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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Meteorological constraints on oceanic halocarbons above the Peruvian Upwelling" *by* S. Fuhlbrügge et al.

S. Fuhlbrügge et al.

sfuhlbruegge@geomar.de

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General Comments: Referee #1: This paper presents a new dataset of halocarbon observations along the Peruvian coast and the upwelling region nearby. The observations add to a scant dataset of halocarbons and helps in completing the global picture in addition to explaining some local differences. Additionally the fluxes calculated will undoubtedly be useful to modelling groups, which have been struggling with getting a complete emission inventory for several of the compounds measured here. I recommend the manuscript is published in ACP, after the authors have addressed a few points that are detailed below.

Author's response: We first would like to thank the reviewer 1 for reviewing the

manuscript and for the overall positive evaluation of the paper, which she/he describes as helpful in completing the global picture of halocarbons observations and useful to modelling groups with getting a complete emission inventory. Below you find our point-by-point answers to your comments (highlighted in italic).

Referee #1: Major comments: 1) Although the authors mention that the fluxes are different to the other locations, such as the Mauritanian upwelling, there isn't much discussion about the reasons for this. One reason that is mentioned is the difference in the wind speed and the ocean atmosphere gradient. Why do the authors rule out biological processes? Maybe some light can be shed on this using ocean colour data, and/or phytoplankton speciation data.

Author's response: We agree with the reviewer that biological processes in the oceans often play an important role for the concentration distribution of brominated and iodinated VSLS, and therefore also for their concentration gradient, being a major driver for their sea-to-air fluxes. The analysis of biological parameters was not part and scope of this manuscript. The relation of pigments, phytoplankton groups, dissolved organic matter and bacteria to the halogenated VSLS are covered in an accompanying manuscript by Hepach et al. (submitted January 2016). For further discussion on the distribution of the oceanic halocarbons and biological processes, see Hepach et al. (2016, submitted). Fluxes for CH3I were much higher in the Peruvian upwelling (M91 cruise) than in the Mauritanian upwelling (DRIVE cruise), because of the higher oceanic concentrations. This can be probably linked to biological production, as high correlations with Chl a and diatoms were found, in contrast to lower concentrations of CH3I in surface waters of the Mauritanian upwelling during June 2010, linked to photochemical production (Hepach et al., 2014). Production of bromocarbons was seemingly much lower in the Peruvian upwelling than in the Mauritanian upwelling, although biological parameters as total chlorophyll concentrations where similar in both regions. As iodinated compounds were much higher in the Peruvian upwelling, different production mechanisms for bromocarbons and iodocarbons can be hypothesized.

Ambient conditions and different phytoplankton species in the Peruvian upwelling may have favoured production of iodocarbons rather than of bromocarbons during the time (December 2012) and in the region of the M91 cruise. The lower concentrations of bromocarbons and lower wind speeds both reduce the sea to air fluxes via both the concentration gradient and kw leading to much lower sea-to-air fluxes in the Peruvian upwelling than in the Mauritanian upwelling.

Referee #1: 2) The authors have mentioned that the transport paths might explain the elevated IO observed by Schönhardt et al. However, the transport paths take about 5-8 days, which is much longer than the lifetime of CH3I and hence its contribution should not be as high. Very low concentrations of IO have also been observed at the Galapagos Islands, although higher CH3I was observed. Closer analysis of the CH3I data had indicated a local source rather than transport from the Peruvian upwelling region (Gomez-Martin et al., 2013).

Author's response: We agree with the reviewer that the lifetime of methyl iodide is too short to be transported from the cruise track towards the equatorial East Pacific and Galapagos Islands before being degraded and that therefore local sources appear likely. However, the observed elevated methyl iodide mixing ratios during the cruise could explain part of the elevated IO above the Peruvian upwelling (Hepach et al., 2016, submitted) as was also observed by Schönhardt et al. (2008). We clarified this in the manuscript now by writing: "A contribution of oceanic emissions from the Peruvian Upwelling to the free troposphere is only achieved in the inner tropics after a transport time of 5 – 8 days, where the VSLS abundances are transported into higher altitudes. Since the lifetime of methyl iodide is only 4 days in the MABL a significant contribution of methyl iodide from the Peruvian upwelling to the observations made by Yokouchi et al. (2008) at San Cristobal, Galapagos is not to be expected. However, it can partly explain the elevated IO observed above the Peruvian upwelling (Hepach et al., 2016, submitted;Schönhardt et al., 2008)."

Referee #1: 3) The quantitative analysis of the dependence of the flux is only limited to

doing Spearman correlations and the dependence between boundary layer and concentrations is shown in a figure. Considering the low spearman's coefficients and high P values (0.05), I suggest that the authors conduct a two dimensional principal component analysis of the dataset considering all the different parameters measured. This will help in better understanding the major driving factors, rather than doing simple correlation coefficient calculations, especially, which do not have a high significance (<0.01). Several of the measured parameters could correlate, but that does not necessarily show any causality as evidenced in table 3.

Author's response: According to the reviewers suggestion we conducted a two-dimensional principle component analysis (PCA). However, a PCA transforms a number of correlated variables into a number of uncorrelated variables. Thus considering all the different parameters measured with their relatively low correlation coefficients a PCA in this case appears unnecessary. Nevertheless we performed a PCA on the relative humidity, wind speed, sea surface temperature (SST), surface air temperature (SAT), MABL height and atmospheric mixing ratios of CHBr3, CH2Br2 and CH3I, which are correlated to each other. The according 'loadings plot' (Figure 1) reveals two cluster. The first cluster includes the atmospheric VSLS mixing ratios of CH3I, CHBr3 and CH2Br2 and the relative humidity. The second cluster includes the MABL height, SST and SAT. These two clusters are forming, since the variables in one cluster are negatively correlated to the variables in the opposite cluster. However, the wind speed with its low spearman correlation coefficients reveals to be no driving factor of the remaining variables. We will add this to the manuscript: "A principle component analysis of the parameters in Table 3 furthermore revealed a distinct relation between SAT, SST, MABL height, relative humidity and atmospheric mixing ratios of CHBr3 and CH2Br2 (not shown here)."

Figure 1: Loadings plot of 1st and 2nd principle component (PC). Two clusters form: 1. CHBr3, CH2Br2 and relative humidity (relH). 2. SAT, SST and MABL height (MABLh).

Referee #1: Minor comments: 1) Please mention the P values for the correlation coef-

ficients in section 3.5

Author's response: Done.: "Indeed, we also find significant ($p < 0.05$) high correlations [. . .]"

Referee #1: 2) The Martin et al 2013 reference should be Gomez-Martin et al, 2013

Author's response: Done.

References Hepach, H., Quack, B., Ziska, F., Fuhlbrügge, S., Atlas, E., Krüger, K., Peeken, I., and Wallace, D. W. R.: Drivers of diel and regional variations of halocarbon emissions from the tropical North East Atlantic, Atmos. Chem. Phys., 14, 10.5194/acp-14-1255-2014, 2014. Hepach, H., Quack, B., Tegtmeier, S., Engel, A., Bracher, A., Fuhlbrügge, S., L., G., Atlas, E., Lampel, J., Frieß, U., and Krüger, K.: Biogenic halocarbons from the Peruvian upwelling region as tropospheric halogen source, to be submitted, 2016. Schönhardt, A., Richter, A., Wittrock, F., Kirk, H., Oetjen, H., Roscoe, H., and Burrows, J.: Observations of iodine monoxide columns from satellite, Atmospheric Chemistry and Physics, 8, 637-653, 10.5194/acp-8-637-2008, 2008. Yokouchi, Y., Osada, K., Wada, M., Hasebe, F., Agama, M., Murakami, R., Mukai, H., Nojiri, Y., Inuzuka, Y., Toom-Sauntry, D., and Fraser, P.: Global distribution and seasonal concentration change of methyl iodide in the atmosphere, Journal of Geophysical Research-Atmospheres, 113, 10.1029/2008JD009861, 2008.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/15/C12965/2016/acpd-15-C12965-2016-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 15, 20597, 2015.

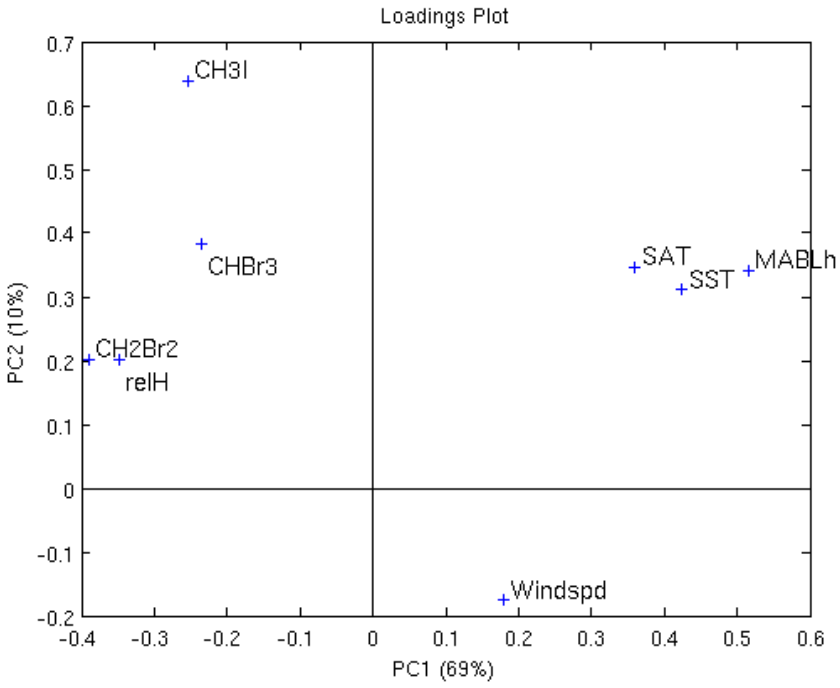

Fig. 1.