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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

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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 #3: There has been a long-standing mystery of why the atmospheric concentration of carbon tetrachloride has declined much slower than predicted after its use was banned by the Montreal Protocol. The SPARC (2016) report resolved only part of this mystery by assessing a slightly longer atmospheric lifetime and by increasing estimates of industrial bottom-up emissions. However, a reconciliation of the top-down and bottom-up estimates was not achievable unless the error bars were stretched to their limits.

The present study by Park et al. utilizes high precision measurements of a suite of halocarbons at a background air monitoring station at Gosan, South Korea, to identify the origins of large fugitive emissions of CCl4 and to estimate their overall emission rates between 2008-2015. The analysis determines that emissions from heavily industrialized regions of China can account for roughly 24 +/- 7 Gg/yr CCl4 between 2011 and 2015 instead of the 4-5 Gg/yr reported bottom-up emissions rates. Surprisingly, emission rates do not seem to have declined over this time period. The additional 19 Gg/yr of fugitive emissions from China would account for over half of the global CCl4 emissions, and perhaps be enough to resolve the remaining mystery of carbon tetrachloride. Thus, this paper represents a very important scientific advance indeed.

The atmospheric measurements are of high quality and the method of using back air trajectories combined with empirical correlations with a reference compound (HCFC-22) is supported by an independent derivation of HCFC-22 emissions that agrees with prior estimates. The industrial source apportionment using the Positive Matrix Factorization (PMF) model yielded several strong relationships, pointing to multiple sources

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of CCl4 associated largely with emissions with other compounds. The interpretation is that the fugitive emissions are occurring at the factory level during production of various chlorocarbons. This seems highly plausible, as the production of these compounds are co-located, whereas the consumption of these compounds are expected to be more widely distributed.

Overall, the writing and figures are clear, and the methodology maximizes the functionality of a high quality dataset. I encourage the publication of this important work, with only a few minor edits suggested below.

1. Pg 2, line 6. The relevant soil sink reference is: Rhew & Happell, 2016, not Rhew et al., 2008.

»> Changed. Thanks much!

2. Pg 3, line 10. Here it would be helpful to have a reference or more description about the Gosan station. A brief description of the sample intake line, its height and its proximity to other major landscape features would be helpful details.

»> 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."

3. Pg 3, line 20. The authors should specify that the remote background station in the Northern Hemisphere is Mace Head, Ireland.

»> We've specified Mace Head station as a NH remote monitoring site (underlined words are the edits): "Note that the "background" concentrations at GSN agree well with the background concentrations observed at the Mace Head station (53°N, 10°W) in Ireland that represents a remote background monitoring station in the Northern Hemisphere and are declining at a similar rate to the global trend (Fig. S4)."

On a related note, it appears that no other AGAGE station comes anywhere close to the pollution level events that Gosan station experiences. Expressing this, perhaps in a quantitative way (standard deviation?) would add to the argument that the Gosan station is uniquely situated among the network to capture the primary region of fugitive emissions. After seeing the data published online from all the other stations, it seems clear that this is so.

»> A point well-taken. We've revised the description about the time series plot of the atmospheric CCl4 concentrations observed at Gosan (Fig. 1) in the section 2 (underlined words are the edits): "The 8-year observational record of CCl4 analyzed in this study is shown in Fig. 1. It is apparent that pollution events (red dots) with significant enhancements above "background" levels (black dots) occur frequently, resulting in daily variations of observed concentrations with relative standard deviations (RSDs) of 4–20% in contrast to the RSDs of 0.1–1.5% shown in all the remote stations operated under the AGAGE program. It clearly implies ongoing emission of CCl4 in East Asia."

4. Section 4. Although the time periods may differ, it may be useful to compare these results with some ground based measurements within China that are closer to the source regions. For example, prior studies have found very high concentrations of halocarbons in the Pearl River Delta region of China. Zhang et al., (JGR 115, D15309,2010)

measured elevated concentrations in 2007 and report “The high correlation between CCl4 and CFCs suggests that this source was more related to the production than the consumption of refrigerants.” How important is the Pearl River Delta region compared to other regions in the present study? It is difficult to assess based on the maps.

»> This is a good suggestion. The Pearl River Delta (PRD) region denoted by blue circles in Fig. S9 shown below is one of important source regions in China.

Referring to the reviewer’s comments on Zhang et al. (2010), we’ve added the following sentences after the discussion about the potential source distributions (Fig. S9) in the section 5 (5. Industrial source apportionment of atmospheric CCl4 in East Asia): “Our results are also consistent with a previous study on halocarbons observations in the Pearl River Delta region of Guangdong (Zhang et al., 2010), which revealed using a source profile analysis that the emissions of CFCs and CCl4 from an industrial source related to chemical (i.e., refrigerant) production increased by 1.4–2.0 times from 2001–2002 to 2007, even though atmospheric mixing ratios of these compounds did not change much for the 6 years. It implied increased use of CCl4 in chemical productions.”

5. Section 4. It would be interesting to see if CH3Br adds any clarity to the model – it is not shown in Figure 4 but shows a high correlation to many other compounds (Figure S5), including CCl4. CH3Br is also banned by the Montreal Protocol but has substantial natural as well as anthropogenic sources. As there are no major natural sources of CCl4, the elevated concentrations of CH3Br may be associated with previously unknown anthropogenic sources. It may be outside the scope of this particular paper, but it would be worth investigating if CH3Br is also emitted from CH3Cl production sites.

»> A very interesting suggestion. The time series of atmospheric CH3Br concentrations in 2008–2015 at Gosan shows below the continuous concentration enhancements as high as ∼30 ppt. As the reviewer mentioned, the observed enhancements of CH3Br are also in a high correlation to many other anthropogenic compounds (now shown in Fig. S6) but are in a poor correlation with CHBr3 (not shown) - an ocean

source tracer. This suggested negligible influence of oceanic source but consistent emissions from nearby fumigant-related source regions.

One previous study in my group estimated CH3Br emission from East Asia to be 6.5 (4.8–8.9) Gg yr-1 based on atmospheric CH3Br concentrations observed from Nov. 2007 to Dec. 2008 at Gosan (Li et al., 2011). This contributed to 50% of the global emission for 1996–2007 (13.8 Gg yr-1, Yvon-Lewis et al., 2009) from "fumigation-quarantine and pre-shipment" derived based on government and industry statistics (UNEP Methyl Bromide Technical Options Committee, 2006). Later, in a following study (Li et al., 2014) we applied a positive matrix factorization (PMF) model to the enhanced concentrations of 18 halogenated compounds including CH3Br obtained for the period from Nov. 2007 to Dec. 2011 and found that CH3Br was grouped in a separate factor from other compounds (see the left panel below). In addition, potential source region analysis revealed that the factor distinguished by a high contribution of CH3Br was predominant along the coastal area in Korea, Yangtze river delta region, and near the Vladivostok. Therefore, the high contribution of CH3Br in the factor was most likely explained by fumigation use in "quarantine" and "pre-shipment" treatments (QPS), which is exempt for all countries under the Montreal Protocol. Since we could not notice any change in the observed enhancements of CH3Br when comparing Nov. 2007–2011 vs. 2012–2015 data and thus expected a separate factor for QPS identified by dominant contribution of CH3Br in PMF results, we excluded CH3Br in the PMF analysis to simplify the results and to better focus on CCl4 related factors. Nonetheless, as the reviewer suggested, it must be worth monitoring if CH3Br could be categorized together with industrially-emitted chemical compounds in future.

Reference: Yvon-Lewis, S.A., Saltzman, E. S., Montzka, S. A.: Recent trends in atmospheric methyl bromide analysis of post-Montreal Protocol variability, Atmos. Chem. Phys., 9, 5963–5974, 2009.

6. Pg 9, line 4. The data repository for the Gosan dataset will need to be updated, as the website specified does not appear to have accessible data repositories.

»> We've updated the data repository by specifying the sub-folder on the website, http://agage.eas.gatech.edu/data_archive/agage/gc-ms-medusa/

7. Figure S1. The Gosan station should be highlighted with a larger symbol. Also: the dark blue obscures the text and border slightly.

»> The station location was emphasized with a star symbol. The border line and texts were moved in front of the plots to minimize their obscurity. While updating, we realized that the analysis period stated in the original figure caption was wrong, and it was corrected: "2008" to "2008-2015".

8. Figure S5: The color scheme helps, but the text is very hard to read. Please make the graphic large enough such that the numbers are readable. It appears that the image can potentially be increased 25% in size while still fitting in the margins. Subscripts can also be added to the left side labels.

»> The figure was updated by enlarging the image along with a bigger font size for numbers. The Y labels were also corrected with subscripts

9. Figure S7. Why is 2010 in bold and red? »> In developing countries, the regulations on production and consumption of CCl4 started to go into effect in 2010. We'd intended to indicate the phase-out year in yearly correlation slopes. The following sentence has been added in the figure caption: "Note that CCl4 production and consumption for dispersive applications in developing countries were phased out in 2010".

10. Figure S8. What do the colors of the legend indicate?

»> The unit of ppt was added in the color scale.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2018-220/acp-2018-220-AC3-supplement.pdf

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-220, 2018.

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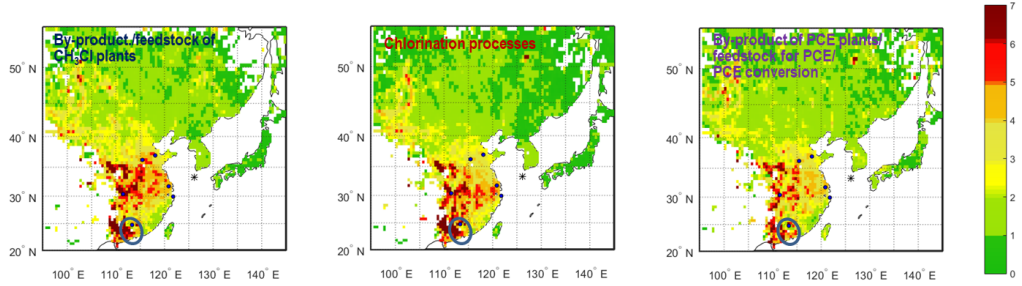

Fig. 1.

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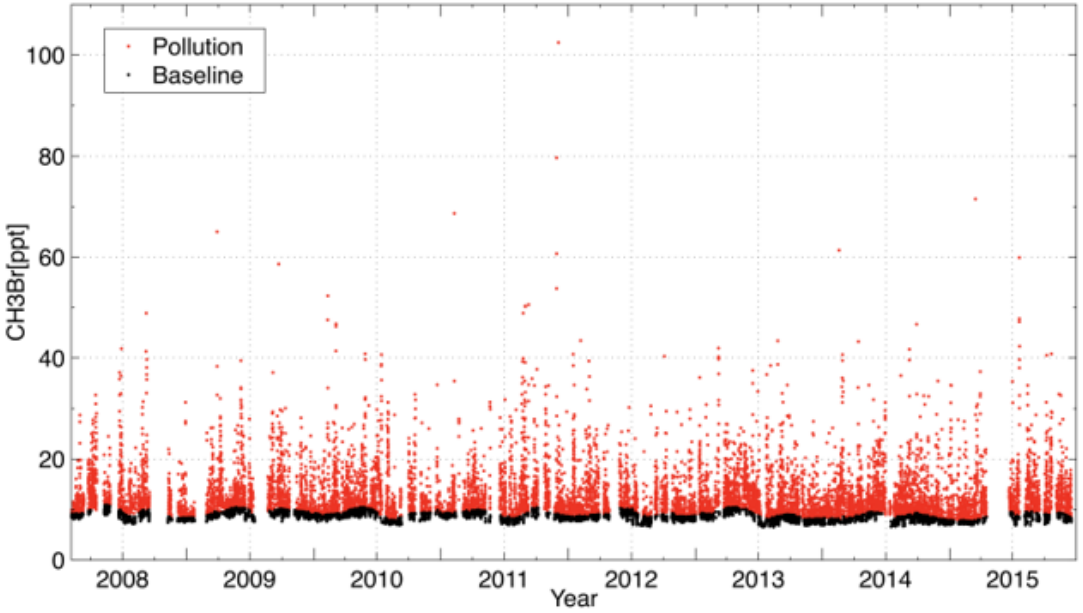

Fig. 2.

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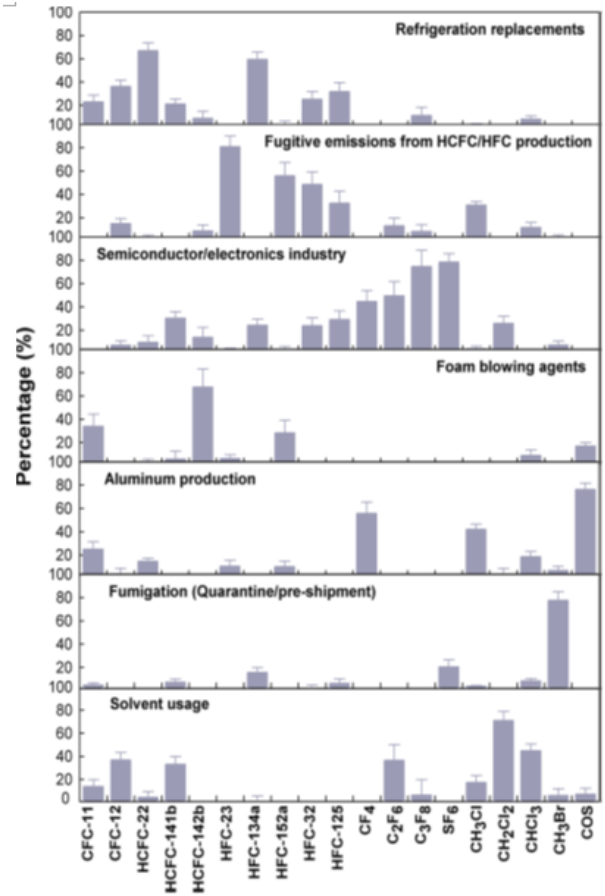

Fig. 3.

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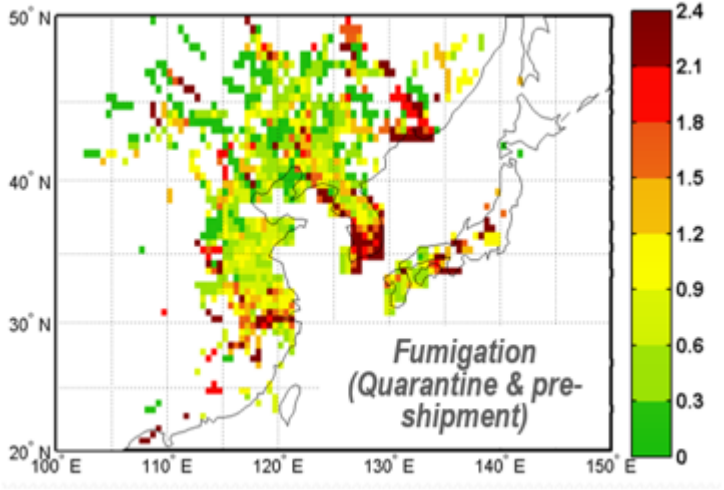

Fig. 4.

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