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Atmospheric Chemistry and Physics Discussions

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.

Anonymous Referee #2

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This study presents some measurements of bromocarbons (and CH3I) at the Cape Verde Observatory, attempts to explain them in the light of halocarbon emissions estimates of and around the Mauritanian upwelling, and to assess the contribution of bromocarbon and seasalt sources to BrO in the MBL in this region. The paper is generally well presented. However, the paper as a whole is rather confusing and could be better structured (I note that Rev#1 has made detailed suggestions here). I also have some major reservations on the model-measurement comparisons and approach. In particular,

(1) Bromocarbon measurements/emissions: The background CHBr3 concentrations of

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4 pptv (p 4348) measured at Cape Verde are an order of magnitude higher than the N. Atlantic open ocean means measured by Butler et al. (2007) of 0.4-0.5 pptv in a comprehensive measurement study of the global oceans. This should be noted in the paper. There would seem to be 3 possible reasons for this: (a) air from over the upwelling or some other non-local source , (b) local sources of CHBr3, presumably from seaweeds since these are a strong source in coastal waters (c) calibration differences. These are already discussed in the paper but I have some comments :

(a) There are published values for CHBr3 and CH2Br2 fluxes in the Mauritanian upwelling from Quack et al., 2007 (JGR) and Carpenter et al. 2008 (ACP); the fluxes from these studies appear to agree well at around 30-40 nmol m-2 d-1 CHBr3 in the peak upwelling region. So why not use these in the model as a starting point for the Hotspot emissions and then discuss differences or otherwise, rather than using arbitary values for fluxes as a basis for discussion ? Also note that the longitudinal extent of the upwelling assumed in the HiBr case of 20-30oW is not realistic. This would have the upwelling extending right out to Cape Verde archipelago and beyond, whereas in reality it does not extend west past about 19 oW.

(b) Other non-local sources. The very high values of CHBr3 previously measured off the NW Africa coast (15-20 pptv) , e.g. Quack et al., 2004, Carpenter et al., 2007, are apparently observed when air passes over the African continent/coast only. Was this the case for the very high values of bromocarbons observed at Cape Verde?. More recent data (see above) shows that these high concentrations in air are not due to the upwelling itself but to some other source.

(c) If there are no seaweed beds at Cape Verde (the possibility of this should be discussed), strong local sources seem unlikely. The authors discuss the potential for a local photochemical source because of the diurnal variability in the measurements. This is an interesting possibility (although there appears to be no evidence of this so far in the literature) - but have they absolutely ruled out transport issues, i.e. stochastic changes in trajectories over this rather short period of 3 days? Although the trajectories

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indeed look rather similar, there are small changes over the day.

(d) This issue is raised briefly on p 4343 and it appears there are calibration differences with other measurements at the site. Because the measurements of CHBr3 at least are unusually high, it would strengthen the paper and bolster discussions regarding other sources if there was more information on calibrations and intercalibarions, for example was the standard used recently certified by NOAA?

(2) Modelling P 4352. The statement that sea salt over the open ocean makes almost no contribution to BrO is in direct contradiction to more detailed modelling studies (e.g. von Glasow et al., 2002) which produce several pptv from seaspray at moderate wind speeds (˜ 6 ms-1). It seems that differences in wind speed are insufficient to explain these differences (since this study required 13 ms-1 to make several pptv BrO). The authors suggest that errors in parameterisations for sea-air fluxes of SSA are a potential reason – but this does not explain the difference in predicted bromine by this and other studies that use the same Monahan treatment. What about differences in chemical (e.g. lack of iodine in this model) or microphysical treatments? It would be desirable to have other model outputs to compare with previous results. For example what is the predicted sea salt concentration and how does this compare to measurements? The reader is left pondering on a result which is apparently quite different from that in the published literature, but with no real sense of whether these differences are real (i.e. there is actullay a much lower bromine source to the atmosphere here compared to otehr regions) or are due to differences in modelling assumptions.

Minor comments Fig 2. The positioning of the error bars is a bit strange. Why not simply put them on the measurements?

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