Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-220-RC3, 2018

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.

Anonymous Referee #3

Received and published: 2 May 2018

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 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.

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.

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

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.

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.

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.

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

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.

9. Figure S7. Why is 2010 in bold and red?

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

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