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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Emissions of Carbon Tetrachloride (CCl_4) from Europe" *by* Francesco Graziosi et al.

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Response to reviewers

The authors would like to thank the reviewers for the very useful suggestions that allowed us to improve the robustness of our estimates.

Main changes:

The use of an alternative a priori did not produce significant differences in the emission estimates. Updated emission fluxes have been reported whenever applicable. However, we believe that the various tests performed contributed in improving the robustness of the results, as shown in the Supplementary Material detailed description and as also reported in the main text.

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Discussion paper

The detailed analysis of CCl4 emission factors required the inclusion of a new section (3.3).

Figures numbering has been changed according to the revised text. In addition, Figures 4 and 6 (current numbering) have been updated to comply with the revised text and results.

We made all the suggested changes along the text.

In the following we provide detailed answers to the specific comments.

Reviewer #1

CCl4 is measured at MHD by GC-MS and GC-ECD - the latter data are preferred because there are inherent problems in AGAGE in measuring CCl4 by GCMS. Do these problems exist for GC-MS at JFJ, and, if they do, do they impact on this analysis. Reply: We want to use as much receptors as possible in order to improve the model performance. However, in this case we found the following: we run the inversion removing JFJ time series and we found a difference in the a posteriori for the whole EGD < 5%. At the macro-area level this difference is relevant for CH macro-area only (>35%) but, being the contribution of CH very small (1.5% of the EGD emissions), this difference is smoothed when considering the whole EGD. This is probably due to the fact that at JFJ the CCl4 GC-MS time series is quite noisy and therefore, in this specific case, the signal do not contribute significantly to the inversion. Also the overlapping of the footprint of CMN and JFJ can be another cause. We also tested the GC-MS time series at MHD, finding a significant increase (40% higher) in emissions, and the correlation between the modelled and observed time series decreased from r2 0.72 to 0.2. The important role of MHD time series in the inversion results is due to the fact that the noisy GC-MS time series at MHD is not balanced by any nearby receptor. Finally, please note that at CMN we use a GC-MS system but this differs from the GC-MS system used at JFJ and MHD in the trapping temperature and GC column, giving a better signal to noise ratio.

Line 165: a priori emissions. I suggest the following prior could be used - the Xiao et al. European emissions should be released according to the E-PRTR distribution of industrial emissions. Hu et al. (2016) showed conclusively the US emissions of CCl4 (and presumably European emissions of CCl4) are not significantly related to population distributions but are related to the distribution of chemical industrial activity. Why bias your prior in the likely wrong direction using largely (96%) population distributed emissions. This could lead to a significantly better a priori. Reply: Thanks for this advice. Following your suggestion, we tested alternative a priori emission fields. The detailed description of the a priori emission field tested is provided in the Supplementary Material, along with an evaluation of their performance. After these tests we have chosen an a priori that, as the reviewer suggested, takes into account the distribution of industrial emission. This new approach produced a posteriori EGD emission values very similar to that obtained with the reference a priori previously used, but with better correlation values. Some differences are found at the macro-area level. In the revised manuscript all the emission values and trend have been updated, as well as the discussion (when necessary).

Line 260: this study and Hu et al. show that the CCl4 emissions are coming from industrial chemical hot-spots and are not related to population distributions. Landfills and domestic bleach sources tend to follow population distributions and these studies therefore tend to down-play landfills and domestic bleach as significant sources although tentative, I think this important conclusion can be made. Reply: The results obtained using the revised approach showed that this is the case in the EGD too and we added a statement on this. In addition, we would like to point out that the industrial activities in the E-PRTR also include emissions from landfills.

3.2.4 Comparison with NAME: why not run the NAME inversion using all 3 observation sites not just MHD? Reply: The meteorology available to the NAME model is not sufficiently high resolution over the Alps and northern Italian mountains to accurately capture the flow in these challenging areas. Meteorology of the order of a km would be

required to enable a reasonable estimate of the flow and therefore be of benefit to the inversion system.

Line 270 - Figure 6 compares UK and NWEU emissions of CCl4 with the latter significantly higher. At this point it would be instructive to compare the relative size of the chemical industries in these two regions - for example compare their chlor-alkali productions Reply: We didn't find any correlation between the size of chemical industries and the CCl4 emission fluxes, suggesting that it is not possible to identify an emission factor applicable to all industries. This is the reason why we didn't provide any graphical information.

Line 284: per capita emissions. Since it has been shown that CCl4 emission distributions do not follow population distributions, then something better than per capita emissions could be calculated as a reference indicator, such as CCl4 emissions per unit of chemical production. I have done this for Hu et al USA emissions and Fraser et al. Australian emissions, as a function of chloro-alkali production - USA (0.39 kg CCl4/tonne Cl and Australia (0.41 kg CCl4/tonne/Cl). European Cl production numbers are available - it would be interesting to see what the European CCl4/Cl emission factor is. Reply: thank you for your suggestion, we have modified the analysis and the text accordingly. In particular we moved the paragraph with the comparison with global emission trend to section 3.2.1. Section 3.3 now reports a detailed analysis of industrial emission factors.

Reviewer #2

At the end of the discussion section (or in the conclusions) when putting their European emissions into a global context I wonder if the authors could summarise the current state of play regarding the CCl4 story. It seems from the references given that recent US, European, Australian and even Chinese top-down emissions still may still not add up to the total amount required to maintain the current atmospheric abundance. Is there

still a missing source, or is the budget balanced within the various levels of uncertainty? Reply: Beside some still missing emission sources, there is also a re-consideration on the CCl4 lifetime. A new study by Butler at al. has been published on ACP while the present paper was under revision. This reconsideration narrowed the gap between top-down and bottom-up estimates. We added a reference to this paper and the related findings.

Line 35: "European emissions correspond to 4.0% of global emissions for 2006-2012". Do the authors mean cumulative emissions over the 7-year period or is it an average of 4% each year? Please clarify. Reply: It is the average on the period. We modified the text to make it clearer

Line 61: "total chlorine in the troposphere". Firstly, do the authors mean total organic chlorine? Secondly, which part of the troposphere are they referring to? Reply: Yes it is total organic chlorine in the whole troposphere. We added this information in the text.

Line 136: I am intrigued as to why the MHD data is taken from the GC-ECD instrument rather than the Medusa-GC-MS that also operates at the site? At JFJ they are using data from a similar (identical?) Medusa GC-MS instrument, but the authors choose not to report the GC-MS data from MHD. Is there a reason for this? Reply: when measuring CCl4, the performance of the GC-ECD is better than the Medusa system. Therefore, when available, GC-ECD data are used. For a detailed explanation of the implications for the inversion see reply to reviewer 1.

Line 144: "at least twice" is not the same as "regularly calibrated". The working tanks are prepared at SIO and are calibrated (at SIO) at the beginning and end of the life of the tank? Reply: yes this was a mistake. Tanks are calibrated at the beginning and at the end of life. We deleted "regularly".

Line 167: Is there a reference or web link for the E-PRTR database? Reply: yes, we added it in the text

Line 215-216: how can emissions be negative? Please explain in the text. Reply: we added the definition in the text

Line 216: is there a reference for the UNEP production database? Reply: Yes we added it in the text

Line 217-218: "Such discrepancy holds also . . ." This sentence doesn't really make sense. Please explain and expand. Reply: Done

Figure 2: What actually are the time series? Are they averaged in any way or are they individual samples Reply: The time series are raw data divided into baseline (black) and polluted (red)

What is the dip seen in the CCl4 concentrations at CMN in 2006? This does not appear to be seen at MHD which suggests it is a local phenomenon. How can such a drop below the expected NH background be accounted for? The period seems to last for several months so presumably cannot be put down to a stratospheric event or southern hemisphere air. Does this period of abnormally low concentrations have any impact on the inversions? Reply: we cannot explain the deep but data have not been flagged because we do not have any instrumental reason to flag them. However it should be noted that the inversion procedure is more affected by the extent of the enhancement above the baseline rather than the baseline absolute value.

Why is the baseline signal in the middle panel so much more variable than the other 2? Perhaps this also relates back to the choice of ECD over MS at Mace Head? Reply: Yes, see reply above

Figure 4: What do the error bars in Panel a represent? Please add an explanation in the caption. Reply: the error bar represents the uncertainty of the emission estimates. The uncertainty is found by the inversion routine, as described in the Supplementary material. The information is added in the caption

Figure 7: I am not entirely convinced by the regression lines in Figure 7 or the trends

described in lines 280-284. Could the yellow trend line be biased by the slightly higher value in 2006 and the slightly lower value in 2012? With the very large uncertainties highlighted by the error bars can you really say there is a statistically significant difference between the blue and yellow lines? It is hard to see from this Figure as they are plotted on different y axes. Can the authors say with any certainty that European emissions were falling faster than global emissions over this period? Reply: We reported two different trends: one for the entire period in which we run the inversion (2006-2014, red line) and one for the period for which we can make a comparison with the Global trend (2006-2012, blue line). We agree that the caption is not clear and we modified it. We agree with the reviewer that over the period 2006-2012 a statistically significant difference between the EGD emission estimates and the global ones cannot be detected. Moreover, the use of the alternative a priori emission field suggested by Reviewer# 1 produced a trend for the EGD emissions closer to the global one.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/acp-2016-326/acp-2016-326-AC1-supplement.pdf

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