Response to Referee #2

We would like to thank reviewer 2 for reviewing the manuscript. Below you find our point-by-point answers to your comments (*highlighted in italic*).

Referee #2:

The contribution of oceanic halocarbons to marine and free troposphere air over the tropical West Pacific by Fuhlbrügge et al. This paper presents seawater and atmospheric measurements of CHBr3, CH2Br2 and CH3I obtained during the ship cruise and aircraft campaign of the SHIVA project. Samples were obtained around Borneo in November-December 2011 and are used here to derive ocean emission fluxes in the region and, with the aid of transport modelling, the contribution of the above gases to the free troposphere. Given the likely importance of this region for the transport of air masses to the stratosphere, and given that the region is poorly sampled (in terms of VSLS), this paper is a useful addition to the literature, providing a good synthesis of the SHIVA measurements. I have no major objections to the method and therefore recommend the paper for publication.

My main concern with the paper is that I found it extremely difficult to read and somewhat convoluted in many parts. I encourage the authors to carefully check the manuscript for places where the text could be streamlined to improve readability and where the main messages could be distilled to avoid them being diluted by so many numbers and detail. I had to stop listing technical corrections given the sheer enormity of the task.

We first thank the reviewer for the general positive evaluation of the paper, which she/he describes as a useful addition to the literature. We agree with the reviewer that the text can be written more concisely and distilled to improve readability, if we omit explaining all details of the method which may have convoluted the main messages. Thus, we intensively revised the paper to streamline it and to make it easier to read and follow. The changes for the revision include shifting of section 2.2.3 ("Convective energy"), 3.2 ("CAPE and humidity") and 5.1.1 ("R/V SONNE - R/A FALCON: identifying observations of the same air mass") to the supplement; shortening and substantial rewriting of sections 2.4.2 ("VSLS source-loss estimate in the MABL"), 4.3 ("VSLS intercomparison: R/A FALCON and R/V SONNE"), 5.1 ("Timescales and intensity of vertical transport") and 5.2 ("Contribution of oceanic emissions to VSLS in the MABL"), 5.3.1 ("Identification of MABL air and their contained VSLS in the FT") and 5.3.3 ("Discussion"). These changes are clearly marked in the revised manuscript. We also have asked a native speaker for revisions of the language.

I also encourage the authors to check that the most appropriate citations are given throughout the manuscript. Citing older classic papers is fine (and good) but in many places the discussion would be better served by citating the most up-to-date literature in addition.

For example, in the introduction numbers are given for the "mean atmospheric lifetime" of CHBr3, CH2Br2 and CH3I. I don't understand why the authors refer to such old papers here (Ko et al. 2003 and Solomon et al. 1994) when the most recent and comprehensive evaluation of the lifetimes of these compounds is given in the 2014 WMO O3 Assessment (Chapter 1: Carpenter and Reimann et al.). The concept of a mean atmospheric lifetime for VSLS can be somewhat problematic. I suggest quoting the tropical MBL local lifetime and range from the 2014 report.

We replaced the mean MABL and mid tropospheric lifetimes to mean tropical MABL and mid tropospheric (at 10 km altitude, given in the brackets) lifetimes and also added the reported lifetime range from Chapter 1 of the WMO (Carpenter et al., (2014)):
"Annually averaged mean tropical lifetimes of these halogenated very short-lived substances (VSLS) in the boundary layer are 15 (range: 13 – 17) days for $CHBr_3$, 94 (84 – 114) days for CH_2Br_2 and 4 (3.8 – 4.3) days for CH_3I. The according mean tropospheric lifetimes at 10 km height are 17 (16 – 18) days, 150 (144 – 155) days, respectively 3.5 (3.4 – 3.6) days (Carpenter et al., 2014)."
Due to these new lifetimes the former Figure 12, (now 10) and Figure 13 (now 11) and the Table 3, 4, 5 and A1 (now S-Table 1) have been changed and the corresponding text was adjusted to it (Sections 5.2 and 5.3).

Abstract:

Line 10: The sentence beginning "Elevated oceanic concentrations.." is long. Consider using the word "respectively" in the second half; i.e. change to "... with high corresponding oceanic emissions of 1486, 405, and 433, respectively, characterize.."

We agree and shortened the sentence to: "Elevated oceanic concentrations for bromoform, dibromomethane and methyl iodide of on average 19.9, 5.0 and 3.8 pmol L^{-1} in particular close to Singapore and at the coast of Borneo with high corresponding oceanic emissions of 1486, 405 and 433 pmol m^{-2} h^{-1}, respectively, characterize this tropical region as a strong source of these compounds. Atmospheric mixing ratios in the MABL were unexpectedly relatively low with 2.08, 1.17 and 0.39 ppt for bromoform, dibromomethane and methyl iodide."

Line 24: Change "origins" to "originates"

Done.

Introduction:

Line 2: Change "the atmospheric ozone" to "atmospheric ozone" Add "e.g." before citations to Solomon (1999) and Saiz-Lopez and von Glasow (2012).

Done.

Line 4: Change "via photochemical and heterogeneous reaction cycles from" to "following the photochemical breakdown of".

Thanks, done.

Line 14: Change "the halogenated very short lived substances" to "these halogenated very short-lived substances".

Done.

Line 16: "Climate change could strongly affect marine biota. . . ". Are there not other recent papers that also suggest this? For example: Hughes, C., et al. (2012), 'Climate induced change in biogenic bromine emissions from the Antarctic marine biosphere', Global Biogeochem. Cycles.

We added Hughes et al. (2012), Leedham et al. (2013) and Hepach et al. (2014), who reported on possible influences of climate change on marine halocarbon production leading to enhanced oceanic production and oceanic emissions of brominated and iodinated compounds:
"Climate change could strongly affect marine biota and thereby halogen sources and the oceanic emission strength (Hughes et al., 2012;Leedham et al., 2013;Hepach et al., 2014)."

Line 23: Change "methyl iodide" to "CH3I". Generally, why bother keep using the full names bromoform, dibromomethane and methyl iodide throughout the text once they have been defined? Check full text and at least be consistent.

The idea of using the full names throughout the manuscript was to make it easier to understand for non-chemists, since chemical formulas generally tend to confuse these readers. Nevertheless, we searched through the whole manuscript and kept on using the chemical formulas consistently now.

Line 25: The sentence beginning "Significantly lower. . ." should be amended. Why talk about just model runs looking at the impact of bromine when the previous discussion was iodine-focused. Numerous recent papers from the Saiz-Lopez group have examined the impact of bromine and iodine on tropospheric O3 (e.g. Saiz-Lopez et al. 2014, iodine chemistry in the troposphere and its effect on ozone, ACP, 2014). As we are talking about VSLS in this paper, an appropriate citation would also be to Hossaini et al. (2015, Nature Geoscience) who examined their impact on UTLS O3. Please include these additional citations and add "e.g." before the list.

We included the suggested references and changed the text to:
"Recent studies reported significant contributions of bromine and iodine to the total rate of tropospheric and stratospheric ozone loss (e.g. von Glasow et al., 2004;Yang et al., 2005;Saiz-Lopez et al., 2014;Yang et al., 2014;Hossaini et al., 2015)."

Line 17: The sentence beginning "The goal of SHIVA" is odd. Was that really the main objective? Consider "was to combine observations of VSLS and models to better understand the processes contributing to ozone loss in the stratosphere and how such factors could respond to climate change." This seems more accurate to me.

Thanks, this part has now been removed for further streamlining of the manuscript.

<u>Data and Methods:</u>

Why does the sub-sub section "2.1.2 Aircraft campaigns" come under the SHIVA SONNE subsection? Could Section 2.1 simply be named something like "Overview of ship cruise and aircraft campaign"? Given the length of these sections, I don't think the subsections are needed.

We agree and renamed section 2.1 to "Ship cruise and aircraft campaign". Section 2.1.1 and 2.1.2 were merged into section 2.1.

<u>Section 4.2:</u>

Line 20: Is it possible to comment more on the possible different sources for CH3I compared to the bromocarbons here?

Methyl iodide has different sources, e.g. phytoplankton, macro algae and photochemical production, the latter is assumed to drive the major part of the sea – air flux of CH_3I (e.g. Manley and Dastoor, 1988;Manley and de la Cuesta, 1997;Richter and Wallace, 2004). This is added to Section 4.2 now. We try to summarize different possible sources, however the statements remain speculative. Still the fact, that methyl iodide reveals a different pattern than the other two compounds indicate different source and/or loss processes. We clarified this in the manuscript:

CH_3I concentrations range from 0.6 – 18.8 pmol L^{-1} with a mean of 3.8 pmol L^{-1} and show a different distribution along the ship track which might be ascribed to additional photochemical production of CH_3I in the surface waters (e.g. Manley and Dastoor, 1988;Manley and de la Cuesta, 1997;Richter and Wallace, 2004).

Line 27 on river run: This point needs expanding. Why would the bromocarbons be elevated due to river run and how is the influence of river run detected?

See also our response to anonymous Reviewer 1: Elevated bromoform is found in chlorinated and ozonised waste water, from e.g. cooling plants and municipal effluents. High concentrations are also often measured at coastlines, due to either natural emissions, mainly from macro algae or due the above described anthropogenic input (see Quack and Wallace, 2003 and references therein). Therefore a plausible explanation for the elevated bromoform concentrations, measured within the contaminated Singapore Strait is a likely influence by anthropogenic effluents. Elevated bromoform concentrations close to Bornean coastal sites and cities with river run-off, and its negative correlation with salinity, indicate riverine sources for the compound. While it is therefore clear that riverine transport from coastal or inland sites is the cause for the elevated coastal concentrations, it cannot be completely resolved, whether anthropogenic sources alone are responsible or whether coastal natural sources may contribute as well. We clarified the text in this regard and changed it to:

"Along the west coast (November 19 - 23, 2011) and northeast coast of Borneo (November 25, 2011), bromocarbon concentrations are elevated, and especially $CHBr_3$ concentrations increase in waters with lower salinities, indicating an influence by river run off. Elevated $CHBr_3$ concentrations are often found close to coasts with riverine inputs caused by natural sources and industrial and municipal effluents (e.g. Quack and Wallace, 2003;Fuhlbrügge et al., 2013 and references therein)."

Discussion:

Line 10: WMO (2015) should be WMO (2014)

We changed the reference to Carpenter et al. (2014).

References

Carpenter, L. J., Reimann, S., Burkholder, J. B., Clerbaux, C., Hall, B. D., Hossaini, R., Laube, J. C., and Yvon-Lewis, S. A.: Update on Ozone-Depleting Substances (ODSs) and Other Gases of Interest to the Montreal Protocol, in: Scientific Assessment of Ozone Depletion: 2014, edited by: Engel, A., and Montzka, S. A., World Meteorological Organization, Geneva, 2014.

Fuhlbrügge, S., Krüger, K., Quack, B., Atlas, E., Hepach, H., and Ziska, F.: Impact of the marine atmospheric boundary layer conditions on VSLS abundances in the eastern tropical and subtropical North Atlantic Ocean, Atmospheric Chemistry and Physics, 13, 6345-6357, 10.5194/acp-13-6345-2013, 2013.

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.

Hossaini, R., Chipperfield, M., Montzka, S., Rap, A., Dhomse, S., and Feng, W.: Efficiency of short-lived halogens at influencing climate through depletion of stratospheric ozone, Nature Geoscience, 8, 186-190, 10.1038/NGEO2363, 2015.

Hughes, C., Johnson, M., von Glasow, R., Chance, R., Atkinson, H., Souster, T., Lee, G., Clarke, A., Meredith, M., Venables, H., Turner, S., Malin, G., and Liss, P.: Climate-induced change in biogenic bromine emissions from the Antarctic marine biosphere, Global Biogeochemical Cycles, 26, 10.1029/2012GB004295, 2012.

Leedham, E., Hughes, C., Keng, F., Phang, S., Malin, G., and Sturges, W.: Emission of atmospherically significant halocarbons by naturally occurring and farmed tropical macroalgae, Biogeosciences, 10, 3615-3633, 10.5194/bg-10-3615-2013, 2013.

Manley, S., and Dastoor, M.: Methyl-iodide (CH3I) production by kelp and assoviated microbes, Marine Biology, 98, 477-482, 10.1007/BF00391538, 1988.

Manley, S. L., and de la Cuesta, J. L.: Methyl iodide production from marine phytoplankton cultures, Limnology and Oceanography, 42, 142-147, 1997.

Quack, B., and Wallace, D.: Air-sea flux of bromoform: Controls, rates, and implications, Global Biogeochemical Cycles, 17, 10.1029/2002GB001890, 2003.

Richter, U., and Wallace, D.: Production of methyl iodide in the tropical Atlantic Ocean, Geophysical Research Letters, 31, 10.1029/2004GL020779, 2004.

Saiz-Lopez, A., Fernandez, R., Ordonez, C., Kinnison, D., Martin, J., Lamarque, J., and Tilmes, S.: Iodine chemistry in the troposphere and its effect on ozone, Atmospheric Chemistry and Physics, 14, 13119-13143, 10.5194/acp-14-13119-2014, 2014.

von Glasow, R., von Kuhlmann, R., Lawrence, M., Platt, U., and Crutzen, P.: Impact of reactive bromine chemistry in the troposphere, Atmospheric Chemistry and Physics, 4, 2481-2497, 2004.

Yang, X., Cox, R., Warwick, N., Pyle, J., Carver, G., O'Connor, F., and Savage, N.: Tropospheric bromine chemistry and its impacts on ozone: A model study, Journal of Geophysical Research-Atmospheres, 110, 10.1029/2005JD006244, 2005.

Yang, X., Abraham, N., Archibald, A., Braesicke, P., Keeble, J., Telford, P., Warwick, N., and Pyle, J.: How sensitive is the recovery of stratospheric ozone to changes in concentrations of very short-lived bromocarbons?, Atmospheric Chemistry and Physics, 14, 10431-10438, 10.5194/acp-14-10431-2014, 2014.