori* information projections of global total emissions from Ashford et al. (2004) that were slightly adjusted to make them fit with the AFEAS (2007) values for the year 2005, the last year available with non-forecast data. They estimated that a total of 12 Gg and 10 Gg of HCFC-22 were emitted from 7 EU countries in 2005 and 2006, respectively. Saikawa et al. (2012) provided European (geographical, excluding Russia) emission estimates from 2005 to 2009, ranging from 13.7 to 7.6 Gg per year, using observations (continuous and flask) at different sites around the globe, the MOZART v4 (Model for Ozone and Related Chemical Tracers version 4) chemical transport model, with a resolution for the regional inversion of 1.9° latitude, 2.5° longitude, and 56 vertical levels, and an *a priori* emission field based on UNEP 2011 consumption data and the emission inventory by McCulloch et al. (2003). As meteorological fields the Modern Era Retrospective-analysis for Research and Applications (MERRA) was used. Finally, Keller et al. (2012) estimated, for 2009, 13.4 Gg from 27 countries in western and Eastern Europe by means of a Bayesian inversion, using global and regional emission data as *a priori* information combined with observations from Mt. Cimone (CMN, Italy), MHD and a Hungarian site (K-Puszta), considering a domain that does not include the Scandinavian countries. Their *a priori* information was based on global and regional emission data together with assumptions on the share of these emissions among the individual countries.

In most cases, these techniques make use of *a priori* information, which allows higher resolution in the inversion result. From a Bayesian perspective, an inversion using *a priori* information searches the most likely solution in view of both the *a priori* emissions and the measured data (Stohl et al., 2009). In this study, in order to derive European emissions of HCFC-22 from 2002 to 2012, we used observations from two European sites, MHD and CMN, in combination with FLEXPART and a Bayesian Inversion method developed by Seibert (2000, 2001), which was improved by Eckhardt et al. (2008) and Stohl et al. (2009, 2010) using different sources of information for creating the *a priori* emission field.

Our results complement the previous studies, providing estimates on the emissions of HCFC-22 on a European scale, down to the country level, and analysing the trend of such emissions over an 11 year period, during which the accelerated restrictions on HCFCs production and consumption decided in 2007 at the 19th Meeting of the Parties to the Montreal Protocol have entered into force.

2. Method

2.1. HCFC-22 observations

In Europe, high-frequency long-term observations of HCFC-22 in ambient air are conducted, via gas chromatography-mass spectrometry (GC−MS) preceded by on-line sample enrichment, at the two WMO GAW (World Meteorological Organisation Global Atmosphere Watch) global stations of Mt. Cimone (Italy) and Mace Head (Republic of Ireland). CMN is located on the top of the highest peak of the Northern Apennines, at 2165 m of altitude above the sea level. The station is representative of the free troposphere, even if episodically reached by polluted air masses originated by the close-by Po valley (Fischer et al., 2003; Henne et al., 2010). MHD, on the western coast of Ireland, is ideally located to study trace gases present both in marine and continental air masses (Grant et al., 2010). MHD is an AGAGE station, making use of the GC−MS MEDUSA system adopted in all the AGAGE sites (Miller et al., 2008). CMN, where a different GC−MS system is used, is an AGAGE affiliated station. Details on the analytical methodology and calibration protocol adopted at CMN and MHD are reported in Maione et al. (2013, 2014) and in Miller et al. (2008) and Simmonds et al. (1996), respectively. At CMN, the relative standard deviation (RSD over 1 year) evaluated from the repeated working standard measurements of HCFC-22 was 0.9% and 0.4% before and after January 2008, respectively. The improvement in the RSD is due an upgrade of the instrumentation completed after January 2008. At MHD % RSD is below 0.26%. In spite of the differences in the analytical methodologies, measurements at the two stations are fully intercomparable, because both system are operated via the Linux-based chromatography software (GCWerks, gcwerks.com) developed within the AGAGE programme and the same calibration scale (SIO-2005, Scripps Institution for Oceanography, La Jolla, CA, USA) is adopted.

2.2. Determination of the background

In order to calculate atmospheric long-term trends and annual growth rates of HCFC-22 it is necessary to careful evaluate background mixing ratios at the receptor sites. For a station like MHD, where prevailing winds from the west to south-west sectors bring clean background air to the site, a meteorological filter can be applied in order to clearly identify atmospheric baseline conditions (Ryall et al., 2001). On the contrary, CMN is surrounded by complex topography and emission fields and the determination of the baseline requires the use of statistical methods. For this aim, we have developed specifically for CMN a two-step procedure that we have also applied to time series recorded at MHD (Giostra et al., 2011). In the first step the measurement data are detrended using an appropriate time interval. In the second step the uncertainty in the determination of baseline mixing ratios, which includes instrumental error and natural background variability, is found. The overall observed probability distribution function (PDF) obtained consists in the sum of a Gaussian and a gamma distribution, where the Gaussian distribution corresponds to the well-mixed background atmosphere state, i.e. data given by emissions undergoing long range transport, and the gamma distribution corresponds to a non-well-mixed state, i.e. data containing recent emission inputs. If the number of available data points is large, the decomposition of the overall PDF as the sum of a Gaussian plus a gamma becomes stable and reliable.

2.3. Dispersion modelling and Bayesian inversion

The inversion is based on 20-day backward simulations obtained with the FLEXPART Lagrangian particle dispersion model (Stohl et al., 1998, 2005; Seibert and Frank, 2004). Meteorological data used as input for this study were the European Centre for Medium-Range Weather Forecasts (ECMWF) global analyses at $1° \times 1°$ resolution for the period 2002–2012 over the domain shown in Fig. 1. In addition, nested meteorological data with a resolution of $0.25° \times 0.25°$ in the European domain (from 12° W to 28°E and from 35° to 65°N) were available for 2008 and 2009, which we call the ECMWF_nest. For each run, 40,000 particles were released backward from the observing stations, at three-hourly intervals. In this way, we obtain the footprint emission sensitivity, which we call the source receptor relationship (SRR). The SRR has been described by Seibert and Frank (2004) as the sensitivity of a "receptor" element to a "source". The SRR value (s kg^{-1}) in a particular grid cell is proportional to the particle residence time in that cell and measures the simulated mixing ratio at the receptor that a source of unit strength (1 kg s^{-1}) in the cell would produce (Stohl et al., 2009). The SRR was calculated without consideration of any chemical removal processes.

The footprint emission sensitivity in the lowest model layer is then multiplied by the emission flux taken from an appropriate emission inventory (the a priori emission field), thus giving the simulated mixing ratio at the receptor, which can be compared with the observations. Fig. 1 shows the footprint emission sensitivity for the period January 2008–December 2008 for a) both MHD and CMN and b) and c) for the two single stations. Emission estimates we derive are based only on areas with an annual average sensitivity >2 ps kg^{-1}.

The inversion algorithm used in this study was developed by Seibert (2000, 2001) and improved by Eckhardt et al. (2008). The method was further improved by Stohl et al. (2009, 2010) who derived a baseline in the observations that is adjusted as part of the inversion process. The basic idea of inversion procedures is to optimise the agreement between the model output and the measurements, at the same time minimising the deviation from the a priori emissions as well as the uncertainties in the emissions. The "optimum" agreement is calculated as the sum of the squared errors inversely weighted with the uncertainty variances. Even if the number of observations exceeds the number of unknown emission values, not all regions are well resolved by the observations. The addition of an a priori knowledge of the emission distribution and of the emission uncertainty is necessary in order to prevent an unstable solution.

Therefore, a term, which provides the deviation of the solution from the a priori emissions and is inversely weighted by the assumed emission uncertainties, is added to the so-called cost function J. The cost function to be minimised is the following:

$$J = (M\tilde{x} - \tilde{y})^T \mathrm{diag}\left(\sigma_o^{-2}\right)(\boldsymbol{M}\tilde{x} - \tilde{y}) + \tilde{x}^T \mathrm{diag}\left(\sigma_{prior}^{-2}\right)\tilde{x} \qquad (1)$$

The model-observation misfit is measured by the first term on the right hand side of equation (1), where the operator **diag** ( ) yields a diagonal matrix, $\boldsymbol{M}$ represents the SRR matrix determined by FLEXPART backward simulations; $\tilde{y}$ is the difference between the observed concentration vector and a priori simulated concentration vector, and $\tilde{x}$ is the difference between an unknown emission vector and an a priori vector. The second term measures the deviation from the a priori values. The vector of standard errors of the observation is represented by σ_o (this error also includes the model
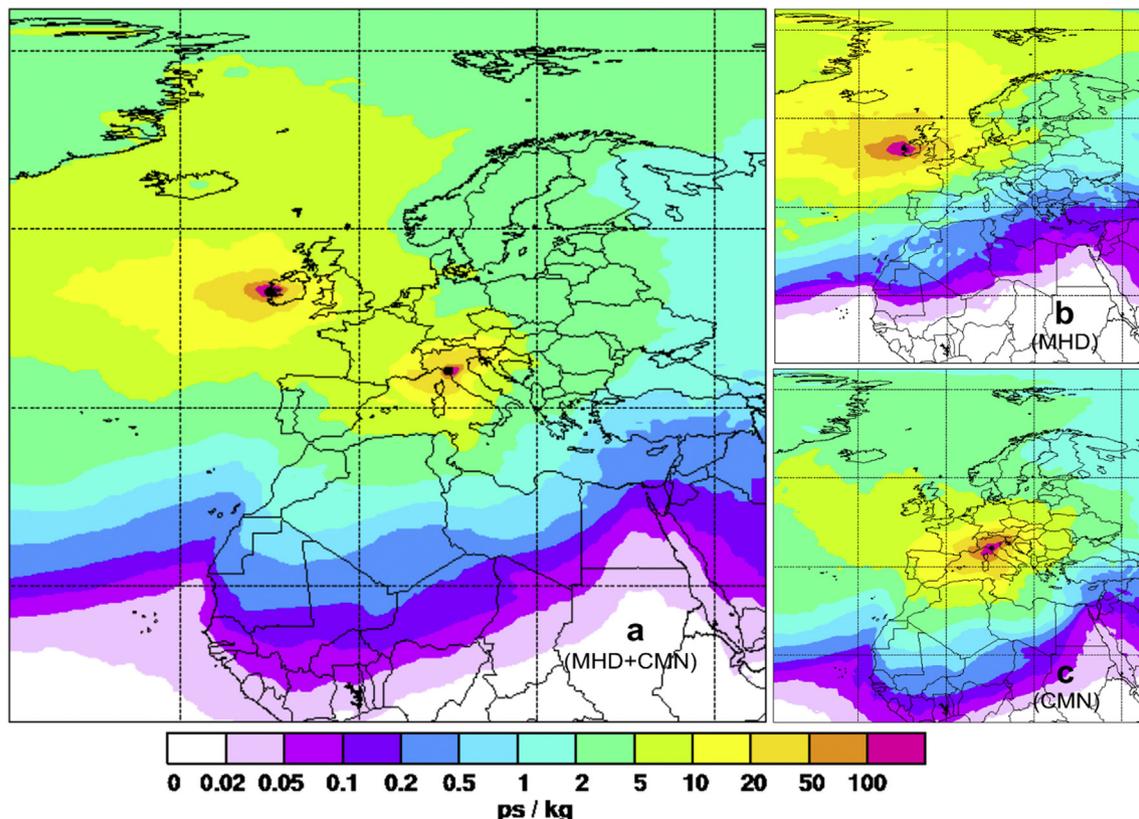

Fig. 1. Footprint emission sensitivity in picoseconds per kilogram (ps kg^{-1}) obtained from FLEXPART 20 d backward calculations averaged over all model calculations over two years (Jan 2008–Dec 2009). Measurement sites are marked with black dots. a) MHD and CMN combined; b) MHD only; c) CMN only.

error) and that of the *a priori* emission values by σ_{prior}. The inversion method used for this study is the same as in Stohl et al. (2009, 2010). Details on the application of this method can also be found in Maione et al. (2014).

Detailed descriptions of the *a priori* emission field creation and of the sensitivity tests performed in order to evaluate the model performance are reported in the Supplementary Material section.

3. Results and discussion

3.1. Atmospheric trends

HCFC-22 time series recorded at CMN and MHD from 2002 to 2012 are reported in Fig. 2. In order to evaluate HCFC-22 trends and annual growth rates, we derived the background mixing ratios (black dots) using the statistical method described in Giostra et al. (2011). This method identifies a threshold above which concentrations are due to episodic "pollution" events from European emissions (red dots).

Elevations above the baseline show a decrease of both yearly frequency of occurrence (green line) as well as yearly average magnitude (blue line) during the last part of the record at both stations. This decrease is more evident at CMN where, in addition, particularly intense elevations are observed in 2006 and 2008 consistently with the EGD UNEP aggregated HCFC-22 consumption data reporting that consumption decreased from 2009 onward.

Trends in the background values are driven by global emissions. Overall 11-y trends of the atmospheric mixing ratios of HCFC-22 at CMN and MHD, derived using the monthly mean baseline mole fractions and the empirical model as in Simmonds et al. (2004), were 6.9 ± 0.4 and 7.0 ± 0.2 ppt y^{-1} ($R^2 = 0.98$), respectively. The averaged annual growth rates (reported in Fig. 3) increase until 2008, with growth rates in 2008 approximately two times higher than in 2004. This was reported by Montzka et al. (2009) who suggested that this was due to the exponential increase in developing country production and consumption of HCFC-22. After 2008, however, we observe a decline in the growth rate, especially in the last two years. The slowing down of the growth rate increase suggests that the annual increase in global emissions determined for past years (Saikawa et al., 2012) likely slowed after 2008.

3.2. Emission estimates

The described inversion procedure has been used to derive HCFC-22 emission intensity and distribution in the EGD as well as in individual macro-regions within it. The maps in Fig. 4 show the *a priori* (Fig. 4a) and *a posteriori* (Fig. 4b) distribution of emission fluxes for a single year (2007). The posterior emission distribution is much less smooth than the prior distribution, suggesting emission hot spots, some of which will be discussed below. The annual HCFC-22 estimated emissions from the EGD and from eight macro areas within the EGD are given in Table 2. Emissions are reported together with an error estimate calculated from the overall relative uncertainty derived as described in the sensitivity tests section (see Supplementary Material).

As also shown in Fig. 5a, HCFC-22 emissions decreased steadily down to about one third of the initial value throughout the study period, with a maximum of 38.2 ± 4.7 Gg in 2003 and a minimum of 12.1 ± 2.0 Gg in 2012, reflecting the effectiveness of provisions within the Montreal Protocol. 2003, 2008 emission values represent the only significant deviation from this trend. The 2003 increase is not reflected by the UNEP consumption data. However, in 2003 a particularly strong heat wave affected Europe during the summer. This translated into large increases in air conditioning equipment sales volume in countries such as Italy, Spain, and France. (Daikin Industries Ltd, 2004 Annual Report), which may have contributed to the increase in emissions we derive for 2003. The slight 2008 deviation could be related to an enhanced use of stockpiles driven by the accelerated phase out schedule for HCFC-22 agreed during the 19th Meeting of the Parties to the Montreal Protocol in 2007, calling for 75% reduction, relative to 1989 base year, in consumption of the HCFCs by January 2010.

The plot in Fig. 5a also shows that the relative emission contributions of the eight macro areas do not vary significantly during the study period. Therefore, the contribution from each macro-area can be expressed as an average percentage value, reported in Fig. 6, together with the percent average maximum error. The highest average contribution is from the FR macro area (France), corresponding to ca. 19% of total EGD emissions. A similar contribution is obtained for the much larger macro area comprised of 11 countries in Eastern Europe. An alternative way of interpreting this information is in terms of per capita emissions. Estimates split into eight macro areas (reported in Fig. 5b) show that the lowest per capita emissions are from Eastern Europe and the Eastern Adriatic regions, whereas FR and IE-UK have the highest per capita emissions. The Scandinavian countries (FI-NO-SE) show unexpectedly high per-capita emissions. However, this result may not be totally robust, as the uncertainty in emissions derived for this area is relatively large (approaching 50%) due either to the low model sensitivity in this region or partly to an inversion artefact, since higher baseline values are expected when air masses come from the north (see Fig. 1Sb). Also, this result could be partly affected by an artefact due to the inversion assigning to the elevations (and therefore to emissions) higher baseline values of the air masses coming from the North, actually ascribable to a Meridional gradient.

Concerning the role of the Montreal Protocol in the protection of climate, converting EGD HCFC-22 emissions from Gg yr^{-1} into CO_2 equivalent (CO_2-eq), we estimated that emissions have decreased from $58,000 \pm 4000$ Gg CO_2-eq in 2002 down to $22,000 \pm 2000$ in 2012.

Fig. 7 shows the comparison of our results (red dots) with previously reported European emission estimates based on different top-down approaches and with the *a priori* emission field used for this study (red open circles), described in the Supplementary Material. O'Doherty et al. (2004) reported HCFC-22 emission estimates for the year 2002 obtained with an inversion based on MHD observations combined with NAME and an annealing technique (grey diamonds) as well as estimates based on commercially sensitive industry data (purple triangle). The NAME domain is somewhat smaller than the domain used in this study and the industry data refer to EU-15. For better comparability, we extrapolated from our EGD inversion results the fluxes from a domain similar to the NAME one (red square). Our estimates are comparable with the NAME ones but significantly lower than the industry data, which were considered as overestimated also by O'Doherty et al. (2004).

Stohl et al. (2009) (green triangles) used the same modelling approach and study domain as we have used here but they used a different *a priori* emission field based on the global annual HCFC-22 emissions from Ashford et al. (2004) and partly different observation data also including time series from the Zeppelin Station (ZEP) in the European Arctic. Their results are within our uncertainty range, with only a 0.2% and 11% difference to our values for 2005 and 2006, respectively.

The largest differences to our results of all other inverse modelling studies for Europe were reported by Saikawa et al. (2012) (blue squares in Fig. 8), with their values being systematically lower than ours for the entire period (2005–2009) of the study. On average, our estimates are 87% higher than theirs. As previously described, the methodology used by Saikawa et al. is based on a different observation network, modelling approach, and *a priori*
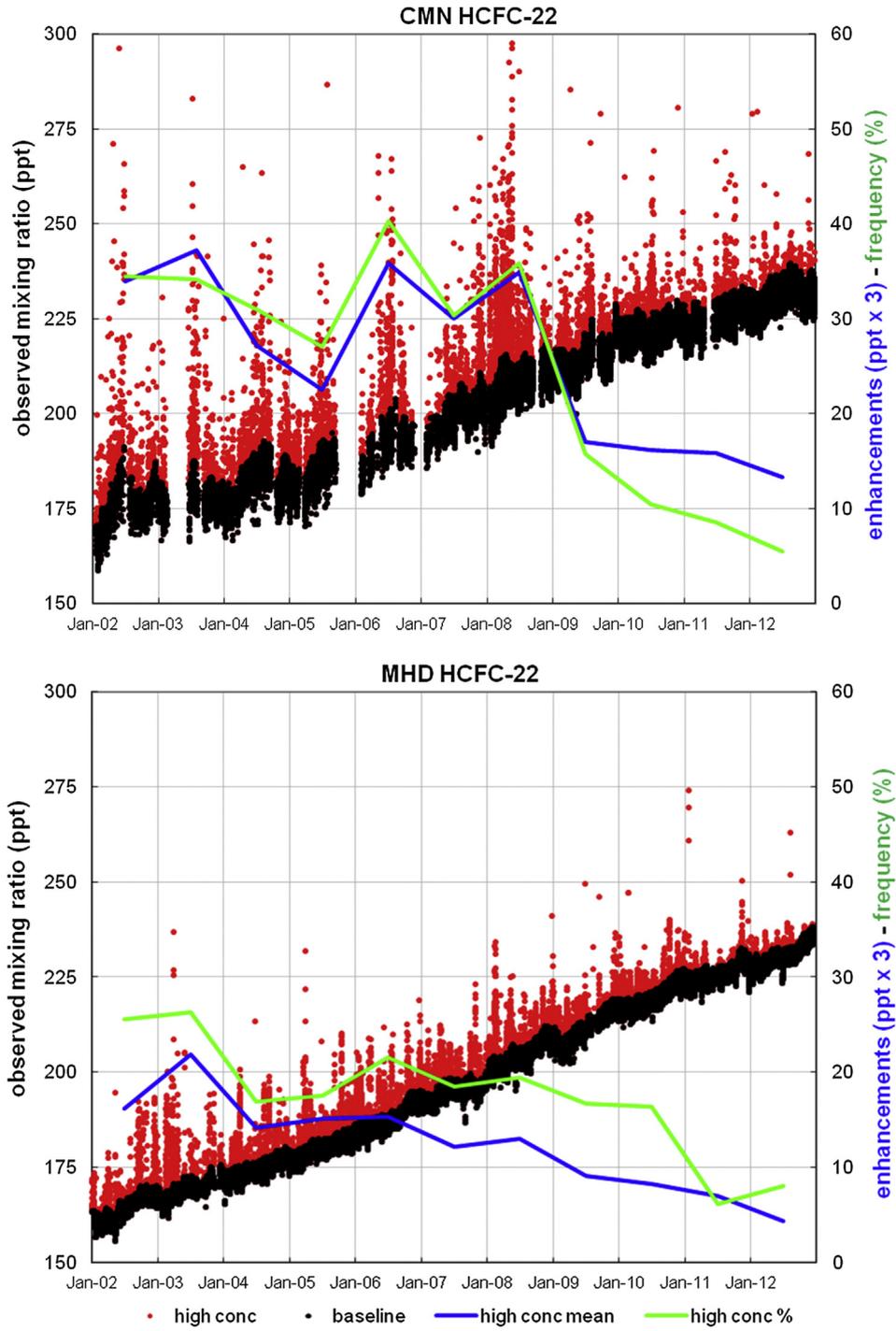
Fig. 2. HCFC-22 time series at CMN (top) and MHD (bottom). Black dots: baseline, red dots: enhancements above the baseline. Frequency (in %) of occurrence of enhanced values above the baseline (green line, right axis) and enhancements' average annual magnitude, in ppt * 3 (blue line, right axis). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

emission field. In order to investigate if the differences in the *a priori* emission fields used in the two studies could be responsible for such a large discrepancy, we re-ran the inversion using the *a posteriori* European emissions given by Saikawa et al. (2012) as our *a priori* (not shown) for 5 years (from 2005 to 2009). However, we still obtained emission fluxes significantly higher (73%) than those reported by Saikawa and, on average, only 14% lower than our reference estimates, confirming that the *a posteriori* emission field obtained through the Bayesian inversion we have used here is rather stable even when using significantly different *a priori*

emission fluxes.

Despite the different *a priori* field and station geometry, Keller et al.'s (2012) emission estimate (light blue dots) for 2009 is within the error bar of our estimate for the same domain (red diamond). Again, at the macro-areas level differences are larger. For instance, our emission fluxes for the DE-DK-NL and UK-IE macro areas are higher than theirs by a factor of about two, and our estimates for PT-ES and the macro area including eastern European countries is lower by 50% compared to theirs. This is probably due to their better constraint on emissions in Eastern Europe provided
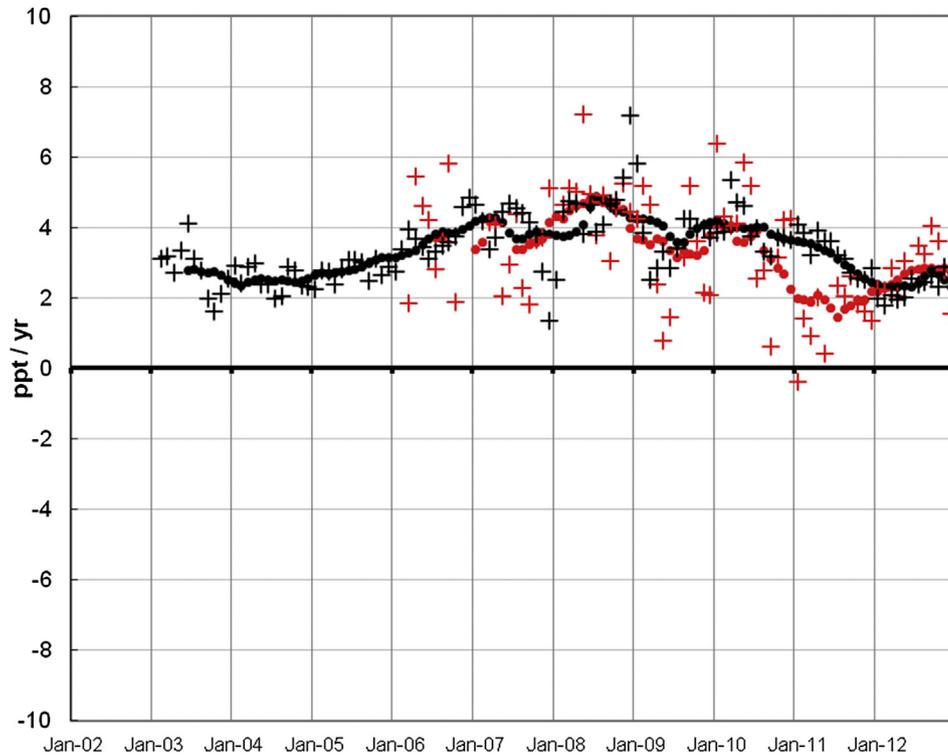
Fig. 3. Average monthly growth rates of HCFC-22 from measurements at CMN (red dots) and MHD (black dots). Tropospheric growth rates are derived from smoothed 12-month differences in the baseline mixing ratio means over the previous 12 months. CMN (red pluses) data have been used starting from 2006, due to gaps of observations in the first part of the record; for MHD (black pluses), the full data set (2002—2012) has been used. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

by their measurement station in Hungary and the different station geometry leading to a different emission distribution within the study domain.

In addition, in order to investigate the influence of the seasonality in the emission fluxes, we performed seasonal inversions, whose results showed that emissions in the Southern European countries facing the Mediterranean basin are higher by some $25 \pm 8\%$ in the warmer months than in fall and winter. On the contrary, seasonal variations for the extra-Mediterranean countries are not significant. The seasonality in the emissions has been described also by Miller et al. (2012) in a study reporting emission estimates for the U.S, and by Xiang et al. (2014) for the global scale. This difference could be explained by a significantly more intense use of air conditioning systems during the warmer months in the southernmost regions and may result from greater leakage from the working compressors.

3.3. HCFC-22 banks

Relating emissions to the banks of non-released material is crucial for predicting future halocarbon atmospheric trends. This is particularly important in the case of HCFC-22, whose dominant emissions are from banks. We attempted to estimate the extent of the European banks using HCFC-22 UNEP consumption data and the different end-use categories reported in the AFEAS data set, all combined with McCulloch's et al. (2006) EF, as previously explained in the description of the *a priori* emission field creation. Fig. 8 shows the extent of banks estimated in our domain from 2002 to 2012.

In Fig. 9 we report the comparison between our EGD emission estimates and those derived from the emissions from the banks showed in Fig. 8. The emissions from the estimated banks are in good agreement with the inversion estimates, being on average only 22% higher. Moreover, the fits of the two curves exhibit

exponential decay constants differing only by 10%. Notwithstanding the general agreement, the two approaches show some differences, with the inversion estimates providing additional information as the deviations from the general trend in 2003 and 2008 that could be due to increased HCFC-22 consumption as a consequence of the heat wave in 2003 and of the accelerated HCFCs phase out decided in the 2007 Montreal Protocol revision, respectively. The good agreement between the results obtained using the two procedures supports the reliability of the bank estimates and emission functions of McCulloch et al. (2003).

In Fig. 9 we also report two possible scenarios for HCFC-22 emissions from the EGD up to 2030, the year in which, under the Montreal Protocol, production and consumption of HCFCs will be completely phased out in non-Article 5 parties. The UNEP HCFC-22 consumption data exhibit a sharp decrease between 2009 and 2010, with 2010 consumption dropping to one tenth of the 2009 value. The annual EGD consumption data between 2010 and 2012 range from 1.16 to 1.36 Gg, well below the 3.8 Gg allowed for 2015 by the Montreal Protocol. We hypothesised: i) a conservative scenario (A) where the average (2010—2012) UNEP consumption has been applied up to 2020, when the consumption value of 0.19 Gg has been adopted, following the Montreal Protocol prescriptions; ii) an optimistic scenario (B) where the 2020 limit (0.19 Gg) has been advanced to 2013 and the 2030 limit (0.0 Gg) has been advanced to 2020. Even if the extent of banks in the scenario A is about twice that of scenario B (in 2020 and 2021), the emissions produced over the entire period do not differ significantly, approaching zero towards the last five-year period. Assuming that the UNEP consumption data are correct, the 20% difference could be ascribed to an inaccurate EF estimate. This suggests that future HCFC-22 emissions from banks could be higher.

In terms of CO_2-eq, projected emissions of HCFC-22 in 2020 will be of 4000 ± 800 Gg CO_2-eq, however, those emissions are likely to
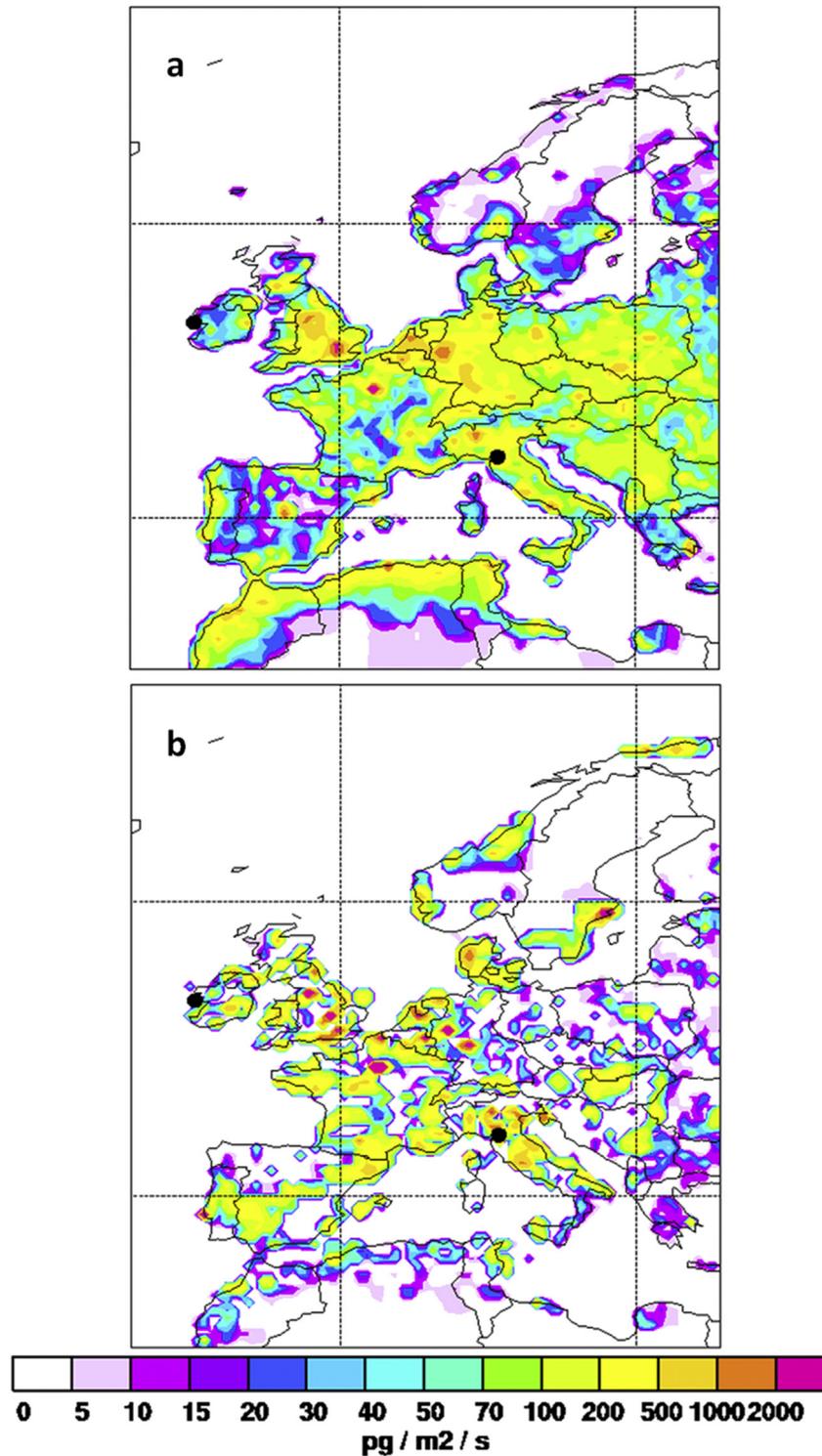
Fig. 4. a) A *priori* distribution of HCFC-22 emissions from the EGD, reference year 2007; b) a *posteriori* distribution for the same domain and year. Measurement stations are marked with a black dot.

be off set in part by the increase in the HFCs used as HCFC re-placements, depending on the properties of the HFCs used as substitutes.

4. Conclusions

We analysed HCFC-22 time series obtained through long term high-frequency atmospheric measurements carried out at the two European GAW-WMO global stations CMN and MHD. The study was done for an 11 year period, from January 2002 to December 2012, during which the accelerated restrictions on HCFC production and consumption decided in 2007 at the 19th Meeting of the Parties to the Montreal Protocol have entered into force. Back-ground values of HCFC-22 as measured by the two European sta-tions over the study period are still increasing as a consequence of global emissions, likely more recently dominated by developing

Table 2
Annual HCFC-22 emission estimates from the EGD and eight macro areas included in the EGD.

| Gg/yr	EGD	FR	ES-PT	AT-CH-IT	IE-UK	BE-DE-DK-LU-NL	AL-BiH-HR-EL-ME-SI	FI-NO-SE	BG-BY-CZ-EE-HU-LT-LV-MD-RO-PL-SL
2002	32.3 ± 4.3	5.0 ± 0.2	2.5 ± 0.3	3.5 ± 0.1	5.1 ± 0.1	3.4 ± 0.4	2.0 ± 0.1	0.9 ± 0.5	8.3 ± 1.6
2003	38.2 ± 4.7	6.8 ± 0.6	7.8 ± 0.8	5.8 ± 0.1	5.0 ± 0.1	4.8 ± 0.5	1.3 ± 0.2	0.8 ± 0.3	4.5 ± 0.8
2004	27.4 ± 3.2	4.3 ± 0.4	1.3 ± 0.1	3.4 ± 0.1	5.7 ± 0.1	5.2 ± 0.9	1.2 ± 0.2	1.1 ± 0.3	4.0 ± 0.8
2005	24.6 ± 3.9	6.0 ± 1.0	3.1 ± 0.4	3.7 ± 0.1	3.0 ± 0.1	1.9 ± 0.3	1.9 ± 0.7	0.6 ± 0.2	3.6 ± 0.3
2006	20.8 ± 2.8	4.1 ± 0.2	2.2 ± 0.3	2.9 ± 0.1	3.4 ± 0.1	2.5 ± 0.2	1.1 ± 0.4	0.4 ± 0.2	3.5 ± 0.6
2007	19.7 ± 2.7	2.5 ± 0.5	1.7 ± 0.3	3.9 ± 0.1	3.3 ± 0.2	3.5 ± 0.1	0.5 ± 0.1	0.5 ± 0.2	2.9 ± 0.6
2008	22.8 ± 3.1	4.3 ± 0.2	2.2 ± 0.4	3.8 ± 0.2	2.7 ± 0.1	2.2 ± 0.3	0.5 ± 0.1	0.4 ± 0.2	6.1 ± 1.0
2009	14.4 ± 1.8	2.5 ± 0.1	1.3 ± 0.2	2.0 ± 0.1	2.2 ± 0.1	3.0 ± 0.2	0.3 ± 0.1	0.5 ± 0.2	1.4 ± 0.4
2010	16.1 ± 2.8	3.2 ± 0.2	2.8 ± 0.8	2.3 ± 0.1	2.2 ± 0.1	1.6 ± 0.1	0.2 ± 0.1	0.3 ± 0.1	2.7 ± 0.8
2011	15.2 ± 3.1	3.2 ± 0.3	1.1 ± 0.2	1.8 ± 0.1	1.5 ± 0.1	1.7 ± 0.3	0.9 ± 0.2	0.8 ± 0.3	2.8 ± 0.4
2012	12.1 ± 2.0	2.7 ± 0.2	0.6 ± 0.1	1.5 ± 0.1	1.2 ± 0.2	1.6 ± 0.2	0.4 ± 0.1	0.4 ± 0.1	2.0 ± 0.3
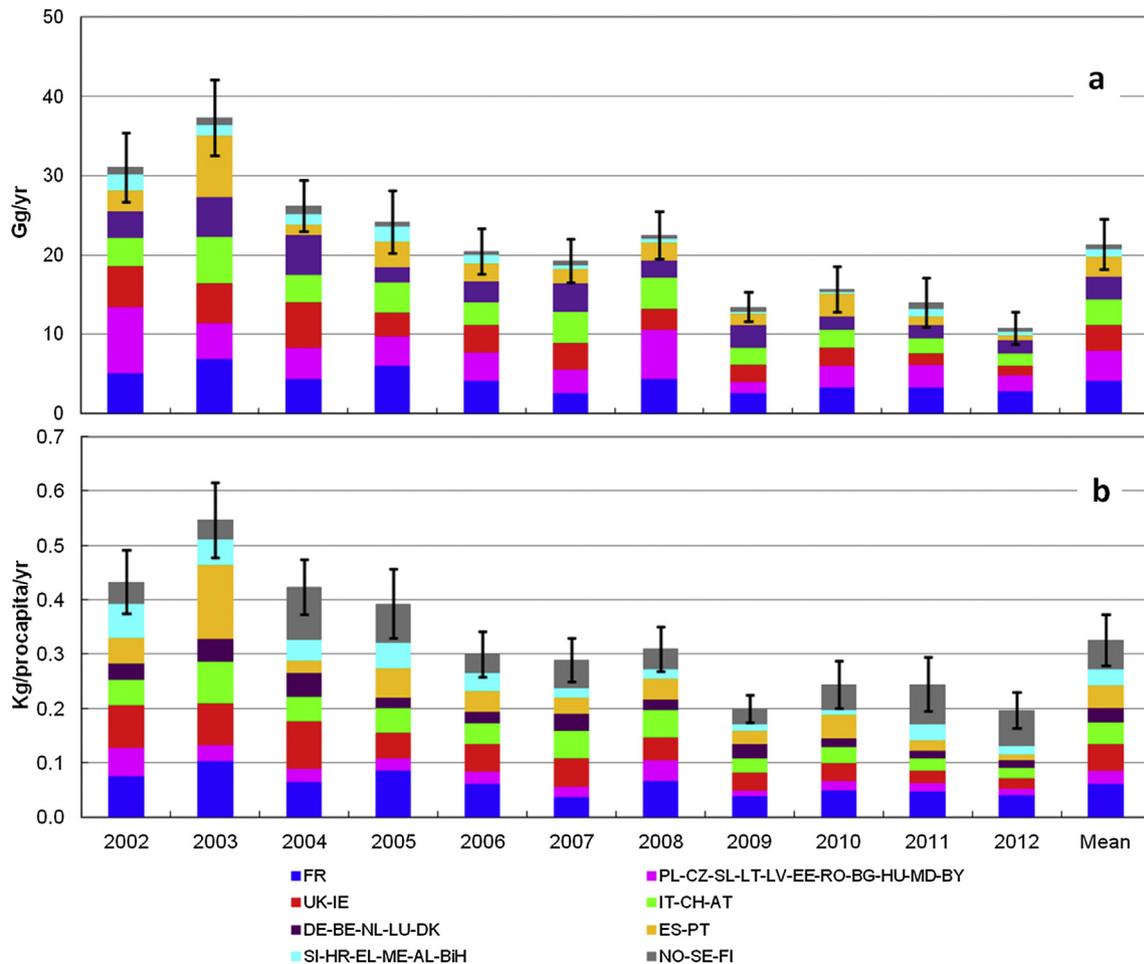
Fig. 5. a) Annual HCFC-22 emission estimates (Gg yr^{-1}) from the EGD split into eight macro areas. Error bars represent the total EGD emission uncertainty as described in the sensitivity tests section. Uncertainties in each region are characterised by those shown in Fig. 1S b) Annual per capita emission estimates (kg y^{-1}) from the EGD split into eight macro areas. The rightmost column shows the 11-y average. Error bars represent the EGD emission uncertainty as described in the sensitivity tests section.

countries. After a steady increase of the atmospheric HCFC-22 growth rate until 2008, indeed a decrease in the atmospheric growth rate of HCFC-22 has been recorded since then. This suggests that is likely that global emissions are not growing as rapidly as before 2008, as also reported by Montzka et al. (2014).

Combining the atmospheric data with a Bayesian inversion method, we estimated emissions of HCFC-22 in Europe down to the country level. Annual emissions from the European Geographic Domain derived in this study, show a constant decrease with two slight deviations from this trend in 2003 and 2008. We attribute the largest fraction of our estimated emissions to two regions, France and a large macro area including 11 eastern European countries

(BG, BY, CZ, EE, HU, LT, LV, MD, PL, RO, and SL), followed by IE-UK, AT-CH-IT, and BE-DE-DK-LU-NL. Highest per-capita emissions are from FR and IE-UK, followed by FI-NO-SE- and AT-CH-IT.

In general, our results show a good agreement with those reported in some previous studies. Comparing our European estimates for 2005 and 2006 with those published by Stohl et al. (2009) who used a similar approach, we found an excellent quantitative agreement, with only minor discrepancies at the country level and mainly in regions with poor observational constraints. A similar result is obtained from the comparison of fluxes estimated, using a similar approach, by Keller et al. (2012) for 2009. Once again we obtained an excellent agreement on the European scale, and some
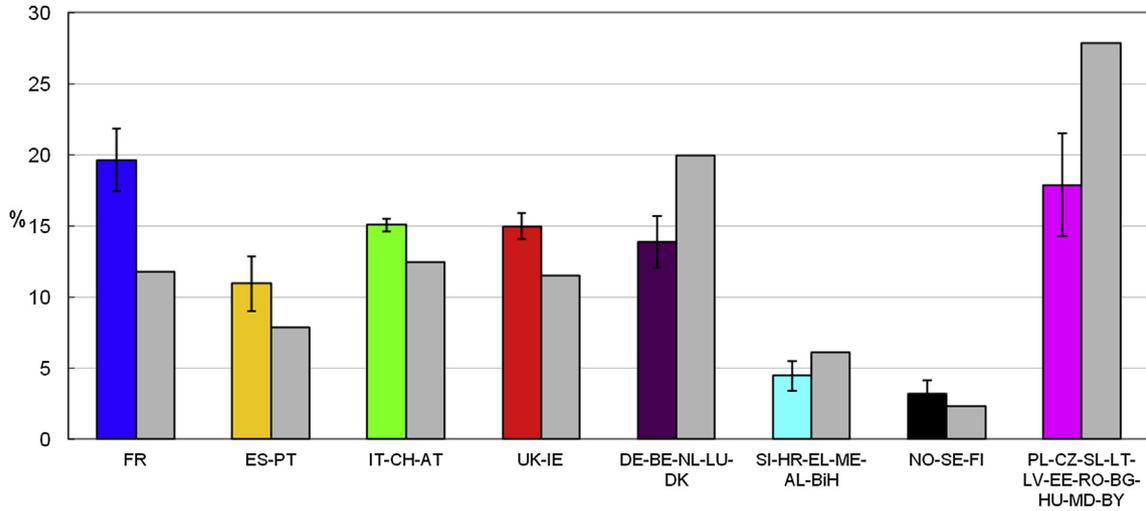
Fig. 6. 11-y average relative contributions to HCFC-22 emissions from eight macro areas in the EGD. The uncertainty is defines as the percent average maximum error. The corresponding *a priori* emissions from each group of countries are represented by the grey bars.
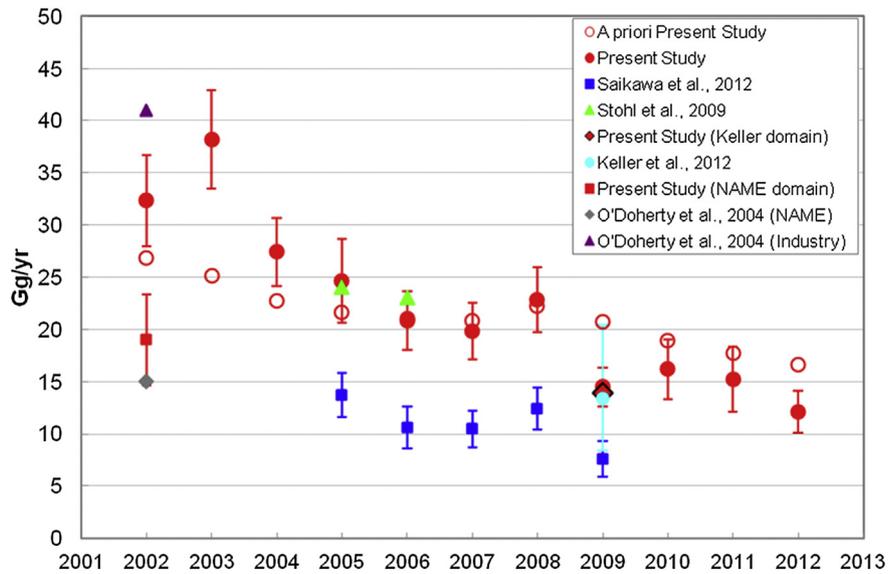

Fig. 7. Comparison of European emissions estimated in the present study with previous top-down estimates and with the *a priori* emissions used for this study. Notice that different domains are considered in some cases, i.e. O'Doherty et al., 2004 results (grey diamond) and the sub region from the present study (red square); Keller et al. (2012) results (light blue dots) and the sub region from this study (red diamonds). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
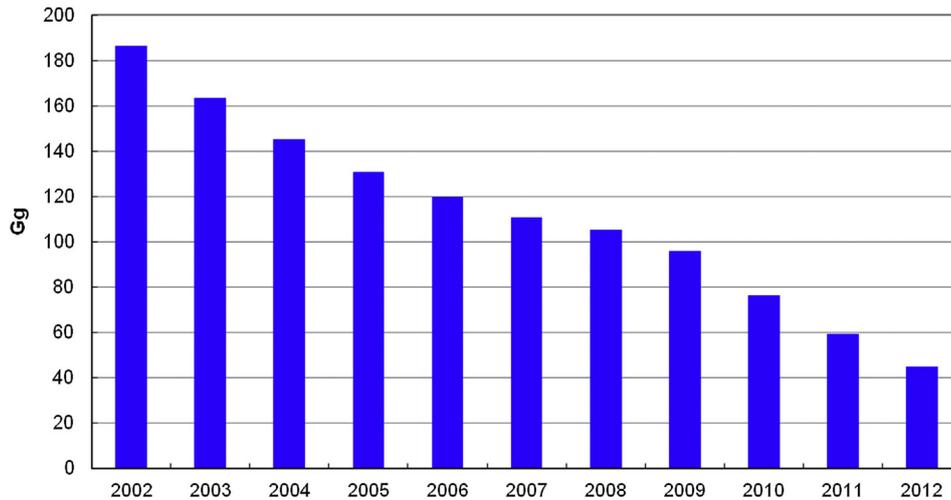

Fig. 8. Extent of HCFC-22 banks in the EGD as obtained combining UNEP consumption data, specified for HCFC-22 only and McCulloch's et al. (2006) EF.
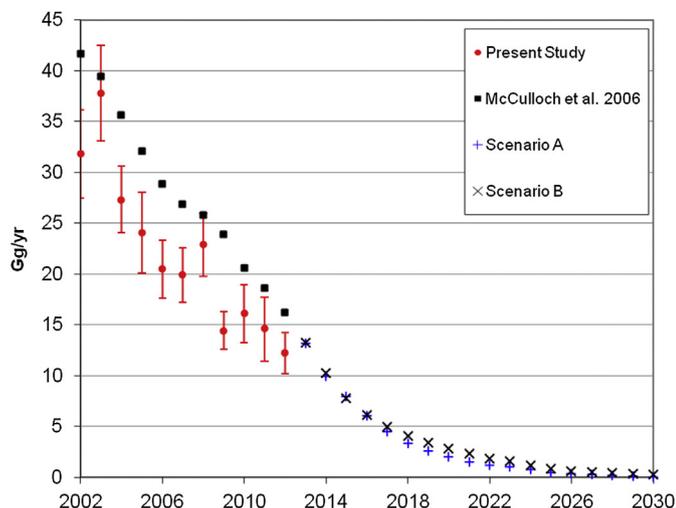
Fig. 9. Comparison of the Bayesian inversion results (red dots) with European emission estimates based on UNEP consumption data combined with the EF reported by McCulloch et al. (2006) (black squares). Emission projections up to 2030, according to two different consumption scenarios, are shown as well. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

differences at the macro-areas level. A significant deviation is observed when comparing our estimates with those calculated by Saikawa et al. (2012) for the period 2005–2009, with our estimates being nearly twice as high. Three monthly inversions allowed us to identify a seasonal cycle in HCFC-22 emissions in Southern Europe. In the Southernmost countries adjacent to the Mediterranean basin the emissions in summer are ca 25% higher than those in the colder months, likely because of a more intensive use of refrigeration and air conditioning systems during the summer. Comparing our estimates with inventories based on UNEP consumption data combined with the emission rates projection given by McCulloch et al. (2006), we also obtained a good agreement with an average difference of 22% between the two estimates, confirming the reliability of the proposed banks evaluation of banks sizes and the general emission functions. The projection of HCFC-22 emissions from the EGD up to 2030 shows a fast decrease and approaches zero after 2025.

Converting the EGD HCFC-22 emissions from Gg yr^{-1} into CO_2 equivalent (CO_2-eq), emissions have decreased from $58,000 \pm 4000$ Gg CO_2-eq in 2002 down to $22,000 \pm 2000$ in 2012, with projected emissions of 4000 ± 800 Gg CO_2-eq in 2020.

In conclusion, this study complements the main results obtained by previous studies and bottom up estimates, extending such results to 2012 and providing a detailed and updated picture of HCFC-22 European emission estimates down to the country (or group of countries) level. In addition, our study provides an assessment of the size of the HCFC-22 bank in Europe and an outlook on future emissions based on atmospheric data rather than solely on bottom up methods.

Acknowledgements

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.04.042.

References

Ashford, P., Clodic, D., McCulloch, A., Kuijpers, L., 2004. Emission profiles from the foam and refrigeration sectors comparison with atmospheric concentrations. Part 2: results and discussion. Int. J. Refrig. 27, 701–716.

Daniel J.S., Velders G.J.M., (Lead Authors), Morgenstern O., Toohey D.W., Wallington T.J., Wuebbles D.J., Akiyoshi H., Bais A.F., Fleming E.L., Jackman C.H., Kuijpers L.J.M., McFarland M., Montzka S.A., Ross M.N., Tilmes S., Tully (Cohauthors) M.B., Andersen S.O., Langematz U., Midgley P.M. (Contributors), 2011. A Focus on Information and Options for Policymakers. Chapter 5 in Scientific Assessment of Ozone Depletion: 2010. Global Ozone Research and Monitoring Project–Report No. 52, 370 pp., World Meteorological Organization, Geneva, Switzerland.

Eckhardt, S., Prata, A.J., Seibert, P., Stebel, K., Stohl, A., 2008. Estimation of the vertical profile of sulfur dioxide injection into the atmosphere by a volcanic eruption using satellite column measurements and inverse transport modelling. Atmos. Chem. Phys. 8, 3881–3897.

Fisher, D.A., Midgley, P.M., 1993. The production and release to the atmosphere of CFCs 113, 114 and 115. Atmos. Environ. 27A (2), 271–276.

Fischer, H., Kormann, R., Kluepfel, T., Gurk, C., Koenigstedt, R., Parchatka, U., Mühle, J., Rhee, T.S., Brenninkmeijer, C.A.M., Bonasoni, P., Stohl, A., 2003. Ozone production and trace gas correlations during the June 2000 MINATROC intensive measurement campaign at Mt. Cimone. Atmos. Chem. Phys. 3, 725–738.

Giostra, U., Furlani, F., Arduini, J., Cava, D., Manning, A.J., O'Doherty, S.J., Reimann, S., Maione, M., 2011. The determination of a regional atmospheric background mixing ratio for anthropogenic greenhouse gases: a comparison of two independent methods,. Atmos. Environ. 45, 7396–7405.

Grant, A., Witham, C.S., Simmonds, P.G., Manning, A.J., O'Doherty, S., 2010. A 15 year record of high-frequency, in situ measurements of hydrogen at Mace Head, Ireland. Atmos. Chem. Phys. 10, 1203–1214.

Henne, S., Brunner, D., Folini, D., Solberg, S., Klausen, J., Buchmann, B., 2010. Assessment of parameters describing representativeness of air quality in-situ measurement sites. Atmos. Chem. Phys. 10, 3561–3581.

Keller, C.A., Hill, M., Vollmer, M.K., Henne, S., Brunner, D., Reimann, S., O'Doherty, S.J., Arduini, J., Maione, M., Ferenczi, Z., Haszpra, L., Manning, A.J., Peter, T., 2012. European emissions of halogenated greenhouse gases inferred from atmospheric measurements. Environ. Sci. Technol. 46, 217–225.

Maione, M., Giostra, U., Arduini, J., Furlani, F., Graziosi, F., Lo Vullo, E., Bonasoni, P., 2013. Ten years of continuous observations of stratospheric ozone depleting gases at Monte Cimone (Italy) - comments on the effectiveness of the Montreal protocol from a regional perspective. Sci. Total Environ. 445–446, 155–164.

Maione, M., Graziosi, F., Arduini, J., Furlani, F., Giostra, U., Blake, D.R., Bonasoni, P., Fang, X., Montzka, S.A., O'Doherty, S.J., Reimann, S., Stohl, A., Vollmer, M.K., 2014. Estimates of European emissions of methyl chloroform using a Bayesian inversion method. Atmos. Chem. Phys. 14, 9755–9770. http://dx.doi.org/10.5194/acp-14-9755-2014.

McCulloch, A., Midgley, P.M., Ashford, P., 2003. Releases of refrigerant gases (CFC-12, HCFC-22 and HFC-134a) to the atmosphere. Atmos. Environ. 37 (7), 889–902.

McCulloch, A., Midgley, P.M., Lindley, A.A., 2006. Recent changes in the production and global atmospheric emissions of chlorodifluoromethane (HCFC-22). Atmos. Environ. 40 (5), 936–942.

Midgley, P.M., Fisher, D.A., 1993. The production and release into the atmosphere of chlorodifluoromethane (HCFC-22),. Atmos. Environ. 27A (14), 2215–2223.

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

Miller, J.B., Lehman, S.J., Montzka, S.A., Sweeney, C., Miller, B.R., Karion, A., Wolak, C., Dlugokencky, E.J., Southon, J., Turnbull, J.C., Tans, P.P., 2012. Linking emissions of fossil fuel CO_2 and other anthropogenic trace gases using atmospheric $^{14}CO_2$. J. Geophys. Res. 117, D08302. http://dx.doi.org/10.1029/2011JD017048.

Montzka, S.A., Hall, B.D., Elkins, J.W., 2009. Accelerated increases observed for hydrochlorofluorocarbons since 2004 in the global atmosphere. Geophys. Res. Lett. 36, L03804. http://dx.doi.org/10.1029/2008GL036475.

Montzka S. A., Reimann S. (coordinating lead authors), Engel A., Krueger K., O'Doherty S., Sturges, W. T., Blake D., Dorf M., Fraser P., Froidevaux L., Jucks K., Kreher K., Kurylo M. J., Mellouki A., Miller J., Nielsen O.-J., Orkin V. L., Prinn R. G., Rhew R., Santee M. L., Stohl A., and Verdonik, D., 2011. Ozone-Depleting

Substances (ODSs) and Related Chemicals, Chapter 1, in Scientific Assessment of Ozone Depletion: 2010. Global Ozone Research and Monitoring Project–Report No. 52, 370 pp., World Meteorological Organization, Geneva, Switzerland.

Montzka, S.A., McFarland, M., Andersen, S.O., Miller, B.R., Fahey, D.W., Hall, B.D., Hu, L., Siso, C., Elkins, J.W., 2014. Recent trends in global emissions of hydrochlorofluorocarbons and hydrofluorocarbons-reflecting on the 2007 adjustments to the montreal protocol. J. Phys. Chem. A. http://dx.doi.org/10.1021/jp5097376, 11/2014.

Myhre, G., Shindell, D., Breon, F.-M., Collins, W., Fuglestvedt, J., Huang, J., Koch, D., Lamarque, J.-F., Lee, D., Mendoza, B., Nakajima, T., Robock, A., Stephens, G., Takemura, T., Zhang, H., 2013. Anthropogenic and natural radiative forcing. In: Qin, T.F.D., Plattner, G.-K., Tignor, M., Allen, S.K., Boschung, J., Nauels, A., Xia, Y., Bex, V., Midgley, P.M. (Eds.), Climate Change 2013: the Physical science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.].

O'Doherty, S., Cunnold, D., Manning, A., Miller, B.R., Wang, R.H.J., Krummel, P.B., Fraser, P.J., Simmonds, P.G., McCulloch, A., Weiss, R.F., Salameh, P., Porter, L.W., Prinn, R.G., Huang, J., Sturrock, G., Ryall, D., Derwent, R.G., Montzka, S.A., 2004. Rapid growth of hydrofluorocarbon 134a and hydrochlorofluorocarbons 141b, 142b, and 22 from advanced global atmospheric gases Experiment (AGAGE) observations at Cape Grim, Tasmania, and Mace head, Ireland. J. Geophys. Res. 109 (D6), 2156–2202. http://dx.doi.org/10.1029/2003JD004277.

Ryall, D.B., Derwent, R.G., Manning, A.J., Simmonds, P.G., 2001. Estimating source regions of European emissions of trace gases from observations at Mace Head. Atmos. Environ. 32, 2507–2523.

Saikawa, E., Rigby, M., Prinn, R.G., Montzka, S.A., Miller, B.R., Kuijpers, L.J.M., Fraser, P.J.B., Vollmer, M.K., Saito, T., Yokouchi, Y., Harth, C.M., Mühle, J., Weiss, R.F., Salameh, P.K., Kim, J., Li, S., Park, S., Kim, K.-R., Young, D., O'Doherty, S., Simmonds, P.G., McCulloch, A., Krummel, P.B., Steele, L.P., Lunder, C., Hermansen, O., Maione, M., Arduini, J., Yao, B., Zhou, L.X., Wang, H.J., Elkins, J.W., Hall, B., 2012. Global and regional emission estimates for HCFC-22. Atmos. Chem. Phys. 12, 10033–10050. http://dx.doi.org/10.5194/acp-12-10033-2012.

Seibert, P., 2000. Inverse modelling of sulphur emissions in Europe based on trajectories. In: Kasibhatla, P., Heimann, M., Rayner, P., Mahowald, N., Prinn, R.G., Hartley, D.E. (Eds.), Inverse Methods in Global Biogeochemical Cycles, vol. 114. American Geophysical Union, pp. 147–154. ISBN:0-87590-097-6. Geophys. Monogr.

Seibert, P., 2001. Inverse modelling with a Lagrangian particle dispersion model: application to point releases over limited time intervals. In: Schiermeier, F.A., Gryning, S.-E. (Eds.), Air Pollution Modeling and its Application XIV. Kluwer Academic Publ., pp. 381–389.

Seibert, P., Frank, A., 2004. Source-receptor matrix calculation with a Lagrangian particle dispersion model in backward mode. Atmos. Chem. Phys. 4, 51–63.

Simmonds, P.G., Derwent, R.G., McCulloch, A., Gaudry, A., 1996. Long-term trends in concentrations of halocarbons and radiatively active trace gases in Atlantic and European air masses monitored at Mace Head, Ireland, from 1987–1994. Atmos. Environ. 30 (3), 4041–4063.

Simmonds, P.G., O'Doherty, S., Derwent, R.G., Manning, A.J., Ryall, D.B., Fraser, P., Porter, L., Krummel, P., Weiss, R., Miller, B., Salameh, P., Cunnold, D., Wang, R., Prinn, R., 2004. AGAGE observations of methyl bromide and methyl chloride at the Mace Head, Ireland and Cape Grim, Tasmania, 1998-2001. J. Atmos. Chem. 47 (3), 243–269.

SPARC, 2013. SPARC report on the lifetimes of stratospheric ozone-depleting substances, their replacements, and related species. In: Ko, M., Newman, P., Reimann, S., Strahan, S. (Eds.), SPARC Report No. 6, WCRP-15/2013.

Stohl, A., Hittenberger, M., Wotawa, G., 1998. Validation of the Lagrangian particle dispersion model FLEXPART against large scale tracer experiment data. Atmos. Environ. 32, 4245–4264, 1998.

Stohl, A., Forster, C., Frank, A., Seibert, P., Wotawa, G., 2005. Technical note: the Lagrangian particle dispersion model FLEXPART version 6.2. Atmos. Chem. Phys. 5, 2461–2474.

Stohl, A., Seibert, P., Arduini, J., Eckhardt, S., Fraser, P., Greally, B.R., Lunder, C., Maione, M., Mühle, J., O'Doherty, S., Prinn, R.G., Reimann, S., Saito, T., Schmidbauer, N., Simmonds, P.G., Vollmer, M.K., Weiss, R.F., Yokouchi, Y., 2009. An analytical inversion method for determining regional and global emissions of greenhouse gases: sensitivity studies and application to halocarbons. Atmos. Chem. Phys. 9, 1597–1620.

Stohl, A., Kim, J., Li, S., O'Doherty, S., Mühle, J., Salameh, P.K., Saito, T., Vollmer, M.K., Wan, D., Weiss, R.F., Yao, B., Yokouchi, Y., Zhou, L.X., 2010. Hydrochlorofluorocarbon and hydrofluorocarbon emissions in East Asia determined by inverse modelling. Atmos. Chem. Phys. 10, 3545–3560.

UNEP, 2009. Handbook for the Montreal Protocol on Substances that Deplete the Ozone Layer. PO Box 30552–00100, eighth ed. United Nations Environment Programme, Ozone Secretariat, Nairobi, Kenya. Retrieved from. http://ozone.unep.org/Publications/VC_Handbook/VC-Handbook-2009.pdf.

UNEP, 2013. UNEP Data Access Centre available at: http://ozone.unep.org/new_site/en/ozone_data_tools_access.php.

Velders, G.J.M., Andersen, S.O., Daniel, J.S., Fahey, D.W., McFarland, M., 2007. The importance of the Montreal protocol in protecting climate,. PNAS 104 (12), 4814–4819. http://dx.doi.org/10.1073/pnas.0610328104.

Velders, G.J.M., Solomon, S., Daniel, J.S., 2014. Growth of climate change commitments from HFC banks and emissions. Atmos. Chem. Phys. 14, 4563–4572. http://dx.doi.org/10.5194/acp-14-4563-2014.

Xiang, B., Patra, P.K., Montzka, S.A., Miller, S.M., Elkins, J.W., Moore, F., Atlas, E.L., Miller, B.R., Prinn, R.G., Wofsy, S.C., 2014. Global emissions of refrigerants HCFC-22 and HFC-134a: unforeseen seasonal contributions. Proc. Natl. Acad. Sci. U. S. A. 111/49 http://dx.doi.org/10.1073/pnas.1417372111.