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Comment on acp-2021-699

Anonymous Referee #1

Referee comment on "Top-down and bottom-up estimates of anthropogenic methyl bromide emissions from eastern China" by Haklim Choi et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-699-RC1, 2021

Review of Choi et al, 'Top-down and bottom-up estimates of anthropogenic methyl bromide emissions from eastern China'

This manuscript is based on a substantial set of high-quality observations of CH3Br and CFC-11 from the Gosan observatory. An interspecies correlation technique is used to derive CH3Br emissions from eastern China based on these observations. The work is important in light of stratospheric ozone depletion and the regulations of the Montreal Protocol. While I have no doubts about the measurement data quality, the interpretation and the estimation of the emissions raise several concerns.

General major comments

Is there a particular reason why the focus was set on Chinese CH3Br emissions? By looking at Figure S2b it appears that (despite a 'proximity' bias) Korean emissions are on a similar order of magnitude. Also, by comparing Figure 4, where maximum enhancements are around 10-13 ppt, and Figure 2, where there are many much larger pollution events, it suggests that other large emitters are nearby.

My main concern is about why the authors can exclude oceanic algae and marshland production of CH3Br from being an important contributor in the observations at Gosan? How conservative is the CH3Br concentration in air advected over over the oceans? Is algae CH3Br production in the waters around Gosan and between China and Gosan less than what one would e.g. assume for Mace Head? For example, Fig 6, intended to show correlation of CH3Br with CFC-11 and some other tracers of both anthropogenic/natural origin, show such nice correlation for 20 May. However, for the period of 28-30 May, large pollution events of CH3Br are not matched with enhancements of CFC-11, benzene, toluene, ethane, and hence are not originating from biomass burning or general anthropogenic activities. Could this be an example of oceanic origin of CH3Br? I suggest to

produce Fig 5 (map with potential source regions) in a way that allows sources in the ocean.

I question the robustness of the ISC correlations (shown in Fig. S4). The data look strongly biased towards a few large concentration enhancements. What happens if e.g. the highest 10-20 points each are removed? Many of the data plots in S4 suggest that many of the data points in the high concentration range are rather scattered (as suggested on line 246) but some suggest distinctly different branches. The data suggests that factors other than population activity (CFC-11 emissions) seem to contribute to some of these. If the high-CH3Br points had a natural component, and if these were removed, it could significantly reduce the anthropogenic emissions. Have the authors tried to apply another filter to understand if some of these branches are biased towards other sources (rapeseed, biomass, oceanic)? For example, a filter could be applied by looking at correlations of CH3Br to another substance, e.g. CFC-12. If the high-CH3Br samples stick out again compared to CFC-12, then that could be an indication of a natural source.

Given the large dynamics of CFC-11 emissions from this region over the past years, an inspection of time-records of yearly (or monthly) CFC-11 emissions and CH3Br/CFC-11 enhancement ratios (from Fig. S4) would be very informative and could be added to Fig. S3.

Using Mace Head and Cape Grim as reference background station: Is Mace Head a good choice for a NH background extraction given its large local oceanic sources? Is the pollution filter working well for a station with presumably high local sources?

Mentioning of SO2F2

In my view, the authors miss a chance to strengthen their CH3Br study by not including a similar analysis for SO2F2. It would be a strong plausibility test of the CH3Br results and help in the interpretations. If the decline of the CH3Br emissions from reported consumption (1.44 Gg to 0.73 Gg) from 2008 to 2019 is not at least partially matched by a similar-magnitude increase of SO2F2 (assuming insignificant use of other, presumably more expensive alternatives), then this could be supporting the conclusions of this work. I don't understand the logic behind the ISC of CH3Br vs SO2F2 (l. 372 ff, Figure S8, Table S3), if one is a replacement for the other, then why should they correlate? Why was the analysis not done of SO2F2 vs CFC-11? Also, I am confused about the statement of a remaining discrepancy of 3.5 Gg/yr (l. 371 and 373) when before the discussion was about a discrepancy of 3 Gg/yr.

Is the alternative SO2F2 really that much more expensive and less effective? I am just surprised that the Chinese authorities would tolerate another forbidden use of a MP substance after they were caught with CFC-11.

Minor comments

Abstract:

l. 26: I am having difficulties to understand reproduce the value of -0.13 ppt/yr from the decline from 8.5 to 7.4 ppt over the course of the eleven years.

l. 29: I suggest to extend 'estimate anthropogenic ...' to 'estimate mean anthropogenic ..'. Please make clear if the +- 1.3 Gg/yr is simply the variability in the yearly estimates, or if this includes some uncertainty estimate.

l. 32: Why the term 'largely'? Is this word an expression of quantiy or uncertainness in the origin of the discrepancy?

l. 51 'reduced completely' is an expression that doesn't make sense.

l. 53 'reduction of 60'000 tonnes' Over what time frame? Consider using same units as later in the text (Gg).

l. 55 '.. due to the phase-out of other uses ..' This is a confusing part of the sentence. Is it necessary?

l. 57 'As a consequence ..' This statement assumes that natural sources of CH3Br have remained constant over this time frame, which seems rather speculative.

l. 58: Define 'ppt' the first time used in the text

l. 62, natural emissions: Is there an estimate of the total natural CH3Br emissions from all these studies in the literature? If so, could you mention it? What fraction could potentially be assigned to the region of interest'

l. 77: It would be instructive to give a typical 'activity factor' for these applications.

l. 84: The word 'resultant' is confusing. Is it necessary?

l. 114: Suggest to extend 'of most the Medusa...' to '... of most of the Medusa ...'.

l. 123: Remove the first 'and'. What is similar to the annual cycles at Gosan and Mace Head -- the amplitude, phase.

l. 125: See also abstract: How do the authors derive a decline of 0.13 ppt/yr from 8.5 ppt to 7.4 ppt in 11 years?

l. 127: 'data in 2011-2012': Why only this period? Does this suggest that in other years, it is not consistent, or are data missing, or is there another reason? please clarify.

l. 159: Specify which boundaries are meant (modeling boundaries, geographical boundaries, boundaries to what/where?)

l. 198. 19 and 21 May, which year?

l. 197 paragraph: The authors point out the good correlation between CH3Br and the tracers benzene, ethane, toluene, which have both biomass burning and also other anthropogenic sources. Based on that, wouldn't then CO be a good tracer for ISC, to capture the sum of biomass burning and anthropogenic sources??

l. 212: extend 'enhancements' to 'concentration enhancements'.

l. 221: 'of the estimated CH3Br'. What are the units for the uncertainties? If unitless, then say so, if with units, then something is wrong here as SigmaE-CFC-11 would need to have the same units as the Sigma-alpha.

l. 231: Suggest to extend to '..the estimated emissions...'

l. 241: suggest to extend to '... residual errors for both X and Y ...'

l. 248: Suggest to change to '.. For most of the observation' (add 'the', remove 'entire')

l. 249: The (e.g. R=0.7 in 2009) is not really a typical example (e.g.) but it is the best taken.

l. 249: is the < symbol correct, shouldn't it be >?

l. 260: The statement of the emissions being 'relatively' constant is rather subjective. Same for 'small fluctuations'. One could argue that year-to-year fluctuations are huge in two cases.

l. 268, wildfires: If wildfires could be responsible for the 2010 and 2013 peaks, then what could wildfires be in other years. As far as I understand, these are not included in the bottom-up estimates. The contribution of wildfires should be clarified semantically and quantitatively in the paragraph on biomass burning (301 ff).

l. 278: Second last sentence. It is unclear, why this observation is particularly worth mentioning.

l. 285: Suggest to change '... actual difference in ...' to either '...the actual difference in...' or to ' .. actual differences in ...' (and then 'are' instead of 'is').

The paragraph on biomass burning (301ff) is confusing and needs improvement. Is the fraction 'agricultural open-field burning' (l. 303) the same as the 'agricultural waste' (l. 313)? If this is the same, and, according to l. 316 turns out to be insignificant (0.07 Gg/yr compared to 3 Gg/yr for the difference between top-down and bottom-up) then why do the authors think this would be seen in a seasonality plot (Fig. S5)? If 'biofuel' burning is a substantial contribution, then would one not expect peak CH3Br observations in winter? Where are 'wildfires' included and where aren't they?

l. 314: 'from the field experiment'...? From which experiment. Perhaps this is should say '... based on field experiments...' or '... based on a field experiment....'

l. 314: For the number '1.1 g tonnes-1'. Please be more specific, is this tonnes of fuel,

tonnes of dry fuel?

It seems that the authors do not include CH3Br from fires other than agricultural and biofuel, i.e. wildfires. Are these negligible?

l. 318: I suggest to replace 'results' by 'resulted'.

l. 346. Are there studies supporting the statement that CH3Br is more effective than e.g. SO2F2. And have the authors verified that CH3Br is indeed significantly cheaper than SO2F2. I am just surprised that the Chinese authorities would tolerate another forbidden use of a MP substance after they were caught with CFC-11.

l. 386: I suggest to replace 'In recent years, CH3Br accounts for ...' to 'In recent year, CH3Br has been accounting for ...'.

l. 388: I suggest to state this a bit more carefully, e.g. 'if any potentially unreported ...'

l. 395: I checked data availability. on /gc-ms-medusa there appears to be a data set with monthly mean results and one with high-resolution. The Gosan CH3Br data is only in the former, but should also be in the latter, after all, analysis was done on individual measurements (ISC).

Figure 4: Caption: Clarify if these are all data, or already filtered for a specific sector of origin. Maximum enhancements are in the range of 10-13 ppt, and when compared to Figure 2, it would suggest that the data in Fig 4 are already a selection. However, also comparing with Figure 2, it appears that large and frequent emissions are also derived from other regions. It re-iterates the question on why this paper only focusses on China, if presumably there are other large emitters.

Figure 5: Does the back trajectory analysis put any CH3Br sources over the ocean? Where, how much? For a compound with both anthropogenic and natural sources, would it make sense to include these in the plot? Same comment for Fig. S6 for SO2F2. This could actually help to understand the differences in the oceanic/marshland contribution of CH3Br assuming that there are no sources of SO2F2. It would be usefult to mark the Gosan station on these maps.

The contribution of CH3Br from South Korea appears small on Fig 5 but the pollution events from Korea (Fig S2b) seem large. Is this apparent discrepancy fully explained by

the proximity of South Korea to the Gosan station?

Figure 8: What uncertainties are included in the grey band? Only those of the CFC-11 emissions? I suggest to include all important uncertainties (CH3Br/CFC-11) slope ratio uncertainties, others? I am missing a short paragraph in the text with a discussion on the uncertainties, that allows the reader to understand where the largest uncertainties are expected from.

Table 1. The table should be self-explanatory, so clearly state whether these are concentrations above baseline or actual concentrations during pollution events. Also, explain if this is a data set filtered for a specific region. Re-check all captions if they allow understanding of the numbers and figures without the main text.

Table 2, caption: Clarify if (and which) activity factors were used to convert consumption to emissions for the bottom-up estimates.

Summary and Conclusion

When mentioning additional contributions, please separate rapeseed and biomass burning, the latter is, according to the authors, insignificant.

Supplement:

Figure S1: How does one have to interpret these figures. Does a dark green mean that there is high residence time? This would then suggest a long residence time over the oceans. As stated earlier, how can the authors exclude that potential oceanic sources have lead to the high CH3Br observed at Gosan?

Figure S2b: Legend: Does this correspond to the classification in Fig? What regions are 'East China'? What regions are 'Korea'? I suggest to move the low

er y-axis limits to negative such that data points and tick marks don't interfer. 'Red' and 'Purple' can bearily be distinguished on printed copies, I su

ggest to change colors. The jargon 'enhanced concentration' should be avoided as it is not clearly understandable when not used together with the text. 'enhancement of CH3Br

above background' (like described in S4) is much clearer.

Figure S3: See general comments. Also, this Fig S3 is only referred to in the main text, but should also have some reference in the supplement.

Figure S4: This is an important figure because it demonstrates the quality and limitations of the ISC method. I suggest to consider showing it in the main text (e.g. by replacing the current Fig. 6 of the main text, which seems far less important). The figure needs improvement. The tick labels, the x and y text labels, and the subfigure titles (years) are too small. Are the scales all the same? I suggest to make uniform scales for all subplots as a comparison between the individual plots is far more important than a potential loss of resolution in some subplots. label the red lines with the numeric values of the slopes. It would be rather informative to draw a (dashed) line that would correspond to the CH3Br/CFC-11 ratio, which one would obtain to match the bottom up emission estimate (still using CFC-11 from earlier studies). In the caption, re-iterate that these are filtered data based on air mass classification and that the selection is made for a specific region.

Figure S5: State what the vertical bars mean.

Table S2: Add references for the UNEP reported data.