

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

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The authors would like to thank both reviewers for their constructive comments. We address specific comments from anonymous referee #1 below. All page and line numbers refer to those in the updated version of the manuscript.

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.

Of course, we agree that in principle, the best way to have co-ordinated this exercise would have been via a neutral co-ordinator with no association to the measurements, however in practise there is no formal facility or funding currently available to support

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



these inter-comparisons of VSLH measurements, and it was our opinion that it was better to organise an inter-calibration ourselves within the community, rather than to have no inter-calibration at all.

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.

The date of the initial analysis carried out by NOAA (immediately after preparation) and the dates of each laboratory's analyses are provided in Table 1. For clarity, we have also added the following sentence (Page 5 L142-144): "The initial quantification of VSLH in SX-3570 was carried out by NOAA in September 2009. Analyses by UK research groups took place between June and November, 2010."

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.

We acknowledge that the lack of a post-inter-comparison analysis is indeed a limitation, and note in the manuscript (Page 17) that re-analysis is required in the near-future. However the stability of CH₃I, CH₂Br₂ and CHBr₃ in gas standards prepared by NOAA has been extensively monitored, in several different canisters and over periods of several years. NOAA-ESRL tests demonstrate only very small changes in concentration (<5 %/yr - so within the uncertainty of the measurements in this study). We note that we should have included a statement to this effect and have modified the manuscript to include this as follows: Page 5, L144-151: "Stability studies of NOAA halocarbon gas standards prepared and contained under the same conditions as SX-3570 indicate that CH₃I, CH₂Br₂ and CHBr₃ mixing ratios are generally relatively stable over this timescale, with drift rates of <2 - 5 % yr⁻¹ (Butler et al., 2007, suppl. material). In addition, NOAA-ESRL have carried out longer term stability tests on six such canisters containing continental background mixing ratios of CHBr₃, CH₂Br₂, and CH₃I (< 1 ppt) over a 3 year period (2004-2007; during the International HALocarbons in Air Compar-

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ison Experiment (IHALACE), manuscript in preparation), and all three gases showed no significant changes over this time.”

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.

Apologies for the oversight on our part in not providing these details initially. The same regulator was used for each groups analysis – details given on Page 6, L155-157, as follows: “For all analyses a high-purity stainless steel HFS4A pressure regulator (Swagelok) was used to supply the SX-3570 gas standard at a constant pressure (30 psig)“.

The following sentences have also been added to detail the pre-sampling flushing volumes used by each lab: Page 6 L165: “Prior to trapping the system was flushed with sample gas at 100ml/min for 70 seconds.” Page 7 L205-207: “Each sample or calibration chromatogram was generated as follows: the system was flushed with ~1 litre gas prior to sampling, after which a flow (~10 ml min⁻¹) of either sample or calibration air was passed through a dual bed adsorbent...”. Page 8 L238-239: “The regulator and inlet system were flushed three times with standard gas prior to each analysis, using a volume of ~80 ml of gas.” Page 11 L313-314: “Sample lines were flushed with 100 ml sample gas prior to trapping.”

5) I disagree with the assertion that the behavior in tanks of CH₂Br₂, CHBr₃, and CH₃I (at pptv levels) is any better known than many of the other short-lived gases. . . particularly CHBr₂Cl, CHBrCl₂, and CH₂BrCl. 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 labo-

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Interactive Discussion

Discussion Paper



Interactive
Comment

ratories 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).

As discussed above in the response to point 3, the stability of CH₃I, CH₂Br₂ and CHBr₃ in NOAA standards has been described previously (Butler et al., 2007, suppl. mat., as referred to in Butler et al., 2010) whereas to our knowledge there is no published material on the stability of the other gases in Essex canisters. In order to make this clearer, the sentence has been rephrased as follows (Page 12 L346-351): "In addition, NOAA-ESRL have characterised the stability of these species in compressed gas cylinders over prolonged periods (Butler et al, 2007, supp. material), whilst to date the stability of shorter-lived iodine-containing VSLH such as CH₂I₂ and CH₂ICl has not been well studied. Thus, although these iodine containing dihalomethanes arguably play an equally important role in tropospheric halogen photochemistry, their analysis has been excluded from the following discussion."

The compounds CH₃I, CH₂Br₂ and CHBr₃ were targeted specifically in this study not just as a result of their relative stability, but predominantly because these were the compounds highlighted by the community (via the Butler et al 2010 paper) as those most important to target for inter-calibrations, since they are the most extensively measured (and modelled) of the VSLH. Many of the other VSLH are not measured by all groups, whereas these 3 compounds are routinely reported by all laboratories taking

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Interactive
Comment

part in the inter-comparison. We have modified the sentence beginning Page 12 L 340 in order to stress that the general interest regarding these gases, for atmospheric modellers as well as with regard to measurements, was our main motivation for targeting these species as follows: “Butler et al. (2010) recommend that in the first instance, inter-laboratory comparisons should focus upon the species CH₃I, CH₂Br₂ and CHBr₃, since these are the most widely reported of the short-lived halocarbons in both the atmosphere and ocean (e.g. Quack and Wallace, 2003; Chuck et al., 2005; Yokouchi et al., 2005; Butler et al., 2007; Quack et al., 2007; Carpenter et al., 2009) and have also been the focus of the majority of tropospheric VSLH modelling studies to date (e.g. Warwick et al., 2006; Palmer and Reason, 2009).”

The UoY laboratory has previously carried out stability tests on iodocarbon gas standards prepared “in-house”, and whilst iodocarbons such as CH₂ICI and CH₂I₂ stored in Silco Steel cylinders tend to be relatively stable over a few weeks (i.e. the duration of a typical field campaign), over longer periods these gases were not stable. However, gas stability can vary greatly depending upon the type of canister and humidity of the gas, and we do not yet have data on the stability of these species in the NOAA standard (as long-term studies of these compounds have yet to be carried out). Therefore, we felt it best to exercise caution when comparing measurements of these species. Since it was not possible to achieve analysis of the NOAA inter-calibration standard by all groups within a few weeks (due to various other commitments of the individual laboratories), we feel that it would be unfair to report comparisons for these species at this stage.

One of the major advantages of a field-based inter-comparison for the VSLH is that it requires all groups to be co-located and performing analyses simultaneously, thus removing the uncertainty associated with stability of certain VSLH in canisters. We have modified the sentence on Page 16 L479-483 as follows to make this point clearer: “In order to achieve a reliable inter-comparison of those VSLH that are potentially less stable in canisters and have even shorter lifetimes than CH₃I, CH₂Br₂ and CHBr₃ (such

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as CH₂I₂ and CH₂Cl₂), the general consensus is that co-locating all instruments to perform simultaneous measurements, for example via an in-situ field-based comparison, would be the best approach”. Another merit of conducting an inter-comparison through performing ambient measurements is that it would compare the whole measurement and analysis system, and not just the calibration scale. See Page 16 L483 – L488: “As some of the poly-halogenated VSLH are rapidly photolysed by sunlight and can also be less volatile and susceptible to wall losses, the sampling technique used when quantifying these species is potentially as important as the calibration method itself. Simultaneous analyses of VSLH in ambient air would allow for a more thorough inter-comparison, testing the whole measurement system in addition to the calibration scale.”.

6) I don't understand how the Cambridge group corrected their value for combined CH₂Br₂ + CHBrCl₂ without knowing the individual response factors for each compound. And what do they do for real environmental samples? If they don't analyze CH₂Br₂ and CHBrCl₂ 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 CHBrCl₂, and use it to calculate CH₂Br₂. . .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 CH₂Br₂ must also include the uncertainty in the assignment of CHBrCl₂ due to estimated instability.

It is made clear in the footnote to the Table that this is not a direct measurement but merely an assigned value calculated by subtracting the NOAA-assigned CHCl₂Br mixing ratio from the combined CHCl₂Br and CH₂Br₂ signal and assuming the same instrument response for CHCl₂Br and CH₂Br₂.

Whilst making field measurements of halocarbons on a research cruise in 2010, the separation between CH₂Br₂ and CHBrCl₂ achieved by the Cambridge GC used for the inter-comparison improved sufficiently to allow two gaussian peaks to be fitted to each

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compound (ie a partial separation). The instrument response for CH₂Br₂ relative to CHBrCl₂ over the 19 day long campaign (46 calibrations) was then assessed, and the response for CHBrCl₂ was 0.84 that of CH₂Br₂ (not the factor of 1 initially assumed for the inter-comparison). Applying this factor to the inter-comparison results yields a slightly higher estimate compared to the value initially reported, and this updated value has now been included in Table 1, to take into account the different response factors (3.01 ± 0.46 ppt).

The uncertainty in the CHBrCl₂ mixing ratio (~10%) has been incorporated into the uncertainty associated with the CH₂Br₂ mixing ratio reported by UoC. We have added a sentence to this effect on Page 8 L227-229: “The uncertainty in the NOAA assigned CHBrCl₂ mixing ratio (estimated to be 10 %, 1σ) is incorporated into the uncertainty in the CH₂Br₂ mixing ratio reported by the University of Cambridge (see below).”

7) I was also struck by the imprecision of the measurements of CH₃I 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?

The Cambridge instrument response to CH₃I is less linear compared with other target compounds, and the peak is generally more tailed than for other analytes. However, the instrument precision typically improves during long term deployments, when left to stabilise during continuous analysis over several days. In addition, slightly higher precision has more recently been achieved by fitting an exponentially modified peak. The level of precision reported here is still of scientific value as this compound often shows a large short term variability in the marine boundary layer (a factor of 10 variation can occur within a few days). The Cambridge group deploy this instrument to areas where long term measurements have never been made, so even measurements of reduced precision are valuable.

8) One issue that deserves more discussion is the comparison between calibrations

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Interactive
Comment

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 CH₃I and CHBr₃. 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.

(Also see related response to comment from reviewer 2) We have added the following discussion of the discrepancies (Page 14, L405-412): “The apparent discrepancies between aqueous and gas phase CH₃I and CHBr₃ calibrations result in PML under-estimating CH₃I and over-estimating CHBr₃ mixing ratios in the SX-3570 gas standard. Over-estimation of CHBr₃ might potentially be explained by incomplete sparging of CHBr₃ from seawater standards(although purge efficiencies have previously been measured, and are taken into account in the PML calibrations, see section 2.2.4), whilst under-estimation of CH₃I could result from breakthrough when sampling SX-3570 gas onto the sorbent tubes. CH₃I is the most volatile of the three VSLH studied here, and thus most susceptible to breakthrough.”

In addition, we have added the following consideration as to how to conduct future inter-comparisons between gas phase and aqueous VSLH calibrations (Page 15 L456-467): “Given the apparent discrepancies between aqueous and gas phase calibrations for CH₃I and CHBr₃ observed in this study, we suggest that future comparisons between aqueous and gas phase instruments should (a) use a range of primary liquid standards when preparing working standards to assess the potential variability of using liquid compared to gaseous standards and (b) evaluate any systematic differences between gas phase and aqueous phase analyses of different methods. The latter could be achieved by using a common gaseous standard for calibration of instruments, in-conjunction with analysis of a common aqueous sample (analyses of aqueous samples would have to be carried out near simultaneously to avoid any degradation). Groups

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using liquid standards should be able to report the comparability of these from one campaign to the next, i.e. be able to compare to a primary standard. Likewise, groups using NOAA gaseous standards for calibration should routinely return cylinders for re-analysis. ”

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