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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Toward resolving the mysterious budget discrepancy of ozone-depleting CCl_4: An analysis of top-down emissions from China" *by* Sunyoung Park et al.

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Referees' comments on "Toward resolving the budget discrepancy of ozone-depleting CCl4: An analysis of top-down emissions from China" by Sunyoung Park, Shanlan Li, Jens Mühle, Simon O'Doherty, Ray F. Weiss, Xuekun Fang, Stefan Reimann, Ronald G. Prinn

We thank the referees for their thoughtful and thorough reviews. We are pleased that all the reviewers see our manuscript as a valuable contribution to the field. We have made changes to the manuscript to answer the suggestions of the reviewers and clarified a few points raised in review. We respond to the referee's comments below and a revised

version of the manuscript including most of the changes suggested by the reviewers will be submitted to the editor. We thank the reviewers and the editor for their time and effort and appreciate the recommendation for publication in Atmospheric Physics and Chemistry.

Reviewer comments:

Referee #2:

Park et al presented a top-down emissions estimate of CCl4 from East Asia based on high frequency surface measurements of halocarbons at the Gosan sites. This paper is timely. Results presented in this paper provide crucial pieces of information that closes the CCl4 global budget as well as providing the atmospheric observational evidence that unreported CCl4 emissions during chloromethans and PCE production. However, the writing in many places can use some improvements. I recommend the authors go through the entire manuscript thoroughly to improve the clarity and accuracy. The paper should be published in ACP after the following comments are addressed.

1. P1 L15, "the 2010" -> "a 2010"

»> Done

2. P2 L5-7. You should state that the global top-down emissions are derived based on both the CCl4 lifetimes and the observed global decline rate.

»> A point well-taken. We have changed it to what the reviewer suggested (underlined words are the edits): "To verify these reported bottom-up estimates, independent CCl4 emission studies have used the total lifetime of CCl4, atmospheric observations, i.e., the observed decline rate of CCl4 concentrations and atmospheric transport models to derive "top-down" estimates."

3. P2 L9. The global emissions number from Liang et al, 2014 was 39Gg/yr, not 30Gg/yr.

»> We realized from the reviewer's comments that the citation was incorrect. The 39 Gg/yr emission from Liang et al. (2014) had been updated into the value of 30 Gg/yr with the new 33-year lifetime of CCl4 in the SPARC report (Liang et al., 2016). So we've changed the original sentence into the following to clarify the updated estimate: "A recent top-down study based upon the observed temporal trend and inter-hemispheric gradient of atmospheric CCl4 (Liang et al., 2014) consistently derived global CCl4 emissions of 30±5 Gg yr-1 in 2000–2012 with the newly determined relative strength of the oceanic sink vs. the soil loss (Liang et al., 2016)."

4. P2 L11-12. I am not sure why you say "unidentified sources and/or unreported anthropogenic emissions". CCl4 is a predominantly man-made compound, therefore the emissions sources are anthropogenic.

»> Agreed. For clarification the word "anthropogenic" has been edited into "industrial". We think unidentified old, contaminated soils and/or facilities can be "unidentified sources" here.

5. In many places, need to change the "," after the references to ";".

»> Corrected

6. P2 L27-30. You need to merge these two sentences and present the results from these studies in a less confusing way with a correct referencing style. In the present form, it is hard for the readers to figure out from which studies the 4.3 and 5.2 Gg/yr were from.

»> The sentences have been merged and edited to clarify that those numbers were updated as new bottom-up emission estimates (underlined words are the edits): "Most recently, Bie et al. (2017) published post-2010 bottom-up emission estimates for China of 4.3 (1.9–8.0) Gg yr-1 in 2011 and 5.2 (2.4–8.8) Gg yr-1 in 2014, which updated a previous estimate of zero emission (Wan et al., 2009) by including the conversion of C2Cl4 emissions to CCl4 as well as a source of CCl4 from coal combustion smog."

7. P2 L30. Change to "8-year continuous high frequency, high precision atmospheric CCl4 concentrations measured. . .."

»> Changed

8. P3 L2. Change "below the " to "to the south of .."

»> Changed

9. P3 L7. I am not sure what do you mean by "well situated to allow monitoring of long-range transport from the surrounding region". Is this because of elevation or it is in remote clean ocean? By surrounding region, what regions are you referring to? China? The Korean Peninsula? Please clarify.

»> We now provide more explicit description of the station in the Supplementary Information as well as give more information in the figure caption (Fig. S1): "Gosan station (GSN, 33.25°N, 126.19°E, Jeju Island, Korea) located on the boundary between the Pacific Ocean and the Asian continent (Fig. S1) is characterized by warm wet East Asian Summer Monsoon and cold dry winter, and by distinct seasonal wind patterns with strong northern winds in winter, and southern influence during summer. These wind patterns are favorable for monitoring air masses passing through East Asia, especially China and Korea. Clean background conditions are observed when a clean stream of air flows in directly from northern Siberia in winter and during transport of southerly oceanic winds in summer (Fig. S2)."; "Fig. S1. The Gosan AGAGE (Advanced Global Atmospheric Gases Experiment) station is located atop a 72-m cliff (air intake elevation: 89 meter above sea level) on the remote south-western tip of Jeju Island, 100 km south of the Korean peninsula, allowing for monitoring of long-range transport from the surrounding region."

10. P3 L10. Please include the actual values than just say "high-precision and high frequency"

»> The data frequency has been given as "every two hours from 2008 to 2015" and the

experimental precision has also been stated in the sentence: “Precisions (1σ) derived from repeated analysis (n = 12) of a working standard of ambient air are better than 1 % of background atmospheric concentrations for all the compounds, e.g. $\pm$ 0.8 ppt (1σ) for 85.2 ppt of CCl4.”

11. P3 L22. You need to define what do you mean by “baseline values”. This is jargon.

»> We have added the following text in parentheses: “(i.e., background values representing regional clean condition without regional/local pollution events)”.

12. P4 L6-7. It would be good to add references here.

»> We’ve added the website http://eng.chinaiol.com/, where the locations of the main factories producing HFCs, HCFC-22 and fluorocarbons are given. The locations were also denoted in Fig. S9.

13. P7 L11. It is interesting that CFC-11 showed up in the source factor. Does this indicate that CFC-11 is also produced in the CM plants?

»> Given the fact that CFC-11 can be readily produced by the reaction of by-produced impurity, CCl4 with HF, the observed high contribution of CFC-11 in the fugitive emissions group is explainable in association with production of chloromethanes and their feedstock use for fluorinated compounds. For further comments regarding recent enhancements of CFC-11 observed at Gosan, please see the last response below.

14. P7. It will be of great value to CCl4 source identification to link the discussions in the source factors to the industrial production, usage, and potential emissions pathway in Sherry et al. (2017). Such a discussion will help to build link from bottom-up inventory-based estimate to atmospheric observation based top-down estimate.

»> Agreed. According to the reviewer’s suggestion, we’ve revised the conclusions to better discuss a link of the industrial sources identified from a factor analysis based on atmospheric observations to the SPARC bottom-up inventory-based estimations. The revised conclusions now read: “A factor analysis combining the observed con-

centration enhancements of 18 species was used to identify key industrial sources for CCl4 emissions and to link our atmospheric observation based top-down identification of potential sources with bottom-up inventory-based estimates (e.g., Liang et al., 2016; Sherry et al., 2017). Three major source categories accounting for 89$\pm$6 % of CCl4 enhancements observed at GSN were identified as advertent or inadvertent coproduction and escape of CCl4 from CH3Cl production plants (factor (A)) and during industrial C2Cl4 production (factor (C)), and fugitive emissions (factor (B)) from feedstock use for the production of other chlorinated compounds (e.g., CHCl3) and process agent use. These sources are largely consistent with the bottom-up CCl4 emissions pathways identified in SPARC (Liang et al., 2016). The SPARC estimate of global CCl4 emissions from chloromethanes and PCE plants (pathway B from Liang et al. (2016) and Sherry et al. (2018)) was 13 Gg yr-1, as the most significant source. Fugitive feedstock/process agent emissions, denoted as pathway A by Liang et al. (2016) and Sherry et al. (2018), were estimated to be $\sim$2 Gg yr-1. These emissions for pathways B and A had contributions from China of 6.6 Gg yr-1 and 0.7 Gg yr-1, respectively. If we assume that the emission rates from the sources correspond to the relative contributions of the corresponding source factors to the total Chinese emission rate (23.6$\pm$7.1 Gg yr-1 for the years 2011–2015), source factors (A), CCl4 emissions from chloromethane plants, and (C), emissions from PCE plants, amount to 13$\pm$4 Gg yr-1 for China. This is as high as the global bottom-up number of 13 Gg yr-1 for pathway B emissions, and more than 50% higher than Chinese estimate of 6.6 Gg yr-1. This could point to a higher than assumed ratio of CCl4 being emitted from these processes into the atmosphere, although factor (C) could possibly include influence of fugitive emissions as a chlorination feedstock for PCE production. Furthermore, also source factor (B), fugitive feedstock emissions are estimated at $\sim$7$\pm$2 Gg yr-1 from China alone, which again contrasts with Chinese estimate of $\sim$0.7 Gg yr-1 and even a lower global estimate of only 2 Gg yr-1 for pathway A from Liang et al. (2016) and Sherry et al. (2018).”

15. Figure 3 and related discussions. (1) I wonder if part of the difference between the

Vollmer et al., 2009 and this study is due to the location of Gosan vs. Shandianzi. The location of Gosan captures most of the outflow from the industrial central and south China, where all the CCl4 production industries are located (as suggested by Figure 2), while Shandianzi captures mostly the air influenced by N. China, without much CM production. Should consider add a related discussion on this in the manuscript.

»> Yes, this is an important point to mention. We agree with the reviewer that difference in the location of monitoring sites and thus in their footprint distributions of compounds of interest must be one of potential reasons for discrepancies found between emission estimates derived from different monitoring sites. Interestingly, however, the CCl4 emission rate of 16.8 $\pm$ 5.6 Gg yr-1 in 2008 we derived in this study was statistically consistent with the 2007 emission rate of 15 (10–22) Gg yr-1 given in Vollmer et al. (2009) within their uncertainties. The agreement could be coincidental, but it could also be consistent with the fact that even though the CM-related production facilities are more likely located in industrial central and south China (Fig 2 and Fig S9), the increase in both the feedstock production sector of CCl4 and emissions from CCl4 by-production was reported only since 2011, i.e. post-2010 (Bie et al., 2017: see Fig. 2 in the paper). In this respect, it is possible that the 2007 emission estimate derived from Shandianzi and the 2008 estimate from and Gosan were not much different, even if Shandianzi is known to capture mostly the air masses influenced by north China – covering most down to Shandong and Anhui for CCl4 (Vollmer et al., 2009) and to Jiangsu and Anhui for CO (An et al., 2014), and thus could possibly miss the influences from Henan, Hubei, and Guangdong provinces. Therefore, it seems that further discussion about potential differences in emissions estimate for CCl4 between Gosan vs. Shandianzi, particularly in relation to the location of CCl4 emission sources can be made when further analysis on the CCl4 data and results of post-2010 from Shandianzi are published.

Reference: An, X., Yao, B., Li, Y., Li, N., Lingxi Zhou, L.: Tracking source area of Shangdianzi station using Lagrangian particle dispersion model of FLEXPART, Meteo-

rol. Appl. 21: 466–473, 2014.

(2) The covariance of CFC-11 and CMs (source factor 2) is very interesting. Does this mean CFC-11 is also an intendended by-product during the industrial process and the recent increase in CFC-11 unreported emissions (Montzka et al. 2018) is to some extent linked to the CCl4 emissions increase in China between 2012-2016?

»> As we noted in response to the comment above regarding the high contribution of CFC-11 shown in the fugitive emissions group, CFC-11 can be readily produced by the reaction of by-produced impurity, CCl4 with HF and thus it would be possible that the observed high contribution of CFC-11 in the fugitive emissions group could be association with production of chloromethanes and their feedstock use for fluorinated compounds, whether it is intended or not Recent increase in unreported CFC-11 emissions discussed in Montzka et al. (2018) is indeed consistent with recent enhancements in CFC-11 pollution signals observed at Gosan (see figures below). It would also be possible that these enhancements might be associated with production of many fluorinated compounds using chloromethanes as feedstock and thus with persistent CCl4 emissions in East Asia, as shown in this study. This reviewer's question is one of the most important issues these days. So, if allowed we'd like to complete a separate analysis for CFC-11enhancements at Gosan and address this issue further in another manuscript.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2018-220/acp-2018-220-AC2-supplement.pdf

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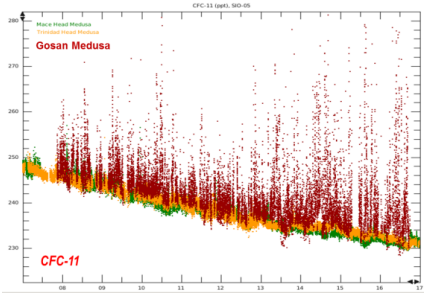
Gosan Medusa
CFC-11

Fig. 1.

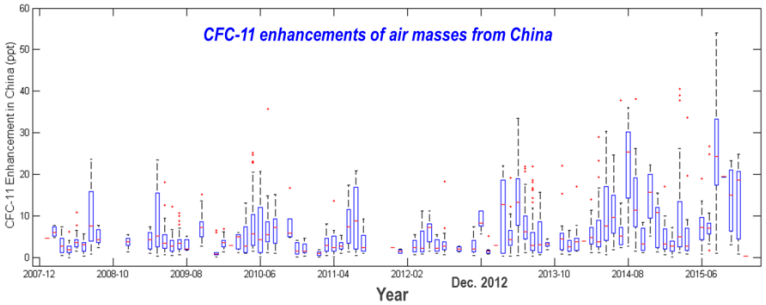
CFC-11 enhancements of air masses from China
CFC-11 Enhancement in China (ppt)
Year
Dec. 2012

Fig. 2.