

Interactive comment on “Results from the first national UK inter-laboratory calibration for very short-lived halocarbons” by C. E. Jones et al.

Anonymous Referee #1

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This manuscript describes the results of the first laboratory comparison from research groups in the UK for several of the commonly measured short-lived halocarbons in the ocean and atmosphere. It is anticipated that this exercise could expand into the broader international community of researchers involved in trace gas measurements. Thus, it is of interest to see how the process was organized and what results were obtained. This type of exercise is valuable to do, but often gets overlooked.

The manuscript is well-written and the results are pretty straightforward. The manuscript could be published, with attention to comments below.

1) It is unfortunate that there was no neutral referee to compile the results. Future comparisons should be organized so that the standards are known only to a neutral referee.

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2) It would be useful to have a timeline of the history of the standard, from when it was prepared, and how long it took to circulate among the research groups.

3) The fact that there was no analysis of the tank before and after the tank was circulated is a major limitation to the results of this paper, and this should be noted somewhere.

4) In the discussion of the analytical protocol, it would be useful to include if a single regulator (and what kind) was used on the NOAA standard, and what flushing volumes were used by each lab.

5) I disagree with the assertion that the behavior in tanks of CH_2Br_2 , CHBr_3 , and CH_3I (at pptv levels) is any better known than many of the other short-lived gases... particularly CHBr_2Cl , CHBrCl_2 , and CH_2BrCl . Since fewer measurements have been done on the iodine compounds, this assertion may be true for them. The reference to the Butler 2010 paper on this topic is just a repetition of this assertion, with no reference data. If the authors can provide some specific information about stability tests, that would be valuable. In my experience, each laboratory that uses gas standards in tanks has some way to monitor stability of the compounds that are reported. Since the laboratories involved here often report these other gases, and also use canisters, I suspect that they have relevant information on compound stability in their standard tanks for all of the compounds they measure. If not, how can they report anything? I also suspect that they did measure the other iodine and bromine compounds in the NOAA standard. If they don't report the results, they are missing an opportunity to share some important (and little seen) data on how groups compare to a common reference (even if absolute values may be unknown). I strongly encourage that any results on other compounds that were reported be included in this manuscript. (I also disagree that a better way to deal with these more “difficult” compounds is through an in field comparison... If you can't measure a common reference material first, then the field comparison is a waste of time).

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6) I don't understand how the Cambridge group corrected their value for combined $\text{CH}_2\text{Br}_2 + \text{CHBrCl}_2$ without knowing the individual response factors for each compound. And what do they do for real environmental samples? If they don't analyze CH_2Br_2 and CHBrCl_2 separately as part of their normal procedure, they shouldn't report separate results here. Further, I would say that the authors can't have it both ways regarding standard stability. Here, they want to believe the NOAA assigned value for CHBrCl_2 , and use it to calculate CH_2Br_2 . . .but then they say that have no confidence in the stability of the compound in the tank! It seems that it is stable! Finally, the uncertainty for CH_2Br_2 must also include the uncertainty in the assignment of CHBrCl_2 due to estimated instability.

7) I was also struck by the imprecision of the measurements of CH_3I by the Cambridge group compared to all others. Since ambient measurements are typically single analyses, this level of imprecision would seem to make data from this system not particularly useful. Can the authors provide some comment on why this might be occurring?

8) One issue that deserves more discussion is the comparison between calibrations of aqueous versus gas phase measurements of these halocarbons. A critical factor for air-sea exchange calculations is to have consistent calibration between gas and aqueous phase measurements. The group did a good effort for this experiment, but notably their measurements were significantly different for CH_3I and CHBr_3 . It would be helpful if these experts could provide some comment on why they think the results are different. The authors might want to consider discussion of how an experiment might be organized to include both air and seawater measurements of VSLs.

Interactive comment on Atmos. Meas. Tech. Discuss., 4, 765, 2011.