Anonymous Referee #2

Overall, the field observations presented in this study contribute a valuable dataset of simultaneous atmospheric and surface ocean halocarbon concentrations, and resulting sea-to-air flux estimates, in a potentially important source region for these gases. Observations of these gases (particularly simultaneous air and seawater measurements) remain sparse, so this type of study is crucial for improving our understanding of the natural occurrence and distribution of marine halocarbons.

One general criticism of this manuscript is that in some instances the language used can be a bit difficult to follow. While I do not think that there is a major problem in this respect, I would encourage the authors to look carefully at the writing style, with a view to improving the readability of the manuscript. Some specific examples of this are highlighted in the individual comments below.

We thank referee #2 for the very helpful input and suggestions which help improving and clarifying the key points of the manuscript in its current form. We look through the manuscript and try to improve the readability. We answer the specific comments below.

Detailed comments:

Page 19702 L14: In the sentence beginning "Atmospheric mixing rations" – presumably "rations" should be "ratios"?

The word has now been removed during the rephrasing of the sentence (see next comment).

Page 19702 L14-16 – Reword this sentence for clarity – particularly the part ". . . and 1.8, 12.8, respectively 2.2 ppt at a Cape Verdean coast. . .".

The sentence is rephrased as follows: *"Atmospheric CH_3I, $CHBr_3$, and CH_2Br_2 of up to 3.3, 8.9, and 3.1 ppt respectively were detected above the upwelling, as well as up to 1.8, 12.8, and 2.2 ppt at the Cape Verdean coast."*

Page 19703 L15-17: The sentence "Phytoplankton produces these trace gases as well and especially upwelling regions where cold, nutrient rich water is brought up to the sea

surface contains large amounts of these compounds" would be much clearer if reworded as follows: "These halocarbons are also produced by phytoplankton, and as such elevated concentrations of these compounds are often observed in upwelling regions, where cold, nutrient rich water is brought up to the sea surface".

Thank you for this suggestion. We agree, and reword the sentence according to the reviewer's suggestion.

Page 19704 L8: "The tropical Mauritanian upwelling is an example for a recently intensified. . ." – change to ". . .an example of a recently intensified. . .".

We rephrase this sentence accordingly.

Page 19704 L25: Change "RegIonal" to "Regional".

The capitalized "I" in "**R**eg**I**onal" refers to the campaign name "D**RI**VE", which stands for "*D*iurnal and *R*eg*I*onal *V*ariability of halogen *E*missions". We therefore leave the letter capitalized but try to clarify the link by italic letters.

Page 19705 L26: Change "were" to "where".

This is corrected.

Page 19706 L19-20: Please provide details of the standards used for calibration - e.g. concentrations and number of points on calibration curve.

10 ml of standard were prepared on board by adding 5 µl of each compound to methanol. This standard was diluted with methanol from 1:1000 to 1:25,000, 1:50,000, 1:100,000 and 1:1,000,000. Previous laboratory experiments have shown that a standard prepared freshly in methanol is stable over the time span of a four week cruise (such as DRIVE). Our experience shows also that the drift within the instrumental set up during the cruises is usually very low, which is why we perform a complete calibration curve once a week using these four dilutions, each in triplicate. To monitor and correct for the potential drift within the system, the 1:50,000 diluted standard, was injected three times on a daily basis. Additionally, we have

measured gaseous NOAA-standards on board every week as well to ensure comparability to the atmospheric samples. We add some more details for the calibration method in the manuscript.

Page 19706 L23-24: The air samples in canisters were analyzed for halocarbons within one month of sampling - can the authors comment on the stability of the halocarbons in these canisters over this time period?

See also our answer to Reviewer #1. Stability and integrity of sample composition during storage is an important consideration in whole air sampling. Often, the stability will depend on canister surface properties, the type of sample (wet/dry), and potentially unknown factors. However, it is not often practical to do stability tests under all conditions of sampling and storage. Thus, after initial testing of canisters, we rely on the measurements themselves to reveal something about the canister stability. We look for consistency between samples collected along a track to reflect sample stability. Our experience indicates that outliers due to compound loss in canisters are usually easy to identify. Other tests we have done are to compare samples collected in the same locations but analyzed by separate laboratories. Typically, sample comparisons between labs show good correlation, with most differences attributed to calibration offsets. One example of comparison between different canister samplings has been conducted during the TransBrom SONNE cruise showing very good agreement (Brinckmann et al., 2012). We also have compared some of the compounds directly from the canister measurements (with storage time) to in-situ measurements with the µ-dirac on a recent cruise (Quack and Krüger, 2013), and despite a large standard deviation in the direct measurements, the overall concentrations compare well. More will be done in some upcoming research which will provide even better insights into sample stability. The bottom line answer to the question about stability is that the canisters we have used have appeared to work well during many previous campaigns, and the results from DRIVE look consistent. From this we conclude that sample stability over the storage time until analysis was not a significant issue. We include more detail into the manuscript.

Page 19707 L5-6: It is stated here that the pigments were analyzed from seawater samples taken from ships' underway system, whereas the halocarbon samples were taken from the ships moon pool. Does this mean that the seawater samples for phytoplankton pigment analysis were taken from a different water supply to the

halocarbon samples? If so, why was this the case, and what are the implications for comparisons between pigments and halocarbons (if any)?

Thank you for pointing out this confusing section. Both halocarbons and pigment samples were taken from the same water supply. This is clarified in the manuscript now: *"1 L of sea surface water from the continuously working pump in the ships moon pool was filtered through 25 mm Whatman GF/F filters and stored at -80° C until analysis."*

Page 19707 L9: Does "waters" refer to the HPLC manufacturer? If so, this should be capitalized, as in "Waters".

"Waters" indeed refers to the manufacturer, and is now corrected again in the revised manuscript.

Page 19709 L14-15: Suggest re-wording the sentence beginning "The beginning ceasing of the upwelling. . .".

We change this sentence to: *"Although the upwelling had already ceased, stations S3 – S6 are defined as upwelling and coastal stations (further on called coastal stations) due to the lower SSTs observed there."*

Page 197010 L4-5: The authors should be clear that the average CH_3I concentration reported for open ocean water is in fact determined based on measurements at only 2 stations. Furthermore, from table 2 it seems that the mean and range of CH_3I concentrations at S2 are very similar to the concentrations observed at the coastal stations, and as such the reported open ocean average concentration appears to be somewhat skewed by the measurements at the S1 station.

We appreciate the reviewer's advice. We clarify at the end of section 3 in the manuscript that values from fewer stations were used to derive the average open ocean concentrations to address this concern: *"Due to the classification of the stations into two regions, average values of both open ocean stations together are based on fewer measurements than average values of the four coastal stations."*

As to the second remark, the reviewer's comment that oceanic CH_3I at S2 was close to coastal values is certainly correct. However, we have chosen to classify these two stations as open ocean according to both physical and biological parameters. We are aware that while SST and salinity observed at S1 were more characteristic for tropical surface water, which was associated with higher mean CH_3I, SST and salinity of S2 were comparable to some of the coastal stations. Regardless of SST and salinity though, Chl *a* concentrations, MABL height, and distance to the coast were more characteristic for the open ocean region which is why we decided to put these two stations into the same cluster. We believe that both these stations represent the (low regional) range of open ocean CH_3I during the campaign.

Page 19710 L4: Rephrase the sentence "Oceanic CH_3I was with 2.4 pmol L^{-1} on average higher at the open ocean stations S1 and S2 that at coastal stations S3 - S6 with 1.8 pmol L^{-1}".

Both this and the following sentence are edited to: *"Higher mean oceanic CH_3I of 2.4 pmol L^{-1} was found at the open ocean stations S1 and S2 than at coastal stations S3 – S6 with a mean of 1.8 pmol L^{-1} (Figure 2b, Table 2). Maximum mean oceanic CH_3I of 3.0 (1.7 – 5.4) pmol L^{-1} was observed at S1. S3 showed the lowest mean CH_3I concentrations of 1.2 (0.2 – 2.1) pmol L^{-1} during 24 h."*

Page 19710 L5-7: Rephrase the sentence beginning "While maximum mean (max-min) oceanic CH_3I. . ."

See previous comment.

Page 19711 L25-27: Can the authors offer any explanation / interpretation of the measurements at the S5 station, where low oceanic CH_3I coincided with high atmospheric mixing ratios, which gave rise to a net deposition flux of CH_3I from the air to sea?

We found the largest diel variability of all halocarbons for CH_3I. Although no general characteristic diel cycles could be observed, oceanic CH_3I was often lower during the night time, which was the case at S5. The higher daytime CH_3I concentrations, possibly caused by photochemical or biological production, may be diluted. A drop in SST could be observed at the time of the low oceanic CH_3I at S5 which could indicate either freshly upwelled water or nightly mixing within the water column (or both) which would then dilute higher concentrated surface water with lower CH_3I water from below leading to lower surface concentrations (Happell and Wallace, 1996). Together with the elevated atmospheric CH_3I coinciding with low MABL heights (elaborated in Fuhlbrügge et al. (2013)), this led to a decrease in sea-to-air fluxes of CH_3I at this moment.

Page 19712 L3-4: Is there any significant difference in the mean CH_3I fluxes from open ocean vs coastal sites? I would assume that the uncertainty in these values would be at least 10%, which would imply that the mean open ocean and coastal fluxes are essentially equivalent.

As indicated by the reviewer, the flux parameterization by Nightingale et al. (2000) does certainly comprise some uncertainties, especially with regard to the wind speed dependent compound specific transfer coefficient k_w. However, we have calculated large supersaturations for both open ocean stations (Figure 4) due to low atmospheric and higher oceanic CH_3I concentrations. Hence, these two stations have the potential for considerably higher sea-to-air fluxes in comparison to the coastal stations. We therefore suggest that sea-to-air fluxes of CH_3I from the open ocean are usually higher than sea-to-air fluxes from the upwelling in the investigation region as a result of slightly higher oceanic CH_3I and lower atmospheric CH_3I. We add a statement emphasizing the potential for elevated sea-to-air fluxes in the open ocean region in comparison to the coastal area in the discussion chapter 5.1.1.

Page 19713 L10: Change "were" to "where".

This is done.

Page 19713 L15-18: This sentence requires re-wording, as it is difficult to follow in the current form.

We rephrase the sentence in the hope that the content is now presented clearer: *"Higher atmospheric bromocarbon mixing ratios were measured at CVAO with $CHBr_3$ mean (variability) of 6.7 ppt (43 %), and mean CH_2Br_2 of 1.4 ppt (16 %) on June 4, and of 6.8 ppt (35 %) and 1.5 ppt (14 %) respectively on June 6 to 7 (Figure 3b and c, Table 2)."*

Page 19714 L2-3: Reword this sentence. Take care that the word "respectively" is used correctly.

We edit the sentence to: *"Surface* $CHBr_3$ *and* CH_2Br_2 *correlated significantly with Chl a at the 95 % level with correlation coefficients* R^2 *of 0.38 and 0.49 (Table 3, Figure 2a)."*

Page 19716 L13: The quoted upper limit value for the CH_3I seawater concentrations reported by Jones et al. 2010 appears to be too high. Jones et al report CH_3I concentrations in seawater in this region of up to 26.1 pmol L^{-1}.

The reviewer's concern is justified that the values reported by Jones et al. (2010) appear to be lower than what we have chosen to report. However, we state total ranges from minimum to maximum concentrations from our measurements in the manuscript, while Jones et al. (2010) listed their range in 10th – 90th percentiles. To better compare these two studies, we have chosen to use their full data range measured during the RHaMBLe campaign which can be accessed via the HalOcAt data base (https://halocat.geomar.de/) published by Ziska et al. (2013). We now refer to this in the mauscript.

Page 19718 L4-7: As part of the comparison of CH_3I fluxes derived in this work and in previous studies, the authors should clearly state that the spatial resolution of the measurements presented here is relatively limited compared to both the Jones et al 2010 and Richter and Wallace 2004 studies. All three of these studies indicate that there is a great deal of variability in the CH_3I flux within this particular ocean region (e.g for this study -1.7-941.6 pmol m^{-2} h^{-1}), so perhaps it is not entirely surprising that the mean flux derived from observations at 2 - 4 discrete measurement sites differs from the mean flux derived from the more spatially resolved surveys? To this end, it may be more insightful to also compare the total range of fluxes determined from this study and the other studies, rather than just the mean values.

We thank the reviewer for these suggestions, and include the range of sea-to-air fluxes from the mentioned studies for a better comparison in discussion chapter 5.1.2 of our manuscript. We agree that it would be more helpful to insert information on the regional distribution of measurements from these other studies which we do now. Nonetheless, we have stated in the manuscript that the large diel variability in CH_3I was partly much higher than the regional variability. We therefore believe that measuring the diel variability of this compound at the six diel stations covered most of the possible range in oceanic concentrations during our study in the investigated region. Consequently, in our opinion the reason for the larger sea-to-air fluxes from the other studies is the generally higher oceanic CH_3I concentration independent of a higher spatial resolution which is also included in the manuscript.

Page 19718 L12-14: This sentence needs re-wording.

We rephrase this sentence.

Page 19719 L27: Suggest replacing the expression “could be a hint for” with “may indicate” or “may imply”, or similar.

We change this sentence according to the reviewer’s suggestion.

Page 19720 L8: Correlation coefficients of wind speed and sea-air flux are given in Table 4, not Table 5.

We correct the number.

Page 19720 L21: Regarding comparisons of $CHBr_3$ fluxes derived from this study and those of Carpenter et al 2009 – see comment above regarding comparisons of CH_3I fluxes with those of other studies.

On the one hand, the range in oceanic $CHBr_3$ and CH_2Br_2 is very similar to the range observed during DRIVE which is why we think that our observed bromocarbon concentrations cover most of the possible oceanic concentrations in the region during that particular season. On the other hand, atmospheric bromocarbons were very low in Carpenter et al. (2009) which in combination with similar wind speeds and environmental conditions caused their higher sea-to-air fluxes. However, we agree that the comparison to Carpenter et al. (2009) would benefit from additional information, thus, we add the sea-to-air flux range and the spatial resolution by Carpenter et al. (2009) to this passage.

Page 19723 L1-9: Can the authors offer a clearer explanation for the overestimation in the atmospheric concentrations of all three halocarbons at S5?

To investigate how local oceanic halocarbon sources contribute to the elevated atmospheric mixing ratios, we have put a very complex system comprising oceanic sources, advection, and MABL height into a simple box model. We decided to use a fetch of 200 km, because this range covers almost the whole investigated region, but is still rather local. In the open ocean region, the sea-to-air flux within this fetch was not sufficient to explain the observed atmospheric mixing ratios, as was expected. On the other hand, the fetch of 200 km led to a large overestimation of atmospheric halocarbons at S5. Since large sea-to-air fluxes, low MABL heights, and the most elevated atmospheric halocarbons coincided only at S5, we believe that this is a very local and extreme phenomenon constrained to the boundaries of station S5. We believe that the overestimation is a result of the extrapolation of local high sea-to-air fluxes to the large fetch of 200 km. Our conclusion from the box model is a) atmospheric mixing ratios at the open ocean stations originate from sources further outside of our fetch of 200 km, b) the general source strength of the Mauritanian upwelling can mostly maintain the atmospheric mixing ratios found in this region in combination with the MABL height, but c) very elevated mixing ratios such as were observed at S5 are a result of very local conditions like high sea-to-air fluxes and very low MABL heights. We state our findings clearer in chapter 5.4.1, especially with regard to the overestimation of atmospheric mixing ratios at S5.

Page 19723 L25: Delete "regionally" from this sentence.

This word is deleted.

Page 19724 L15: This sentence is a little confusing - please re-phrase.

We delete this sentence, and hope this will reduce the confusion.

Page 19725 L22-23: The statement "The regional oceanic CHBr3 and CH2Br2 distributions and emissions were a result of biological production. . ." seems a bit strong. The observations in this study may suggest that this was the case, but the authors cannot be 100% certain, and so this conclusion should be less strongly worded.

We rephrase this statement accordingly: *"The matching regional distribution of* $CHBr_3$ *and* CH_2Br_2 *concentrations and emissions with phytoplankton indicators imply a biological source, albeit with no clear diurnal cycles."*

A final comment - some of the figures could be improved by increasing font size (Fig 2) and changing data markers such that when several datasets are displayed on the same plot the separate datasets can be easily identified (Fig 3).

We edit all the figures with regard to the font size and clarity of presentation.

References:

Brinckmann, S., Engel, A., Bönisch, H., Quack, B., and Atlas, E.: Short-lived brominated hydrocarbons – observations in the source regions and the tropical tropopause layer, Atmos. Chem. Phys., 12, 1213-1228, 10.5194/acp-12-1213-2012, 2012.

Carpenter, L. J., Jones, C. E., Dunk, R. M., Hornsby, K. E., and Woeltjen, J.: Air-sea fluxes of biogenic bromine from the tropical and north atlantic ocean, Atmos. Chem. Phys., 9, 1805-1816, 2009.

Fuhlbrügge, S., Krüger, K., Quack, B., Atlas, E. L., Hepach, H., and Ziska, F.: Impact of the marine atmospheric boundary layer on vsls abundances in the eastern tropical and subtropical north atlantic ocean, Atmos. Chem. Phys., 13, 6345-6357, 10.5194/acp-13-6345-2013, 2013.

Happell, J. D., and Wallace, D. W. R.: Methyl iodide in the greenland/norwegian seas and the tropical atlantic ocean: Evidence for photochemical production, Geophys. Res. Lett., 23, 2105-2108, 10.1029/96gl01764, 1996.

Jones, C. E., Hornsby, K. E., Sommariva, R., Dunk, R. M., Von Glasow, R., McFiggans, G., and Carpenter, L. J.: Quantifying the contribution of marine organic gases to atmospheric iodine, Geophys. Res. Lett., 37, L1880410.1029/2010gl043990, 2010.

Nightingale, P. D., Malin, G., Law, C. S., Watson, A. J., Liss, P. S., Liddicoat, M. I., Boutin, J., and Upstill-Goddard, R. C.: In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers, Glob. Biogeochem. Cycle, 14, 373-387, 10.1029/1999gb900091, 2000.

Quack, B., and Krüger, K.: Rv sonne fahrtbericht / cruise report so218 shiva 15.-29.11.2011 singapore - manila, philippines stratospheric ozone: Halogens in a varying atmosphere part 1:

So218- shiva summary report (in german) part 2: So218- shiva english reports of participating groups, GEOMAR, Kiel, Germany, 2013.

Ziska, F., Quack, B., Abrahamsson, K., Archer, S. D., Atlas, E., Bell, T., Butler, J. H., Carpenter, L. J., Jones, C. E., Harris, N. R. P., Hepach, H., Heumann, K. G., Hughes, C., Kuss, J., Krüger, K., Liss, P., Moore, R. M., Orlikowska, A., Raimund, S., Reeves, C. E., Reifenhäuser, W., Robinson, A. D., Schall, C., Tanhua, T., Tegtmeier, S., Turner, S., Wang, L., Wallace, D., Williams, J., Yamamoto, H., Yvon-Lewis, S., and Yokouchi, Y.: Global sea-to-air flux climatology for bromoform, dibromomethane and methyl iodide, Atmos. Chem. Phys., 13, 8915-8934, 10.5194/acp-13-8915-2013, 2013.