

## ***Interactive comment on “Toward resolving the mysterious budget discrepancy of ozone-depleting CCl<sub>4</sub>: An analysis of top-down emissions from China” by Sunyoung Park et al.***

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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) characterise 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 CCl<sub>4</sub>. Showing where the CCl<sub>4</sub> is emitted in China is a major contribution to our understanding of the input of CCl<sub>4</sub> to the atmosphere but to then assign emissions to particular industrial processes based solely on correlation with emissions of other chemicals is

C1

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.

The SPARC report on CCl<sub>4</sub> [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 CCl<sub>4</sub> (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 CCl<sub>4</sub>. 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.

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 CF<sub>4</sub> emissions that arise in aluminium production.

C2

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.

From the point of view of assigning geographical locations of CCl<sub>4</sub> 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 CCl<sub>4</sub> are geographically co-located with enhanced emissions of other species, with the results shown in Figure 4.

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 CCl<sub>4</sub>, 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.

In Figure 4, panel 2, 32% of CCl<sub>4</sub> 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 40.1°C) 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 (CH<sub>2</sub>F<sub>2</sub>, difluoromethane) but use as feedstock does not result in significant emission of DCM. The conclusion must be that 32% of the CCl<sub>4</sub> emissions found are co-located with the areas where DCM is emitted

C3

from its use, principally as a solvent.

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<sub>4</sub> emissions are co-located with solvent emissions of tetrachloroethene.

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

Figure S5 shows correlations between observations of the atmospheric concentrations of 26 halocarbons. Of these, some 19 have correlation coefficients versus CCl<sub>4</sub> higher than 0.6 (average 0.72). The conclusion that CCl<sub>4</sub> 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.

Apparently, in China some 90 Gg/y of CCl<sub>4</sub> 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 CCl<sub>4</sub>. 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. The evidence presented by the authors is entirely consistent with a higher figure for

C4

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.

The sentence on page 8 lines 31 to 32 “This seems plausible, as evaporative losses of CCl<sub>4</sub> 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 CCl<sub>4</sub> in the air in a storage tank ventilated to the atmosphere is the equilibrium vapour pressure at the temperature of the liquid CCl<sub>4</sub> 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 CCl<sub>4</sub>. 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.

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 CCl<sub>4</sub> and other emissions. The present text is wrong in almost all respects.

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C5

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C6