

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

Interactive comments:

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In many respects this is an excellent paper that uses high frequency atmospheric measurements that have low and well defined uncertainty to a) estimate the magnitude of carbon tetrachloride emissions in air reaching the Gosan observatory and b) characterize the geographical location of those emissions. However, the authors go several steps too far when they assign physical processes to the sources of releases of CCl₄.

>>> We thank Dr. McCulloch for his thoughtful and thorough comments. We are very pleased that he considered our manuscript as a valuable contribution to the field. Based on Dr. McCulloch's perspective, we realize possible confusion over terminology (e.g., fugitive emissions from feedstock use vs. escape of by-product), which might mislead the readers. We are very careful with our definitions and terminology throughout the manuscript. We have also made changes to the manuscript to answer the suggestions of the reviewers. We hope that we've clarified a few points and concerns raised in Dr. McCulloch's comments below and have satisfactorily addressed these concerns in the revised version of the manuscript. [In the following, Dr. McCulloch's comments are in bold Courier New and our responses and are in Time New Roman font]

Showing where the CCl₄ is emitted in China is a major contribution to our understanding of the input of CCl₄ to the atmosphere but to then assign emissions to particular industrial processes based solely on correlation with emissions of other chemicals is an over-interpretation of the data presented and contradicts practical evidence used to build bottom-up inventories for both China and the world as a whole. Consequently, the discussion of results and conclusions on pages 7 to 9 needs to be completely rewritten taking into account that the measurements relate to emissions and do not relate to contemporaneous production in either quantity or location.

>>> It appears that there is a misunderstanding in that “to assign emissions to particular industrial processes based solely on correlation with emissions of other chemicals is an over-interpretation of the data presented.”

We did use the correlation with HCFC-22 exclusively for estimating the total Chinese emissions of CCl₄, based on HCFC-22 emission numbers for China. For the assignment of the CCl₄ emissions to particular industrial processes (e.g., pathways A vs. B) the results from a far more sophisticated PMF receptor model was used. The PMF was applied to the enhanced concentrations (i.e, in which the influence of the regional background levels on the measurements has been removed by subtracting baseline values) of all 18 species for their pollution source apportionment. Each resulting source category (i.e., factor) was characterized by a *distinctive combination of high-contribution species* and was defined accordingly based on the source profiles.

For the phrase of “to assign emissions to particular industrial processes contradicts practical evidence used to build bottom-up inventories for both China and the world as a whole.”, our analysis identified three major source categories of (A) CH₃Cl production plants (B) fugitive emissions from feedstock use for the production of other chlorinated compounds (e.g., CHCl₃) and from process agent use, and (C) PCE production plants. These sources are largely consistent with the bottom-up CCl₄ emissions pathways identified in SPARC (Liang et al., 2016; Sherry et al., 2018).

For the sentence of “the measurements relate to emissions and do not relate to contemporaneous production in either quantity or location”, we agree that the observed concentrations are related to emission and not directly to contemporaneous production. It was the reason why we used a factor analysis on the measurements to suggest source apportionment for industry-related compounds. The PMF results pointed to a few source categories of CCl₄, which were defined based on the source profiles associated with other compounds. Since we note the production and feedstock use of those compounds can be co-located, whereas general consumption and legacy release are more widely distributed, we believe our interpretation CCl₄ emissions are occurring at the factory level during production of various halocarbons is highly plausible.

In addition, one of primary motivations for this study is to suggest first observational based estimates for industrial sources in comparison with the SPARC industrial bottom-up emissions, thereby providing insight into a link between the different approaches. Thus, the discussion of results and conclusions on pages 7 to 9 in the original text served the distinct and deliberate purpose and thus we have left the main messages in the discussion as they were.

**The SPARC report on CCl₄ [SPARC, 2016] and subsequently Sherry et al. [2018] showed the principal sources of emission to be inadvertent and unreported, arising from:
manufacture and use of chlorine, including as a disinfectant;
leakage from historic landfill;
unreported emissions of material produced during the manufacture of legitimate chemical products and then used in emissive applications in contravention of regulations.**

Of the 25 Gg/y emissions estimated [SPARC, 2016] only 2 Gg/y were calculated to be fugitive emissions. Actual fugitive emissions, that is emissions from the plant during the production of CCl₄ (either as desired product or as by-product) or its use as a chemical feedstock, are better understood than any of the other sources and account for only a few percent of the global emissions of CCl₄.

>>> For our current understanding of the fugitive emissions, we found a bit difference between the SPARC report (and Sherry et al.) vs. your statement here of “Actual fugitive emissions ... are better understood than any of the other sources and account for only a few percent of the global emissions of CCl₄.”

Fugitive feedstock/process agents emissions (SPARC pathway A) derived based upon UNEP reported, feedstock emission factors of 0.5–2% and assumed 95% fraction of total production for feedstock use according to the post-1995 reporting to UNEP (Montzka and Reimann, 2011), were estimated to be ~2 Gg yr⁻¹. The underlying assumption is that (1) UNEP reported total production and the reported amounts used as feedstocks have completed globally and regionally even after recent rapid increase in production of various halocarbon compounds and (2) the approximation of 0.5% to 2% leakage from contained feedstock production is accurate. We also note that the fugitive emissions defined in both the SPARC report (pathway A) and Sherry et al. (pathway C) include not only feedstock usage, but also process agents use.

There is an important distinction between fugitive emissions, which are (or at least can be) controlled and which are an economic loss to the manufacturer and material that is disposed of “usefully” but which is, in the end, emitted into the atmosphere.

>>> For clarification we described our factor (A), which was now re-named to make it easier to compare them to the SPARC report as asked for by one of reviewers, as advertent or inadvertent co-production and *escape* of CCl₄ during CH₃Cl generation in the chemical plants.

At the root of the problem with the paper is the naive assertion that all emissions arise from chemical production. Among the 26 halocarbons reported in the paper, this is true only for: HFC-23 (which arises from HCFC-22 production and where 90% of emissions are from the chemical plant itself [Simmonds et al., 2018]) and that part of CF₄ emissions that arise in aluminium production.

>>> We did not intend to give a wrong impression that “all emissions of 26 halocarbons arise from chemical production”. Addressing emission sources of individual “26” species is certainly beyond

the scope of this study. As discussed in the section of “Industrial source apportionment of atmospheric CCl₄ in East Asia”, only CCl₄, CH₃Cl, CH₂Cl₂, CHCl₃, CFC-11, HFC-23 and CH₂Cl₂ of 18 species analyzed in the PMF model were discussed in terms of association with chemical manufacturing of various halogenated compounds, because importantly, it turned out that these compounds were grouped together in a couple of source factors.

For the rest, emissions occur during use of the substance or when equipment containing the substance is scrapped at the end of its life. This is well known, indeed it forms the basis for the national estimates of fluorinated greenhouse gases submitted to UNFCCC, and the authors have no grounds for asserting otherwise.

>>> As shown in the section of “Industrial source apportionment of atmospheric CCl₄ in East Asia”, potential emissions occurring during use, recycling and old equipment destruction were discussed in separate source factors: “refrigerant use” and “foam blowing”, in which we noticed no CCl₄ contribution (see SI text).

From the point of view of assigning geographical locations of CCl₄ emissions, the important species are methyl chloride, dichloromethane, tetrachloroethene and HFC-23. These form part of the suite of chemicals used by the authors in the analysis of the observation to show how emissions of CCl₄ are geographically co-located with enhanced emissions of other species, with the results shown in Figure 4.

>>> Yes, it is an important point that the production and feedstock use of the suite of chemicals can be co-located, whereas general consumption and legacy release are more widely distributed. Therefore, the interpretation of the results shown in Fig. 4 that the emissions of CCl₄ as co-product/by-product and as feedstock/process agent occur at production level is reasonable.

Combustion processes in which the fuel contains chloride ion (much of Chinese coal, municipal solid waste and biomass) account for most of the methyl chloride emitted into the atmosphere by human activity and there is a substantial natural source (five times larger than anthropogenic) [Carpenter & Reimann, 2014]. Sherry et al. [2018] show 26 Gg/y of methyl chloride is made in China from CCl₄, so the statement in Figure 4, panel 1 that 38% of release is due to methyl chloride production implies a fugitive emission rate of 35% - ludicrous both from economic and public health points of view.

>>> It appears that the numbers above need to be clarified. 38% of the CCl₄ enhancements from source factor (A) and 19% of CCl₄ from factor (C) correspond to advertent or inadvertent co-production and escape of CCl₄ during CH₃Cl and C₂Cl₄ production in the chemical plants. They are described as CM plants and PCE/CTC plants in the section of CTC production in Sherry et al. (2018), respectively.

Therefore, as stated in the conclusion, if assuming that those relative contributions of the factors correspond to the source emissions, the unreported, non-feedstock emissions from CCl₄ production amount to ~13 Gg yr⁻¹ of CCl₄ in China alone. Then the emission rate of CCl₄ would be ~6% of 203 Gg yr⁻¹ for global CCl₄ production, and ~17% of 77 Gg yr⁻¹ for CCl₄ production in China (Sherry et al., 2018), with the assumption that the UNEP reported amounts are complete.

In Figure 4, panel 2, 32% of CCl₄ emissions are co-located with 78% of DCM emissions. DCM has a high solvent power for oils and greases and for some polymeric materials. These properties, coupled with its volatility (boiling point 40.1oC) have led to its wide use as an industrial solvent in applications such chemicals and pharmaceuticals production and to a lower extent as food extraction solvent, for metal cleaning and paint removal. It is also a component of special adhesives and has been used in PU foam blowing, in aerosols, paint strippers and as laboratory agent. Many of these uses can result in much of the DCM employed being emitted into the environment (so-called emissive uses). More recently, smaller quantities of DCM have been used as chemical feedstock to produce HFC-32 (CH₂F₂, difluoromethane) but use as feedstock does not result in significant emission of DCM. The conclusion must be that 32% of the CCl₄ emissions found are co-located with the areas where DCM is emitted from its use, principally as a solvent.

>>> Yes, our PMF results were also consistent with the fact that CH₂Cl₂ (DCM) has been widely used as an industrial solvent. The 26±14 % contribution of CH₂Cl₂ shown in the factor (G) seems to suggest its use as a cleaning solvent, because the factor was characterized by high contributions of SF₆, C₂F₆, and CF₄, and thus explained as the source factor for semiconductor/electronics manufacturing processes (see SI text).

Importantly, a large fraction of CH₂Cl₂ was also shown in the source factor (B) with consistently high contributions of CHCl₃ and CCl₄, which are known to be produced along with CH₂Cl₂ as by-products of chlorination, and used as feedstocks or solvents in chemical manufacturing. This factor was also distinguished by a high contribution of HFC-23, a typical by-product of HCFC-22 generation where CHCl₃ is used as a feedstock.

As CHCl₃ and CH₂Cl₂, short-lived, Cl-contained species are still allowed for emissive uses, their high percentages could be explained in part by ubiquitous industrial use. However, when

considering that the observed enhancements of HFC-23, CHCl_3 , and CH_2Cl_2 are grouped together into a single factor with CCl_4 and CFC-11 that have been banned for emissive (dispersive) use, this factor for CCl_4 (also for CFC-11) should represent emissions occurring as desired product/by-product and as feedstock/process agent during chemical manufacturing processes (for the details of CFC-11, see the response to Reviewer #2's comments).

Exactly the same can be said about Figure 4, panel 3. Here the co-location demonstrated is with tetrachloroethene. Like DCM, this is used in many applications as a solvent, particularly in textile and metal cleaning, which is where most of the emissions arise. Compared to the amount that is produced and used, feedstock emissions are small. So, a further 19% of CCl_4 emissions are co-located with solvent emissions of tetrachloroethene.

>>> As we stated earlier, PCE (C_2Cl_2) is also allowed for dispersive uses with various applications as an industrial solvent like CH_2Cl_2 , and thus its emission could be widely distributed geographically. However, the factor (C) was distinguished by both CCl_4 and PCE, which means that CCl_4 emissions are co-located with PCE emissions, just as commented. In other words, there are possible co-emissions during their productions and consumptions (uses). Then the explanation for CCl_4 that is not allowed for its dispersive use should be escape emissions from co-production during industrial C_2Cl_4 production and in part fugitive emissions of CCl_4 being used as a chlorination feedstock for C_2Cl_4 production, both occurring at the chemical production level. Furthermore, potential source region distributions of the three emission sources for CCl_4 shown in Fig. S9 (note its original number was S8) are very similar. It consistently supported the argument that the three sources are more likely related to chemical manufacturing industry including production/by-product production and feedstock/process agent use of related compounds, rather than related to dispersive use and/or legacy emissions, which are expected to be widely distributed with different patterns among the three source factors.

The first two panels of Figure 4 also show that 70% of CCl_4 emissions are co-located with 90% of HFC-23 emissions. CCl_4 is not directly involved in the chemical processes that make or use HFC-23.

>>> HFC-23 is not either produced on purpose or used (only less commonly used in semiconductor fabrication). Therefore, any compounds except HCFC-22 cannot be “directly involved in the chemical processes that make or use HFC-23”, because it is a typical by-product of HCFC-22 production.

CHCl_3 is used as a feedstock for HCFC-22 production. CHCl_3 is produced in chloromethanes plants from the reaction of hydrochlorinating methanol (CH_3OH) with HCl to form methyl chloride (CH_3Cl), and subsequent chlorination to produce CH_2Cl_2 , CHCl_3 , and CCl_4 . The reaction of CCl_4

with H₂ to form CHCl₃ and HCl is also possible. In this sense, fugitive emissions of CCl₄ as an impure co-product of CHCl₃ and/or as feedstock for CHCl₃ can be associated with HCFC-22 production, and thus indirectly related to emission of HFC-23.

The authors present no evidence to attribute the co-location of these emissions and those of DCM, chloroform and CFC-11 to "fugitive emissions.....at the factory level during various chemical manufacturing processes in China" (page 7, lines 20-21). This is an assumption that, as discussed above, has no basis in fact.

>>> We've interpreted our results, which reveal that the regulated CCl₄ has been emitted with significant amounts, 4–5 times larger than the inventory-based bottom-up emissions estimate, and the emitted CCl₄ has shared its source factors with CHCl₃, CH₂Cl₂, CH₃Cl, HFC-23, CFC-11 and PCE.

For a compound like CCl₄ fully regulated for dispersive uses, if it is co-emitted with other compounds produced as co-products or by-products of each other and consumed as feedstocks/process agents/solvents in chemical industries, which source could you suggest as an alternative explanation for their co-emissions except emissions occurring at the factory level when CCl₄ is produced as a by-product and used as feedstock/process agent during various chemical manufacturing processes?

Figure S5 shows correlations between observations of the atmospheric concentrations of 26 halocarbons. Of these, some 19 have correlation coefficients versus CCl₄ higher than 0.6 (average 0.72). The conclusion that CCl₄ is a ubiquitous contaminant of polluted air samples arising from industrial regions of China is obvious. However, the co-locations demonstrated are for emissions of all the substances, not emissions of one against production of the others.

>>> Fig. S5 (now Fig. S6 in the revised SI) shows one-to-one correlations between enhanced concentrations of 26 halocarbons, mainly to provide a measure when selecting a reference compound for the interspecies correlation method, which was used to estimate the total emissions of CCl₄ in China. It is correct that CCl₄ is a ubiquitous contaminant of polluted air samples in China, just like any other long-lived, anthropogenic compounds. Note that HFC-23, which can be expected to be emitted from point sources, showed high correlations of > 0.6 with some 13 species. Therefore, the high one-to-one correlations do *not* demonstrate co-locations either, because the correlations shown in Fig. S5 (now Fig. S6) were determined from the combined data of all the air masses originated from China. This plot cannot be served to argue that co-locations and thus co-emissions are demonstrated.

Apparently, in China some 90 Gg/y of CCl₄ are co-produced with other chloromethanes [Zhang et al., 2015]: this represents only 3% of the total Chinese production of methyl chloride, dichloromethane and chloroform, nevertheless it is the main production source of CCl₄. SPARC [2016] and Sherry et al. [2018] were able to account for 13 Gg/y globally as “unreported” emissions from NON-FEEDSTOCK USE. As mentioned above, feedstock emissions were calculated separately and shown to be 2 Gg/y.

>>> According to Sherry et al. (2018), the CCl₄ production in China from chloromethanes plants and PCE plants were 76.5 Gg yr⁻¹ and 0 Gg yr⁻¹, respectively. The “fugitive emissions” denoted as pathway A by Liang et al. (2016) and Sherry et al. (2018) are calculated to be 2 Gg yr⁻¹, and they included not only “feedstock emissions” but also “process agent emissions”.

The evidence presented by the authors is entirely consistent with a higher figure for these unreported emissions from China which would come from industrialised areas, as found. There is, however, no evidence to support the assertion that they arise during production of other chemicals. All that has been proved is that their emissions are geographically co-located with emissions of these other chemicals.

>>> As stated earlier, our discussion given in this manuscript was started with a question of how come the banned CCl₄ could be co-emitted with CHCl₃, CH₂Cl₂, CH₃Cl, HFC-23, CFC-11 and PCE, and interestingly, resulting source apportionments were consistent with the SPARC report (2016) and Sherry et al. (2018).

The sentence on page 8 lines 31 to 32 “This seems plausible, as evaporative losses of CCl₄ during its use as feedstock and/or process agent and from storage reservoirs of factories are easily overlooked and very poorly constrained” is simply wrong. The highest concentration of CCl₄ in the air in a storage tank ventilated to the atmosphere is the equilibrium vapour pressure at the temperature of the liquid CCl₄ in the tank. In practise the vapour above the liquid is not well mixed, so the vapour pressure represents an absolute maximum. At 20°C, the vapour pressure is such that a full to empty and refill cycle in such a storage tank could release 0.04% of the CCl₄. This is well known, easily calculated, and forms the basis of default estimates of fugitive emissions (such as the 0.5% default factor in the IPCC Greenhouse

Gas Reporting Guidelines) [IPCC, 2006]. This sentence will become redundant when the discussion of Figure 4 and the conclusions are completely rewritten.

>>> Both Sherry et al. (2018) and SPARC mentioned about “potential fugitive leakage during transport and storage” in the section of “Fugitive emissions from usage of CTC” and “some transport leakage, storage leakage” in the section of “CCl₄ usage (feedstock, process agent) and destruction”, respectively. However, for the sake of argument, we’ve removed the statements.

In summary, the authors need to accept the difference between emissions and production and to rewrite pages 7 to 9 recognising that their observations relate only to emissions. It might help if they were to co-opt one of the authors of the SPARC report or the Sherry et al. [2018] paper to help them write robust conclusions about the relationships between CCl₄ and other emissions. The present text is wrong in almost all respects.

>>> See our earlier comment that addressed the discussion in the original pages 7 to 9.

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