Halocarbon Intercomparison Workshop
4 February 2008
Novartis Institute
London, UK

(Jointly sponsored by COST, SOLAS, and NERC)

On 4 February, 2008, thirty-five scientists from seven nations countries gathered in London at the Novartis Institute to discuss the need for an international effort that would ensure traceability of measurements of short-lived, volatile halocarbons to a common calibration scale. The need for this workshop was driven by the recognition that, although many measurements of these gases have been made in the atmosphere and ocean, they cannot always be relied upon to draw distinctions in regional or temporal trends beyond those ascribing nearly order-of-magnitude differences. Most studies in the past have focused on local phenomena or have relied on the results from single expeditions. Efforts to put these results together into a common data base could be to naught, in that, without ensuring common calibration scales, the combined data would likely yield incorrect information owing mainly to differences in calibration.

The role of these short-lived halocarbons in atmospheric chemistry has become increasingly recognized in recent years as scientists understand more clearly both stratospheric ozone depletion and tropospheric oxidation. The first of these issues affects the amount of erythemal radiation striking the earth and the second influences the ability of the atmosphere to cleanse itself. Ultimately, both are human health issues.

Though only one day in length, the workshop was well attended throughout. The schedule was packed and aimed at 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. Sessions held following introductory presentations by Tom Bell of UEA and Jim Butler of NOAA included (1) presentations and discussion of the scientific need for this effort led by Roland von Glasow of UEA, (2) presentations and discussion of measurement uncertainties led by Lucy Carpenter of York University, (3) a review and discussion of existing standardization approaches, led by Brad Hall of NOAA, (4) presentations and discussion of issues in comparing data, led by Birgit Quack of IFM-Kiel, and (5) a general discussion of a path forward.

Introduction and Overview

Tom Bell pointed out that if the community is to engage in any form of Earth System Modeling, then global data sets would be necessary to provide the informational products sought and that the value of these data depended upon their comparability which, for short-lived halocarbons, was largely unknown. These products begin with determining global budgets and fluxes, but they also go to tropospheric and stratospheric chemistry in more complex models. Jim Butler further made it clear from the recent Scientific Assessment of Ozone Depletion that these short-lived halocarbons were an increasingly important issue, accounting for 15-45 % of the ozone-depleting bromine in the stratosphere and deriving almost entirely from the ocean. Currently we understand little of their variability in the ocean and atmosphere, much less the potential influence of climate change on their emission. Because production and emission of these gases from the ocean contribute such a large proportion of the bromine and iodine in the atmosphere, modeling efforts that engage the ocean-atmosphere interface in essence must begin with flux estimates.

Butler showed several examples of disagreement and “fortuitous” agreement among oceanic and atmospheric measurements taken simultaneously by different investigators in near or exact locations. Drawing examples for CHBr3, CH3I, and, to a lesser extent, CH2Br2, he underscored how common calibration and measurement efforts to compare approaches would have allowed scientists to draw firm, environmental conclusions from data that, due to this lack of comparison, can only be interpreted with ambiguity. Though some measurements taken simultaneously by different investigators at the same location, such as those by Lucy Carpenter of York and Steve Montzka of NOAA, agreed well, the issue still remains as to how to extrapolate such an understanding to data that are not taken simultaneously in the same location. Data sets that may seem to agree at certain points still cannot be combined without a systematic, on-going effort to compare measurements. Finally, he showed that differences can derive not only from a lack of calibration, but also from analytical approaches. These, too, need to be addressed. He noted that some form of measurement guidelines, even loosely expressed, were probably necessary for the scientific community to begin building global data sets.

Scientific Need for Comparison.

Roland von Glasow introduced this session with a presentation addressing levels of detection needed for modeling processes in the troposphere and detecting changes in the stratosphere. He pointed out large gaps in the data, particularly over the Indian and Pacific Oceans, that, in themselves, made accurate global modeling difficult. He concluded that detection and precision for bromine (for both stratospheric and tropospheric questions) needed to be around 1 ppt and for iodinated compounds about ±50%. During discussion, von Glasow noted that fluxes of shorter lived, iodinated compounds, particularly CH2I2, were more critical than knowing concentrations in the atmosphere because of their short lifetimes. This left some question about how important it was to include CH2I2 in an intercalibration effort.

Measurement Uncertainty

Lucy Carpenter provided a detailed description of uncertainties in gas phase and water phase sampling. Aside from uncertainties associated with calibration, those associated with gas phase sampling include line losses, sample flow rate, atmospheric artifacts (humidity etc), analytical precision, and reproducibility of gas standards. Those associated with water sampling include loss or production during storage, loss or production during purging, sample flow rates, and reproducibility of water standards. With care, it is possible to obtain precision of a few percent for air samples, but this is much higher and variable for water. It was noted during discussion that liquid standards appear to have less uncertainty than perm tubes, analytical precision typically <5% in air (ppt range) – higher for water. Sampling precision of these gases in air is generally limited by analytical precision, but for water it commonly runs around 10-15%.

Don Blake underscored the high variability of these compounds found in the free troposphere. Samples retrieved from aircraft flying side by side typically agree well for CHBr3 and CH2Br2. Over time (thus space), however, CHBr3 varies from 1-10 ppt and agrees well between canisters & in-situ measurements. CH3I and CH2Br2 also agree well when sampled by canister or measured in-situ. Of particular note is that CHBr3 can be high during tropical storms, reflecting the large flux of Br into the free troposphere and potentially stratosphere.

Existing Standardization Techniques

Brad Hall discussed the issues with making and maintaining calibration scales in air. Compressed gas standards prepared through static dilution of a pure compound are portable, can be long lasting, can hold multiple species, and are traceable. However, there are problems with stability, legal issues in transport, and they require several steps of preparation to achieve low ppt levels. Short-lived compounds prepared in this manner at NOAA can be made to within ±5%. This procedure is also used at Scripps Institution of Oceanography (Ray Weiss) and Nippon Institute for Environmental Sciences (Yoko Yokouchi).

Subsequent discussions relating to liquid standards suggested that standards prepared in liquid could be more precise than permeation tubes and that permeation tubes were hard to handle in the field and that reproducibility was poorer. Liquid standards prepared direction by gravimetric dilution of pure compound in solvents (e.g. Methanol) and subsequent volumetric dilutions seem to be a more suitable approach for water samples. Tertiary standard would then be made into halocarbon-free seawater and purged for analysis. It was noted that it can be difficult to get halocarbon-free methanol, that purge efficiency can vary, and that complications can result from introducing a large amount of methanol into the analytical system. Possible reactions with methanol were also noted as uncertainties and it was noted that such standards needed to be kept at -20 C to remain stable.

Preliminary results from IHALACE results were discussed inasmuch as permitted. IHALACE was an international round-robin of four ambient and two sub-ambient air samples circulated to 22 laboratories, but it focused mainly on longer-lived halocarbons. The study unfortunately took 3 years for all laboratories to complete their analyses. CFC11 and CFC12 comparisons were fairly good between labs with their own calibration scales, but there was a greater spread in the results when data from labs which ‘borrow’ the calibration scale from another lab are included. Only 2 labs reported CHBr3 with a 15-20% difference between them.

Current Comparison Issues

Birgit Quack opened this session with a summary of information provided by the attendees. Of these, 19 groups reported analyzing 32 short-lived, halogenated compounds in their studies. Top 10 (in descending order) are CH3I, CHBr3, CH2Br2, CHBr2Cl, CH3Br, CHCl3, CH2ICl, C2H5I, CH3Cl, and CH2IBr. Comparisons made in the past show mixed results. For example, in one study, NOAA and NCAR measurements in air agreed reasonably well for CHBr3 and CH2Br2 at mixing ratios of < 2ppt, but above that reported amounts diverged. Other comparisons showed NOAA measurements in the water agreeing reasonably with those by Kiel. Quack also noted underscored several analytical issues, including destroying cells and releasing gases during sample preparation through heating, purging, filtering, and sonicating. She further noted that storing water samples leads to substantial losses and possibly even increases in the concentrations of these gases. When effort is made to provide consistent measurements, it is still clear that the variability, likely real, in seawater samples is very high. The variability can be driven by seasonal and diurnal variation, species composition, weather, and primary production to name a few contributors. The ensuing discussion led to the recognition that comparing standards in water with those in air had several complications.

Path Forward

Following the guided discussions, the workshop ended with a two-hour discussion of possible ways to begin ensuring that data are all comparable. Hall & Weiss noted that intercomparability, not necessarily accuracy, was the key to being able to combine data sets. Weiss further noted, and got general agreement, that the bottom line in all of these measurements would come from an ability to measure the substances in air, as it had the fewest complications and that many compounds were somewhat stable in canisters of compressed air. In the end it was decided that we should focus on CHBr3, CH2Br2 CH3I, and what dihalomethanes we could get, as there may be issues getting stable standards of dihalomethanes for inter-lab calibration.

The first stage of this effort would compare relative standards rather than absolute calibrated values. It was generally favored that someone could fill multiple canisters with the same air & disseminate them to others for analysis in reasonably short time, thus avoiding long delays such as those encountered during IHALACE. Another alternative offered was to take instruments to a chamber and all investigators could make simultaneous measurements. Though clearly a way to get simultaneous measurements of the same air and offering the possibility of equilibrating water for purge and trap comparisons, this could be an expensive option and not all instruments used are portable. A common field-based campaign was discussed at length, with possible sites being Appledore Island, Sweden, Mace Head. Again this could allow both water and air comparisons, but could get expensive and would require multiple funding sources.

Finally, it was noted that a single intercalibration effort would not be good enough, that approaches need to be taken to compare measurements frequently.

Approaches, Action, Committee

The participants decided that several approaches could be taken to begin comparisons as soon as possible, while developing a longer-term calibration scale. This would ensure that measurements heretofore become more coordinated quickly and with some sense of agreement with regard to calibration, while time is taken to develop a more permanent scale.

- Analysis of long term calibration techniques requires some attention regarding testing stability of canisters for these various compounds. NOAA and SIO are looking into this. The only compound on the target list in this conference not being monitored so far is CH2ICl. CH2I2 is being studied

- Don Blake of volunteered to distribute flasks among participants – both from this workshop and others whom might be identified. This has the advantage of being reasonably inexpensive and, most importantly, possible fairly soon. Brad Hall will transmit results from IHALACE once it is completed and then may be able to lead a wider-based round-robin with the same cylinders, but focusing on the short-lived gases discussed here, and including many who were not on the original IHALACE list.

- It was recognized that field campaigns & chamber studies, though desirable, would take considerably more time to bring together, as would other approaches for comparing analyses of water samples.

- It was agreed that funding agencies for these activities need to be identified and proposals need to be written for anything beyond the circulation of flasks or canisters.

- A Future Directions article (Atmospheric Environment) to ‘advertise’ the intercalibration to other groups may be a good approach to announce that this important need is being addressed and to bring others into the fold of this on-going activity. Other participants, however, would need to have some history of making halocarbon measurements.

- We need to write up report from this meeting & devise a timeline. A committee was designated to begin moving this effort forward. Committee members include, but are not limited to Butler, Barkley, Williams, Blake, Blake, Quack, Carpenter, Bell. Butler will prepare a draft plan and circulate it to committee members for further development before passing it to other participants.

- *Timeline:*
    - 16th April - deadline for report & article (deadline for Sweden)

• Blake canisters to be sent out Autumn 2008
• Proposal
o Though there will be several proposals for certain aspects of this effort, a proposal is needed for a parent organization to embrace the long-term effort. o Possible parent organizations for on-going QA/QC – WMO, SOLAS? o Butler to work through WMO to find a place for hosting this effort, likely one of the GAW Scientific Advisory Groups (greenhouse gases, reactive gases, ozone), but none of which apply directly to these gases.
• Field campaign 1-2 years time?
• Another meeting - 2 years?
• Measurement guidelines – ongoing, initial version Jan 09
• Atmospheric Environment Article – June 2008