

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 #2

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At first reading this is a straightforward manuscript which simply reports the results of initiative to compare calibrations for measurements of three relatively short-lived atmospheric halocarbons among several British research groups. The paper also extends to groups measuring these trace gases in natural waters, where concentrations and methods are quite different. I believe this is an important undertaking for the reasons outlined in the manuscript, and that it is an entirely appropriate subject for publication in AMT.

But on further consideration I find significant shortcomings in the work, which probably result from the blending of contributions from many authors without a sufficiently coherent effort to tie it all together:

- 1) One of the greatest vulnerabilities concerns the NOAA standard that was circulated
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among the laboratories for this calibration effort. As the paper notes, the NOAA laboratory was willing only to assign provisional values to this standard canister, and do so only to two significant digits, because of concerns regarding stability. Yet the NOAA values are described in the text as “certified”, while at end of the manuscript (page 780, lines 24-26) recalibrating this canister at NOAA is described as something that should be done in the future. In my view, it should have been done before this paper was written and submitted for publication. This is a major flaw in the manuscript that is noted also by Anonymous Referee #1 (in his/her comment #3). It is standard procedure in this business, especially when dealing with trace gases that are known not to store easily, to measure “out” and “in” values for a field standard before publishing anything.

- 2) There is mention of “the NOAA scale” but the paper doesn’t say which NOAA scale. Such calibration scales are not absolute, but rather are defined within NOAA and in other groups that do primary calibrations as being related to a specific suite of primary standards. These scales are generally given a name (e.g. NOAA-2005) and have a citable reference or website where details are given. In short, the paper needs to say which NOAA scale is used, and it needs to be clear whether the UEA and UoC measurements used the same NOAA scale or a different one. Finally, although the units of the NOAA scale (dry air mole fraction) can be found in the text, these units should also be given in the caption for Table 1 where the data are listed.

- 3) Instrumental non-linearities and blank corrections are not mentioned anywhere in the discussions of instrumental methods for the five British laboratories in the study. Each laboratory should say whether blanks and instrumental non-linearities were addressed. This is a fundamental part of analytical chemistry.

- 4) Although NOAA-ESRL is not a British laboratory, the dependence of this paper on NOAA calibrations requires that the methods used at NOAA at least be described briefly, and that a reference to the NOAA methods be given.

- 5) In two places in the paper the NOAA calibrations are described as “certified”, yet

the numbers to which this refers are actually described as “preliminary” and are given with limited precision for that reason. In fact, no such calibrations should be regarded “certified” or “correct” — no authority is absolute. It would be better to call the NOAA values “assigned” mixing ratios, or something to that effect.

6) The paper includes many subjective statements that are inappropriate to this quantitative subject, such as that numbers are “in excellent agreement”, “good agreement”, “reasonably good agreement”, or “very close agreement”. Wherever possible these subjective statements should be replaced by objective ones that relate the degree of agreement to what is expected on the basis of measurement statistics.

7) Statistical precisions are reported as \pm one standard deviation, while estimated systematic uncertainties are reported as \pm two standard deviations. This is confusing. But more importantly, the authors should recognize that many systematic errors, such as those caused by contamination or by impure reagents, are not normally distributed and often have only one sign. The use of the standard deviation to describe such errors is therefore inappropriate.

8) I do not agree with the assertion (page 779, lines 22-25) that calibrations are somehow tied to the methods that are used. What is true is that different methods are vulnerable to different kinds of errors, but all methods applied properly ought to give the same answers. Perhaps this statement is just poorly worded. I also agree with Anonymous Referee #1 (in his/her comment #8) that further discussion of the comparisons between gas phase and liquid phase measurements would strengthen the paper significantly. These are quite different communities, and I am sure that there is much to be gained by bringing them closer together and recognizing what steps ought to be taken to reconcile their different approaches. Indeed, some of the answers may lie in issues of blank correction and instrumental non-linearity mentioned above.

9) I agree with Anonymous Referee #1 (at the end of his/her comment #5) that field comparisons are not called for if laboratory comparisons are problematic.

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10) In the description of the UoB measurements, it should be made clearer that there is no Scripps primary calibration for these gases, and that Scripps only checked for drift in the tertiary standard used for the UoB measurements.

In summary, I believe that this work deserves to be published, but only after a substantial effort is made to address the concerns expressed above and by Anonymous Referee #1. The most important concern, namely the re-calibration of the NOAA canister, may be somewhat moot because of the amount of time that has elapsed since the work was done, but it should be done anyway.

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