

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

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Abstract. Very short-lived halocarbons (VSLH) such as CH₃I, CH₂Br₂ and CHBr₃ provide an important source of reactive halogens to the atmosphere, however high spatial and seasonal variability in their ambient mixing ratios and sea-air fluxes gives rise to considerable uncertainty in global scale emission estimates. One solution to improve global flux estimates is to combine the multitude of individually published datasets to produce a database of collated global halocarbon observations. Some progress towards this has already been achieved through the HalOcat (Halocarbons in the Ocean and Atmosphere) database initiative, but the absence of a common calibration scale for very short-lived halocarbons makes it difficult to distinguish true environmental variations from artefacts arising from differences between calibration methodologies. As such, the lack of inter-calibrations for both air and seawater measurements of very short-lived halocarbons has been identified as a major limitation to current estimations of the global scale impact of these reactive trace gases. Here we present the key findings from the first national UK inter-laboratory comparison for calibrations of the halocarbons CH₃I, CH₂Br₂ and CHBr₃. The aim of this inter-calibration was to provide transparency

between halocarbon calibrations from major UK research institutions, an important step towards enabling all measurements from these institutions to be treated as one coherent integrated dataset for global source term parameterisations.

1 Introduction

Very short-lived halocarbons or VSLH (defined as those with atmospheric lifetimes of less than six months, Law and Sturges, 2007) of predominantly biogenic marine origin are thought to supply a substantial fraction of reactive halogens to the marine boundary layer (MBL) (Carpenter et al., 2003; Jones et al., 2010), free troposphere (von Glasow et al., 2004; Yang et al., 2005) and lower stratosphere (Garcia and Solomon, 1994; Sturges et al., 2000; Liang et al., 2010 and references therein), potentially influencing both stratospheric and tropospheric photochemistry and climate.

Photo-destruction of volatile organic iodine- and bromine-containing trace gases to release I and Br atoms within the troposphere can initiate catalytic ozone depletion and impact upon NO/NO₂ and OH/HO₂ chemistry, which in turn affects the atmospheric lifetimes of other climatically important trace gases (Vogt et al., 1999; Bloss et al., 2005; Read et al., 2008; Whalley et al., 2010; Mahajan et al., 2010).



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While the majority of organic iodine compounds (or iodocarbons) are broken down within the troposphere, the relatively longer lived bromocarbons (e.g. CH_2Br_2 and CHBr_3 , with respective lifetimes of 3–4 months and ~3–5 weeks; Quack et al., 2007) are thought to contribute ~15–40 % of stratospheric bromine (Montzka and Reimann, 2011). Bromine-catalysed stratospheric ozone depletion is on average ~60 times more efficient than chlorine-initiated ozone destruction (Law and Sturges, 2007), yet to date sources of stratospheric bromine have been less well quantified.

The number of published VSLH datasets has increased substantially in recent years (including Quack and Wallace, 2003 and references therein; Chuck et al., 2005; Archer et al., 2007; Carpenter et al., 2007; Quack et al., 2007; Laube et al., 2008; Varner et al., 2008; O'Brien et al., 2009; Carpenter et al., 2009; Jones et al., 2010; Kurihara et al., 2010), and includes atmospheric and oceanic measurements, and sea-air flux estimates. However, there remains considerable uncertainty associated with global source term estimates for these gases (e.g. annual global CHBr_3 source estimated as ~10 Gmol Br yr^{-1} , but including the quantifiable uncertainties gives the range 3–22 Gmol Br yr^{-1} ; Quack and Wallace, 2003). This high level of variability is the result of several factors, including the spatial and seasonal variability in VSLH biological production and sea-air transport rates, their short tropospheric lifetimes, the sparse availability of data which may be considered representative of regional sources (i.e. made in the free troposphere or over the open ocean), and the lack of a common calibration scale for these gases. Improved quantification of the global emission budget for these short-lived halocarbons requires an integrated approach, combining as many datasets as possible, in order to maximise the temporal and spatial resolution.

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 CH_4 and CO_2 , 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 inter-calibrations 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.

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. NOAA-ESRL determined VSLH mixing ratios in SX-3570 by gas chromatography with mass-selective detection

Table 1. Summary of CH₃I, CH₂Br₂ and CHBr₃ mixing ratios as assigned by NOAA and determined by the individual UK research laboratories, together with the 2σ precision in the inter-calibration analyses and the estimated 2σ (95.4 % confidence interval) overall uncertainty in the reported mixing ratio (incorporating both systematic uncertainties and precision), U . The number of data points used to derive the reported mixing ratio is given in brackets.

Institution	Date of analysis	Calibration scale	CH ₃ I ($\pm 2\sigma$) (ppt)	U (2σ) (ppt)	CH ₂ Br ₂ ($\pm 2\sigma$) (ppt)	U (2σ) (ppt)	CHBr ₃ ($\pm 2\sigma$) (ppt)	U (2σ) (ppt)
NOAA	9 Sep 2009	NOAA	3.8 ± 0.2	0.79	2.6 ± 0.2	0.56	5.4 ± 0.2	0.58
University of Bristol (Mace Head)	23 Jun 2010	Linde (CH ₂ Br ₂ , CHBr ₃); NIES (CH ₃ I)	3.33 ± 0.14 (13)	0.54	0.70 ± 0.02 (10)	0.56	5.51 ± 0.14 (10)	0.64
University of Cambridge	12 Oct 2010	NOAA	4.76 ± 1.82 (8)	2.05	$*3.01 \pm 0.42$ (8)	0.80	6.26 ± 0.64 (8)	0.90
University of East Anglia	9 Jun 2010	NOAA	3.91 ± 0.04 (4)	0.94	2.62 ± 0.06 (4)	0.66	6.20 ± 0.88 (4)	1.55
Plymouth Marine Laboratory	9 Nov 2010	PML (liquid standards)	1.78 ± 0.20 (8)	0.29	2.93 ± 0.14 (8)	0.18	9.28 ± 1.14 (8)	1.47
University of York	25 Oct 2010	York (permeation oven)	2.97 ± 0.08 (3)	0.34	3.18 ± 0.10 (3)	0.42	5.30 ± 0.20 (3)	0.63
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 CHBrCl₂ and CH₂Br₂ signal (and based on an instrument response for CHBrCl₂ of 0.84 times the CH₂Br₂ response) gives the value indicated.

(GC/MS) (Montzka et al., 1993, 1996). Samples were analyzed relative to gravimetrically-prepared standards (cylinders similar to SX-3570, Butler et al., 2007). The mixing ratios assigned by NOAA for the VSLH targeted for the comparison (CH₃I, CH₂Br₂ and CHBr₃) are given in Table 1. CHBr₃ was calibrated based upon the NOAA-2003 scale, whilst CH₃I and CH₂Br₂ were calibrated according to the NOAA-2004 scale. 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. 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. 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 $<2\text{--}5\%$ yr⁻¹ (Butler et al., 2007, Supplement). 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 Comparison Experiment (IHALACE), manuscript in preparation), and all three gases showed no significant changes over this time.

2.2 Calibration and analysis methods

Details of the analytical systems and calibration techniques used by each group during the inter-comparison are outlined below. 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).

2.2.1 University of Bristol (Mace Head)

All comparisons were carried out using the Medusa-MS (custom pre-concentration device coupled to an Agilent 6890 GC and Agilent 5973 MSD). 2 L samples were pre-concentrated on a trap held at $-150\text{--}170\text{ }^{\circ}\text{C}$ and were subsequently analysed using a single main capillary chromatography column (CP-PoraBOND Q, 0.32 mm ID \times 25 m, 5 μm , Varian Chrompack) with temperature and pressure ramping (Miller et al., 2008). Prior to trapping the system was flushed with sample gas at 100 ml min^{-1} for 70 s.

The MS was operated in EI-SIM (Electron Impact-Selected Ion Monitoring) mode using a single target ion and one or two qualifier ions as a check for the correct ion ratios. The starting column temperature was $40\text{ }^{\circ}\text{C}$, this was ramped on injection of the sample to $200\text{ }^{\circ}\text{C}$ at $28\text{ }^{\circ}\text{C min}^{-1}$. CH₃I was quantified using the CH₃I⁺ ion (m/z 142) with I⁺ (m/z 127) as a qualifier, whilst CH₂Br₂ was quantified via CH₂Br₂⁺ (m/z 174) with CH₂Br⁺ (m/z 93) and CH₂Br⁺ (m/z 95) as qualifier ions, and finally CHBr₃ on CH(⁷⁹Br)(⁸¹Br)⁺ (m/z 173) with CH(⁷⁹Br)(⁷⁹Br)⁺ (m/z 171) as a qualifier ion.

The NOAA standard SX-3570 was compared against a tertiary standard (J-128), filled during relatively clean-air conditions at Trinidad Head using modified diving compressors (SA-6, RIX Industries), and measured against secondary standards at Scripps Institution of Oceanography (SIO) to check for drift before and after usage at Mace Head. In the case of CH_2Br_2 and CHBr_3 , preliminary calibration values were assigned by comparison to a commercial gas standard prepared by Linde Gas Ltd. In the case of CH_3I , a preliminary calibration was assigned via comparison to a gas standard provided by Y. Yokouchi (National Institute for Environmental Studies, NIES, Japan). The precision of the SX-3570 to J-128 measurement was $\sim 2\%$ for CH_3I , $\sim 0.7\%$ for CH_2Br_2 and $\sim 1.2\%$ for CHBr_3 ($n = 10$). No blank corrections were applied to the data. The Medusa-MS has demonstrated linearity for concentrations of up to 12 times higher than typical background ambient mixing ratios for CHBr_3 and 8 times ambient CH_2Br_2 mixing ratios.

2.2.2 University of Cambridge

At Cambridge, the calibration comparison was carried out using a GC-ECD (gas chromatograph with electron capture detection) system similar to that described by Gostlow et al. (2010) but with improved sample pre-concentration (thermally regulated) and separation (longer column). The inter-calibration standard SX-3570 was compared to the Cambridge working standard (NOAA cylinder no. SX-3568; CHBr_3 calibrated according to the NOAA 2003 scale and CH_3I and CH_2Br_2 calibrated based upon the 2004 scale) using a sequence of samples analysed over a 24 h period. The SX-3570 standard was treated as an unknown sample and the Cambridge working standard was used to achieve calibration. The sequence generated 8 sample chromatograms from analysis of SX-3570 and 9 calibration chromatograms of the Cambridge working standard (with sample volumes from 3–50 ml), to produce response curves which were used to calibrate the samples. Blank chromatograms were run following each sample or calibration chromatogram by passing helium carrier gas through the adsorbent bed (these served as a check on desorption efficiency and system impurities, and were sufficiently clean that blank corrections were not necessary).

Each sample or calibration chromatogram was generated as follows: the system was flushed with ~ 11 gas prior to sampling, after which a flow ($\sim 10 \text{ ml min}^{-1}$) of either sample or calibration air was passed through a dual bed adsorbent (1 mg each of Carboxen 1016/1001) held in an Ultimet tube ($1/32'' \text{ od} \times 0.53 \text{ mm id}$, Varian) mounted across a 6 port, 2 position Valco valve set in the “load” position. The adsorbent tube was Peltier-cooled to 15°C , the target sample volume was 20 ml. Oxygen and residual moisture were purged from the adsorbent bed using dry helium before the Valco valve was switched to the “inject” position and the adsorbent tube was heated to 190°C for 15 s in the

helium carrier flow. The column (Restek MXT 502.2, 20 m long, 0.18 m i.d., $1 \mu\text{m}$ film thickness) was held at 28°C for 6 min then heated to 132°C at 6°C min^{-1} , and the helium carrier gas pressure was increased to compensate for the increase in gas viscosity during the temperature program. The analytes were directed into the ECD (Agilent micro volume model no. G2397-60510) running at 250°C . Target peaks in chromatograms from the inter-calibration standard were calibrated using the response curve for each compound generated from the calibration chromatograms using the Cambridge working standard. These enable the tracking of small changes in detector non-linearity, which are taken into account in the work-up of the data. For CHBr_3 and CH_2Br_2 , the response is reasonably linear (Gostlow et al., 2010). 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. The uncertainty in the NOAA assigned CHBrCl_2 mixing ratio (estimated to be 10 %, 1σ) is incorporated into the uncertainty in the CH_2Br_2 mixing ratio reported by the University of Cambridge (see below).

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 (2σ).

2.2.3 University of East Anglia

All samples were dried on-line prior to analysis using a glass tube filled with $\text{Mg}(\text{ClO}_4)_2$. The regulator and inlet system were flushed three times with standard gas prior to each analysis, using a volume of ~ 80 ml of gas. 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 inter-calibration 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 in line with NOAA calibration scales (the 2003 scale for CHBr_3 and 2004 scale for CH_3I and CH_2Br_2) by measuring it against two tertiary standards (351 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. Throughout these analyses, blank signals were much smaller than the reported measurement precision, and were thus not considered. Analysis of the SX-3570 standard demonstrates that this system produces a linear response for CH_3I , CH_2Br_2 and CHBr_3 up to $\sim 2\text{--}5$ ppt.

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, while the secondary and working standards were prepared 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 minutes. 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 $1\text{--}2^\circ\text{C}$. For the purposes of the inter-calibration, 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 (PermapureTM) before being trapped on Markes sorbent tubes as described above. Molar concentrations were derived for components of SX-3570 based upon purge-efficiency-corrected aqueous phase calibrations, and converted to ppt in order to allow comparison with the mixing ratios reported by other institutions. The instrument response was linear for 0.5–2.0 l gas for all three compounds ($R^2 > 0.99$), and no blank corrections were applied.

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 μm 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). The instrument response was linear for CH_3I ($0\text{--}4\text{ pmol l}^{-1}$,

$R^2 > 0.98$), CH_2Br_2 ($0\text{--}14\text{ pmol l}^{-1}$, $R^2 > 0.99$) and CHBr_3 ($0\text{--}15\text{ pmol l}^{-1}$, $R^2 > 0.99$). 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} . The GC oven temperature was held at 40°C for 5 min, increased at $20^\circ\text{C min}^{-1}$ to 200°C and held for 2 min, before increasing at $20^\circ\text{C min}^{-1}$ 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 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 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 (PermapureTM) prior to pre-concentration of volatile components onto a Peltier cooled (-20°C) adsorbent trap (UNITY2TM & CIA8, Markes International Ltd.). Sample lines were flushed with 100 ml sample gas prior to trapping. 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 $\text{CH}_2(^{79}\text{Br})(^{81}\text{Br})^+$ (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.

Sample volumes of 1.0, 1.5 and 2.0 l of the NOAA inter-calibration standard were analysed to produce a linear response curve. No VSLH signals were detected in nitrogen-only blank samples, and as such blank corrections were deemed unnecessary. 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 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 $\sim\text{ppm}$ (parts per million) levels. Loop injections of $25\text{ }\mu\text{L}$ volumes of this gas are diverted to the

instrument to achieve a multi-point calibration at ppt levels, and these calibrations were used to determine mixing ratios of VSLH in the inter-calibration 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 year, to calculate the permeation rates. The estimated uncertainty of this calibration technique is $\pm 12\%$, calculated from the combined uncertainties due to the variance of the 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 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). In addition, NOAA-ESRL have characterised the stability of these species in compressed gas cylinders over prolonged periods (Butler et al., 2007, Supplement), whilst to date the stability of shorter-lived iodine-containing VSLH such as CH_2I_2 and CH_2ICl 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.

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 NOAA-assigned mixing ratios.

The mixing ratios determined by each laboratory are reported in Table 1, together with the associated 2σ analytical precision and estimated 2σ overall measurement uncertainty. The total uncertainties are a combination of bias (e.g. potential wall losses/gains, flow errors, gravimetric errors) and precision errors. The precision error is presumed to behave randomly, with a zero mean. Both the bias and precision are presumed to represent stationary statistical properties of a Gaussian distributed data set. Assuming that the errors are un-correlated, the total uncertainty may be estimated from the sum of squares of all the bias and precision errors (Mofat, 1988).

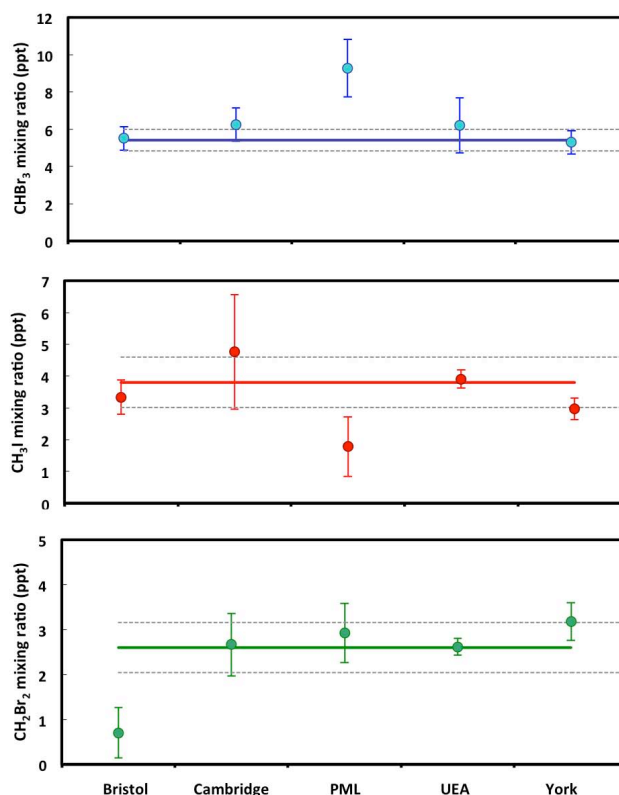


Fig. 1. CHBr_3 , CH_3I and CH_2Br_2 mixing ratios determined by each research group, with estimated 2σ measurement uncertainties. The solid line in each plot corresponds to the NOAA-assigned mixing ratio, and the grey dotted lines indicate the estimated 2σ uncertainty in the NOAA values.

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 that 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 within ~ 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 (within 1%), 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

CHBr₃ mixing ratios in excellent agreement with the NOAA-assigned value (within 2 %), and CH₃I mixing ratios equivalent to the NOAA value, within the measurement uncertainties. UoY calibrated CH₂Br₂ in SX-3570 slightly higher than NOAA (although in reasonable agreement taking into account the measurement uncertainties), whilst UoB calibrated CH₂Br₂ 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 CH₂Br₂ mixing ratio was nevertheless in good agreement with the NOAA analyses (within ~12 %, and equivalent within measurement uncertainties). However, the CH₃I and CHBr₃ mixing ratios reported by PML differed from the NOAA-assigned values by ~25 % and ~45 %, respectively, which is outside of measurement uncertainties.

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 Sect. 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 is most susceptible to breakthrough.

The mean and median of all the independently derived CH₃I, CH₂Br₂ and CHBr₃ mixing ratios are in reasonably good agreement (within 2–15 % for median, 7–21 % for mean) with the NOAA-assigned values. The largest discrepancy is between the average independently derived CHBr₃ mixing ratio and the figure reported by NOAA, however this is skewed by the high PML mixing ratio value; removing this value gives a mean (and median) of ~5.8 ppt CHBr₃, bringing the agreement to within 8 %.

The largest deviation between the reported mixing ratios was observed in the analysis of CH₂Br₂ (41 %), whilst the closest agreement was between CHBr₃ measurements (25 % deviation). Excluding the PML values, the deviation between the CHBr₃ mixing ratios was reduced to ~8 %, and the spread in reported CH₃I 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.

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 CHBr₃, CH₂Br₂ and CH₃I found in this study compared with the current uncertainty in their global budgets. Current global oceanic CHBr₃ flux estimates range from 240–1760 Gg Br yr⁻¹ (Quack and Wallace, 2003; Warwick et al., 2006; Butler et al., 2007), equivalent to ~1000 Gg Br yr⁻¹ ± 75 %, an uncertainty considerably larger than the variation in the CHBr₃ calibration scales identified in this study. Likewise, the CH₃I global budget is estimated as ~330 Gg I yr⁻¹ ± 65 % (ranging from 114–546 Gg I yr⁻¹, Moore and Groszko, 1999; Bell et al., 2002; Butler et al., 2007; Jones et al., 2010), which equates to an uncertainty substantially greater than the spread in CH₃I calibrations. Despite exhibiting the most variability between calibration scales, the ~66 % uncertainty in the estimated global CH₂Br₂ source term (~169 Gg Br yr⁻¹ ± 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 CHBr₃ 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 CHBr₃, there are larger discrepancies between gas phase CH₃I calibration scales, while CH₂Br₂ calibrations proved the least consistent of the VSLH analysed during this comparison.

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 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 reanalysis.

On a national scale, the next desirable stage in this process would be for each institution to submit their CH₃I, CH₂Br₂ and CHBr₃ 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 a Supplement.

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 co-locating all instruments to perform simultaneous measurements, for example via an in-situ field-based comparison, 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. 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. 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 inter-calibrations (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.net/4/865/2011/amt-4-865-2011-supplement.pdf>

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