Response to Referee #1

Referee #1- general comment:

This paper describes a rather comprehensive set of measurements performed in the region of the South China and Sulu Seas that were designed to improve our understanding of the fluxes of three short-lived halogenated hydrocarbons from the ocean to the free troposphere. This is an important region for understanding the input of naturally emitted bromine and iodine to the stratosphere and is woefully under-sampled. Furthermore, the authors have brought many useful resources and ancillary observations to the experiment in addition to just atmospheric mixing ratio measurements to improve our understanding of halocarbon fluxes in this region. Unfortunately, I found the paper very difficult to read and follow. After hours of studying it I was still unsure that the conceptual framework of and conclusions drawn from the simple box-modelling approach were appropriate. I'm concerned with oversimplification of the processes involved. Some of this confusion stems from the language used in the paper. Descriptions often use jargon or short-cut terms that confuse rather than clarify the arguments being presented. Statements are often overly general and imprecise.

Author response to general comment:

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 a comprehensive addition to the understanding of VSLS fluxes from the ocean to the free troposphere. With the very helpful comments and tips we have streamlined the text substantially and thus improved its readability. Thus we also think that the conceptual framework and the conclusions drawn become much clearer. 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 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.

Below you find your comments (*highlighted in italic*) and our point-by-point answers.

Referee 1:

Confusion is enhanced by a main conclusion stated in the abstract that isn't supported by any portion of the text (line 23): "bromoform in the FT above the region origins [sic] almost entirely from the local South China Sea area", despite numbers in the summary that indicate local contributions to free troposphere CHBr3 of 60%, which to me isn't "almost entirely" (see lines 20-26, p. 17917–is the word "originates" meant?). Perhaps some schematics or diagrams showing the magnitudes of fluxes would help. In short, there is substantial room for improving communication of the simple modelling framework so as to enhance the value of the manuscript to potential future readers.

Author response:

We agree that "almost entirely" is overstated for 60 % contribution and are now giving only the number itself (60%). We further changed "origins" to "originates". We agree that a sketch of the fluxes and the involved budget would be very helpful. Thus we suggest replacing the former Figure 11 in the submitted manuscript with the following:

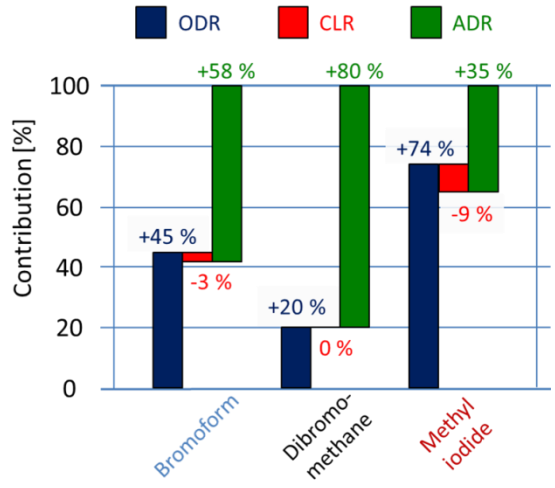

Figure 11: Budgets of the Oceanic Delivery Ratio (ODR, blue), Chemical Loss Ratio (CLR, red) and Advective Delivery Ratio (ADR, green) of $CHBr_3$, CH_2Br_2 and CH_3I.

Other items: Section 2.3, to what degree are conclusions based on the particular air-sea exchange parameterization the authors have chosen (at the exclusion of others)?

We have chosen the Nightingale et al. (2000) parameterization, given its a good mean representation of available air- sea flux parametrizations, which has been discussed in many papers (e.g. Lennartz et al., 2015 ACP). We agree with the reviewer that applying other air-sea flux parameterizations as e.g. discussed by Lennartz et al. (2015) leads to different fluxes (mainly for wind speeds > 10 m/s) and thus to different source-loss estimates. Thus we compare the effect of

two available air – sea flux parameterizations, one from the low (Liss and Merlivat, 1986) and one from the high end of reported parameterizations (Wanninkhof and McGillis, 1999), and included the uncertainty analysis in our discussion (see sentence below). The main conclusions of the paper do not change mainly due to overall moderate wind speed (~ 6 m/s) observed during the cruise:

"Different parameterizations for the transfer coefficient k_w such as Liss and Merlivat (1986) , which is at the lower end of reported parameterizations, and Wanninkhof and McGillis (1999), which is at the higher end, are discussed in Lennartz et al. (2015). Both lead to a reduction of the oceanic contribution to the atmospheric mixing ratios at the observed average moderate wind speeds (~6m s^{-1}) when applied to our data. Still, the general conclusion that local oceanic sources of $CHBr_3$ and CH_3I significantly contribute to MABL mixing ratios remains for the cruise. In times of possible higher wind speeds (>10 ms^{-1}), which are likely for this region, the flux variations between the different parameterizations but also the oceanic contribution to atmospheric abundances would increase."

Lifetimes: are the simple lifetimes calculated for this region of the globe and season of year? Are they a mean over 24 hrs? How do clouds affect trace gas lifetimes in this region and might they explain some of the underestimations of calculated mixing ratios (particularly for CH_3I)?

In the submitted manuscript we used average tropical (± 20° latitude) lifetimes for the MABL from model runs by Hossaini et al. (2010) including degradation by photolysis and OH. According to the comment of Reviewer 2, we now use mean tropical MABL and mid tropospheric (at 10 km altitude, given in the brackets) lifetimes from Chapter 1 of the WMO (Carpenter et al., (2014)): 15 (17) days for bromoform, 94 (150) days for dibromomethane and 4 (3.5) days for methyl iodide. The manuscript is changed accordingly. All lifetimes are annually averaged, which is added to the manuscript as well.

We agree that clouds may influence the atmospheric lifetimes of the compounds via changing photolysis rates (Tie et al., 2003) as well as varying OH fields (Rex et al., 2014). Thus we added the following sentences to the discussion of the uncertainties:

"Additional uncertainties may arise from cloud induced effects on photolysis rates (Tie et al., 2003) and OH levels (Rex et al., 2014) impacting the VSLS lifetimes."

Section 4.1 Line 5-6: mixing ratios are higher afterwards and winds speeds are lower (not higher?).

We have shortened and clarified the sentence in the following way:

"Overall, the three VSLS show a joint pattern of atmospheric mixing ratios along the cruise track with lower atmospheric surface abundances before 21 November 2011 and higher mixing ratios afterwards, which can be attributed to a change in air mass origin (Figure 1)."

Last paragraph: any discussion of age of air inferred from the ratio of two gases (CH2Br2 and CHBr3) seems to require some consideration of the magnitude and variability in the emission ratio. Fortunately, you have measured emissions for both chemicals in this region to provide some information, if one presumes that ratio and variability are appropriate for a much broader region. How variable is their emission ratio and how do the ratios of measured atmospheric mixing ratios compare to this variability? A glance at figure 6d seems to indicate that there is enough variability in their emission ratio in this region of the globe that any discussion of age of air based on the ratio of the ambient mixing ratios of these gases could be not defensible.

We agree that the water concentrations and the emissions hold a large variability along the diverse cruise track. However, inspecting the variability of the ratio for given regimes along the cruise track may give insights into the "relative distance" to oceanic sources, which have often been reported to have a ratio of 0.1 between bromoform and dibromomethane directly at the source (e.g. Yokouchi et al., 2005 and references therein). As dibromomethane and bromoform have different lifetimes, the ratio decreases with a distance from the source. Thus we believe that the ratio between the two gases differentiates between air masses that were subject to the influence of fresher sources, often coastal, versus the influence of more remote air masses. We removed the "age" term and reduced the discussion to an overall description:

"The concentration ratio of CH_2Br_2 and $CHBr_3$ (Figure 4b) has been used as an indicator for the relative distance to the oceanic source, where a ratio of 0.1 was observed crossing strong coastal source regions (Yokouchi et al., 2005;Carpenter et al., 2003). The ten times elevated $CHBr_3$ has a much shorter lifetime, thus degrades more rapidly than CH_2Br_2, which increases the ratio during transport. Overall, the mean concentration ratio of CH_2Br_2 and $CHBr_3$ is 0.6 ± 0.2, which suggests that predominantly older air masses are advected over the South China Sea".

Section 4.2 I find it quite surprising and interesting that in this region of supposedly high natural emissions of VSLS the authors suggest that the highest emissions are apparently associated with anthropogenic influences and river outflow. This seems a significant point that I haven't been aware of being made previously. Can the authors add some additional explanation and provide hard

evidence from the observations made during this experiment to support this assertion? Do any previous studies support these assertions?

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)."

Section 4.3: an indication of the number of comparison measurements and an uncertainty on the values being compared (in the text and in Table 2) is lacking but would be useful. Line 20-24. Regarding the intercomparison, I would think any interpretation of gradients between the free troposphere and the boundary layer should be done with data that are internally consistent so that any potential instrumental influences don't affect the conclusions. In that respect, I don't understand why the mean of the different measurement techniques onboard the aircraft (and that have substantial differences that would seem to be instrumental) is used to compare with the ship-board marine bl results. In a discussion of mean results, sure, mention results from both instruments. But when gradients are being interpreted, it seems only appropriate to use aircraft results that are consistent with those from the ship (good to see that the unbiased result appears in figure 13).

We agree with the reviewer and included the information in the manuscript. We added the corresponding numbers in Table 1 and 2 (Falcon GhOST: n=513, WASP: n=202; SONNE: N=195).

According to Sala et al. (2014) the agreement between the GhOST and WASP instruments for the bromocarbons are within the expected uncertainty range of both instruments. Next to this, WASP measurements were available only up to 6 km altitude and for the bromocarbons. Thus, using measurements from both instruments benefits a larger spatial and temporal resolution of the data set which is considered representative for the region. A possible instrumental offset for CH_3I is discussed. We rewrote lines 16-24 on page 17922 to:

"According to Sala et al. (2014) the agreement between the GhOST and WASP instruments are within the expected uncertainty range of both instruments which is then assumed to be also valid for the ship measurements. The good agreement between WASP and ship data might be caused by the same sampling and analysis method, both using stainless steel canisters and subsequent analysis with GC/MS, while GhOST measures in-situ in a different resolution. Since GhOST and WASP measurements together cover a larger spatial area and higher temporal resolution, a mean of both measurements is used in the following for computations in the free troposphere. For CH3I significantly higher mixing ratios were measured during the meetings between ship and aircraft (Table 2). Whether this offset is systematic for the different methods, needs further investigation.

Figures: 6d, I'd like to be able to see the CH2Br2 results, but they are often obscured by other data.

We improved the visibility of CH2Br2 lines in the former Figure 6 (now Figure 4) by choosing a darker line for them and using non-linear y-axes.

Figure 8, consider making the legend more informative by indicating ship, flask, insitu instead of the instrument acronyms.

According to your suggestions we added the information to the figure legend of the former Figure 8, now Figure 6.

Figure 13, I presume the unadjusted observations from the aircraft are the mean of the two available measurements and the adjust ones are only the data from aircraft flasks? Explicitly stating so would help.

Yes, thanks for pointing this out. We further explain details in the figure caption now. Unadjusted measurements include measurements from both instruments on the aircraft. The "adjustment" only

accounts for methyl iodide. Since flask (WASP) observations are not available for methyl iodide, the in-situ observations are reduced by the percentage of which in-situ measurements on the aircraft and on the ship differed during the two meetings on November 19 and 21, 2011, according to Table 2:

“Mean FT mixing ratios (solid lines) and 1 standard deviation (shaded areas) from in-situ and flask observationson R/A FALCON (Obsv., black) versus simulated mean FT mixing ratios from MABL air (MABL, red) and oceanic emissions (Ocean, blue) observed by R/V SONNE. R/A FALCON in-situ observations have been adjusted for CH3I (Obsv.*, dashed black) according measurements deviations during the meetings of R/V SONNE and R/A FALCON (compare Table 2; Section 4.3).”

References

Carpenter, L., Liss, P., and Penkett, S.: Marine organohalogens in the atmosphere over the Atlantic and Southern Oceans, Journal of Geophysical Research-Atmospheres, 108, 10.1029/2002JD002769, 2003.

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.

Hossaini, R., Chipperfield, M., Monge-Sanz, B., Richards, N., Atlas, E., and Blake, D.: Bromoform and dibromomethane in the tropics: a 3-D model study of chemistry and transport, Atmospheric Chemistry and Physics, 10, 719-735, 10.5194/acp-10-719-2010, 2010.

Lennartz, S. T., Krysztofiak, G., Marandino, C. A., Sinnhuber, B. M., Tegtmeier, S., Ziska, F., Hossaini, R., Krüger, K., Montzka, S. A., Atlas, E., Oram, D. E., Keber, T., Bönisch, H., and Quack, B.: Modelling marine emissions and atmospheric distributions of halocarbons and dimethyl sulfide: the influence of prescribed water concentration vs. prescribed emissions, Atmos. Chem. Phys., 15, 11753-11772, 10.5194/acp-15-11753-2015, 2015.

Liss, P. S., and Merlivat, L.: Air-Sea Gas Exchange Rates: Introduction and Synthesis, in: The Role of Air-Sea Exchange in Geochemical Cycling, edited by: Buat-Menard, P., Reidel, D., and Norwell, M., Springer Netherlands, 113-127, 1986.

Nightingale, P., Malin, G., Law, C., Watson, A., Liss, P., Liddicoat, M., Boutin, J., and Upstill-Goddard, R.: In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers, Global Biogeochemical Cycles, 14, 373-387, 10.1029/1999GB900091, 2000.

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

Rex, M., Wohltmann, I., Ridder, T., Lehmann, R., Rosenlof, K., Wennberg, P., Weisenstein, D., Notholt, J., Kruger, K., Mohr, V., and Tegtmeier, S.: A tropical West Pacific OH minimum and

implications for stratospheric composition, Atmospheric Chemistry and Physics, 14, 4827-4841, 10.5194/acp-14-4827-2014, 2014.

Sala, S., Bonisch, H., Keber, T., Oram, D., Mills, G., and Engel, A.: Deriving an atmospheric budget of total organic bromine using airborne in situ measurements from the western Pacific area during SHIVA, Atmospheric Chemistry and Physics, 14, 6903-6923, 10.5194/acp-14-6903-2014, 2014.

Tie, X., Madronich, S., Walters, S., Zhang, R., Rasch, P., and Collins, W.: Effect of clouds on photolysis and oxidants in the troposphere, Journal of Geophysical Research-Atmospheres, 108, 10.1029/2003JD003659, 2003.

Wanninkhof, R., and McGillis, W.: A cubic relationship between air-sea CO2 exchange and wind speed, Geophysical Research Letters, 26, 1889-1892, 10.1029/1999GL900363, 1999.

Yokouchi, Y., Hasebe, F., Fujiwara, M., Takashima, H., Shiotani, M., Nishi, N., Kanaya, Y., Hashimoto, S., Fraser, P., Toom-Sauntry, D., Mukai, H., and Nojiri, Y.: Correlations and emission ratios among bromoform, dibromochloromethane, and dibromomethane in the atmosphere, Journal of Geophysical Research-Atmospheres, 110, 10.1029/2005JD006303, 2005.