Emissions of Carbon Tetrachloride (CCl_4) from Europe

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Abstract. Carbon tetrachloride (CCl_4) is a long-lived radiatively-active compound able to destroy stratospheric ozone. Due to its inclusion in the Montreal Protocol on Substances that Deplete the Ozone Layer, the last two decades have seen a sharp decrease in its large scale emissive use with a consequent decline of its atmospheric mole fractions. However, the Montreal Protocol restrictions do not apply to the use of carbon tetrachloride as feedstock for the production of other chemicals, implying the risk of fugitive emissions from the industry sector. The occurrence of such unintended emissions is suggested by a significant discrepancy between global emissions as derived by reported production and feedstock usage (bottom-up emissions), and those based on atmospheric observations (top-down emissions). In order to better constrain the atmospheric budget of carbon tetrachloride, several studies based on a combination of atmospheric observations and inverse modelling have been conducted in recent years in various regions of the world. This study is focused on the European scale and based on long-term high-frequency observations at three European sites, combined with a Bayesian inversion methodology. We estimated that average European emissions for 2006 - 2014 were 2.2 (± 0.8) Gg yr^{-1}, with an average decreasing trend of 6.9 % per year. Our analysis identified France as the main source of emissions over the whole study period, with an average contribution to total European emissions of approximately 26%. The inversion was also able to allow the localisation of emission “hot-spots” in the domain, with major source areas in Southern France, Central England (UK) and BE-NE-LUX (Belgium, The Netherlands, Luxembourg), where most of industrial scale production of basic organic chemicals

are located. According to our results, European emissions correspond on average to 4.0 % of global emissions for 2006-2012. Together with other regional studies, our results allow a better constraint of the global budget of carbon tetrachloride and a better quantification of the gap between top-down and bottom-up estimates.

1.Introduction

Carbon tetrachloride (CCl_4) is a near exclusively anthropogenic compound whose first uses as solvent, fire extinguisher, fumigant and rodenticide date back to 1908 (Galbally, 1976; Happell et al., 2014). The rapid increase in its production occurring between the 1950s and the 1980s is linked mainly to its use as a solvent and also to the growth in the production of chlorofluorocarbons (CFCs) made from CCl_4 (Simmonds et al., 1998). This led to a significant increase in the atmospheric mixing ratios of CCl_4, as shown by firn air analysis (Butler et al., 1999; Sturrock et al., 2002). The tropospheric lifetime, of 26 years (SPARC 2013) to 35 years (Liang et al., 2014) is the result of the sum of three partial loss rates: loss in the stratosphere (Laube et al., 2013), degradation in the ocean (Yvon-Lewis and Butler, 2002) and degradation in the soil (Happell et al., 2014).

Main concerns about this long-lived chemical are linked to its capability to destroy the stratospheric ozone layer and as a radiatively active gas, with an ozone depleting potential (ODP) of 0.72 (Harris and Wuebbles et al., 2014) and a global warming potential (GWP) of 1,730 (Myhre et al., 2013). The inclusion of CCl_4 in the Montreal Protocol on Substances that Deplete the Ozone Layer (MP) led to a sharp decrease in the large scale emissive use of CCl_4 and the consequent decline in its atmospheric mixing ratios was observed starting in the early 1990s (Fraser et al., 1994; Simmonds et al., 1998), with peak mole fractions of around 103 part per trillion (ppt) and 101 ppt in 1991 in the Northern Hemisphere (NH) and Southern Hemisphere (SH), respectively (Walker et al., 2000). In 2012 CCl_4 measured global average mole fractions were 84.2 and 85.1 ppt, as measured by the AGAGE (Advanced Global Atmospheric Gases Experiment) and NOAA-GMD (National Oceanic and Atmospheric Administration-Global Monitoring Division) ground-based sampling networks, respectively. The respective decrease rates during 2011-2012 were 1.2 and 1.6% yr^{-1} (Carpenter and Reimann et al., 2014). The contribution of CCl_4 to total organic chlorine in the troposphere in 2012 was 10.3% (Carpenter and Reimann et al., 2014).

Currently, emissive uses of CCl_4 are banned under the MP in signatory countries. Production and use are allowed for feedstock for chemical manufacture, for example for perchloroethylene, hydrofluorocarbon (HFC) and pyrethroid pesticides production (UNEP, 2013). Chemical feedstocks should be converted into new chemicals, effectively destroying the feedstock, but fugitive emissions are possible. With no significant natural sources (Butler et al., 1999; Sturrock et al.,

2002) the possible sources for CCl_4 in the atmosphere are fugitive emissions from the industry sector (Simmonds et al., 1998; Fraser et al., 2014), generation during bleaching (Odabasi et al., 2014) or emissions from a legacy of CCl_4 in old landfill (Fraser et al., 2014).

The persistence of such emissions is suggested by a discrepancy between global emissions as derived from reported production and feedstock usage (bottom-up emissions) and those based on atmospheric observations (top-down emissions). Assuming a total atmospheric lifetime of 26 years and the observed trend in the atmosphere, the top-down global CCl_4 emission estimates suggest for 2011-2012 global CCl_4 emissions are 57 (40–74) Gg yr^{-1}, a value that is at least one order of magnitude higher than estimates based on industrial use (Carpenter and Reimann et al., 2014). In addition the persistence of an inter-hemispheric gradient of about 1.3 ppt (Northern Hemisphere, NH minus Southern Hemisphere, SH) since 2006, shows that CCl_4 is still emitted in the NH (Carpenter and Reimann et al., 2014). Similar results have been obtained by Liang et al. (2014), who deduced that the mean global emissions during 2000-2012 were 39 Gg yr^{-1} (34-45 Gg yr^{-1}) with a calculated total atmospheric lifetime for CCl_4 of 35 (32-37) years.

In order to better constrain the CCl_4 budget, several top-down studies have been conducted in recent years focused on the global and regional scale, the top-down approach having been recognised as an important independent verification tool for bottom-up reporting (Nisbet and Weiss, 2010; Weiss and Prinn, 2011; Lunt et al., 2015).

Xiao et al. (2010) used a three-dimensional inversion model and global CCl_4 observations (AGAGE and NOAA-GMD) to derive emissions from eight world regions over the 1996-2004 period, identifying South-East Asia as being responsible of more than half of the global industrial emissions, which they estimated as 74.1 ± 4.3 Gg yr^{-1} (9-year average).

The role of China as a significant source region of CCl_4 has been highlighted by Vollmer et al. (2009) who, based on 18-month continuous high-frequency observations (October 2006 – March 2008) conducted at a site in the North China Plain and a Bayesian inversion modelling approach, calculated Chinese emissions to be 15 Gg yr^{-1} (10-22 Gg yr^{-1}) out of their global estimates of 53 ± 30 Gg yr^{-1}.

According to Fraser et al. (2014) top-down Australian emissions during 1996-2011 have declined from 0.25-0.35 Gg yr^{-1} to 0.12-0.18 Gg yr^{-1}, a decline of 5% yr^{-1}. In this study potential sources other than those arising from production, transport and use were identified and on the basis of an analysis of pollution episodes, were likely to be associated with contaminated soils, toxic waste treatment facilities and chlor-alkali plants.

In 2012, Miller et al. used a ^{14}C-based top-down method, to derive for the United States an average emission of 0.4 Gg yr^{-1} during 2004-2009, corresponding to 4% of the global emissions given in

Montzka and Reimann et al. (2011). Emission estimates by Hu et al. (2016) during 2008-2012 were 4.0 (2.0-6.5) Gg yr^{-1}. This number is two orders of magnitude greater that emissions reported to the US EPA Toxic Releases Inventory over the same period and one order of magnitude larger that the previous estimates given by Miller et al. (2012). Hu et al.'s estimates were derived using observations from a large observation network including multiple sites across the United States and both a Bayesian and geostatistical inverse analyses.

For Europe, the most recent estimates are given in the above-cited paper by Xiao et al. (2010), who reported that Europe has been responsible, over 1996-2004, for 4% of global emissions. However this study, based on observations conducted at global baseline sites, did not derive regional variations that likely occur across the different European countries and that could help in identifying specific emission sources, including those unrelated to reported production.

In order to derive CCl_4 European emissions at the country scale we conducted a study based on long-term, high-frequency CCl_4 observations carried out at three European sites combined with FLEXPART and the Bayesian inversion approach developed by Seibert (2000; 2001), improved by Eckhardt et al. (2008) and Stohl et al. (2009; 2010) and recently applied to derive emissions of halogenated species at the European scale (Maione et al., 2014; Graziosi et al., 2015).

Even though major source regions are likely to be located in East Asia, our results, in combination with those obtained from other regional studies, are useful in order to better assess the global budget of CCl_4 and better evaluate to what extent future emissions will affect the evolution of the equivalent effective stratospheric chlorine.

2.Method

2.1 Measurements

In Europe CCl_4 long-term, high-frequency observations of CCl_4 are available from three sites, all labelled as WMO-GAW (World Meteorological Organisation-Global Atmosphere Watch) global stations and AGAGE and affiliated stations: Mt. Cimone, CMN (Italy); Jungfraujoch, JFJ (Switzerland) and Mace Head, MHD (Ireland). CMN and JFJ are mountain stations occasionally affected by air masses from the polluted boundary layer; MHD baseline station is mostly affected by oceanic air masses and occasionally by air masses from over Ireland, United Kingdom and continental Europe. All CCl_4 data used in this paper are available from the AGAGE network: different instrumentations and protocols are used to measure in situ CCl_4 at each station: CMN uses a gas chromatograph with mass spectrometric detection (GC-MS), with sample enrichment on adsorbent trap by a commercial thermal desorber (Maione et al., 2013); JFJ uses a gas chromatograph with mass spectrometer detection, with sample enrichment on a custom built thermal desorber-Medusa-GC-MS, (Miller et al., 2008); MHD uses a gas chromatograph with an electron capture detection (GC-ECD), without sample enrichment (Prinn et al., 2000).

All the measurements are reported using the Scripps Institution of Oceanography (SIO), SIO-05 gravimetric primary calibration scale: ambient air measurements are routinely calibrated against whole air working standard that have been filled locally, using a bracketing technique, to override short term instrumental drifts. Working standards are then referenced on a weekly basis to tertiary tank (provided and calibrated by SIO) on site for the GC-MS measurements, i.e. CMN and JFJ. For the Mace Head GC-ECD instrument the tertiary tanks used as the working standard are prepared and calibrated at SIO at least twice, at the beginning and end of the life of the tank (Prinn et al., 2000; Miller et al., 2008). For this reason the contribution of the scale transfer (calibration) uncertainty to the total measurement uncertainty is minimized among stations, constraining the error estimate to the instrumental precision, calculated as the standard deviation (1σ) of the repeated working standard measurements for the covered period, that is typical for each site/setup and almost constant over the years of observation: CMN ± 0.39 ppt; JFJ ± 0.86 ppt and MHD ± 0.24 ppt. In addition, the analytical systems at the three stations are operated via the Linux-based chromatography software GCWerks (gcwerks.com) developed within the AGAGE programme.

2.2 Inverse modelling

Observations have been combined with 20-day backward trajectories of the FLEXPART Lagrangian Particle Dispersion Model (Stohl et al., 2005). FLEXPART runs are based on the European Centre for Medium-range Weather Forecast (ECMWF) wind fields, using 3-hourly ECMWF Re-Analyses, (ERA-Interim) (analysis fields are at 00:00, 06:00, 12:00 and 18:00 UTC, and 3-h forecasts are at 03:00, 09:00, 15:00 and 21:00 UTC) with 1°x1° horizontal resolution and 91 vertical levels. The emission sensitivity map of source-receptor relationships (SRR) generated using the three European stations is reported in Fig.1. The obtained SRR combined with an *a priori* emission field allowed us to estimate the *a posteriori* emission flux for the European Geographic Domain (EGD), using the Bayesian inversion technique.

With the aim of obtaining the best performance of the model in terms of the correlation coefficient between the observations and the modelled time series, we tested seven *a priori* emission fields based on different combinations of: i) CCl_4 emission fluxes estimated by Xiao et al. (2010), ii) CCl_4 emissions in the European Pollutant Release and Transfer Register (E-PRTR, http://prtr.ec.europa.eu/#/home), reporting CCl_4 atmospheric emissions higher than 100 kg yr^{-1} from 30,000 industrial facilities in the domain from 2007 to 2013, iii) information on the potential chlorine production from chlor-alkali plants as in the Eurochlor report (www.eurochlor.org), providing information on the chlorine potential production of each plant from 2006 to 2014 iv) CCl_4

emission factors from the chlor-alkali industry derived by Brinkmann et al. (2014) and Fraser et al. (2014), and v) diffusive emissions from the use of bleach containing cleaning agents (Odabasi et al., 2014). In the seven *a priori* emission fields tested the parameterisation range was: i) from 0.6 to 4.4 Gg yr^{-1} for the total *a priori* emission flux from the EGD, ii) from 3% to 80% for the contribution of industrial activities to the total EGD flux and iii) from 0.03 to 0.4 kg CCl_4 for each tonne of chlorine produced by the chlor-alkali plants listed in Eurochlor.

Despite these large ranges of values, the resulting EGD emission fluxes converged to very similar values, well within the inversion uncertainty, confirming the robustness of the method. For this study we used an “Ensemble” a priori emission field that showed the best model performance. The detailed description of the tests performed is reported in the Supplementary Material.

The inversion grid consists of more than 5.000 grid boxes with different horizontal resolution ranging from 0.5° by 0.5° to 2.0° by 2.0° latitude-longitude in order to assure similar weight on the inversion result. We estimated nine years of European emissions, from January 2006 to December 2014. From January 2006 to December 2014 the inversion was run using the only two stations (CMN and MHD) in which observations were available. During 2010-2014, data from JFJ were also used. A detailed description of the inversion technique and of the related uncertainty is given in the Supplementary Material.

3. Results and discussion.

3.1 Time Series Statistical Analysis

CCl_4 time series (individual data) at three European stations are reported in Fig. 2. Using a statistical approach described in Giostra et al. (2011) we discriminate background mole fractions (black dots) from elevations above the baseline (red dots) due to pollution episodes. The CMN time series shows a dip in 2006 that cannot be explained by instrumental reasons. However, it should be noted that the inversion results are affected by the extent of the enhancements above the baseline rather than by the baseline absolute values. Therefore the 2006 CMN data have not been flagged.

The background data line at JFJ is thicker, reflecting the greater noise in the signal due to inherent problems in measuring CCl_4 with the Medusa-GC-MS. Therefore, we performed some tests running the inversion after removing JFJ time series. Despite the quite noisy JFJ time series, we found a difference in the estimated emissions for the whole European domain $< 5\%$. This can be due to the overlapping of the footprint of CMN and JFJ receptors.

The monthly mean background mole fractions have been used to derive CCl_4 atmospheric trends, applying the empirical model described in Simmonds et al. (2004). Atmospheric trends in the background mole fractions over the common period (July 2010- Dec 2014) are -1.5±0.2, -1.2±0.1, -1.3±0.1% yr^{-1} (R^2 = 0.93, 0.99, 0.98), at CMN, MHD, and JFJ, respectively. Such values are consistent with global trends given in Carpenter and Reimann et al. (2014).

3.2 Inversion Results

CCl_4 emission intensity from the EGD and the emission distribution within the same domain has been estimated using the European observations and the described Bayesian inversion technique. As shown in Figure 3, the main deviations between our estimates ($flux_{post}$) and the *a priori* values ($flux_{prior}$) are found in 2006, and in 2013-2014. The relative percentage bias, given by ($flux_{post}$ – $flux_{prior}$)/$flux_{prior}$ *100), ranges from + 15% to -37%, as shown in the bottom panel of Fig 3. The emission flux uncertainty decreases from 180% of the *a priori* to 33% of the *a posteriori* emission field (average over the study period), supporting the reliability of the results. More details on the method performance are given in the Supplementary Material.

3.2.1 European emissions and emission trends

The inversion results indicate average EGD emissions during the study period of 2.2 (± 0.8) Gg yr^{-1}. CCl_4 total emissions from the EGD have decreased from ~ 2.8 (± 1.0) Gg yr^{-1} in 2006 to ~ 1.5 (± 0.5) Gg yr^{-1} in 2014, corresponding to an average EGD decreasing trend of 6.9 % per year (Figure 4). To put European emissions in a global perspective, we compared our results with global estimates. Global top-down emissions as derived from atmospheric measurements are available only until 2012 (Carpenter and Reimann et al., 2014). For the sake of consistency, this comparison was made considering the same time period, when we estimated EGD average emissions of 2.5 Gg yr^{-1}, corresponding to 4% of the global average. The plot in Fig.4 also shows a comparison between the EGD and the global emission trends. Over 2006-2012, the EGD estimates show an average trend -2.9% yr^{-1} compared with a global trend, for the same period, of -2.2% yr^{-1}. For comparison, during 2004-2011 the decreasing trend in Australian emissions was 5% yr^{-1} (Fraser et al., 2014).

EGD and macro-areas emission estimates for the single years are given in Table I. Such figures cannot be reconciled with potential emissions estimated from European production data reported to UNEP that, along the study period with exception of 2012, are negative, being calculated as the amount of controlled substances produced, minus the amount destroyed and the amount entirely used as feedstock. The discrepancy between the inversion results and the emissions reported to UNEP by industry persists also if a 2% of fugitive emissions and a 75% of destruction efficiency are hypothesised. (UNEP Production database, http://ozone.unep.org/). Also when comparing our estimates with emissions from the industrial activities declared to the E-PRTR, we found the latter to be strongly (on average 35 times) under-estimated, reinforcing the incompleteness of available information.

3.2.2 Emission distribution within the domain and emission hot spots

The obtained EGD *a posteriori* emission fluxes differ from the *a priori* both in intensity (as described above) and in spatial distribution.

In order to quantitatively assess the contribution to the total European emissions of CCl_4 from the various countries, we have divided our domain into ten macro areas (acronyms given in Table 1), whose extension is related to the SRR of the area (see Figure 1). Emissions from the single macro areas and the associated uncertainty (see Supplementary Material) are reported in Table 1 and in Figure 5a. Figure 5b shows the percentage contribution from the single macro areas.

Our estimates identify FR as the main emitter in the EGD over the entire study period, with an average contribution of approximately 26%. Six macro areas (ES-PT > NEE > DE-AT > SEE> UK-IE > IT) contribute between 13.2 and 7.6%, while the remaining regional contributions average 4% each. Emissions from France reached a maximum in 2010. Emissions from IT and CH show a faster decreasing trend with respect to the average EGD rate and the remaining macro areas decreased according to the overall average EGD emissions. As a result, starting from 2008, the percent contribution of France is about the 30 % of total EGD emissions.

Beside the overall picture given by the analysis of the aggregated macro area emission estimates, the analysis of the spatial distribution of the emission fluxes provides additional insights. The map in Figure 6 shows the *a posteriori* average distribution of emission fluxes over the study period, obtained with the "Ensemble" *a priori* emission field.

The geo-referenced emission sources as reported by the E-PRTR inventory, are represented as open circles, with the dimension of the circles referring to the amount released. Crosses refer to the geo-referenced Eurochlor chlor-alkali plants, for which the information on CCl_4 fluxes is not available.

Figure 6 shows how, in general, the localisation of the main emission sources declared by E-PRTR is well captured by the inversion, as in the case of Southern France, Central England (UK) and BE-NE-LUX. In addition, many hot spots are coincident with the chlor-alkali industries reported in Eurochlor, see e.g. the Bavarian region in Southern Germany, Sardinia (Italy) and Southern Spain. These hot spots are observed even when the inversion is run using the *a priori* emission field that does not include the E-PRTR and/or Eurochlor information on industrial emissions (not shown), indicating that the emission hot spots are not forced by the *a priori* flux.

In order to facilitate the comprehension of the map in Fig. 6, we compared the E-PRTR emission fluxes with estimates from the grid cells included in the corresponding hot spot areas identified through the inversion. We found that emission fluxes for the hot spots in Southern France and Central England were one order of magnitude larger than the reported ones and for BE-NE-LUX emissions were five times larger than those declared in the E-PRTR inventory. These results suggest either an under-reporting of current emissions and/or the occurrence of additional sources not reported by the E-PRTR inventory and/or emissions from the chlor-alkali industry and/or from historical production (such as landfill) (Fraser et al., 2014).

3.2.3 Comparison with NAME

For comparison, we ran an alternative top down approach based on observations at MHD combined with the UK MetOffice Numerical Atmospheric dispersion Modelling Environment (NAME) to simulate the dispersion and an iterative best fit technique (the simulated annealing) to derive regional emission estimates (Manning et al., 2011). This alternative top-down approach differs from our procedure in the dispersion model, in the inversion technique, in the absence of an *a priori* emission field and in the use of a single receptor. The use of a single station narrows the study area to a sub-EGD that includes eight countries in North West Europe (NWEU), i.e. BE-NE-LUX, DE, DK, FR, IE and UK. Figure 7 reports a comparison of the results obtained using the two different approaches for UK only and for the NWEU domain. Overall, a fair agreement is observed, with the differences between the two estimates always within the emission uncertainty. Such encouraging results endorse the reliability of the estimated emissions.

3.3 Industrial emission factors

UNEP (2009) identified chlor-alkali plants as potential accidental sources of CCl_4. Consistently, in the U.S. Hu et al. (2016) reported emission hot-spots in areas where chlor-alkali plants are located. In addition, Fraser et al. (2014) suggest that plants based on the out dated Hg cells technology could be the main responsible for CCl_4 emissions. In Europe, the last two decades have seen efficient improvements in the chlor-alkali production technologies and Brinkmann et al. (2014) estimated an emission factor (EF) of 0.03 kg CCl_4 $tonne^{-1}$Cl produced. From our estimates we derived an average EF from the EGD of 0.21 kg CCl_4 $tonne^{-1}$Cl produced during 2010-2014 that, as shown in paragraph 3.2.2, follows the distribution of industrial plants. These figures can be compared against a value of 0.39 calculated (Fraser, personal communication) for 2008-2011 on the base of U.S. emission estimates given by Hu et al. (2016), and a value of 0.41 for 2004-2011, based on Australian emissions (Fraser et al., 2014). Indications on the reasons of discrepancies between our EF and that given by Brinkmann et al. (2014) and between our EF and that calculated for U.S. and Australia, could be provided by an analysis at the macro area level. Our estimates show how the emission factors are not homogeneous across the macro areas in the EGD, with DE-AT, BE-NE-

LUX and SCA exhibiting EFs of the same order of magnitude of those given in Brinkmann et al., whereas values for the remaining macro areas are one order of magnitude higher. Indeed, CCl_4 emission fluxes estimated for the different macro areas of the EGD (reported in Figure 5), even after subtraction of the diffuse share (following the population density), are not directly related to the chlorine potential production in the same macro-areas (Eurochlor, 2014; for further details see Figure 6S, in the Supplementary Material). A reason of this lack of correlation could be ascribable to the inhomogeneous penetration of the different technologies in the various EGD macro areas (Eurochlor, 2014; for further details see Figure 7S, in the Supplementary Material), suggesting that CCl_4 fluxes are more related to the adopted technology rather than to the amount of chlorine produced. The determination of such emission rates is made even more difficult by additional factors, like i.e. lack of obligation, for the chlor-alkali plants allowed to use CCl_4 as process agent for the elimination of nitrogen trichloride and the recovery of chlorine from tail gases, to report the actual amount used and/or the transfer of the allocated quota (Brinkmann et al., 2014).

4. Conclusions

In this study we have estimated European emissions of carbon tetrachloride combining atmospheric observations at three European sites with a Lagrangian dispersion model (FLEXPART) and a Bayesian inversion method. This procedure allowed us to assess the CCl_4 emission field with a high spatial resolution within the domain.

We estimated average emissions from the European Geographic Domain during 2006-2014 of 2.2 (± 0.8) Gg yr^{-1}, with a decreasing rate of 6.9% per year. Such an emission flux corresponds to the 4% of the global emissions estimates given by Carpenter and Reimann et al. (2014) over the period 2006-2012.

When comparing emissions derived with the top-down approach with those evaluated through bottom-up methods, large discrepancies are observed. Such discrepancies are expected with regard to the information contained in the UNEP database, which reports production (without allowing for stock change but quoting destruction as a negative production) and consumption for emissive uses. Also emissions reported in the E-PRTR inventory, that should include data related to those industrial processes (including waste treatment) that can potentially emit CCl_4, represent only about 3% of our estimates. However, in spite of the discrepancy in the quantification of emissions, the inversion is able to localise the main source areas reported in the E-PRTR. In addition, we note that many areas where chlor-alkali plants are located are identified as source areas by the inversion, even when the information related to such plants is not included in the *a priori* emission field. Thus, the estimated *a posteriori* emission flux seems to confirm that chlor-alkali plants are mainly responsible for CCl_4 emissions in the domain (UNEP, 2009).

We have also calculated the rate of CCl_4 emitted into the atmosphere per amount of chlorine produced in the chlor-alkali industry obtaining an average emission factor for Europe of 0.21 kg CCl_4 $tonne^{-1}$Chlorine produced. This value is lower than those for the U.S. (0.39) and Australian (0.41) plants. This European average emission factor includes a high variability across the various macro areas in the domain, showing the inadequacy of the chlorine potential production as a proxy of CCl_4 emissions as well as the relevance of the chlorine production technologies adopted by the chlor-alkali industry (including the direct use of CCl_4 to abate nitrogen trichloride emissions).

To summarize, this study allowed us to estimate CCl_4 emission fluxes at the European regional scale. Thanks to the good sensitivity in most of the EGD, the emission field can be reconstructed with a resolution level able to show, for each country, the main inconsistencies between the national emission declarations and the estimates based on atmospheric observations. Our results could allow a better constraint of the global budget of CCl_4 and a better quantification of the gap between top-down and bottom-up estimates, even if our estimates together with those derived by other regional studies (Fraser et al., 2014; Hu et al., 2016; Vollmer et al., 2009) still do not add up to the total amount required to comply with the current atmospheric abundance as in Carpenter and Reimann (2014). Such a discrepancy can be ascribed either to missing sources or to a lack of data from un-sampled regions of the world or to an incorrect evaluation of CCl_4 atmospheric lifetime, as recently shown in a study by Butler et al. (2016), whose reconsideration of CCl_4 total lifetime could contribute to narrowing the gap between top-down and bottom-up estimates.

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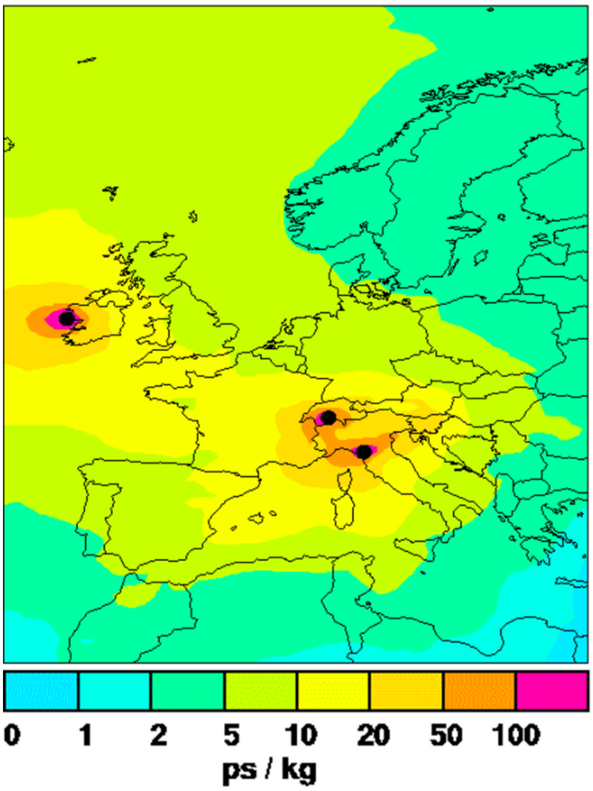


Figure 1. Footprint emission sensitivity in picoseconds per kilogram (ps kg^{-1}) obtained from FLEXPART 20 days backward calculations averaged over all model calculations over two years (Jan 2008- Dec 2009). Measurement sites are marked with black dots.

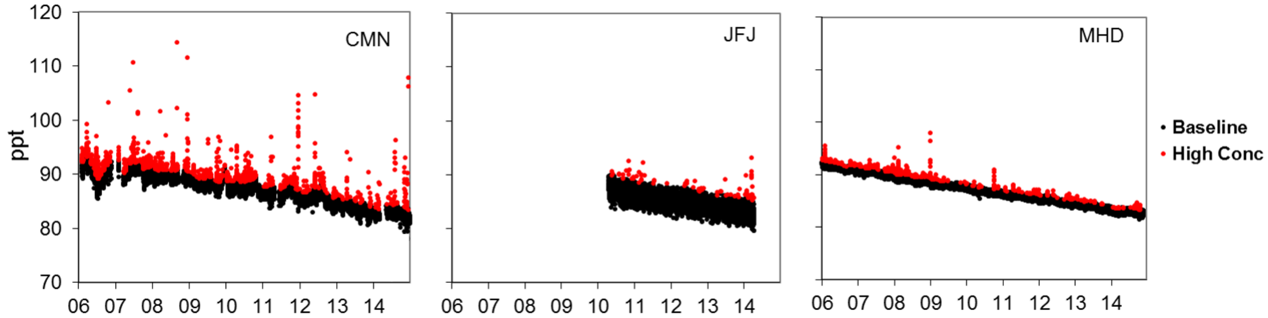
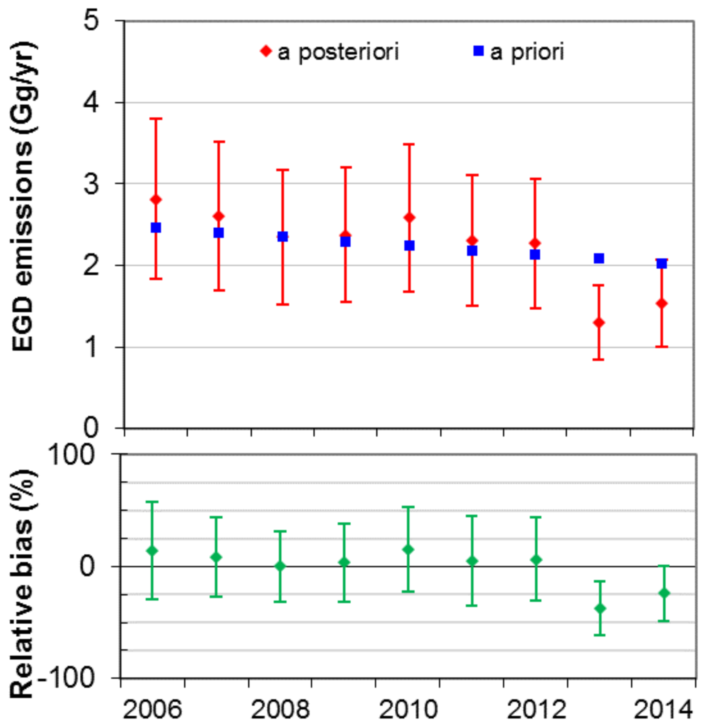


Figure 2. CCl_4 time series at three European sites. Black dots: baseline, red dots: enhancements above the baseline.



595 **Figure 3. Upper panel: comparison between the *a priori* (blue squares) and *a posteriori* (red diamonds) CCl_4 emission fluxes from the European Geographic Domain during 2006-2014. Bottom panel, percentage relative bias between the *a priori* and *a posteriori* time series (green diamonds).**

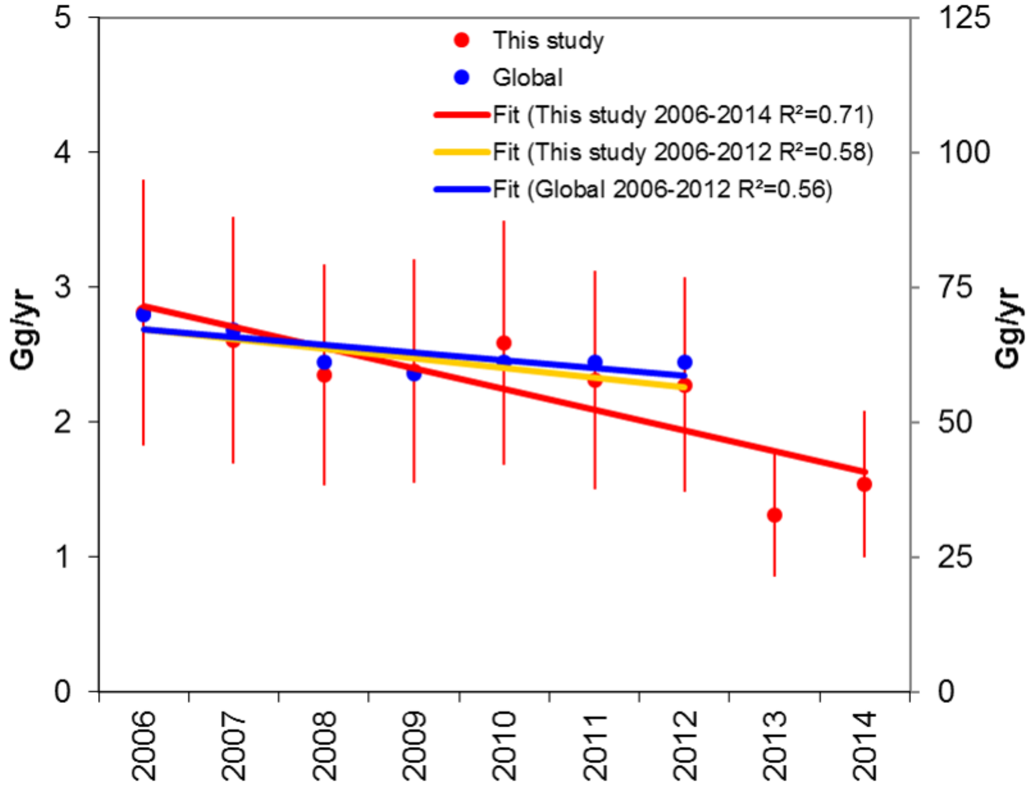


Figure 4. European Geographic Domain CCl_4 emission fluxes derived in this study (red dots, left axis) compared with the global ones reported in Carpenter and Reimann et al. (2014) (blue dots, right axis). The red line represents the linear regression of our estimates over 2006 to 2014 (-6.9% yr^{-1}). Orange line: as for red lines but over 2006-2012 (-2.9 % yr^{-1}). Blue line: linear regression of global fluxes over 2006-2012 (-2.2 % yr^{-1}).

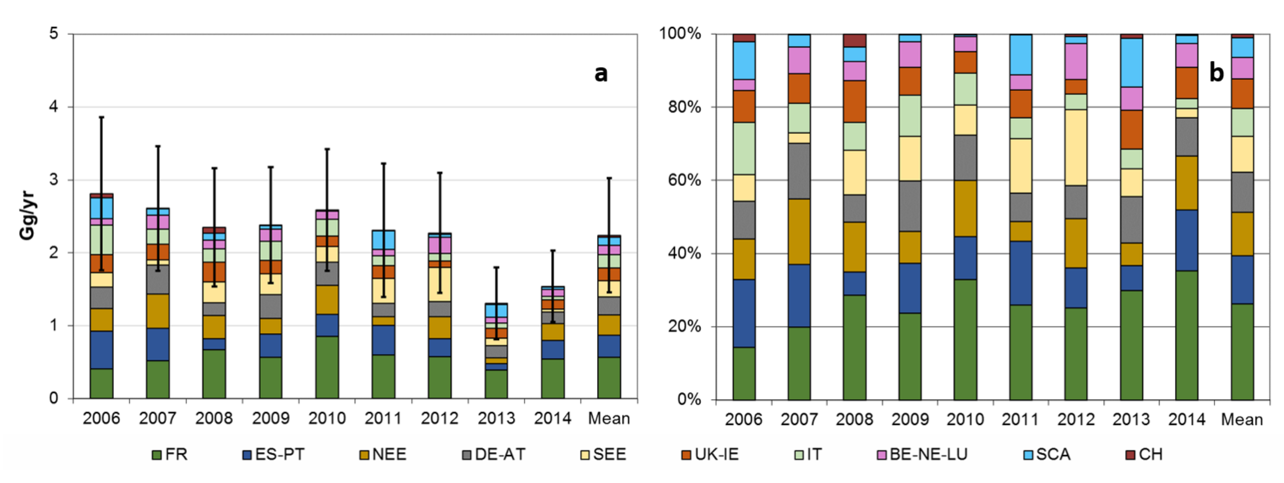


Figure 5. a) Carbon tetrachloride estimated emission over the study period given in Gg yr^{-1} from ten macro areas in the EGD. Error bars represent the uncertainty in emissions as derived by the inversion routine (see Supplementary Material) b) Yearly percent contribution of the single areas to total EGD emissions.

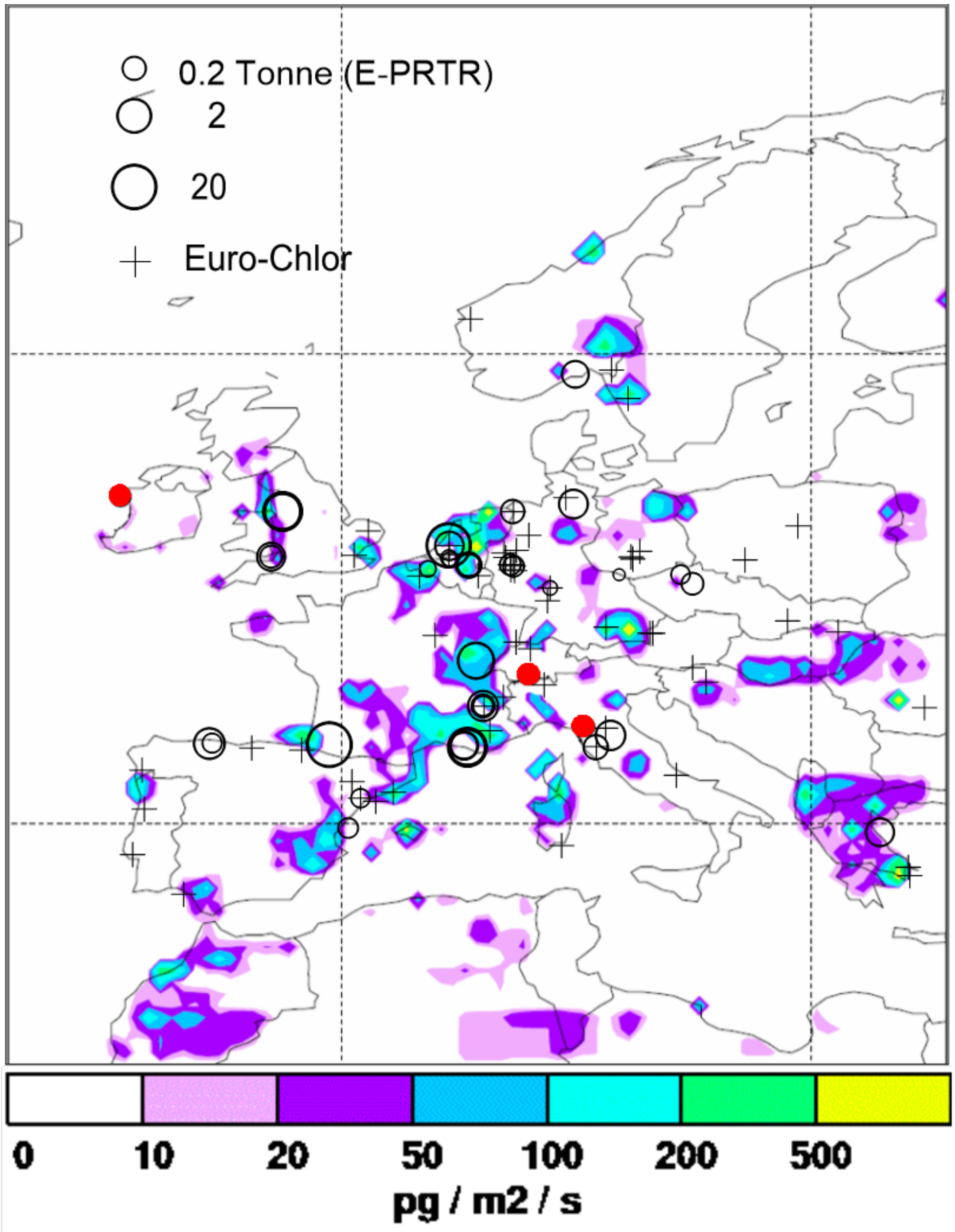


Figure 6: Average *a posteriori* distribution of CCl_4 emissions from the European Geographic Domain over the study period. Measurement stations are marked with red dots. Open circles represent emissions to atmosphere as reported by the E-PRTR inventory and crosses correspond to the location of chlor-alkali plants listed in Eurochlor.

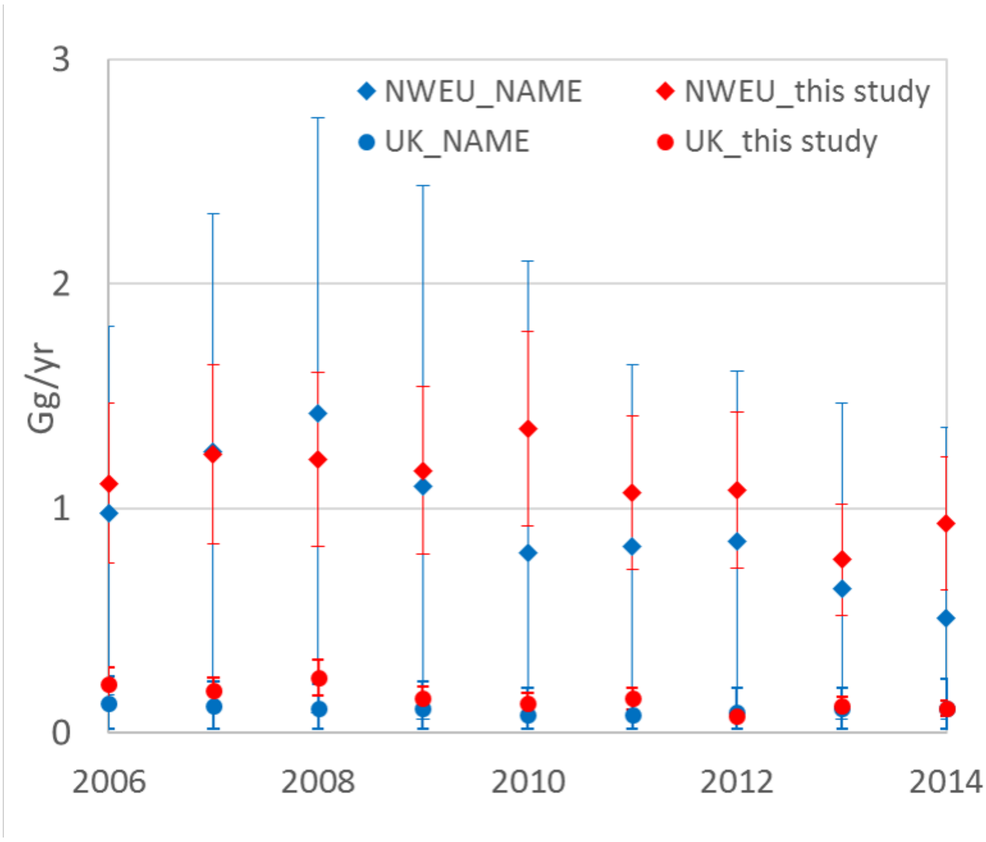


Figure 7. Comparison between emissions from UK (circles) and the NWEU domain (diamonds) estimated through the NAME (blue) and the Bayesian (red) approach.

Table 1: Carbon tetrachloride emission estimates (Gg yr^{-1}) and associated uncertainty, percent yearly emission trends and 9-yr average percent contribution from the EGD and from ten macro areas in the EGD over the study period. Macro areas, listed according to their emission intensity are: FR (France); ES-PT (Spain, Portugal); NEE (Poland, Czech Republic, Slovakia, Lithuania, Latvia, Estonia, Hungary, Romania, Bulgaria); UK-IE (United Kingdom, Republic of Ireland); DE-AT (Germany, Austria); IT (Italy); SCA (Norway, Sweden, Finland, Denmark); SEE (Slovenia, Croatia, Serbia, Bosnia-Herzegovina, Montenegro, Albania, Greece); BE-NE-LUX (Belgium, The Netherlands, Luxembourg), CH (Switzerland).

Areas	CCl_4 yearly emissions (Mg yr-1)									Trend %yr-1	Mean
	2006	2007	2008	2009	2010	2011	2012	2013	2014		
EGD	2812±1058	2606±853	2348±807	2376±800	2586±837	2308±913	2272±822	1305±488	1538±485	-6.9	
FR	405±109	519±140	671±181	563±152	849±229	597±161	572±154	391±106	542±146	0.0	26.2
ES-PT	519±189	444±162	151±55	323±118	303±110	405±148	248±90	87±32	257±94	-10.1	13.2
NEE	311±118	468±177	318±120	209±79	399±151	123±47	305±115	81±31	226±86	-9.9	11.8
DE-AT	290±81	396±110	176±49	327±91	319±89	181±50	206±57	166±46	161±45	-8.7	11.0
SEE	205±120	76±45	286±168	291±171	213±125	342±201	471±277	100±59	38±22	-1.3	9.8
UK-IE	241±60	212±53	269±67	181±45	149±37	175±44	88±22	138±35	132±33	-9.7	8.0
IT	405±117	208±60	179±52	265±77	228±66	131±38	98±28	70±20	43±12	-19.9	7.6
BE-NE-LUX	88±15	189±32	121±20	167±28	109±18	95±16	224±38	82±14	98±16	-1.9	5.9
SCA	287±236	88±72	95±78	46±38	11±9	252±207	44±36	175±144	35±29	-9.3	5.4
CH	61±12	6±1	82±16	4±1	6±1	7±1	16±3	15±3	6±1	-23.8	1.0