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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Drivers of diel and regional variations of halocarbon emissions from the tropical North East Atlantic" *by* H. Hepach et al.

Anonymous Referee #1

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This manuscript addresses the oceanic sources of three volatile halocarbon compounds that contribute to potentially important aspects of atmospheric chemistry. The paper provides information on the distribution and air-sea flux of these compounds with a focus on the Mauritanian Upwelling region as a source of high amounts of these compounds. Measurements of halocarbons in seawater are relatively rare and even less common are reports that combine these with atmospheric measurements and the environmental factors, including biological variables that may influence their production and emission. In this respect the manuscript is appropriate subject matter for ACP and is a potentially valuable addition to the special issue. The manuscript aims to com-

pare distributions of the halocarbons between oceanic waters and the more productive, coastal upwelling regions and provides estimates of the air-sea fluxes in each location. In general the authors do a good job of this aspect of the manuscript. What is less convincing is the determination of the sources of the compounds which relies almost entirely on correlative analyses between, in some cases, poorly constrained proxies of biological variables. I think this evidence is over-interpreted with little explanation of the uncertainties involved or potential alternative sources not tested. The manuscript is well written and results are well presented. An important point is the extent of overlap, with the Fühlbrugge et al. submission to the same Special Issue; particularly in relation to the conclusion regarding the MABL height and its impact on atmospheric mixing ratios.

Specific concerns:

1. P19706 2.1 L19. Was an internal standard used in the analyses and if not, how was drift in instrument sensitivity monitored?

2. P19706 2.1 L19. It would be useful to report the purge efficiencies for each of the compounds

3. P19706 2.1 L21. More detail is required regarding how precision was calculated from duplicates? Normally, assessment of precision requires at a minimum, triplicate samples. Were' true replicate samples analysed – i.e. replicate water samples collected from the moon pool, or were the duplicates from the same sample?

4. P19707 2.1 More details of how the intercalibration was performed would be useful, as would evidence of the stability of the individual compounds in the gas samples in the canisters over the approximately 1 month of storage.

5. P19707 2.2 L18. Fixation of samples for flow cytometry may cause cell loss, particulary amongst nanophytoplankton, was this considered in the analyses?

6. P19710. 4.1.1 L5, Sentence starting 'While maximum. . ..,' requires rephrasing.

7. P19710. 4.1.1 L14. Please explain how the difference in 'regional variability' between air and ocean CH3I concentrations was determined.

8. P19711 4.1.3. I would suggest presenting the results of the saturation anomalies and concentration gradients, fluxes and air-sea flux collectively for the 3 compounds. At present the separate sections involve a fair amount of duplication.

9. Fig. 4, it would make the figures clearer if the black and grey lines used, were more distinct.

10. P19716, 5.1.1 L20+ Sources of CH3I. The conclusion that a lack of correlation between CH3I with Prochlorococcus, divynl chorophyll a, diagnostic diatom pigments and chlorophyll is not sufficient evidence to discount a biological source. For several reasons, i) correlations are a relatively weak means of determining a source, especially if the variables are being cycled at different rates ii) since both production and loss processes determine the observed concentrations; iii) there is evidence that heterotrophic bacterial processes may be involved in CH3I production (Manley and Dastoor 1988, Amachi et al. 2001, 2004, and others) and these correlations do not take account of these potential processes.

11. 19718, 5.1.2. Comparison to previous studies: The authors should at least try to explain the large difference in concentrations measured for CH3I, between this study and that of Jones et al. 2010 and Richter and Wallace 2004? There is considerable debate at present regarding the relative contribution of different sources of reactive iodine to the tropical MABL and the 10-fold difference in concentrations between studies make this even harder to assess unless some explanation is provided.

12. 19719, 5.2.1, L5. Measurements of algal abundance or pigments do not constitute 'algal activity', they may be a useful proxy for algal biomass.

13. 19719, 5.2.1 Sources of bromocarbons. As for CH3I, the strength of correlation between observed concentrations and specific phytoplankton taxonomic groups is rel-

atively weak evidence of a source. Firstly, attributing specific pigments concentrations to specific phytoplankton taxonomic groups is itself generally a weak proxy. For instance, how was diatom biomass determined in the present assessment? If it is based on the concentrations of fucoxanthin, then this compound is also found in the majority of haptophytes. The authors need to explain: i) how and which marker pigments were attributed to which phytoplankton groups; ii) make clear the uncertainty in their assessment of the link between these defined groups and the concentrations of the halocarbons; iii) point out that observed concentrations represent a balance between production and loss processes, e.g. a compound could exist at low concentrations but have both high production and high loss rates.

14. 5.1 and 5.2 Discussion: Air-sea flux estimates and determination of the drivers: In a number of ways this paper demonstrates the need to now go beyond wind-based parameterizations of transfer velocity to estimate flux rates and to explore what really determines the flux. Several reports have recently demonstrated the value of using a more comprehensive, albeit more complex, algorithm to estimate and explore the controls on air-sea flux. The authors should, at least, address the limitations of their approach and explain what additional measurements would be required to implement an approach such as the COARE model (Fairall et al. 2003) for their flux estimates. [Fairall, C. W., E. F. Bradley, J. E. Hare, A. A. Grachev, and J. B. Edson (2003), Bulk parameterization of air to sea fluxes: Updates and verification for the COARE algorithm, J. Clim., 16, 571–591.]

15. 5.4. 19722-3. Atmospheric lifetimes. The authors should explain whether their assessment of the contributions to atmospheric halocarbon mixing ratios takes into account losses within the atmosphere, and if not, why this is not required.

16. P19723 – 19726, 5.4.2. and 6. Discussion and Conclusion. The conclusion that MABL height has an influence on the air-sea flux of the bromocarbons is interesting but would benefit from some explanation of what may control that height and how that may change in the future, if at al.

17. Finally, the authors should also make it clear that these three compounds are only a subset of the suite of volatile halocarbons that may exchange between ocean and atmosphere and explain why they focus particularly on these specific compounds.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 19701, 2013.