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Results from the first national UK inter-laboratory calibration for very short-lived halocarbons

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765

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766

The Halocarbons in the Ocean and Atmosphere (HalOcat) database project is a current SOLAS/COST initiative hosted by IFM-GEOMAR, which aims to collate atmospheric and oceanic VSLH observations from across the international research community (<https://halocat.ifm-geomar.de>). However, the lack of formal comparisons between the various calibration techniques used by different research groups to quantify halocarbons has been identified as one of the major limitations to effectively utilising this type of integrated dataset to improve global emissions estimates. Indeed it is currently difficult to discern with any certainty whether observational differences are naturally occurring, or are simply artefacts of differences in measurement and calibration techniques. Given the potential benefits of compiling a coherent global database for measurements of very short-lived halocarbons within the atmosphere and ocean, there is a general consensus within the community for the need to link individual datasets to a common calibration scale (Butler et al., 2010). Such calibration scales are already in place for longer lived atmospheric trace gases, such as CH₄ and CO₂, however the comparative instability of shorter-lived gases in metal canisters for prolonged periods (Finlayson-Pitts and Pitts, 2000), coupled with the very limited number of stability studies, makes large scale intercalibrations for these gases less straightforward.

A meeting of international scientists from the halocarbon measurement community in London in February 2008 highlighted the need for more formal inter-laboratory calibrations for these short-lived gases (Butler et al., 2010). Whilst the ultimate goal would be to undertake an international inter-calibration, encompassing all research laboratories that routinely monitor very short-lived halocarbons, funding and logistical constraints mean that to date this has not been achieved. However, the UK halocarbon measurement community has taken an initial step towards this goal, and we report here the key findings from the first formal UK inter-laboratory comparison of calibrations for very short-lived halocarbons.

769

2 Methods

Research groups from the following institutions participated in the UK inter-laboratory comparison of calibrations for very short-lived halocarbons, as part of the UK National Environment Research Council (NERC) Quantifying and Understanding the Earth System (QUEST) initiative, between June and November, 2010:

- The University of Bristol (UoB, Mace Head Atmospheric Station, Ireland)
- The University of Cambridge (UoC)
- The University of East Anglia (UEA)
- Plymouth Marine Laboratory (PML)
- The University of York (UoY)

2.1 The inter-calibration gas standard

Each laboratory's existing calibration technique was compared to the NOAA (National Oceanic and Atmospheric Administration, US) calibration scales, through the exchange of a compressed gas standard, SX-3570. The multi-component gas standard (in an electropolished stainless steel canister, Essex Cryogenics, St. Louis, MO, US) containing both VSLH and longer-lived halocarbons in modified continental background air (from Niwot Ridge, Colorado) was prepared and analysed by the NOAA Earth System Research Laboratory (ESRL) Global Monitoring Division in Boulder, Colorado. For those halocarbons with very low background air concentrations, the standard was spiked with additional volumes of high concentration halocarbons, in order to generate mixing ratios ~2–5 ppt above ambient levels. Mixing ratios assigned by NOAA for the VSLH targeted for the comparison (CH₃I, CH₂Br₂ and CHBr₃) are given in Table 1. The SX-3570 gas standard also contains other short-lived polyhalogenated methanes, including CH₂I₂, CH₂ICl and CHBrCl₂, however the stability of these gases in canisters has not been well characterised, and hence only provisional mixing ratios were assigned for these compounds.

770

chromatograms using the Cambridge working standard. With the current chromatographic set-up, CH_2Br_2 and CHBrCl_2 co-elute (O'Brien et al., 2009). For this comparison, the SX-3570 CHBrCl_2 mixing ratio assigned by NOAA was subtracted from the combined value for the unresolved CH_2Br_2 and CHBrCl_2 peaks determined by Cambridge, in order to allow as close a comparison of the CH_2Br_2 mixing ratios as possible.

Measurement precision is calculated for each target compound as the standard deviation of the 8 replicates of the standard SX-3570. The uncertainty in the reported dry air mole fraction for each target compound is calculated directly from the estimated scale uncertainties from NOAA-ESRL: 10% for CHBr_3 and 20% for CH_3I and CH_2Br_2 (two standard deviations).

2.2.3 University of East Anglia

All samples were dried on-line prior to analysis using a glass tube filled with $\text{Mg}(\text{ClO}_4)_2$. Subsequently the condensable trace gases were pre-concentrated from ~250 ml of air at -78°C in a 1/16" sample loop filled with an adsorbent (Hayesep D, 80/100 mesh) which was heated to 100°C immediately after injection. Separation was carried out using an Agilent 6890 gas chromatograph with an Agilent GS-GasPro column (length 30 m, ID 0.32 mm) coupled to a high sensitivity tri-sector (EBE) mass spectrometer from Micromass/Waters Corporation (AutoSpec Premier). The MS was operated in EI-SIR (Electron Impact-Selected Ion Recording) mode, at a mass resolution of 1000. The column temperature was held at -10°C for two minutes and then ramped from -10°C to 200°C at $10^\circ\text{C min}^{-1}$ (Laube et al., 2010). CH_3I was quantified using the I^+ ion (m/z 126.91) whilst CH_2Br_2 was quantified via $\text{CH}_2(^{79}\text{Br})^+$ (m/z 92.93) and CHBr_3 on $\text{CH}(^{79}\text{Br})(^{81}\text{Br})^+$ (m/z 172.84).

The intercalibration standard SX-3570 was measured four times against an internal standard (Aculife-treated aluminium cylinder) filled with remote tropospheric air from Niwot Ridge near Boulder, USA. The latter was brought inline with NOAA calibration scales by measuring it against two tertiary standards (35I electropolished stainless

steel canisters from Essex Cryogenics, also from Niwot Ridge, measurements in May 2010, four repeats each) which were obtained from, and calibrated by, NOAA-ESRL in 2009.

2.2.4 Plymouth Marine Laboratory

VSLH in seawater were analysed based upon the methods outlined by Hughes et al. (2008). Calibration and quantification of VSLH were performed using laboratory-prepared liquid standards, by dilution of the pure compounds into HPLC-grade methanol. The primary standards were prepared gravimetrically, the secondary and working standard by serial dilution. Microlitre volumes of the working standards were injected into seawater, and these standards were used to achieve multi-point calibrations, taking into account individual purge efficiencies of the VSLH.

Halocarbons were extracted from the water phase by purging with ultra high purity (BIP) nitrogen at 90 ml min^{-1} for 10 min. Aerosols and moisture were removed from the purge gas stream using glass wool contained within a section of glass tubing, and a counterflow Nafion drier using oxygen-free nitrogen at 180 ml min^{-1} . Halocarbons were trapped on triple-bed stainless steel solid sorbent tubes (Markes International Ltd.) containing Tenax, Carbograph and Carboxen. During sample collection, the tubes were held in a Peltier temperature-controlled block held at $1-2^\circ\text{C}$. For the purposes of the intercalibration, sample volumes of 0.5, 1.0, 1.5 and 2.0 l of the NOAA SX-3570 standard were passed through a Nafion drier (Permapure™) before being trapped on Markes sorbent tubes as described above. Molar concentrations were derived for components of SX-3570 based upon aqueous phase calibrations, and converted to ppt in order to allow comparison with the mixing ratios reported by other institutions.

Seawater calibration standards and SX-3570 samples were analysed using an Agilent GC-MS (5973N), coupled to a Markes Unity thermal desorption (TD) platform. The GC is fitted with a 60 m DB-VRX capillary column ($0.32\ \mu\text{m}$ film thickness, J & W Ltd.), and the MS was operated in electron ionization (EI)/single ion mode (SIM) throughout the analyses. CH_3I was quantified using the CH_3I^+ ion (m/z 142), CH_2Br_2

via $\text{CH}_2(^{79}\text{Br})(^{81}\text{Br})^+$ (m/z 174) and CHBr_3 on $\text{CH}(^{79}\text{Br})(^{81}\text{Br})^+$ (m/z 173). Within unity, the sample tube was heated to 200 °C, and the sample refocused onto a cold trap held at -10 °C. Following this, the cold trap was rapidly heated at 100 °C s⁻¹ to 290 °C, introducing the sample to the GC column with a helium carrier gas flow rate of 2 ml min⁻¹.
5 The GC oven temperature was held at 40 °C for 5 min, increased at 20 °C min⁻¹ to 200 °C and held for 2 min, before increasing at 20 °C min⁻¹ to 240 °C, and held for 4 min. GC-MS sensitivity drift was monitored and corrected for by injecting constant volumes of deuterated halocarbons (CD_3I , $(\text{CD}_3)_2\text{CDI}$) into each sample (prepared as for calibration standards from pure compounds) (Hughes et al., 2006, 2008). Total
10 measurement uncertainties for each compound were estimated from the combined uncertainties (root sum of squares) of the following; volumes of liquid halocarbon standard additions at each stage during serial dilution, volumes of liquid standard additions to seawater samples, purge flow rate, and the uncertainty in the calibration linear regression. Precision was estimated as the standard deviation of repeat measurements
15 performed during the calibration.

2.2.5 University of York

Analyses were carried out using an Agilent Technologies 6850 gas chromatograph coupled to a 5975C mass selective detector with an electron ionization source and operating in single ion mode (SIM). All samples were passed through a Nafion drier
20 (Permapure™) prior to pre-concentration of volatile components onto a Peltier cooled (-20 °C) adsorbent trap (UNITY2™ & CIA8, Markes International Ltd.). Analytes were thermally desorbed by heating the trap to 300 °C, and separated using an HP5-MS column (25 m, 0.25 mm ID, 0.25 micron film, Agilent J&W). CH_3I was quantified using the CH_3I^+ ion (m/z 142) with I^+ (m/z 127) as a qualifier, whilst CH_2Br_2 was quantified via
25 $\text{CH}_2(^{79}\text{Br})(^{81}\text{Br})^+$ (m/z 174) with $\text{CH}_2(^{79}\text{Br})(^{79}\text{Br})^+$ (m/z 172) as a qualifier ion, and finally CHBr_3 on $\text{CH}(^{79}\text{Br})(^{81}\text{Br})^+$ (m/z 173) with $\text{CH}(^{79}\text{Br})(^{79}\text{Br})^+$ (m/z 171) as a qualifier ion.

775

Sample volumes of 1.0, 1.5 and 2.0 l of the NOAA intercalibration standard were analysed to produce a response curve. Calibration of VSLH was achieved using a permeation oven based dynamic dilution technique based on Wevill and Carpenter (2004). Individual permeation tubes (Eco Scientific) containing pure VSLH liquids
5 are contained in one of two temperature controlled ovens (thermostatic at 40 and 70 °C) and each tube permeates a single gaseous VSLH at a steady rate. Zero grade nitrogen flows through the system at 100 ml min⁻¹ and dilutes the VSLH permeation gas to ~ppm (parts per million) levels. Loop injections of 25 µl volumes of this gas are diverted to the instrument to achieve a multi-point calibration at ppt levels, and these
10 calibrations were used to determine mixing ratios of VSLH in the intercalibration standard SX-3570. The permeation tubes are weighed periodically (using a KERN 770 mass balance, accurate to 0.01 mg) typically every 6 weeks over a period of ~1 yr, to calculate the permeation rates. The estimated uncertainty of this calibration technique is ±12%, calculated from the combined uncertainties due to the variance of the
15 permeation tube weighings, the calibration linear regression, and uncertainties in loop volumes and flow rates.

3 Results

Butler et al. (2010) recommend that in the first instance, inter-laboratory comparisons should focus upon the species CH_3I , CH_2Br_2 and CHBr_3 , since these are the most
20 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). In addition, long term studies have characterised the stability of these species in compressed gas cylinders over prolonged periods (Butler et al., 2010), whilst the stability of other VSLH such as CH_2I_2 and CH_2ICI
25 has not been well studied. As such, although the iodine containing dihalomethanes CH_2I_2 and CH_2ICI arguably play an equally important role in tropospheric halogen photochemistry, the lack of information regarding their long-term stability in pressurised gas

776

canisters means that at this stage, analyses of these gases have been excluded from the following discussion.

Each laboratory that participated in the inter-comparison used their existing measurement and calibration technique (detailed above) to determine the mixing ratios of CH_3I , CH_2Br_2 and CHBr_3 within the NOAA standard SX-3570. The results of these analyses are summarised in Table 1 and Fig. 1. The comparisons were carried out blind (i.e. the halocarbon mixing ratios in the NOAA SX-3570 gas standard were unknown), with the exception of the University of York calibration, where, as coordinators of the comparison, the scientists carrying out the analyses had prior knowledge of the certified mixing ratios.

It is important to stress that several different calibration scales exist for these gases, and there is no formal consensus as to which is the most accurate. As such, the data points with greater deviation from the NOAA-assigned values should not necessarily be considered “incorrect”. The purpose of this study is simply to identify systematic offsets between observations from the different institutions, in order to improve comparability between datasets.

The two institutions which already use the NOAA scale for VSLH calibration (University of Cambridge and University of East Anglia) reported mixing ratios which were most consistently in good agreement with the NOAA-assigned values across all compounds (ranging from ~0.5–25% depending upon the species). Although both institutions report CHBr_3 mixing ratios ~0.8 ppt larger than the NOAA-assigned value, and in excellent agreement with each other (which could indicate some degradation of CHBr_3 in the UoC and UEA standards, or an upward drift of CHBr_3 in SX-3570), all three values are consistent within the uncertainties of the measurements. The UoC, UEA and SX-3570 VSLH gas standards were all prepared and analysed by the NOAA laboratory at around the same time (August–September 2009).

Despite not currently using the NOAA scale for VSLH calibrations, both the Universities of York and Bristol report CHBr_3 mixing ratios in excellent agreement with the NOAA-assigned value, and CH_3I mixing ratios equivalent to the NOAA value, within

777

the measurement uncertainties. UoY calibrated CH_2Br_2 in SX-3570 slightly higher than NOAA (although in reasonable agreement taking into account the measurement uncertainties), whilst UoB calibrated CH_2Br_2 some ~2–3 times lower than NOAA.

The group based at Plymouth Marine Laboratory primarily analyse VSLH concentrations in seawater, and do not routinely make atmospheric measurements of these gases. As such, their normal sampling methods had to be modified in order to carry out the gas-phase calibrations, and this should be taken into consideration when interpreting their reported values. The PML-assigned CH_2Br_2 mixing ratio was nevertheless in excellent agreement with the NOAA analyses, however, the PML values for CH_3I and CHBr_3 were in less good agreement.

The mean and median of all the independently derived CH_3I , CH_2Br_2 and CHBr_3 mixing ratios are in reasonably good agreement (within 15% for median) with the NOAA-assigned values. The average CHBr_3 mixing ratio is higher than the figure reported by NOAA, however this is skewed by one high value, and removing the PML mixing ratio gives a mean (and median) of ~5.8 ppt CHBr_3 , in very close agreement with the NOAA mixing ratio.

The largest deviation between the reported mixing ratios was observed in the analysis of CH_2Br_2 (41%), whilst the closest agreement was between CHBr_3 measurements (25% deviation). Excluding the PML values, the deviation between the CHBr_3 mixing ratios was reduced to ~8%, and the spread in reported CH_3I values was also reduced, from 33% to ~20%.

4 Conclusions and future work

The results from the first UK national comparison for short-lived halocarbon calibrations provide a significant step forward to achieving the long-term goal of an internationally recognised calibration scale. This in turn will facilitate use of a coherent central database, containing a vast quantity of globally distributed VSLH measurements, and hence potentially lead to improved global source term parameterisations for these gases.

778

Since the ultimate long-term aim of these comparisons is to reduce the uncertainty in global emission estimates, we consider the spread in calibration scales for CHBr_3 , CH_2Br_2 and CH_3I found in this study compared with the current uncertainty in their global budgets. Current global oceanic CHBr_3 flux estimates range from 240–1760 Gg Br yr^{-1} (Quack and Wallace, 2003; Warwick et al., 2006; Butler et al., 2007), equivalent to $\sim 1000 \text{ Gg Br yr}^{-1} \pm 75\%$, an uncertainty considerably larger than the variation in the CHBr_3 calibration scales identified in this study. Likewise, the CH_3I global budget is estimated as $\sim 330 \text{ Gg I yr}^{-1} \pm 65\%$ (ranging from 114–546 Gg I yr^{-1} , Moore and Grozsko, 1999; Bell et al., 2002; Butler et al., 2007; Jones et al., 2010), which equates to an uncertainty substantially greater than the spread in CH_3I calibrations. Despite exhibiting the most variability between calibration scales, the $\sim 66\%$ uncertainty in the estimated global CH_2Br_2 source term ($\sim 169 \text{ Gg Br yr}^{-1} \pm 66\%$; Butler et al., 2007; Liang et al., 2010) still outweighs the discrepancies which might result from use of the different calibration scales reported here.

The results from this study suggest that gas phase CHBr_3 calibrations made by UK atmospheric research institutes are in good agreement, however this comparison also indicates that cross-calibrating between gaseous and dissolved VSLH is not straightforward. Compared to CHBr_3 , there are larger discrepancies in CH_3I calibration scales, while CH_2Br_2 calibrations proved the least consistent of the VSLH analysed during this comparison. Differences in the analytical techniques employed by the institutions involved in this study (see Sect. 2.2) may also have contributed to differences in their reported mixing ratios. For example, different detection techniques (ECD vs. MS), separation methods (type of GC column and conditions) and sample collection and preparation methods are all factors which could potentially influence the calibrations to some extent.

On a national scale, the next desirable stage in this process would be for each institution to submit their CH_3I , CH_2Br_2 and CHBr_3 observations to the HalOcat database, calibrated both according to their existing calibration scale, and adjusted for the common, NOAA, scale. As well as achieving comparability on a national level, this will

also enable measurements from the UK research groups that took part in this inter-calibration to be interpreted alongside the large database of CH_3I , CH_2Br_2 and CHBr_3 observations already published using the NOAA scale (Butler et al., 2007). A summary of relevant VSLH publications from the institutions that took part in this inter-calibration is provided as an Appendix.

In order to achieve a reliable inter-comparison of those VSLH that are potentially less stable in canisters and have even shorter lifetimes than CH_3I , CH_2Br_2 and CHBr_3 (such as CH_2I_2 and CH_2ICl), the general consensus is that an in-situ field-based comparison, with groups simultaneously measuring VSLH in ambient air, would be the best approach. 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. Furthermore, this approach would also provide a mechanism through which inter-laboratory comparisons could be extended to include measurements of VSLH in seawater. Comparisons of dissolved VSLH may prove more challenging than gas phase intercalibrations (since sparging efficiencies add an additional level of complexity, and degradation within the water may make sequential sampling of one standard over a period of a few months impractical), however these studies are necessary, since seawater measurements form a critical component of the global VSLH budget.

In the long-term, this national inter-laboratory comparison of VSLH calibrations should be repeated at frequent intervals (ideally on an annual basis), in order to maintain confidence in the level of comparability, and should ideally also be extended to include other international institutions. In addition, explanations for the differences in the calibration scales highlighted here should be explored, and the VSLH standard SX-3570 should be returned to the NOAA-ESRL for reanalysis, in order to assess any drift in mixing ratios which may have occurred since the initial analyses. Funding for this type of activity is generally not readily available, yet establishing a robust, long-term inter-laboratory comparison protocol for VSLH calibration is crucial to creating a coherent, integrated global database for these gases, and will underpin any future studies

aiming to use such a database to achieve improved estimates for global VSLH source terms.

Supplementary material related to this article is available online at:

<http://www.atmos-meas-tech-discuss.net/4/765/2011/>

5 **[amtd-4-765-2011-supplement.pdf](http://www.atmos-meas-tech-discuss.net/4/765/2011/amtd-4-765-2011-supplement.pdf)**

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785

Table 1. Summary of CH₃I, CH₂Br₂ and CHBr₃ mixing ratios as certified by NOAA and determined by the individual UK research laboratories, together with the 1σ precision in the intercalibration analyses and the estimated 2σ uncertainty in the reported mixing ratio (including systematic uncertainties in the measurement, but excluding precision), *U*. The number of data points used to derive the reported mixing ratio are given in brackets.

Institution	Date of analysis	Calibration scale	CH ₃ I (±1σ) (ppt)	<i>U</i> (ppt)	CH ₂ Br ₂ (±1σ) (ppt)	<i>U</i> (ppt)	CHBr ₃ (±1σ) (ppt)	<i>U</i> (ppt)
NOAA	9 Sep 2009	NOAA	3.8 ± 0.10	0.76	2.6 ± 0.10	0.52	5.4 ± 0.10	0.54
University of Bristol (Mace Head)	23 Jun 2010	Linde (CH ₂ Br ₂ , CHBr ₃); NIES (CH ₃ I)	3.33 ± 0.07 (13)	0.52	0.70 ± 0.01 (10)	0.56	5.51 ± 0.07 (10)	0.62
University of Cambridge	12 Oct 2010	NOAA	4.76 ± 0.91 (8)	0.95	*2.66 ± 0.21 (8)	0.53	6.26 ± 0.32 (8)	0.63
University of East Anglia	9 Jun 2010	NOAA	3.91 ± 0.02 (4)	0.94	2.62 ± 0.03 (4)	0.66	6.20 ± 0.44 (4)	1.27
Plymouth Marine Laboratory	9 Nov 2010	PML (liquid standards)	1.78 ± 0.10 (8)	0.21	2.93 ± 0.07 (8)	0.12	9.28 ± 0.57 (8)	0.93
University of York	25 Oct 2010	York (permeation oven)	2.97 ± 0.04 (3)	0.33	3.18 ± 0.05 (3)	0.41	5.30 ± 0.10 (3)	0.60
Mean			3.35		2.42		6.51	
Median			3.33		2.66		6.20	
% standard deviation			33%		41%		25%	

* Note that the University of Cambridge GC-ECD was not able to distinguish between CH₂Br₂ and CHBrCl₂, which co-elute on their system. However, subtraction of the NOAA-assigned CHBrCl₂ mixing ratio from the combined CH₂Br₂ and CHBrCl₂ signal (and assuming the same instrument response for CHBrCl₂ and CH₂Br₂) gives the value indicated.

786

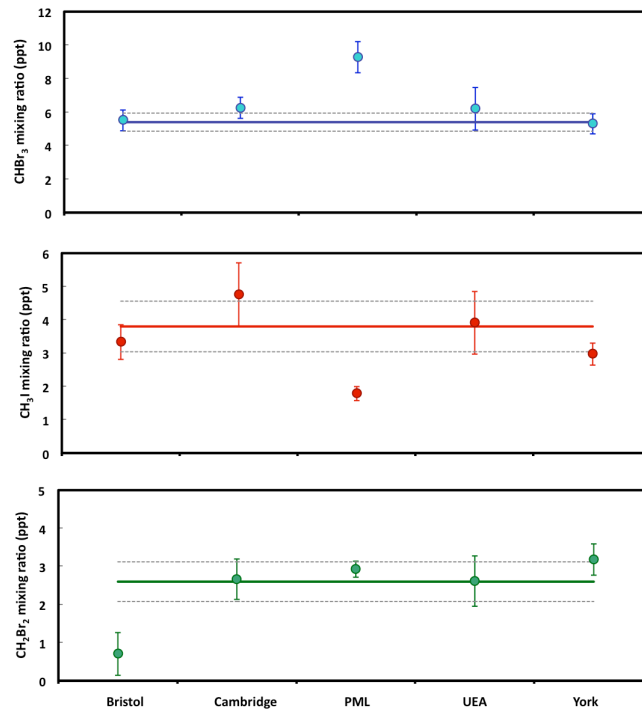


Fig. 1. CH₃I, CH₂Br₂ and CHBr₃ mixing ratios determined by each research group, with estimated measurement uncertainties. The solid line in each plot corresponds to the NOAA-assigned mixing ratio, and the grey dotted lines indicate the estimated uncertainty in the NOAA values.