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Interactive comment on “Bromocarbons in the tropical marine boundary layer at the Cape Verde Observatory – measurements and modelling” *by* L. M. O’Brien et al.

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We thank the editor for the chance to address these concerns directly.

1 Instrument performance

The available house-keeping data (which is quite detailed) indicates that the instrument performance was good in Cape Verde. Figure 1 (http://people.pwf.cam.ac.uk/adr22/ - ACPD O’Brien et al.,
2009 - reply to editor comments) shows 3 chromatograms (an atmospheric sample with high $CHBr_3$, a calibration run and a blank) from that deployment. A small memory

effect for $CHBr_3$ and CH_2Br_2 is visible in the blank, but nothing significant.

Before the campaign, the same instrument was deployed at the Weybourne Observatory on the North Norfolk coast, UK. The comparison for C_2Cl_4 with AGAGE Mace Head measurements in the second half of the period (when the winds were from the Atlantic, rather than from Europe as in the first half) is good; that for $CHCl_3$ is less good, and is consistent with an offset we see in later comparisons with UEA data in Borneo. The $CHBr_3$ values in this period were typically between 3 and 5 ppt, which is comparable to the North Norfolk values of 1.7 ppt (cliff top) and 7.9 ppt (near a seaweed bed) reported by Baker et al. (Chemos., 3, 93, 2001).

2 Stability of calibration standard

During the time at Cape Verde, the calibration approach consisted of a series of 20 scc aliquots of calibration gas standard from NOAA and the microDirac samples (also 20scc) were scaled to that to calculate the atmospheric mixing ratio. The NOAA Essex standard (moist) was transferred into an onboard gas bottle (Restek Sulfinert treated 500 cc high pressure sample cylinder, filled to 60 bar).

The NOAA standard gas cylinder (Essex) was certified in December 2005 and the Cape Verde measurements were 18 months later in May/June 2007. The standard was humidified in order to passivate the canister walls and so increase long-term stability (important for some gases). We have no direct side-by side comparisons with other standards before going to Cape Verde. One of the reasons we went to Cape Verde was to make side-by-side measurements with the GC-MS from the University of Bristol. As stated in the paper, comparisons with their preliminary data showed real differences, but their data has not been published yet so we cannot make a meaningful comparison with them at this time.

However a year after Cape Verde, the same instrument was in Danum Valley for OP3 and ran side-by-side with the UEA GC-MS. The results for $CHBr_3$ and CH_2Br_2 are shown in Fig 2 (from Gostlow et al, submitted to AMTD). The two sets of measurements generally agree well for both gases. For $CHBr_3$ the agreement is particularly good and for both sets of data there is usually good agreement in the variability at the sub-ppt level. For CH_2Br_2 our values in Danum valley are slightly lower than the UEA measurements (despite an expected overestimation of CH_2Br_2 with μ-Dirac because of its co-elution with $CHBrCl_2$). Our NOAA (Essex) standard was also directly measured by the UEA GC-MS during OP3 and a preliminary value for bromoform of 8.1 ppt (compared to the NOAA 2005 value of 9.0 ppt) based on UEA running standards was given. Whole air samples collected at a coastal site (Tawau) and measured by UEA since then show continued good agreement. There is thus strong evidence that the concentrations in the calibration gas itself have not changed much.

This leaves the possibility of an error in the transfer of the standard gas from the NOAA cylinder to the on-board cylinder. However the concentrations of gases such as methyl chloroform were the same as simultaneous measurements by NOAA and AGAGE, so any problem was gas specific. We have had problems when transferring air from our dry NOAA standard (Aculife) into other cylinders, but none have been identified when using the moist standard. In particular we transferred standard gas to the same cylinder used in Cape Verde in both the Weybourne and Borneo deployments with no apparent ill effect. Unfortunately, no comparison was made with our laboratory standard when the on-board cylinder was returned to the laboratory as the cylinder was by then empty (3.5 months after the measurements ended).

3 Co-elutants

We can never be certain that there are no co-elutants since we use an ECD, and so there could be an unknown compound hiding underneath the peak we are calling bromoform. However a comparison with the preliminary $CHBr_3$ values from Bristol showed very similar time variations with peaks being seen at the same time in both instruments indicating that, if there is a co-elutant, its source must be similar to that of $CHBr_3$. Further the $CHBr_3$ peak in Fig 1 is a well defined and symmetric peak. Any co-elutant must therefore have almost exactly the same retention time. We have done a lot of work looking for a possible co-elutant in the laboratory. The only possible compound found to date is iodopentane. We know no reason why this should be present in the air in Cape Verde in significant quantities (multi-ppt would be required to affect the $CHBr_3$ measurement, assuming a similar sensitivity to CH_3I); furthermore to affect our measurement it would also need to correlate with $CHBr_3$. This does not mean there is no co-elutant with $CHBr_3$, but we do think that any co-elutant is unlikely to be present in major quantities in the Cape Verde samples.

On the other hand we do have a problem for dibromomethane as already described in the paper. Figure 3 shows the correlation plots between $CHBr_3$ and (a) CH_2Br_2 and (b) $CHBr_2Cl$. There is an intercept on the CH_2Br_2 axis consistent with the problem already identified. A similar feature is present in the $CHBr_2Cl$ plot which presumably indicates a problem with $CHBr_2Cl$ rather than with $CHBr_3$.

We are not aware of a co-elutant with CH_3I, except possibly for C_2H_5Br. The CH_3I peak is in a much more crowded part of the chromatogram than the $CHBr_3$ peak and so we are not as confident about this as for $CHBr_3$. We are still working on the coelution issues and are collaborating with Johannes Laube and others from UEA on this issue.

4 Explanation in conjunction with other results

We agree that the measurements we report are surprisingly high and we have looked hard for a convincing instrumental explanation, without success to date. Despite extensive investigations, we cannot find anything wrong with our approach and conclude

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that we present real measurements. Our calibration procedures have certainly improved since that deployment (Gostlow et al., submitted to AMT), but our reliance on the NOAA-ESRL calibration standard and its apparent stability since that time give us faith in the calibration of these Cape Verde measurements.

One possible explanation for the high values we observe is that they are influenced by the presence of seaweed along the foreshore near the Cape Verde Atmospheric Observatory (CVAO) and therefore not seen in other measurements made in the region (Carpenter et al., 2009; Quack et al., JGR, 2007ab). If these local seaweed beds are a source of halocarbons and the release rate is increased by greater stress from higher solar radiation and higher ambient air/sea temperatures, then the higher release rate emissions might compensate for the relatively small amount of seaweed compared to Mace Head, for example.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 4335, 2009.