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Technical Note: Ensuring consistent, global measurements of short-lived halocarbon gases in the ocean and atmosphere

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Short-lived halocarbons are significant sources of reactive halogen in the troposphere and likely the lower stratosphere. Quantifying ambient concentrations in the surface ocean and atmosphere is essential for understanding the impact of fluxes of these gases on marine boundary layer oxidation and lower stratospheric ozone-depletion processes. Despite the body of literature increasing substantially over recent years, calibration issues complicate comparison of results and limit the utility of building larger-scale databases that would enable further development of the science (e.g. sea-air flux quantification, model validation, etc.). With this in mind, thirty-two scientists representing eight nations and from both atmospheric and oceanic halocarbon communities gathered in London in February 2008 to discuss the scientific issues and plan an international effort toward a common calibration scale. Here, we discuss the outputs from this meeting, suggest the compounds that should be targeted initially, identify opportunities for beginning calibration and comparison efforts, and make recommendations for ways to improve the comparability of previous and future measurements.

1 Introduction

Short-lived halocarbons (lifetimes less than ~six months) have been implicated as significant sources of reactive halogen in both the marine boundary layer and the lower stratosphere. In the marine boundary layer, inorganic bromine (Br) and iodine (I), which are involved in free radical chemistry, originate in part from their organic counterparts and are responsible for a sizeable fraction of oxidation (von Glasow et al., 2004; Yang et al., 2005; Salawitch, 2006). In the lower stratosphere, Br dramatically accelerates the chlorine-driven depletion of ozone. Long-lived source gases alone cannot account for the total amount of inorganic bromine (Br_y) in the lower stratosphere (Dorf, 2005; Law and Sturges, 2007). About 20–35% of the Br in the lower stratosphere likely derives from short-lived halocarbons that are rapidly convected from the marine boundary layer (Kritz et al., 1993; Law and Sturges, 2007).

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Quantifying sources of short-lived halocarbons is challenging. The combination of short tropospheric lifetimes and a variety of natural sources leads to substantial variability in mixing ratios and fluxes. Although substantial progress has been made, improving our understanding of the contribution of these important halogen sources to stratospheric and tropospheric chemistry is limited, in part, by a lack of calibration and comparison of measurements among laboratories. For example, Quack et al. (2007b) reported an uncertainty factor of ~ 2.5 in ocean-atmosphere CHBr_3 fluxes related to analytical and calibration differences between two groups collecting data on the same cruise and O'Brien et al. (2009) report substantial differences between atmospheric concentrations of very short-lived halocarbons measured by two groups at the Cape Verde Observatory. Other studies also highlight variability in oceanic concentrations and atmospheric fluxes, with reported values varying by several orders of magnitude in individual investigations, and also varying widely among the various reports (for example, see Figs. 1 and 2). These variations result, in part, from natural spatial and temporal differences, but it is not always clear how much the discrepancies emanate from analytical or calibration dissimilarities. Without these distinctions, one cannot differentiate between spatial/temporal variability and systematic offsets, and quantifying relative contributions of organic and inorganic forms to the reactive species that drive oxidation is difficult. Consistency of calibration is particularly important for experiments involving multiple investigators and multiple platforms in which the principal aim is to quantify fluxes of very short-lived source and product gases entering the upper troposphere. Despite an increasing volume of publications and important results, calibration issues continue to limit the ability of researchers to take full advantage of expanding data sets. Combining data into a global dataset without reference to calibration could diminish the utility of the database as a whole.

Seeking to address this issue, thirty-two scientists from eight nations gathered in February, 2008 at the Novartis Institute in London (see Appendix A). The aim was to plan for an international effort that would ensure traceability to common calibration scales for oceanic and atmospheric measurements of short-lived, volatile halocar-

bons. Discussions focused on determining the scope of the scientific need, identifying which compounds should be targeted for the greatest scientific benefit, identifying opportunities for beginning calibration and comparison efforts, and prescribing a way forward for improving the comparability of measurements. It was clear from discussion at the meeting that calibration remains a nagging issue in the community (see <http://tinyurl.com/c9cg58> for more details). Many scientists are eager to compare and share information; they just seem to lack a coordinator or group dedicated to initiating discussion and information exchange.

2 Discussion

Efforts at improving calibration methods, traceability, and confidence in long-term records of these gases are needed. Bi-lateral comparisons have been performed during field studies, and the results of some of these comparisons have led to increased interest in calibration procedures, but a broader, on-going comparison effort is desired. One complication is that some investigators mainly study aqueous species whereas others focus on atmospheric gaseous measurements, yet both sets of measurements are required for estimating fluxes to the atmosphere. The approach to standardization in the community must thus consider both liquid and gaseous media. It was generally agreed, however, that initial efforts should focus on the measurement of substances in air, as this presented the fewest complications. Thus, the exchange of air samples in cylinders was suggested as an immediate goal. Further, since there are a number of species of interest, the initial comparisons would focus on a few select species thought to be the most important in terms of bromine and iodine (CHBr_3 , CH_2Br_2 , and CH_3I). This also takes advantage of the fact that knowledge of stability in gas cylinders (at both low and high pressures) is more mature for these gases. Additional species such as CH_2BrCl , CH_2I_2 , etc. could be measured, of course, but air sample preparation would likely focus on the target species.

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For the initial comparison involving air samples, the pros and cons of different approaches were discussed. One approach involves the circulation of a few large cylinders, such as is frequently done within the CO₂-measurement community. The advantage of this type of approach is that the capital costs are often lower, and the cylinders can be linked relatively easily by one or more central labs. A disadvantage is that such an experiment can take a long time to complete. The International HALocarbons in Air Comparison Experiment (IHALACE) involved 21 labs and took three years to complete. These types of experiment have been successfully carried out by the WMO Global Atmosphere Watch program and other coordinated groups for long-lived trace gases such as CO₂, CH₄, CO, and N₂O (e.g. CarboEurope, <http://tinyurl.com/csrsq5>), however, the time required to circulate cylinders remains an issue (WMO, 2005). A second approach involves sending samples in small containers to each laboratory simultaneously. The advantage is that the experiment can be completed quickly and can be operated on a continuing basis. Disadvantages include potentially high capital costs (the purchase of many small flasks or cylinders), and the burden placed on one or more labs to prepare samples and link all samples to common scales. This can also be complicated by the fact that stability cannot be guaranteed and must be verified by the coordinating lab. It was decided at the meeting that the circulation of many smaller flasks or cylinders was preferred, although a source of funding to initiate the project was not determined.

Beyond efforts to establish an initial or on-going comparison study involving air samples there was great interest in an intensive study in which several investigators would make measurements at a common site. This was suggested as a near-term goal and would involve investigators that could measure constituents in air, water, or both. An intensive study involving a large number of investigators is critical to resolving analytical issues. Finally, it was noted that a single comparison effort would not be enough. A plan to compare measurements regularly would need to be developed. With better calibration and comparison efforts, the scientific community could develop a global halocarbon dataset, with much more confidence in its reliability than today.

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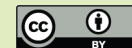
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An immediate result of the London meeting was the apparent increase in communication and bi-lateral comparison. Several groups exchanged air samples and data as a direct result of the meeting. In the end, however, the community needs to find a home for this coordination effort. Currently, the WMO Global Atmosphere Watch program hosts scientific advisory groups for greenhouse gases, ozone, reactive gases, aerosols, and precipitation chemistry. The WMO advisory groups work with the atmospheric community to establish calibration centres, measurement guidelines, and assist in comparison efforts so that future participants can ensure the value of their measurements to the global community. Perhaps unfortunately, naturally-occurring short-lived halocarbons do not fit neatly into any of the current groups: short-lived halocarbons are largely of marine origin, which brings in a strong aquatic component, and are big players in both stratospheric (ozone) and tropospheric (reactive gases) chemistry.

Work is underway to improve calibration and comparison efforts. Interested investigators involved in the measurement of short-lived halocarbons and other related trace gases should contact one of the authors for information on current comparison activities. Alternatively, please visit the Surface Ocean – Lower Atmosphere Study (SOLAS) project integration website for more information (<http://tinyurl.com/4xwzpa>).

Appendix A

Scientists attending the Short-Lived Halocarbon Intercalibration Workshop, London, UK, 2008

Abrahmsson, Katrina	Chalmers University of Tech., Göteborg, Sweden
Atlas, Elliot	University of Miami, USA
Bell, Thomas	University of East Anglia, Norwich, UK
Blake, Don	University of California, Irvine, USA
Butler, James	NOAA Earth System Research Laboratory, USA

Carpenter, Lucy
Hall, Brad
Harris, Neil
Hughes, Claire
Jones, Charlotte
Karlsson, Anders
Laube, Johannes
Maione, Michela
Martino, Manuela
Milton, Martin
Moore, Bob
Morin, Pascal
Nightingale, Phil
O'Doherty, Simon
Oram, David
Quack, Birgit
Raimund, Stefan
Scholer, Heinfried
Schulz-Bull, Detlef
Sive, Barkley
Smythe-Wright, Denise
Von Glasow, Roland
Warwick, Nicola
Weiss, Ray
Williams, Jonathan
Yokouchi, Yoko

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NOAA Earth System Research Laboratory, USA
University of Cambridge, UK
University of East Anglia, Norwich, UK
University of York, UK
Chalmers University of Tech., Göteborg, Sweden
Frankfort University, Germany
University of Urbino, Pesaro, Italy
University of East Anglia, Norwich, UK
National Physical Laboratory, Teddington, UK
Dalhousie University, Halifax, Canada
Station Biologique de Roscoff, France
Plymouth Marine Laboratory, UK
University of Bristol, UK
University of East Anglia, Norwich, UK
IFM-GEOMAR, Keil, Germany
Station Biologique de Roscoff, France
Heidelberg, Germany
University of Heidelberg, Germany
University of New Hampshire, USA
National Oceanography Centre, Southampton, UK
University of East Anglia, Norwich, UK
University of Cambridge, UK
University of California, San Diego, USA
Max Planck Institute for Chemistry, Mainz, Germany
National Institute for Environmental Studies, Ibaraki, Japan

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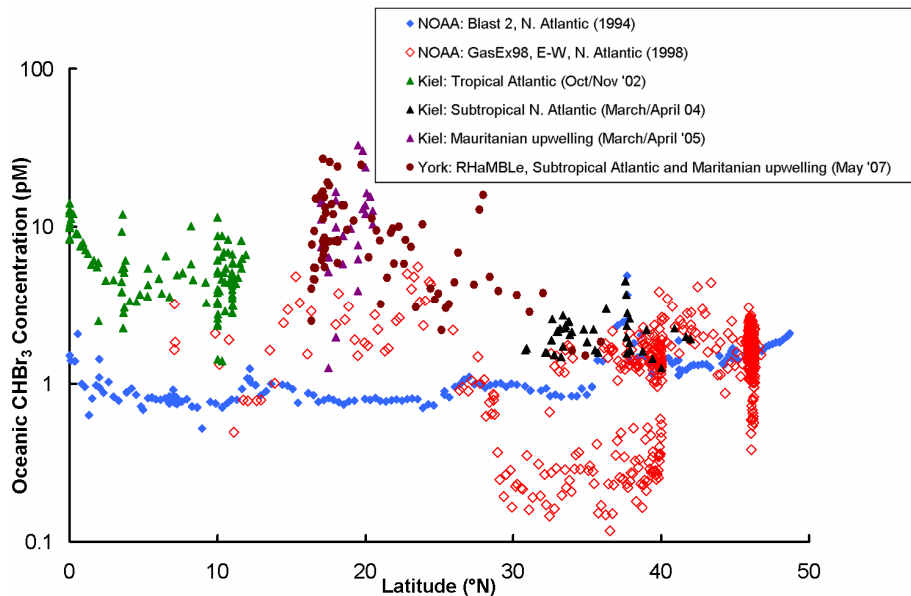


Fig. 1. Oceanic CHBr_3 concentrations (pM) in surface waters of the North Atlantic Ocean. Note the log scale for CHBr_3 concentration. Data from a number of sources (Quack, unpublished data, Meteor 60/5, 2004; Quack et al., 2004, 2007a; Butler et al., 2007; Carpenter et al., 2009).

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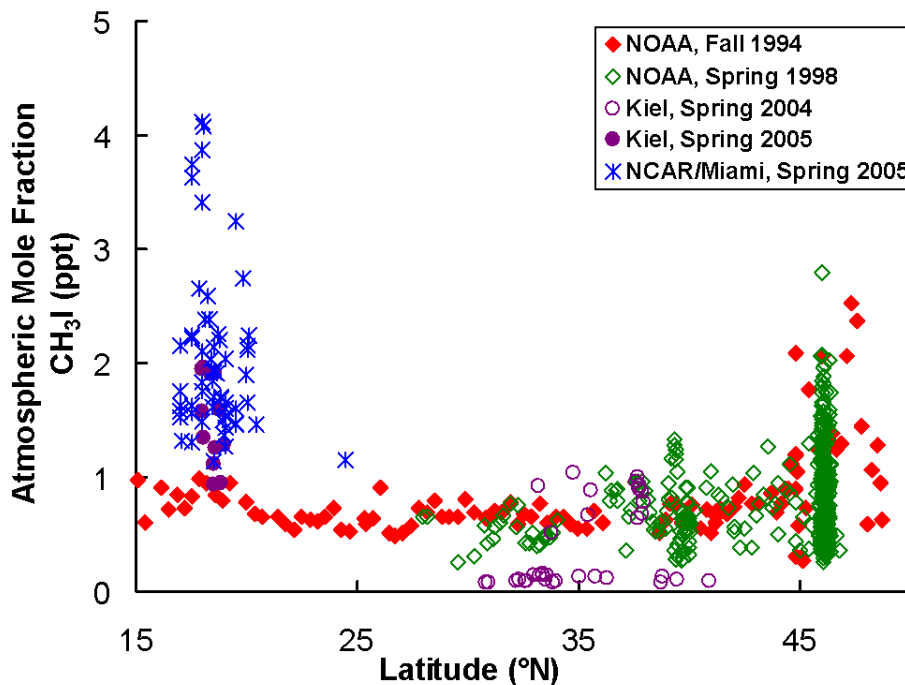


Fig. 2. Atmospheric mole fraction CH₃I (ppt) in the marine boundary layer over the North Atlantic Ocean from 1994–2005. Data from a number of sources (Richter, 2003; Butler et al., 2007; Quack et al., 2007a).

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