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. [In the following, Reviewers' comments are in bold Courier New and our responses and are in Time New Roman font]

Reviewer comments:

Referee #1:

Paper Summary: This paper uses observations from the Korean Gosan station to identify the location of CCl4 sources and the specific industrial processes involved with the CCl₄ emissions. There are two basic techniques used to analyze these data. First, trajectories are used in a source/receptor analysis technique to identify the CCl₄ emission locations. The major sources originate in Eastern China. Second, a positive matrix factorization (PMF) analysis technique is used to finger-print the specific sources of CCl_4 . This analysis reveals that the emissions are primarily from chloromethane production (CH_3Cl) , perchloroethylene production, and fugitive emissions from feedstock usages. These estimates are larger than those from the SPARC CCl₄ report, with the fugitive emissions being 10x larger than SPARC!

Review Summary: This is an excellent paper that NEEDS to be published. My overall comments are with regard to improving the writing in the paper and some of the structure.

Paper Suggestions:

While the paper mentions the SPARC (2016) CCl_4 report, there ought to be more discussion of how this paper seems to resolve the discrepancy between their emissions based upon measurements. SPARC had a top-down emissions calculation of 40 ± 15 Gg/y, a hemispheric gradient method of 30 ± 5 Gg/y, and a regional emission

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estimates of 21.4 ± 7.5 Gg/y. The SPARC regional 21.4 Gg/y had a 15 Gg/y contribution from China. The higher estimate herein of 24 Gg/y from China would bring this 21.4 SPARC number up to 30 Gg/y - in precise agreement with the gradient method and within the uncertainties of the 40 Gg/y top down estimate.

>>> Yes, we agree with the reviewer. This is an important point to mention and we have included the following sentences in the second paragraph of the Conclusions section: "Liang et al. (2016) estimated global top-down emissions as 35 ± 16 Gg yr⁻¹, which was an average estimate based on the estimate of 40 ± 15 Gg yr⁻¹ for the new 33-year total lifetime of CCl4 and an independent top-down method using the observed inter-hemispheric gradient in atmospheric concentrations which yielded 30 ± 5 Gg yr⁻¹. The SPARC sum of regional emissions was estimated as 21 ± 8 Gg yr⁻¹, of which Chinese emissions of 15 (10–22) Gg yr⁻¹ contributed 71 \pm 33% to the total amount, but this result is still lower than the aggregated top-down values. However, if we employ the higher emission estimate of 23.6 ± 7.1 Gg yr⁻¹, which is largely in agreement with the best global emissions estimate of 35 ± 16 Gg yr⁻¹ determined by Liang et al. (2016)."

The discussion in the summary of the CC14 sources should be broken out with more definitive statements. The SPARC report used industrial estimates to characterize potential sources and this paper provides the [Sherry et al., 2016], **first observational basis** for these sources, but this paper also makes the case that Sherry et al. is perhaps too conservative in their estimates.

>>> This comment is also very helpful. The factors were re-named as (A), (B), (C) and so on, and their descriptions in the section of "Industrial source apportionment of atmospheric CCl₄ in East Asia" were also updated to make it easier to compare them to the SPARC report, as suggested by reviewers 1 and 2. The figure legends in Fig. 4 were changed accordingly.

As suggested, 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 concentration 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 bottomup 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 being related to advertent or inadvertent co-production and escape of CCl₄ from CH₃Cl production plants (factor (A)),escape during industrial PCE 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, and possibly from other chloromethanes use in chemical manufacturing. 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/CCl₄ 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 as ~2 Gg yr⁻¹. The emissions contributions from China to pathways B and A were 6.6 Gg yr⁻¹ and 0.7 Gg yr⁻¹, respectively (Liang et al., 2016; Sherry et al., 2018).

If we assume that emission rates from sources correspond to the relative contributions of corresponding source factors to the total Chinese emission rate $(23.6 \pm 7.1 \text{ Gg yr}^{-1} \text{ for the years } 2011-2015)$, source factors (A) (CCl₄ emissions from chloromethane plants) and (C) (emissions from PCE plants) amount to $13 \pm 4 \text{ Gg yr}^{-1}$ 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 the Chinese estimate of 6.6 Gg yr⁻¹. This could represent that the ratio of CCl₄ emissions from these processes into the atmosphere may be higher than previously assumed, although factor (C) could possibly include the influence of fugitive emissions of CCl₄ when using as a chlorination feedstock for PCE production. Furthermore, source factor (B) (fugitive feedstock/process agent emissions) are estimated at ~7 ± 2 Gg yr⁻¹ from China alone, which again contrasts with the Chinese estimate of ~0.7 Gg yr⁻¹ and even with the lower global estimate of only 2 Gg yr⁻¹ for pathway A from Liang et al. (2016) and Sherry et al. (2018)."

The paper is fairly well written, but many of the current paragraphs need to be broken up into more distinct sections or primary thoughts. The extended paragraphs of the current version obscure the thoughts, logic of the paper, and the overall content of the text.

>>> Based on the reviewer's perspective, we realized that discussions should have been better structured in various places in the previous version breaking a long body of paragraph by a single topic. We do think the revised manuscript has been improved according to reviewer's suggestions. Thanks for the reviewer's editorial comments!

For example, the 2nd para of the Introduction (P2, 4-30) talks about top down emissions, bottom up emissions....I would break this up into paras on: 1) top down emissions (4-12); 2) a SPARC bottom up para (12-16); and 3) a discussion of regional emissions.

>>> As the reviewer suggested, we divided this long paragraph into three to make it easier to follow. First, we started with a discussion about the updated bottom-up emissions in the SPARC

report, and introduced the global top-down and hemispheric gradient top-down emissions, pointing out that the revised bottom-up estimate of 25 Gg yr⁻¹ is still lower than the average SPARC-merged top-down emission estimate of 35 ± 16 Gg yr⁻¹. Then we added the summed regional emissions estimate from Australia, East Asia, U.S. and Western Europe, and mentioned its lowering than the global total and the relative significance of East Asia contribution.

In the 1st para of section 3 (P. 4 line 18 to P.5 line 32 - 46 lines!), there are a broad range of paragraph thoughts. The paragraph starts with a discuss of the interspecies correlation and ends with a thought on an underestimate of Chinese emissions. Please break this up to improve the flow of the text.

>>> We have broken up the original, long paragraph, which is now in section 4 of the revised version, into four paragraphs corresponding to "introduction to an interspecies correlation method", "a reference compound and its emission estimate", "determination of the empirical correlations between the observed enhancements of CCl₄ and reference, HCFC-22" and "comparison of the annual CCl₄ emissions in China estimated in present study with previous results".

The "Data Overview" section both discusses the data and shows results. I would restructure sections 2 and 3 into: a data, methods, and results sections. The Supporting Information ought to flow better into these data and methods sections.

>>> We have completely restructured section 2 of the manuscript by breaking it up into two subsections (2.1. Measurements of CCl₄ at Gosan and 2.2. Results), and one independent section (3. Potential source regions of CCl₄ in East Asia). The new section 3 is comprised of three paragraphs: introduction to trajectory statistics as a tool to illustrate the regional distribution of potential CCl₄; input data and conditions for calculation; and description of the resulting map of potential source areas. We've also added specific information on corresponding SI text accordingly in the new section 3. Air mass source country classification that had been discussed in the last paragraph of Data overview section in the original manuscript, now moved to the beginning of section 4, as a transitional paragraph to the following country-specific emission analysis.

Again, break up the single paragraph of the conclusions into short paragraphs. The main messages are lost in this "run-on" paragraph.

>>> We have re-organized the conclusions with four short paragraphs. We hope this can convey ideas more clearly to readers. For the text revision, please see the earlier response.

Figures are good. For Fig. 4, put some vertical lines on the plot to see how the bars line up with chemical names at the bottom.

>>> Done

Fig. S5. What are the colors for? Do they indicate statistical significance?

>>> We now say in the figure caption: "The colors by shade indicate statistical significance."

Referee #2:

Park et al presented a top-down emissions estimate of CC14 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 observational evidence that unreported CC14 atmospheric 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 bottom-up estimates, independent top-down CCl₄ emission studies have used the total lifetime of CCl₄ with atmospheric observations (i.e., the observed decline rate of CCl₄ concentrations) and atmospheric transport models to derive "top-down" emission 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 from 2000 to 2012 when using the newly determined relative strength of oceanic sink versus 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 <u>estimates for China of 4.3 (1.9–8.0) Gg yr⁻¹ in</u> 2011 and 5.2 (2.4–8.8) Gg yr⁻¹ in 2014, which updated the previous zero emissions estimate (Wan et al., 2009) by including the conversion of C₂Cl₄ emissions to CCl₄ as well as the 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) is located on the boundary between the Pacific Ocean and the Asian continent (Fig. S1), which experiences a warm wet East Asian Summer Monsoon, a cold dry winter, and distinct seasonal wind patterns (strong northern winds in winter and a southern influence during summer). These wind patterns are favorable for monitoring air masses passing through East Asia, particularly through 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**. Gosan AGAGE (Advanced Global Atmospheric Gases Experiment) station is located on a 72-m cliff (air intake elevation: 89 m 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 air mass 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 (1 σ) 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. ± 0.8 ppt (1 σ) 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 conditions without regional/local pollution events, black dots)".

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

>>> We've added the website <u>http://eng.chinaiol.com/</u>, 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 concentration 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 bottomup 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 being related to advertent or inadvertent co-production and escape of CCl4 from CH3Cl production plants (factor (A)), escape during industrial PCE 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, and possibly from other chloromethanes use in chemical manufacturing. 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/CCl₄ 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 as ~2 Gg yr⁻¹. The emissions contributions from China to pathways B and A were 6.6 Gg yr⁻¹ and 0.7 Gg yr⁻¹, respectively (Liang et al., 2016; Sherry et al., 2018).

If we assume that emission rates from sources correspond to the relative contributions of corresponding source factors to the total Chinese emission rate $(23.6 \pm 7.1 \text{ Gg yr}^{-1} \text{ for the years } 2011-2015)$, source factors (A) (CCl₄ emissions from chloromethane plants) and (C) (emissions from PCE plants) amount to $13 \pm 4 \text{ Gg yr}^{-1}$ 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 the Chinese estimate of 6.6 Gg yr⁻¹. This could represent that the ratio of CCl₄ emissions from these processes into the atmosphere may be higher than previously assumed, although factor (C) could possibly include the influence of fugitive emissions of CCl₄ when using as a chlorination feedstock for PCE production. Furthermore, source factor (B) (fugitive feedstock/process agent emissions) are estimated at ~7 ± 2 Gg yr⁻¹ from China alone, which again contrasts with the Chinese estimate of ~0.7 Gg yr⁻¹ and even with the 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 CC14 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 ± 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, Meteorol. 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 byproduced 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.



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 CC14 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 back trajectories combined with of using air 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 CC14 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 colocated, 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

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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) is located on the boundary between the Pacific Ocean and the Asian continent (Fig. S1), which experiences a warm wet East Asian Summer Monsoon, a cold dry winter, and distinct seasonal wind patterns (strong northern winds in winter and a southern influence during summer). These wind patterns are favorable for monitoring air masses passing through East Asia, particularly through 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**. Gosan AGAGE (Advanced Global Atmospheric Gases Experiment) station is located on a 72-m cliff (air intake elevation: 89 m 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 air mass 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): "The background concentrations at GSN were determined using the statistical method detailed in O'Doherty et al. (2001), and they agree well with those observed at <u>the Mace Head station (53°N, 10°W) in Ireland (which is representative of a remote background monitoring station in the Northern Hemisphere)</u> 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) occurred 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). These results clearly imply that CCl₄ emissions are emanating from East Asia."

4. Section 4. Although the time periods may differ, it may be results useful compare these with some ground based to 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 Delta region compared Pearl River 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 those of a previous study on halocarbons observations in the Pearl River Delta region of Guangdong (Zhang et al., 2010), which used a source profile analysis to reveal that CFCs and CCl4 emissions 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 there were no significant changes in the atmospheric mixing ratios of these compounds for the 6 years. These results imply the increased use of CCl₄ in chemical production."

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 CC14. 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 CC14, the elevated concentrations of CH3Br may associated with previously be 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, <u>http://agage.eas.gatech.edu/data_archive/agage/gc-ms-medusa/</u>

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.

Toward resolving the budget discrepancy of ozone-depleting carbon tetrachloride (CCl₄): An analysis of top-down emissions from China

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Abstract. Carbon tetrachloride (CCl₄) is a first-generation ozone-depleting substance, and its emissive use and production were 15 globally banned by the Montreal Protocol with a 2010 phase-out; however, production and consumption for non-dispersive use as a chemical feedstock and as a process agent are still allowed. This study uses the high frequency and magnitude of CCl₄ pollution events from an 8-year real-time atmospheric measurement record obtained at Gosan station (a regional background monitoring site in East Asia) to present evidence of significant unreported emissions of CCl₄. Top-down emissions of CCl₄ amounting to 23.6 ± 7.1 Gg yr⁻¹ from 2011 to 2015 are estimated for China, in contrast to the most recently reported, post-2010,

- 20 Chinese bottom-up emissions of 4.3–5.2 Gg yr⁻¹. The missing emissions (~19 Gg yr⁻¹) for China contribute to approximately 54% of global CCl₄ emissions. It is also shown that 89 \pm 6% of CCl₄ enhancements observed at Gosan are related to CCl₄ emissions from the production of CH₃Cl, CH₂Cl₂, CHCl₃, and C₂Cl₄ (PCE) and its usage as a feedstock and process agent in chemical manufacturing industries. Specific sources and processes are identified using statistical methods, and it is considered highly unlikely that CCl₄ is emitted by dispersive uses such as old landfills, contaminated soils, and solvent usage. It is thus
- crucial to implement technical improvements and better regulation strategies to reduce evaporative losses of CCl_4 occurring at the factory and/or process level.

1. Introduction

Carbon tetrachloride (CCl₄) is a long-lived greenhouse gas and an ozone-depleting substance. Its emissive use, production, and consumption are regulated under the Montreal Protocol on Substances that Deplete the Ozone Layer and its Amendments (MP).

- 30 After reaching a peak in the early 1990s, the atmospheric abundance of CCl_4 has been decreasing at a rate of -4.9 ± 0.7 ppt Cl yr⁻¹ (Carpenter et al., 2014) due to the phase-out of CCl_4 use in MP non-Article-5 (developed) countries by 1995. MP Article-5 (developing) countries, including China, were required to cease CCl_4 production and consumption for dispersive applications by 2010. However, CCl_4 production and consumption for non-dispersive use (e.g., as chemical feedstock and as a process agent) continues to be allowed, and thus CCl_4 is still produced and consumed alongside the increasing production of non-ODS
- 35 chemicals (Carpenter et al., 2014). At present, the global bottom-up CCl_4 emissions derived from reporting countries are 3 (0–8) Gg yr⁻¹ for 2007–2013 (Carpenter et al., 2014; Liang et al., 2016).

The recent SPARC report (Liang et al., 2016) updated bottom-up anthropogenic CCl_4 emissions to at most 25 Gg yr⁻¹ in 2014, based on re-consideration of industrial production processes plus usage (15 Gg yr⁻¹), and the upper-limit estimate of 10 Gg yr⁻¹ for the potential escape from legacy sites and unreported inadvertent emissions (Sherry et al., 2017).

- To verify these bottom-up estimates, independent top-down CCl_4 emission studies have used the total lifetime of CCl_4 with atmospheric observations (i.e., the observed decline rate of CCl_4 concentrations) and atmospheric transport models to derive "top-down" emission estimates. Using the most current estimates for the lifetime of CCl_4 in the atmosphere, soil, and ocean (Liang et al., 2016; Rhew and Happell, 2016; Butler et al., 2016), global top-down emissions to the atmosphere were calculated as 40 ± 15 Gg yr⁻¹ from 2007 to 2014 (Liang et al., 2016). A recent top-down study based upon the observed temporal trend and inter-hemispheric gradient of atmospheric CCl_4 (Liang et al., 2014) consistently derived global CCl_4 emissions of 30 ± 5 Gg yr⁻¹
- from 2000 to 2012 when using the newly determined relative strength of oceanic sink versus soil loss (Liang et al., 2016). Therefore, the best estimate of global emissions from top-down methods is 35 ± 16 Gg yr⁻¹, which is significantly higher than reported emissions of 3 Gg yr⁻¹, even when considering large uncertainties relating to soil and ocean CCl₄ sinks (and how those sinks might change over time). Although the revised bottom-up estimate of 25 Gg yr⁻¹ mentioned above contributes considerably to closing the gap between bottom-up and top-down emission estimates, this new bottom-up value is still lower than the average
- SPARC-merged top-down emission estimate of 35 ± 16 Gg yr⁻¹ (though the uncertainty is large). The discrepancy between bottom-up and top-down emission estimates implies the existence of unidentified sources and/or unreported industrial emissions. Regional studies of episodic enhancements of CCl₄ above atmospheric background concentrations observed in several regions using inverse model techniques, have suggested emissive fluxes of 0.11 ± 0.04 Gg yr⁻¹ in 2009–2012 from Australia (Fraser et al., 2014), 15 (10–22) Gg yr⁻¹ in 2007 from East Asia (Vollmer et al., 2009), 4 (2–6.5) Gg yr⁻¹ in 2008–2012 from the U.S. (Hu et al., 2014), 15 (10–22) Gg yr⁻¹ in 2007 from East Asia (Vollmer et al., 2009), 4 (2–6.5) Gg yr⁻¹ in 2008–2012 from the U.S. (Hu et al., 2014), 15 (10–22) Gg yr⁻¹ in 2007 from East Asia (Vollmer et al., 2009), 4 (2–6.5) Gg yr⁻¹ in 2008–2012 from the U.S. (Hu et al., 2014), 15 (10–22) Gg yr⁻¹ in 2007 from East Asia (Vollmer et al., 2009), 4 (2–6.5) Gg yr⁻¹ in 2008–2012 from the U.S. (Hu et al., 2014), 15 (10–22) Gg yr⁻¹ in 2007 from East Asia (Vollmer et al., 2009), 4 (2–6.5) Gg yr⁻¹ in 2008–2012 from the U.S. (Hu et al., 2014), 15 (10–22) Gg yr⁻¹ in 2007 from East Asia (Vollmer et al., 2009), 4 (2–6.5) Gg yr⁻¹ in 2008–2012 from the U.S. (Hu et al., 2014), 15 (10–22) Gg yr⁻¹ in 2007 from East Asia (Vollmer et al., 2009), 4 (2–6.5) Gg yr⁻¹ in 2008–2012 from the U.S. (Hu et al., 2014), 15 (10–20) Gg yr⁻¹ in 2007 from East Asia (Vollmer et al., 2009), 4 (2–6.5) Gg yr⁻¹ in 2008–2012 from the U.S. (Hu et al., 2014), 15 (10–20) Gg yr⁻¹ in 2007 from East Asia (Vollmer et al., 2009), 4 (2–6.5) Gg yr⁻¹ in 2008–2012 from the U.S. (Hu et al., 2014), 15 (10–20) Gg yr⁻¹ in 2008–2012 from the U.S. (Hu et al., 2014), 15 (10–20) Gg yr⁻¹ in 2008–2012 from the U.S. (Hu et al., 2014), 15 (10–14) (Hu et al., 2014), 15 (10–14) (Hu et al., 2014), 15 (10–14) (Hu et al., 2014) (Hu
- 20 2016), and 2.3 ± 0.8 Gg yr⁻¹ in 2006–2014 from Western Europe (Graziosi et al., 2016). The summed emissions were estimated to total 21 ± 8 Gg yr⁻¹ (Liang et al., 2016), with the most significant contribution belonging to East Asia. As the sum of regional emissions quantified to date has not accounted for global top-down emissions, an improved quantification of regional/countryscale and industry-based CCl₄ emissions is required to gain a better insight into the causes of the discrepancy between the regional sums and the global top-down estimate. This would improve our understanding of the unidentified and/or unreported
- 25 industrial emission sources and would help to establish practical and effective regulation strategies. With the aim of resolving the apparent CCl₄ budget discrepancy, this study presents an estimate of regional CCl₄ emissions from China, one of the MP Article 5 countries in East Asia. Due to its recent and ongoing strong industrial growth, current emissions and changes in emission patterns are of special interest. In addition, recent studies based on atmospheric monitoring have consistently reported a significant increase in the emissions of most halocarbons in China (Vollmer et al., 2009, Kim et al., 2010,
- 30 Li et al., 2011). Top-down estimates of Chinese emissions for CCl₄ have been made in previous studies using a Lagrangian inverse model based on ground-based monitoring data (Vollmer et al., 2009) and an interspecies correlation method based on aircraft observations (Palmer et al., 2003; Wang et al., 2014). The estimates made in these studies were quite variable with 17.6 \pm 4.4 Gg yr⁻¹ in 2001 (Palmer et al., 2003), 15 (10–22) Gg yr⁻¹ in 2007 (Vollmer et al., 2009) and 4.4 \pm 3.4 Gg yr⁻¹ in 2010 (Wang et al., 2014), and these studies were conducted prior to the complete phase-out of CCl₄ production for emissive applications in
- China came into effect in 2010. 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 the previous zero emissions estimate (Wan et al., 2009) by including the conversion of C₂Cl₄ emissions to CCl₄ as well as the source of CCl₄ from coal combustion smog.
 In this study, we present an 8-year record of continuous, high frequency, high-precision, atmospheric CCl₄ concentrations measured at the Gosan station (33° N, 126° E) on Jeju Island, Korea for 2008–2015. Using a tracer-tracer correlation method (Li
- 40 et al., 2011) based on a top-down interpretation of atmospheric observations, we estimate yearly emission rates of CCl₄ for China

and examine changes in these rates following the scheduled phase-out for CCl_4 in 2010. Gosan station monitors air masses arriving from a variety of different regions (Kim et al., 2012), and the emission footprints of these cover an area from northeastern China down to south of the Yangtze River, which is the most industrialized region in China. We also analyze the measurements of 17 other anthropogenic compounds to identify key industrial sources of CCl_4 emissions and their potential locations using a Positive Matrix Factorization model in combination with trajectory statistics (Li et al., 2014).

5

2. Data overview

2.1. Measurements of CCl₄ at Gosan

Gosan station (GSN) is located on the remote south-western tip of Jeju Island, which lies to the south of the Korean peninsula (72 m above sea level), and is well situated for monitoring long-range air mass transport from surrounding regions (Fig. S1).
Wind patterns at GSN are typical of the Asian Monsoon, with strong predominant north-westerly and north-easterly continental outflows of polluted air from fall through to spring, clean continental air flowing directly from northern Siberia in winter, and pristine maritime air from the Pacific in summer (Fig. S2). High-precision and high-frequency measurements of 40 halogenated compounds including CCl₄ were made continuously every two hours from 2008 to 2015 using a gas chromatography-mass spectrometer (GC-MS) coupled with an online cryogenic pre-concentration system ("Medusa") (Miller et al., 2008) as part of the

15 Advanced Global Atmospheric Gases Experiment (AGAGE) program. Precisions (1 σ) derived from repeated analysis (*n* = 12) of a working standard of ambient air were better than 1 % of background atmospheric concentrations for all compounds, e.g. \pm 0.8 ppt (1 σ) for 85.2 ppt of CCl₄. The measurements are mostly on calibration scales developed at the Scripps Institution of Oceanography (SIO).

20 2.2 Results

The 8-year observational record of CCl_4 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) occurred 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). These results clearly imply that CCl_4 emissions are emanating from

- East Asia. The background concentrations at GSN were determined using the statistical method detailed in O'Doherty et al. (2001), and they agree well with those observed at the Mace Head station (53°N, 10°W) in Ireland (which is representative of a remote background monitoring station in the Northern Hemisphere) and are declining at a similar rate to the global trend (Fig. S4). The magnitude of pollution data analyzed in this study was defined as the observed enhancements (red dots in Fig. 1) in concentration units above the baseline values (i.e., background values representing regional clean conditions without
- 30 regional/local pollution events, black dots), to exclude the influence of trends and/or variability in background levels from the analysis.

3. Potential source regions of CCl₄ in East Asia

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A statistical analysis combining enhanced concentrations (above-baseline concentrations) of CCl_4 from 2008 to 2015, with corresponding back trajectories, enabled identification of the regional distribution of potential CCl_4 emission sources. The statistical method (see "Trajectory Statistics" in SI) was first introduced in 1994 (Seibert et al., 2004) and has previously been applied to analyses relating to halogenated compounds (e.g., Li et al., 2014; Reimann et al., 2004).

An elevated concentration at an observation site is proportionally related to both the average concentration in each grid cell over which the corresponding air mass has travelled and the air mass trajectory residence time in the grid cell. This allows the method to compute a residence-time-weighted mean concentration for each grid cell by simply superimposing the back trajectory domain on the grid matrix. We used 6-day kinematic backward trajectories arriving at a 500 m altitude above the measurement site that

- 5 were calculated using the HYbrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model of the NOAA Air Resources Laboratory (ARL) based on meteorological information from the Global Data Assimilation System (GDAS) model with a 1°×1° grid cell (Li et al., 2014). The residence times were calculated using the methods of Poirot and Wishinski (1986). To eliminate low confidence level areas, we applied a point filter that removed grid cells that had less than 12 overpassing trajectories (Reimann et al., 2004).
- 10 The resulting map of potential source areas for CCl₄ in East Asia (Fig. 2) shows that emission sources are widely distributed in China, but they are particularly concentrated in north eastern China and south-central China (approximately Shandong, Henan, Hubei, and Guangdong provinces). These provinces include industrialized urban areas that conduct intensive industrial activities, such as chemical manufacturing (<u>http://eng.chinaiol.com/</u>). It is of note that this statistical analysis has little sensitivity to emissions from southwest China, due to the limits of the typical 5- to 6-day back-trajectory domain of the HYSPLIT model.
- 15 Additionally, this method tends to underestimate the inherently sharp spatial gradients in the vicinity of emission hot-spots, because its calculation scheme distributes the measured concentrations evenly throughout grid cells over which a trajectory has passed (Stohl, 1996). Nonetheless, it is clear that the CCl₄ emission sources from East Asia were predominantly located in China.

4. Using observed interspecies correlations to estimate country-based, top-down CCl₄ emissions in China

- To identify pollution events influenced solely related toy Chinese emissions, we classified an event as "Chinese" if the 6-day
 kinematic back trajectories arriving at GSN had entered the boundary layer (as defined by HYSPLIT) only within the Chinese domain, which was defined as a regional grid of 100–124°E and 21–45°N (Fig. S5(a)). This analysis classified 29% of all observed CCl₄ pollution events from 2008 to 2015 (Fig. S5(b)) as "Chinese". An additional 46% were affected by Chinese domain plus another country's; however, these blended air masses were excluded from the determination of Chinese emissions.
- For the Chinese emissions estimate of CCl₄, we use an interspecies correlation method, analogously to many recent emission studies (e.g., Kim et al., 2010; Li et al., 2011; Palmer at al., 2003; Wang et al., 2014). In this method, the emission rate of a comeasured compound of interest can be inferred based on its compact empirical correlation with a reference compound whose country-scale emission has been independently well-defined. This empirical ratio approach provides a simple yet comprehensive method for estimating regional emissions of almost all halogenated compounds measured at GSN, and it minimizes the uncertainties inherent in more complex modeling schemes. This method is particularly useful for compounds such as CCl₄,
- 30 where the associated bottom-up inventories indicate close to zero emissions and/or clearly have large errors, which thus makes it difficult to adequately define the prior emissions required for inverse modeling. However, the ratio method is restricted by its core assumptions: that the emissions of the reference and target compounds are co-located (or at least well mixed) until they reach the measurement site, and that the reference emissions are well-known. The interspecies ratios we observed at GSN showed statistically significant correlations for many compounds at national scales (Li et al., 2011), suggesting that overall these
- 35 core assumptions were satisfied in this study.

An adequate reference compound should be a widely used industrial species with high national emission rates, thereby allowing for robust and compact correlations with many other species and low uncertainties in its own emission estimate. The reference compound was chosen by examining the observed relationships of CCl_4 enhancements above baseline versus the enhancements

above baseline for 25 other halocarbons in air masses classified as "Chinese". We found that the $\Delta CCl_4/\Delta HCFC-22$ ratio (0.13 ppt/ppt) showed one of the most significant correlations ($R^2 = 0.72$, p < 0.01) (Fig. S6). Furthermore, given that China has been the largest producer and consumer of HCFCs since 2003, and that production of HCFC-22 accounts for more than 80% of all Chinese HCFC production (UNEP, 2009), HCFC-22 is the best-suited reference compound for use with China. Additionally,

- 5 strong Chinese HCFC-22 emissions have been determined from atmospheric observations and inverse modeling in previous studies (Kim et al., 2010; Li et al., 2011; Stohl et al., 2010; An et al., 2012; Fang et al., 2012), with estimates ranging from 46 to 146 Gg yr⁻¹ over the period 2007–2009. Our estimates of annual HCFC-22 emissions in China for 2008–2015 were independently derived from atmospheric measurements at GSN using an inverse technique based on FLEXible PARTicle dispersion model (FLEXPART) Lagrangian transport model analysis (Stohl et al., 2010; Fang et al., 2014), and ranged from 89
- 10 Gg yr⁻¹ in 2011 to 144 Gg yr⁻¹ in 2015. The uncertainty in the top-down estimates was 30%, which mainly related to an assumed uncertainty of \pm 50% in annual prior emissions used for the inversion calculation (Fig. S7). Next, we used empirical correlations between observed enhancements of CCl₄ and HCFC-22 (Δ CCl₄/ Δ HCFC-22; annual slopes shown in Fig. S8) to estimate CCl₄ emission rates. The interspecies slopes were determined based on observed enhancements obtained by subtracting regional background values from the original observations, to avoid potential underestimation of the
- 15 slopes due to the high density of low background values (following Palmer et al. (2003)). Estimated uncertainties for our CCl₄ emission estimates comprise the emissions uncertainty of HCFC-22 and an uncertainty associated with the Δ HCFC-22/ Δ CCl₄ slope, which was calculated using the Williamson-York linear least-squares fitting method (Cantrell, 2008), considering measurement errors of both HCFC-22 and CCl₄.
- Figure 3 provides the annual CCl₄ emissions in China for the years 2008–2015, which were calculated based on our interspecies
- 20 correlation method, and also shows a comparison between our results and previous estimates of CCl_4 emissions from China. The CCl_4 emission rate of 16.8 ± 5.6 Gg yr⁻¹ in 2008 found in this study is consistent with 2001 (Palmer et al., 2003) and 2007 (Vollmer et al., 2009) top-down emissions estimates of 17.6 ± 4.4 Gg yr⁻¹ and 15 (10-22) Gg yr⁻¹, respectively. To obtain those results, Palmer et al. (2003) used observed correlations of CCl_4 with CO as a tracer to investigate CCl_4 emissions in aircraft observations of the Asian plume over a two-month period (March to April) in 2001, and Vollmer et al. (2009) estimated the 2007
- 25 emissions using an inverse model based on atmospheric measurements taken from late 2006 to early 2008 at an inland station (Shangdianzi, 40°N, 117°E) located in the North China Plain. Wang et al. (2014) obtained aircraft measurements over the Shandong Peninsula on July 22 and October 27 in 2010 and from March to May in 2011, and estimated CCl₄ emission in 2010 based on observed correlations of CCl₄ with both CO and HCFC-22. However, the estimates from these two different tracers differed by ~100 % (8.8 versus 4.4 Gg yr⁻¹) and were much lower than the two previous results of Palmer et al. (2003) and
- 30 Vollmer et al. (2009) and our 2010 estimate of 32.7 ± 5.1 Gg yr⁻¹. Although the cause of this discrepancy is unclear, it is considered that it could be related to the low numbers of observations obtained in the aircraft campaigns and to difficulties defining regional background values and extracting pollution signals from the aircraft data. It is also possible that the results mostly represent emissions from northern China. Extrapolating to the entire country using data from northern China would lead to an underestimate of emissions, as most industrial activities occur in the south-central and eastern parts of China.
- Our estimates show that Chinese emissions increased sharply before reaching a maximum in 2009–2010 (with a range of 38.2 ± 5.5 to 32.7 ± 5.1 Gg yr⁻¹) immediately prior to the scheduled phase-out of CCl₄ by 2010. The sudden large increase could be attributed to uncontrolled use/production leading to emissions of stored CCl₄ before the scheduled restrictions came into effect. Interestingly, this increase in our emission estimates was also consistent with the increase of about 20 Gg yr⁻¹ in the total annual production of CCl₄ in China from 2008 to 2010, which was mainly related to an increase in the feedstock production sector, i.e.,
- 40 raw material production for non-ODS chemicals (Bie et al., 2017). After a dip in 2012, our estimated emissions in 2013–2015

remain stable and are similar overall to those in 2011, with no statistically discernible differences between these years. It is of note that the average emission rate estimated in this study of 23.6 ± 7.1 Gg yr⁻¹ for the years 2011–2015 is significant, as post-2010 bottom-up emissions of CCl₄ in China have been reported as near zero (Wan et al., 2009), and even the most up-to-date bottom-up estimates (Bie et al., 2017) have indicated emissions of only 4.3 (1.9–8.0) Gg yr⁻¹ in 2011 and 5.2 (2.4–8.8) Gg yr⁻¹ in

5 2014. These discrepancies between bottom-up and top-down emission estimates may suggest that emissions of CCl₄ from either non-regulated feedstock/process agent use, or unreported non-feedstock emissions from the production of chloromethanes (CH₃Cl, CH₂Cl₂,CHCl₃) and PCE, are larger than expected.

5. Industrial source apportionment of atmospheric CCl₄ in East Asia

The Positive Matrix Factorization (PMF) Model was used to characterize key industrial CCl₄ sources based solely on atmospheric observations (Paatero and Tapper, 1994). We included all CCl₄ enhancement events observed at GSN thereby representing better characterization of emission sources throughout East Asia and not just in China. The PMF model has been widely used to identify and apportion sources of atmospheric pollutants (Guo et al., 2009; Lanz et al., 2009, Li et al., 2009; Choi et al., 2010), and is an optimization method that uses a weighted least squares regression to obtain a best fit to the measured concentration enhancements of chemical species (details in SI text) and to resolve the number of "source factors" controlling the observations. A brief mathematical expression of the model is given by Eq. (1),

$$x_{ik} = \sum_{i=1}^{p} g_{ij} f_{ik} + e_{ik} (i = 1, 2, ..., m; j = 1, 2, ..., p; k = 1, 2, ..., n),$$
(1)

where x_{ik} represents enhanced concentrations in the time series of the *i*th compound at the *k*th sampling time; g_{ij} is the concentration fraction of the *i*th compound from the *j*th source; f_{jk} is the enhanced concentration from the *j*th source contributing to the observation at the *k*th time, which is given in ppt; e_{ik} is the model residual for the *i*th compound concentration measured in the

- 20 *k*th sampling time; and *p* is the total number of independent sources (i.e., the number of factors) (Paatero and Tapper, 1994). The number of source factors is an optimal value determined based on the R-squared that measures how close the predicted concentrations are to the observed enhancements of 18 species (including not only CCl₄, major CFCs, HCFCs, HFCs, PFCs, SF₆, carbonyl sulfide (COS), but also CH₃Cl, CH₂Cl₂, CHCl₃, and PCE) to account for the potential chemical intermediate release of CCl₄ during industrial activities. The model's R-squared values, as estimated from a correlation plot between the measured and
- 25 PMF model-predicted concentrations, showed that an eight-source model is most appropriate, suggesting eight potential source categories for those 18 species. Each source factor is defined based on the source profile (i.e., relative abundances of individual species). The percentage contributions of factors to the observed enhancements of individual compounds are shown in Fig 4. Uncertainties were determined from the 1σ standard deviation of factor contributions from 5 sets of 20 runs (total 100 replications) (Reff et al., 2007).
- 30 Factor (A) shown in the Fig. 4 is characterized by $38 \pm 4\%$ of CCl₄ and $97 \pm 2\%$ of CH₃Cl, suggesting advertent or inadvertent co-production and escape of CCl₄ during chloromethane generation in chemical plants (see SI text for chemical reactions). CCl₄ and CH₃Cl co-emitted in smog from coal combustion (Li et al., 2003) are less likely to be the source of this factor because COS, which is a major coal burning tracer, does not contribute to this factor. Source factor (B) is largely related to fugitive emissions in feedstock and process agent use of various compounds; it accounts for a large fraction of CCl₄ ($32 \pm 4\%$) and shows high
- 35 percentages for several compounds: $72 \pm 18\%$ of CH₂Cl₂, $59 \pm 11\%$ of CHCl₃, $39 \pm 10\%$ of CFC-11, and $51 \pm 12\%$ of HFC-23. It is of note that CH₂Cl₂ and CHCl₃ can be produced as by-products of chlorination along with CCl₄ and are used as intermediates or solvents in chemical manufacturing. CCl₄ is a feedstock for PCE, HFC, methyl chloride, and divinyl acid chloride production (Liang et al., 2016) and is also used in CFC production (Zang et al., 2010; Sherry et al., 2018). In addition,

 $CHCl_3$ can be used as a feedstock for HCFC-22 production (Montzka et al., 2011), which is consistent with factor (B) also being distinguished by a high contribution of HFC-23: Chinese emissions of HFC-23 account for ~70% of total global emissions (Kim et al., 2010; Li et al., 2011) and it is a typical by-product of HCFC-22 generation (Fang et al., 2015). HFC-23 is thus emitted at factory level in regions where chemical manufacturing industries are heavily collocated. Overall, the fact that observed

- 5 enhancements of HFC-23, CCl₄, CH₂Cl₂, CHCl₃, and CFC-11 are grouped together into the factor (B) in the PMF analysis implies that this factor most likely represents fugitive emissions of these compounds occurring at the factory level during various chemical manufacturing processes in China. Source factor (C) is distinguished by $19 \pm 1\%$ of CCl₄ and $95 \pm 2\%$ of PCE; it can possibly be explained by advertent or inadvertent co-production and escape of CCl₄ during industrial C₂Cl₄ production and in part by fugitive emissions of CCl₄ used as a chlorination feedstock for C₂Cl₄ production.
- 10 The spatial distributions (Fig. S9) of source factors (A), (B), and (C) derived from trajectory statistics (SI text) are similar and cover areas in and around Guangzhou of Guangdong, Wuhan of Hubei, Zhengzhou of Henan, and Xian of Shaanxi province. These distributions are consistent with the results of PMF analysis, which confirms that CCl_4 emissions from China are more strongly associated with industrial processes than with population density. Our results are also consistent with those of a previous study on halocarbons observations in the Pearl River Delta region of Guangdong (Zhang et al., 2010), which used a source
- 15 profile analysis to reveal that CFCs and CCl₄ emissions 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 there were no significant changes in the atmospheric mixing ratios of these compounds for the 6 years. These results imply the increased use of CCl₄ in chemical production. The three emission source factors (A–C), which account for 89 ± 6% of CCl₄ enhancements observed at GSN, are thus considered to be mostly escaped CCl₄ emissions at the factory level relating to inadvertent by-production, feedstock usage
- 20 for production of chlorinated compounds, and process agent use for chemical processes. Other factors of PMF analysis relate to (D) primary aluminum production (Blake et al., 2004), (E) HFCs production/applications, (F) refrigerant consumption, (G) processes in the semiconductor/electronics industry, and (H) foam blowing agent use, and can mostly be summarized as being distributed emissions. However, the percentage contributions of these other source factors to CCl₄ enhancements are not statistically significant when considering the uncertainty range. The smallest contribution to CCl₄ of
- 25 the sources characterized as general consumption and legacy release could suggest that CCl₄ emissions from old landfills, contaminated soil, and solvent usage have become less significant. A detailed description of factors D–H is provided in the Supporting Information section.

6. Conclusions

An 8-year record of atmospheric CCl₄ observations obtained at GSN provided evidence of ongoing CCl₄ emissions from East 30 Asia during 2008–2015. Based on these measurements, this paper presents a top-down CCl₄ emissions estimate from China of 23.6 \pm 7.1 Gg yr⁻¹ for the years 2011–2015, which is different to a bottom-up estimate of 4.3–5.2 Gg yr⁻¹ given by most current bottom-up emission inventories for post-2010 China.

Liang et al. (2016) estimated global top-down emissions as 35 ± 16 Gg yr⁻¹, which was an average estimate based on the estimate of 40 ± 15 Gg yr⁻¹ for the new 33-year total lifetime of CCl₄ and an independent top-down method using the observed inter-

35 hemispheric gradient in atmospheric concentrations which yielded 30 ± 5 Gg yr⁻¹. The SPARC sum of regional emissions was estimated as 21 ± 8 Gg yr⁻¹, of which Chinese emissions of 15 (10–22) Gg yr⁻¹ contributed $71 \pm 33\%$ to the total amount, but this result is still lower than the aggregated top-down values. However, if we employ the higher emission estimate of 23.6 ± 7.1 Gg yr⁻¹ obtained for China in this study, the summed regional estimate would be 30 ± 10 Gg yr⁻¹, which is largely in agreement with the best global emissions estimate of 35 ± 16 Gg yr⁻¹ determined by Liang et al. (2016).

A factor analysis combining the observed concentration enhancements of 18 species was used to identify key industrial sources for CCl_4 emissions and to link our atmospheric observation-based top-down identification of potential sources with bottom-up

- 5 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 being related to advertent or inadvertent co-production and escape of CCl₄ from CH₃Cl production plants (factor (A)),escape during industrial PCE 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, and possibly from other chloromethanes use in chemical manufacturing. These sources are largely consistent with the bottom-up
- 10 CCl₄ emissions pathways identified in SPARC (Liang et al., 2016). The SPARC estimate of global CCl₄ emissions from chloromethanes and PCE/CCl₄ 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 as ~2 Gg yr⁻¹. The emissions contributions from China to pathways B and A were 6.6 Gg yr⁻¹ and 0.7 Gg yr⁻¹, respectively (Liang et al., 2016; Sherry et al., 2018).
- 15 If we assume that emission rates from sources correspond to the relative contributions of corresponding source factors to the total Chinese emission rate ($23.6 \pm 7.1 \text{ Gg yr}^{-1}$ for the years 2011–2015), source factors (A) (CCl₄ emissions from chloromethane plants) and (C) (emissions from PCE plants) amount to $13 \pm 4 \text{ Gg yr}^{-1}$ 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 the Chinese estimate of 6.6 Gg yr⁻¹. This could represent that the ratio of CCl₄ emissions from these processes into the atmosphere may be higher than previously assumed, although
- factor (C) could possibly include the influence of fugitive emissions of CCl_4 when using as a chlorination feedstock for PCE production. Furthermore, source factor (B) (fugitive feedstock/process agent emissions) are estimated at ~7 ± 2 Gg yr⁻¹ from China alone, which again contrasts with the Chinese estimate of ~0.7 Gg yr⁻¹ and even with the lower global estimate of only 2 Gg yr⁻¹ for pathway A from Liang et al. (2016) and Sherry et al. (2018). Although the analysis provided here may contain uncertainties, it appears that the SPARC industry-based bottom-up emissions are underestimated. Therefore, improvements in
- estimating industry bottom-up emissions of CCl_4 , particularly at the factory and/or process level, are crucial for gaining a better understanding and evaluation of ongoing global emissions of CCl_4 .

Data used in this study are available from http://agage.eas.gatech.edu/data_archive/agage/gc-ms-medusa/.

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References

10

- An, X. Q., Henne, S., Yao, B., Vollmer, M. K., Zhou, L. X., Li Y.: Estimating emissions of HCFC-22 and CFC-11 in China by atmospheric observations and inverse modeling, Sci. China Chem, 55, 10, 2233–2241, https://doi.org/10.1007/s11426-012-4624-8, 2012.
- 5 Bie P., Fang X., Li Z., Hu J.: Emissions estimates of carbon tetrachloride for 1992-2014 in China, Environ. Poll., 224, 670–678, https://doi.org/10.1016/j.envpol.2017.02.051, 2017.
 - Blake, N. J., Streets, D. G., Woo, J. H., Simpson, I. J., Green, J., Meinardi, S., Kita, K., Atlas, E., Fuelberg, H. E., Sachse, G., Avery, M. A., Vay, S. A., Talbot, R. W., Dibb, J. E., Bandy, A. R., Thornton, D. C., Rowland, F. S., Blake, D. R.: Carbonyl sulfide and carbon disulfide: Large-scale distributions over the western Pacific and emissions from Asia during TRACE-P, J. Geophys. Res., 109 (D15), https://doi.org/10.1029/2003JD004259, 2004.
 - Butler, J. H., Yvon-Lewis, S. A., Lobert, J. M., King, D. B., Montzka, S. A., Bullister, J. L., Koropalov, V., Elkins, J. W., Hall,
 B. D., Hu, L., and Liu, Y.: A comprehensive estimate for loss of atmospheric carbon tetrachloride (CCl₄) to the ocean,
 Atmos. Chem. Phys., 16, 10899–10910, https://doi.org/10.5194/acp-16-10899-2016, 2016.
- Cantrell, C. A.: Technical Note: Review of methods for linear least-squares fitting of data and application to atmospheric chemistry problems, Atmos. Chem. Phys., 8, 5477–5487, https://doi.org/10.5194/acp-8-5477-2008, 2008.
- Carpenter, L. J., Reimann, S., Burkholder, J. B., Clerbaux, C., Hall, B. D., Hossaini, R., Laube, J. C., and Yvon-Lewis, S. A.: Ozone-Depleting Substances (ODSs) and other gases of interest to the Montreal Protocol, in: Scientific Assessment of Ozone Depletion: 2014. Global Ozone Research and monitoring Project – Report N. 55, World Meteorological Organization, Geneva, Switzerland, 2014.
- 20 Chen, Z. L., Yang B.: Study on the conversion technology of carbon tetrachloride, Organo-Fluorine Ind., 1, 48–53 (In Chinese with English Abstract), 2013
 - Choi, E., Heo, J. B., Yi, S. M.: Apportioning and locating nonmethane hydrocarbon sources to a background site in Korea, Environ. Sci. Technol., 44, 15, 5849–5854, https://doi.org/10.1021/es903634e, 2010.
- Fang, X., Wu, J., Su, S., Han, J., Wu, Y., Shi, Y., Wan, D., Sun, X., Zhang, J., Hu, J.: Estimates of major anthropogenic
 halocarbon emissions from China based on interspecies correlations, Atmos. Environ., 62, 26–33, https://doi.org/10.1016/j.atmosenv.2012.08.010, 2012.
 - Fang, X., Thompson, R. L., Saito, T., Yokouchi, Y., Kim, J., Li, S., Kim, K. R., Park, S., Graziosi, F., and Stohl, A.: Sulfur hexafluoride (SF6) emissions in East Asia determined by inverse modeling, Atmos. Chem. Phys., 14, 4779–4791, https://doi.org/10.5194/acp-14-4779-2014, 2014.
- 30 Fang, X., Stohl, A., Yokouchi, Y., Kim, J., Li, S., Saito, T., Park, S., Hu, J.: Multiannual top-down estimate of HFC-23 emissions in East Asia, Environ. Sci. Tech., 49, 7, 4345–4353, https://doi.org/10.1021/es505669j, 2015.
 - Fang, X., Velders, G. J. M., Ravishankara, A. R., Molina, M. J., Hu, J., Prinn, R. G.: Hydrofluorocarbon (HFC) emissions in China: An inventory for 2005–2013 and projections to 2050, Environ. Sci. Tech., 50, 4, 2027–2034, https://doi.org/10.1021/acs.est.5b04376, 2016.
- 35 Fraser, P., Dunse, B., Manning, A., Wang, R., Krummel, P., Steele, P., Porter, L., Allison, C., O'Doherty, S., Simmonds, P., Mühle, J., Prinn, R.: Australian carbon tetrachloride (CCl₄) emissions in a global context, Environ. Chem., 11, 77-88, doi.org/10.1071/EN13171, 2014.
 - Graziosi, F., Arduini, J., Bonasoni, P., Furlani, F., Giostra, U., Hermanssen, O., Lunder, C., Manning, A. J., McCulloch, A., O'Doherty, S. J., Reimann, S., Vollmer, M. K., Maione, M.: Emissions of carbon tetrachloride (CCl₄) from Europe, Atmos. Chem. Phys., 16, 12849–12859, 2016.

40

- Guo, H., Ding, A. J., Wang, T., Simpson, I. J., Blake, D. R., Barletta, B., Meinardi, S., Rowland, F. S., Saunders, S. M., Fu, T. M., Hung, W. T., Li, Y. S.: Source origins, modeled profiles, and apportionments of halogenated hydrocarbons in the greater Pearl River Delta region, southern China, J. Geophys. Res.: Atmos., 114, D11302, 2156–2202, http://doi.org/10.1029/2008JD011448, 2009.
- 5 Hu, L., Montzka, S. A., Miller, B. R., Andrews, A. E., Miller, J. B., Lehman, S. J., Sweeney, C., Miller, S., Thoning, K., Siso, C., Atlas, E., Blake, D., de Gouw, J. A., Gilman, J. B., Dutton, G., Elkins, J. W., Hall, B. D., Chen, H., Fischer, M. L., Mountain, M., Nehrkorn, T., Biraud, S. C., Moore, F., Tans, P. P.: Continued emissions of carbon tetrachloride from the U.S. nearly two decades after its phase-out for dispersive uses, Proc. Natl. Acad. Sci., 113, 2880-2885, doi:10.1073/pnas.1522284113, 2016.
- Kim, J., Li S., Kim K. R., Stohl A., Muhle J., Kim S. K., Park M. K., Kang D. J., Lee G., Harth C. M., Salameh P. K., Weiss R.
 F.: Regional atmospheric emissions determined from measurements at Jeju Island, Korea: Halogenated compounds from China, Geophys. Res. Lett., 37, L12801, https://doi.org/10.1029/2010GL043263, 2010.
 - Kim, J., Li, S., Mühle, J., Stohl, A., Kim, S. K., Park, S., Park, M. K., Weiss, R. F., Kim, K. R.: Overview of the findings from measurements of halogenated compounds at Gosan (Jeju Island, Korea) quantifying emissions in East Asia, Environ. Sci.,
- 15 9, 1, 71–80, https://doi.org/101080/194315X.2012.696548, 2012.
 - Lanz, V. A., Henne, S., Staehelin, J., Hueglin, C., Vollmer, M. K., Steinbacher, M., Buchmann, B., and Reimann, S.: Statistical analysis of anthropogenic non-methane VOC variability at a European background location (Jungfraujoch, Switzerland), Atmos. Chem. Phys., 9, 3445–3459, https://doi.org/10.5194/acp-9-3445-2009, 2009.
- Li, S., Kim, J., Kim, K. R.: Emissions of halogenated compounds in East Asia determined from measurements at Jeju Island,
 Korea, Environ. Sci. Technol., 45, 13, 5668–5675, https://doi.org/10.1021/es104124k, 2011.
 - Li, S., Kim, J., Park, S., Kim, S. K., Park, M. K., Mühle, J., Lee, G., Lee, M., Jo, C. O., Kim, K. R.: Source identification and apportionment of halogenated compounds observed at a remote site in East Asia, Environ. Sci. Tech., 48, 1, 491–498, https://doi.org/10.1021/es402776w, 2014.
 - Li, X., Wang, S., Duan, L., Hao, J.: Characterization of non-methane hydrocarbons emitted from open burning of wheat straw and corn stover in China, Environ. Res. Lett., 4, 044015, 2009.
 - Montzka, S. A., and Reimann S.: Ozone-Depleting Substances 1.90 (ODSs) and related chemicals, Chapter 1 in Scientific Assessment of Ozone Depletion: 2010, Global Ozone Research and Monitoring Project—Report No. 52, World Meteorological Organization, Geneva, Switzerland, 2011.
 - Li, S., Park, M. K., Jo, C. O., Park, S. J.: Emission estimates of methyl chloride from industrial sources in China based on high
- 30 frequency atmospheric observations, J. Atmos. Chem. 74, 2, 227–243, https://doi.org/10.1007/s10874-016-9354-4, 2017.
 - Liang, Q., Newman, P. A., Daniel, J. S., Reimann, S., Hall, B. D., Dutton, G., Kuijpers L. J. M.: Constraining the carbon tetrachloride (CCl₄) budget using its global trend and inter-hemispheric gradient, Geophys. Res. Lett., 41, 5307–5315, doi:10.1002/2014GL060754, 2014.
- Liang, Q. Newman, P. A., Reimann, S. (Eds.), SPARC Report on the Mystery of Carbon Tetrachloride. SPARC Report No. 7, WCRP-13/2016, 2016.
 - Miller, B. R., Weiss, R. F., Salameh, P. K., Tanhua, T., Greally, B. R., Mühle, J., Simmonds, P. G.: Medusa: A sample preconcentration and GC/MS detector system for in situ measurements of atmospheric trace halocarbons, hydrocarbons, and sulfur compounds, Anal. Chem., 80, 5, 1536–1545, https://doi.org/10.1021/ac702084k, 2008.
 - Mühle, J., Ganesan, A. L., Miller, B. R., Salameh, P. K., Harth, C. M., Greally, B. R., Rigby, M., Porter, L. W., Steele, L. P., Trudinger, C. M., Krummel, P. B., O'Doherty, S., Fraser, P. J., Simmonds, P. G., Prinn, R. G., and Weiss, R. F.:

40

25

Perfluorocarbons in the global atmosphere: tetrafluoromethane, hexafluoroethane, and octafluoropropane, Atmos. Chem. Phys., 10, 5145–5164, https://doi.org/10.5194/acp-10-5145-2010, 2010.

- O'Doherty, S., Simmonds, P. G., Cunnold, D. M., Wang, H. J., Sturrock, G. A., Fraser, P. J., Ryall, D., Derwent, R. G., Weiss, R.
 F., Salameh, P., Miller, B. R., Prinn, R. G.: In situ chloroform measurements at Advanced Global Atmospheric Gases
 Experiment atmospheric research stations from 1994 to 1998, J. Geophys. Res.: Atmos., 106, D17, 20429–20444,
- Paatero, P., Tapper, U.: Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values, Environ., 5, 111–126, https://doi.org/10.1002/env.3170050203, 1994.
- Palmer P. I., Jacob, D. J., Mickley, L. J., Blake, D. R., Sachse, G. W., Fuelberg, H. E., Kiley, C. M.: Eastern Asian emissions of
- 10 anthropogenic halocarbons deduced from aircraft concentration data, J. Geophys. Res., 108, 4753, D24, https://doi.org/10.1029/2003JD003591, 2003.
 - Poirot, R. L., Wishinski, P. R.: Visibility, sulfate and air-mass history associated with the summertime aerosol in northern Vermont, Atmos. Environ, 20, 7, 1457–1469, https://doi.org/10.1016/0004-6981(86)90018-1, 1986.
 - Reff, A., Eberly, S.I., Bhave, P.V.: Receptor modeling of ambient particulate matter data using positive matrix factorization:
- 15 review of existing methods, J. Air & Waste Manage. Assoc., 57, 2, 146–154, https://doi.org/10.1080/10473289.2007.10465319, 2012.
 - Reimann S., Schaub, D., Stemmler, K., Folini, D., Hill, M., Hofer, P., Buchmann, B., Simmonds, P. G., Greally, B. R., O'Doherty, S.: Halogenated greenhouse gases at the Swiss High Alpine Site of Jungfraujoch (3580 m asl): Continuous measurements and their use for regional European source allocation, J. Geophys. Res., 109, D05307J, https://doi.org/10.1080/10473289.2007.10465319109, 2004.
 - Rhew, R. C., Miller, B. R., Weiss, R. F.: Chloroform, carbon tetrachloride and methyl chloroform fluxes in southern California ecosystems, Atmos. Environ., 42, 30, 7135–7140, https://doi.org/10.1016/j.atmosenv.2008.05.038, 2008.
 - Rhew, R. C., and Happell, J. D.: The atmospheric partial lifetime of carbon tetrachloride with respect to the global soil sink, Geophys. Res. Lett., 43, 2889-2895, doi:10.1002/2016GL067839, 2016.
- 25 Seibert, P., Kromp-Kolb, H., Baltensperger, U., Jost, D. T., Schwikowski, M.: Trajectory analysis of aerosol measurements at high Apline sites, in: Transport and transformation of pollutants in the troposphere, Borrell, P.M., T. Cvitaš, W. Seiler (Eds.), Academic Publishing, Den Haag, 689–693, 2008.
 - Sherry, D., McCulloch, A., Liang, Q., Reimann, S., Newman, P.A.: Current sources of carbon tetrachloride in our atmosphere, Environ. Res. Lett., 13, 2, https://doi.org/10.1088/1748-9326/aa9c87, 2018.
- Stohl, A.: Trajectory statistics: A new method to establish source receptor relationships of air pollutants and its application to the transport of particulate sulfate in Europe, Atmos. Environ., 30, 4, 579–587, https://doi.org/10.1016/1352-2310(95)00314-2, 1995.
 - Stohl, A., Kim, J., Li, S., O'Doherty, S., Mühle, J., Salameh, P. K., Saito, T., Vollmer, M. K., Wan, D., Weiss, R. F., Yao, B., Yokouchi, Y., and Zhou, L. X.: Hydrochlorofluorocarbon and hydrofluorocarbon emissions in East Asia determined by inverse modeling, Atmos. Chem. Phys., 10, 3545–3560, https://doi.org/10.5194/acp-10-3545-2010, 2010.
 - Vollmer, M. K., Zhou, L. X., Greally, B. R., Henne, S., Yao, B., Reimann, S., Stordal, F., Cunnold, D. M., Zhang, X. C., Maione, M., Zhang, F., Huang, J., Simmonds, P. G., Emissions of ozone-depleting halocarbons from China, Geophys. Res. Lett., 36, 15, http://dx.doi.org/10.1029/2009GL038659, 2009.
 - Wang, C., Shao, M., Huang, D., Sihua, L., Zeng, L., Hu, M., Zhang, Q.: Estimating halocarbon emissions using measured ratio
 relative to tracers in China, Atmos. Environ., 89, 816–826, https://doi.org/10.1016/j.atmosenv.2014.03.025, 2014.

40

35

5

20

https://doi.org/10.1029/2000JD900792, 2001.

- Wan, D., Xu, J., Zhang, J., Tong, X., Hu, J.: Historical and projected emissions of major halocarbons in China, Atmos. Environ., 43, 36, 5822–5829, https://doi.org/10.1016/j.atmosenv.2009.07.052, 2009.
- United Nations Environment Programme (UNEP 2009) Ozone Secretariat Data Access Centre; http://ozone.unep.org/reporting/, last access: 11 February 2018.
- 5 Zhang, Y. L., Guo, H., Wang, X. M., Simpson, I. J., Barletta, B., Blake, D. R., Meinardi, S., Rowland, F. S., Cheng, H. R., Saunders, S. M., Lam, S. H. M.: Emission patterns and spatiotemporal variations of halocarbons in the Pearl River Delta region, southern China, J. Geophys. Res., 115, D15309, doi:10.1029/2009JD013726., 2010.

Figure Captions

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Figure 1. Atmospheric CCl_4 concentrations observed from 2008 to 2015 at Gosan station (GSN, 33°N, 126°E) on Jeju Island, Korea. Pollution events (identified as significant enhancements in concentrations from background levels shown in black) are denoted by red dots.

5 **Figure 2**. Distribution of potential source regions calculated from trajectory statistics for enhancement data of CCl₄ observed from 2008 to 2015. The color code (in ppt) denotes a residence-time-weighted mean concentration for each grid cell. The resulting map of potential source areas for CCl₄ shows that emission sources are widely distributed over China. The site of Gosan station is indicated by an asterisk (*).

Figure 3. CCl_4 emissions in China as determined by an inter-species correlation method. A comparison between our results and 10 previous estimates for Chinese emissions is also shown. Note that emissions reached a maximum in 2009–2010 in concurrence with the scheduled phase-out of CCl_4 by 2010, but the average annual emission rate of 23.6 ± 7.1 Gg yr⁻¹ for the years 2011–2015 are still substantial.

Figure 4. Source profiles derived from PMF analysis for 18 compounds, including CCl₄, CFCs, HCFCs, HFCs, PFCs, SF₆, COS, CH₃Cl, CH₂Cl₂, CHCl₃, and C₂Cl₄. The PMF analysis is performed on the time series of enhanced concentrations. The y-axis shows the percentage of all observed enhancements associated with each factor (with 1 σ standard deviation) such that the vertical sum for each species listed on the x-axis is 100.

Figure 1.





Figure 2.





Supporting Information

Toward resolving the budget discrepancy of ozone-depleting CCl₄: An analysis of

top-down emissions from China

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Gosan station

Gosan station (GSN, 33.25°N, 126.19°E, Jeju Island, Korea) is located on the boundary between the Pacific Ocean and the Asian continent (Fig. S1), which experiences a warm wet East Asian Summer Monsoon, a cold dry winter, and distinct seasonal wind patterns (strong northern winds in winter and a southern influence during summer). These wind patterns are favorable for monitoring air masses passing through East Asia, particularly through 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. Gosan AGAGE (Advanced Global Atmospheric Gases Experiment) station is located on a 72-m cliff (air intake elevation: 89 m above sea level) on the remote south-western tip of Jeju Island, 100 km south of the Korean peninsula, allowing for monitoring of longrange air mass transport from the surrounding region.

Trajectory residence time

Residence time trajectory analyses are used extensively to identify source locations and preferred transport pathways of atmospheric trace elements and particulate species (Ashbaugh et al., 1985). Residence times are calculated by the following equation,

$$\tau_{abk} = \sum_{k=1}^{n} \sum_{h=1}^{l} (S_{abkh} / v_{kh})$$
 S(1)

where τ_{abk} is the total residence time for all trajectories over grid cell *a*, *b*; S_{abkh} is the length of that portion of the h^{th} segment of the k^{th} trajectory over the grid cell *a*, *b*; and v_{kn} is the average speed of the air parcel as it travels along the h^{th} segment of the k^{th} trajectory.

The residence time analysis shown in Fig. 2S suggests that the major air masses arriving at Gosan station (GSN) vary seasonally, with predominantly northwesterly and northeasterly continental outflows from fall through spring, and flows of clean air directly from the Pacific in summer and from northern Siberia in winter.



Fig. S2. Residence time analysis for 2008–2015 using 6-day back-trajectories arriving at Gosan station. Seasonal residence time distributions show a distinctive seasonally-varying wind pattern.



Fig. S3. Distribution of averaged residence times of air masses arriving at Gosan for the years 2008–2015. Residence times of over 24 h occurred over both northeastern continental regions and the central southern part of China. The asterisk denotes Gosan measurement station.



Fig. S4. 8-year observation records for CCl₄ analyzed in this study shown as red points (also shown in Fig. 1). For comparison, corresponding observations taken at the Mace Head station (53°N, 10°W) in Ireland are represented using blue points. Note that the "background" concentrations from GSN agree well with the baseline values at Mace Head station, a background station in the Northern Hemisphere, and are declining at a similar rate to its global trend.

Trajectory Statistics

To identify potential CCl_4 source regions, we applied statistical analysis coupled with back trajectories to the time series of observed enhancements in CCl_4 concentrations from 2008 to 2015. The trajectory statistics method has often been applied to estimate the potential source areas of air pollutants (Reimann et al. 2004), and the underlying assumption of this method is that elevated concentrations at an observation site are proportionally related to both the average concentrations in a specific grid cell over which the observed air mass has passed and the residence time of the air mass over that grid cell. Thus, the method simply computes a residence-time-weighted mean concentration for each grid cell by superimposing the back-trajectory domain on the grid matrix. The formula is given by,

$$\overline{C}_{ab} = \frac{\sum_{i=1}^{n} (\tau_{abi}C_i)}{\sum_{i=1}^{n} \tau_{abi}}$$
S(2)

where C_i is the enhanced concentration of CCl₄ at a given i^{th} time; τ_{abi} is the residence time of the trajectory arriving at Gosan at the i^{th} time spent over grid cell *a*, *b* (in 0.5° x 0.5°) within the atmospheric boundary layer; and \overline{C}_{ab} represents the relative strength of the cell *a*, *b* as a potential source region of CCl₄. Back trajectories were calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model of the NOAA Air Resources Laboratory (ARL) using meteorological information from the Global Data Assimilation System (GDAS) model with $1^{\circ} \times 1^{\circ}$ grid cell. The HYSPLIT model was run using 6-day backward trajectories at 500-m altitude above the measurement site. The residence times were calculated using the method of Poirot and Wishinski (1986). To eliminate low confidence level areas, a point filter was applied that removed grid cells over which less than 12 trajectories had passed (Reimann et al. 2004).

This trajectory statistics method can also be applied to illustrate the potential location of each source factor determined from the Positive Matrix Factorization (PMF) analysis. The formula is identical to Eq. S(2) in all respects, except that it uses the normalized strength of each source factor. The enhanced concentrations from the j^{th} source contribute to the observation at the k^{th} time (which is denoted as " f_{jk} " of Eq. (1) in main text). Since the f_{jk} values from all eight sources cover a very wide range of concentrations, the f_{jk} values can be normalized against their time average for the j^{th} source, with the aim of not biasing the statistical significance of one source against the others. Therefore, the normalized time series of f_{jk} values were defined as

$$mjk = fjk / (\sum_{k=1}^{n} fjk) / n$$
S(3)

Eq. S(2) was modified to the following,

$$\overline{m}_{abj} = \frac{\sum_{k=1}^{n} (\tau_{abk} m_{jk})}{\sum_{k=1}^{n} \tau_{abk}}$$

where m_{jk} is the normalized strength of the j^{th} source at a given k^{th} time; τ_{abk} is the residence time of the trajectory arriving at Gosan at the k^{th} time spent over the grid cell a, b (in 0.5° x 0.5°) within the atmospheric boundary layer; and m_{abj} represents the relative strength of the cell a, b as a potential source region of the j^{th} source.



Fig. S5(a). Trajectory attribution: four country domains defined to separate country-specific pollution signals from original observations. The Chinese domain is defined as being within a regional grid of 100–124°E and 21–45°N.



Fig. S5(b). CCl₄ pollution events in 2008–2015 classified according to origin. Air masses from China are shown in red, and purple dots represent blended air masses affected both by China and other countries. Together, these two groups explain approximately 75% of

observed pollution data during 2008–2015. The remaining 25% are shown as gray dots.



Fig. S6. Observed relationships of CCl₄ vs. 26 halocarbons for air masses originating from China. The colors by shade indicate statistical significance. The CCl₄: HCFC-22 ratio (0.13 ppt/ppt) has one of the most significant correlation coefficients ($R^2 = 0.79$, p < 0.01) of the calculated 25-member correlation matrix.



Fig. S7. Annual HCFC-22 emissions in China for 2008–2015 derived from atmospheric measurements data from Gosan station using an inverse technique based on a Lagrangian transport model analysis. Red error bars denote estimation uncertainty of 30%; dashed and solid gray lines represent the average and its 30% uncertainty ranges, respectively, for HCFC-22 emissions during 2008–2015. Estimates are very consistent overall with previous top-down studies and a bottom-up estimate.



Fig. S8. Annual slopes of empirical correlations between observed enhancements of CCl₄ vs. HCFC-22 (Δ CCl₄ vs. Δ HCFC-22). It is important to note that CCl₄ production and consumption of its dispersive applications in developing countries were phased out in 2010. The slopes and uncertainties were calculated using a Williamson-York linear least-squares fitting method.



Fig. S9. Potential source region distributions of the three emission sources accounting for $89 \pm 5\%$ of CCl₄ enhancements observed at Gosan. The areas in and around Guangzhou of Guangdong, Wuhan of Hubei, Zhengzhou of Henan, and Xian of Shaanxi province are identified as the dominant contributors. The six blue dots indicate locations of main factories producing HFCs, HCFC-22, and fluorocarbons; these are provided in http://eng.chinaiol.com/.

Positive Matrix Factorization Model Calculation

PMF optimization uses a weighted least squares regression to obtain a best fit to the measured enhancements in the concentration data. The main constraints that need to be resolved during the analysis are "source factors", and thus this method is often called factor analysis. The mathematical expression of the model is given by Eq. (1),

$$x_{ik} = \sum_{j=1}^{p} g_{ij} f_{jk} + e_{ik} (i = 1, 2, ..., m; j = 1, 2, ..., p; k = 1, 2, ..., n)$$
(1)

where x_{ik} represents enhanced concentrations in the time series of the "*i*" halogenated compound at the k^{th} sampling time; g_{ij} is the concentration fraction of the *i*th compound from the *j*th source; f_{jk} is the enhanced concentration from the *j*th source contributing to the observation at the k^{th} time, which is given in ppt; e_{ik} is the model residual for *i*th compound concentration measured in the k^{th} sampling time; and *p* is the total number of independent sources (i.e., the number of factors) (Paatero and Tapper, 1994). The optimal number of factors (*p*) should be determined by using a function Q, defined in Eq. S(5) below,

$$Q = \sum_{i=1}^{m} \sum_{k=1}^{n} \left(\frac{e_{ik}}{u_{ik} h_{ik}}\right)^2$$
S(5)

where u_{ik} are the uncertainties corresponding to each measurement data point. Following the guideline provided by Polissar et al. (1998) for PMF model input uncertainties, we considered the instrumental measurement uncertainty, monthly standard deviation (1 σ) of background concentrations, and 1/3 of the detection limit value as the overall uncertainty assigned to each data point. The PMF model input uncertainties (in ppt) were constructed as follows,

$$u_{ik} = \sqrt{\mu_{ik}^2 + \sigma_{ik}^2} + d_{ik}/3$$
S(6)

where μ_{ik} is measurement uncertainty; σ_{ik} is the monthly standard deviation of the background; and d_{ik} is the analytical detection limit. The average values of these individual input error terms are listed for all species in Table S1. In Eq. S(5), $h_{ik} = 1$ if $|e_{ik}/u_{ik}| < \alpha$, and otherwise h_{ik} is defined as $|e_{ik}/u_{ik}|/\alpha$. The α is the outlier threshold distance parameter. Appropriate down weighting of outliers in PMF datasets has been conducted in many studies (Polissar et al., 1998; Lee et al., 1999; Lee et al., 2002) using this parameter, to reduce the influence of outliers and extreme values. We constrained the PMF analysis with $\alpha = 4$, which is most commonly used; therefore, when the scaled residual exceeded four times that of the standard deviation, the uncertainty, u_{ik} , was increased to down-weight that concentration.

The model runs with randomly selected initial values for f and g at a given number of factors (p) (varied from 5 to 10 factors) to obtain a minimum Q value in less than 20 iterations (Lee et al., 1999). As the number of factors increases, the corresponding minimum Q values decreases, with a level-off in this case near 7 factors. We carefully examined the solutions with 7, 8, and 9 factors and determined an optimal value based on both goodness of fit to the data and prior knowledge about halogenated compound emissions. The model's goodness-of-fit was estimated from a correlation plot between the measured and model-predicted concentrations. Most of the

compounds (16 out of 18 species) showed good correlations ($\mathbb{R}^2 > 0.6$, see Table S2) for the eight-factor solution. Another way to assess a PMF fit is to examine the distribution of scaled residuals (e_{ik}/u_{ik}). We found the most species except COS lie within ±4, which is considered a typical limit. The seven-factor model cannot separate the foam-blowing-agent factor from the semiconductor/electronics sector factor, which are both well-known sources of halogenated compounds. For the nine-factor analysis, the sources for CH₂Cl₂ and CHCl₃ were split. Therefore, we concluded that an eight–source model provides the most relevant and meaningful interpretation for the enhanced CCl₄ concentrations observed at Gosan.

PMF input uncertainties

The uncertainties (in ppt) imposed on individual concentrations are typically determined in the PMF community as follows,

$$u_{ik} = \sqrt{\mu_{ik}^2 + \sigma_{ik}^2} + d_{ik}/3$$
 S(7)

where μ_{ik} is the measurement uncertainty; σ_{ik} is the monthly standard deviation (1 σ) of the background; and d_{ik} is the analytical detection limit. The average values of these individual input error terms for all species are listed in Table S1.

Compounds	Analytical precision (ppt)	Background uncertainty (ppt)	Detection limit (ppt)		
CFC-11	0.44	1.40	0.72		
CFC-12	0.61	0.82	1.33		
HCFC-22	0.54	1.70	1.47		
HCFC-141b	0.10	0.70	0.22		
HCFC-142b	0.07	0.55	0.12		
HFC-23	0.13	0.26	0.26		
HFC-134a	0.18	1.10	0.47		
HFC-152a	0.08	0.53	0.15		
HFC-32	0.13	0.29	0.28		
HFC-125	0.05	0.20	0.11		
HFC-143a	0.09	0.22	0.19		
CF_4	0.09	0.19	0.20		
C_2F_6	0.03	0.04	0.06		
C_3F_8	0.01	0.02	0.03		
SF_6	0.03	0.08	0.07		
CH ₃ Cl	1.09	11.00	2.36		
CH_2Cl_2	1.55	7.20	3.36		
CHCl ₃	0.17	1.40	0.74		

Table S1. Three individual input error terms and their average values for all species.

CH ₃ Br	0.05	0.38	0.11
CCl_4	0.80	1.09	1.76
COS	2.92	14.00	6.36
PCE	0.02	0.42	0.04

Goodness of PMF model fit

The goodness of fit of the PMF model can be assessed by comparing the predicted compound concentrations with the original measurements. We found R-squared of larger than 0.6 for most of the halogenated compounds, as shown in Table S2.

CFCs and HCFC _s		HFCs		PFC_s and SF_6		Others					
Compounds	\mathbb{R}^2	p valve	Compounds	\mathbf{R}^2	p valve	Compo	unds R ²	p valve	Compounds	\mathbf{R}^2	p valve
CFC-11	0.58	< 0.01	HFC-23	0.70	< 0.01	CF_4	0.67	< 0.01	CCl ₄	0.76	< 0.01
HCFC-22	0.78	< 0.01	HFC-134a	0.68	< 0.01	C_2F_6	0.55	< 0.01	CHCl ₃	0.77	< 0.01
HCFC-141b	0.74	< 0.01	HFC-143a	0.27	< 0.01	SF ₆	0.81	< 0.01	CH_2Cl_2	0.95	< 0.01
HCFC-142b	0.75	< 0.01	HFC-32	0.88	< 0.01				CH ₃ Cl	0.99	< 0.01
			HFC-125	0.86	< 0.01				C_2Cl_4	0.99	< 0.01
									COS	0.99	< 0.01

Table S2. Goodness-of-fit statistics for plot of observed concentrations versus PMF model estimates at number of factors (p) = 8.

Description of PMF source factors

The factor (D) is characterized by high percentages of CF_4 (50 ± 9%) and COS (94 ± 24%). COS is mostly emitted from coal and biomass burning, and from various industrial processes including primary aluminum production (Blake et al., 2004). The aluminum production industry, particularly in China, is a well-known emission source of PFCs (Mühle et al., 2010). Although approximately 9 ± 4% of CCl₄ enhancements are attributed to this factor, there are no known processes that could release CCl₄ from this source.

The source factor (E) is characterized by high percentages of HFCs ($89 \pm 1\%$ of HFC-125, $78 \pm 1.3\%$ of HFC-32, $52 \pm 1.4\%$ of HFC-143a, and $43 \pm 5\%$ of HFC-134a). These compounds are used in air conditioning and refrigeration applications and are predominantly produced in China (Fang et al., 2016). Their azeotropic blends, such as R-410A (50% HFC-32, 50% HFC-125 by weight), R404A (52% HFC-143a, 44% HFC-125 and 4% HFC-134a), R-407C (23% HFC-32, 52% HFC-134a, 25% HFC-125) and R-507A (50% HFC-125 and 50% HFC-143a), are also increasingly used in China (Fang et al., 2016). The small percentages of contributions from these fourth and fifth sources to CCl₄ enhancements are not statistically significant when considering the uncertainty range, but they may suggest that CCl₄ is emitted to some extent by coal fired power plants located close to primary aluminum smelters and to production facilities for air-conditioning systems and refrigerant units. It is notable that the sixth, seventh, and eighth factors do not contribute to observed CCl₄ enhancements.

The factor (F) shown in Fig. 4 in the main text, which is interpreted as arising from refrigerant consumption, explains approximately $80 \pm 2\%$ of the HCFC-22 and $32 \pm 4\%$ of observed HFC-134a enhancements. HCFC-22 and HFC-134a are the most abundant species in the HCFC and

HFC families, respectively, and show their increasing use in refrigeration units and air conditioning systems as CFCs replacements (Montzka et al., 2011).

Many species contribute significantly to factor (G); in particular, $88 \pm 20\%$ of SF₆, $41 \pm 3\%$ of C₂F₆, and $40 \pm 13\%$ of CF₄. SF₆ is widely used in the high-voltage electrical equipment sector as a gaseous dielectric medium and is also used as an etching/cleaning agent in the semiconductor/electronics sector (Forster et al., 2007). There has been a recent increase in the use of PFCs (CF₄ and C₂F₆ foremost among them) for plasma etching and chamber cleaning in semiconductor/electronics manufacturing processes (Mühle et al., 2010). These large contributions of SF₆ and PFCs suggest that this source factor is related to processes in the semiconductor/electronics industry.

The last factor (H) shown in Fig. 4 is composed of $92 \pm 4\%$ HCFC-142b, the most widely used CFC replacement in foam blowing agents for extruded polystyrene boards (Derwent et al., 2007). The foam blowing factor also explains $23 \pm 2\%$ of CFC-11, indicating that this CFC is still emitted from remaining bank use or old building materials.

Chlorination reactions for CCl₄ production and use

<u>CH₃Cl/CCl₄ plants</u> (Sherry et al., 2018) CH₃OH+HCl→**CH₃Cl**+H₂O CH₃Cl+Cl₂→**CH₂Cl₂+HCl** CH₂Cl₂+Cl₂→**CHCl₃+HCl** CHCl₃+Cl₂→**CCl₄+HCl**

<u>Feedstock for production of chloromethanes and PCE</u> CCl₄+H₂→CHCl₃+HCl (e.g., Zang and Beard, 1998) 3CCl₄+CH₄→4CHCl₃ (e.g., Bae et al., 2007) 2CCl₄+2H₂→C₂Cl₄+4HCl (Sherry et al., 2018) CCl₄+4Cl₂+CH₄→C₂Cl₄+4HCl 2CCl₄+H₂→C₂Cl₆+2HCl CCl₄+HF→CCl₃F[CFC-11] + HCl

References

- Ashbaugh, L. L., Malm, W. C., Sadeh, W. Z.: A residence time probability analysis of sulfur concentrations at Grand Canyon National Park., Atmos. Environ., 19, 8, 1263–1270, 1985, <u>https://doi.org/10.1016/0004-6981(85)90256-2</u>, 1985.
- Bae, J. W., Lee, J. S., Lee, K. H.: Disposal of CCl₄ by disproportionation reaction with CH₄, Ind. Eng. Chem. Res. 46, 22, 7057-7065, 2007.
- Derwent, R. G., Simmonds, P. G., Greally, B. R., O'Doherty, S., McCulloch, A., Manning, A., Reimann, S., Folini, D., Vollmer, M. K.: The phase-in and phase-out of European emissions of HCFC-141b and HCFC-142b under the Montreal Protocol: Evidence from observations at Mace Head, Ireland and Jungfraujoch, Switzerland from 1994 to 2004, Atmos. Environ., 41, 4, 757–767, https://doi.org/10.1016/j.atmosenv.2006.09.009, 2007.
- Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D. W., Haywood, J., Lean, J., Lowe, D. C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., Van Dorland, R.: Changes in Atmospheric Constituents and in Radiative Forcing, in: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., Miller, H. L (Eds.), Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2007.
- Lee, E., Chan, C. K., Paatero, P.: Application of positive matrix factorization in source apportionment of particulate pollutants in Hong Kong, Atmos. Environ., 33, 19, 3201–3212, https://doi.org/10.1016/S1352-2310(99)00113-2, 1999.
- Lee, J. H., Yoshida, Y., Turpin, B. J., Hopke, P. K., Poirot, R. L., Lioy, P. J., Oxley, J. C.: Identification of sources contributing to Mid-Atlantic regional aerosol, J. Air & Waste Manage. Assoc., 52, 10, 1186–1205, <u>https://doi.org/10.1080/10473289.2002.10470850</u>, 2002.
- Montzka S. A., Reimann, S. (Eds): Ozone-depleting substances (ODSs) and related chemicals, in: Scientific Assessment of Ozone Depletion 2010, World Meteorol Org, Geneva, 1–108., 2010.
- Mühle, J., Ganesan, A. L., Miller, B. R., Salameh, P. K., Harth, C. M., Greally, B. R., Rigby, M., Porter, L. W., Steele, L. P., Trudinger, C. M., Krummel, P. B., O'Doherty, S., Fraser, P. J., Simmonds, P. G., Prinn, R. G., and Weiss, R. F.: Perfluorocarbons in the global atmosphere: tetrafluoromethane, hexafluoroethane, and octafluoropropane, Atmos. Chem. Phys., 10, 5145–5164, https://doi.org/10.5194/acp-10-5145-2010, 2010.
- Paatero, P., Tapper, U.: Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values, Environ., 5, 111-126, https://doi.org/10.1002/env.3170050203, 1994.
- Poirot, R. L., Wishinski, P. R.: Visibility, sulfate and air-mass history associated with the summertime aerosol in northern Vermont, Atmos. Environ, 20, 7, 1457–1469, https://doi.org/10.1016/0004-6981(86)90018-1, 1986.

- Polissar, A.V., Hopke, P. K., Paatero, P., Malm, W. C., Sisler, J. F.: Atmospheric aerosol over Alaska: 2. Elemental composition and sources, J. Geophys. Res., 103, D15, 19045–19057, https://doi.org/10.1029/98JD01212, 1998.
- Reimann S., Schaub, D., Stemmler, K., Folini, D., Hill, M., Hofer, P., Buchmann, B., Simmonds, P. G., Greally, B. R., O'Doherty, S.: Halogenated greenhouse gases at the Swiss High Alpine Site of Jungfraujoch (3580 m asl): Continuous measurements and their use for regional European source allocation, J. Geophys. Res., 109, D05307J, https://doi.org/10.1080/10473289.2007.10465319109, 2004.
- Wan, D., Xu, J., Zhang, J., Tong, X., Hu, J.: Historical and projected emissions of major halocarbons in China, Atmos. Environ., 43(36), 5822-5829, 2009.
- Zhang, Z.C., Beard, B.C.: Genesis of durable catalyst for selective hydrodechlorination of CCl₄ to CHCl₃. Appl. Catal. A, 174, 33–39, 1998.