Questions Referee #1:

Question 1: A minor question - given that the mixing ratios of these gases are so low, it seems unlikely that they are normally distributed. Is there any evidence that they are? I could imagine that the atmospheric levels over the oceans represent a dilution of the emissions with "zero air" from above. In that case, wouldn't a log-normal distribution better describe the data? If so, then a geometric mean (and variance) might be more appropriate.

Reply: This objection is justified. The mixing ratios along the cruise track in the West Pacific are not normally distributed, which is due to the uneven distribution of sources and sinks. So, the use of arithmetic mean and standard deviation, as suitable for a normal distribution, is problematic in this case. As you expected, the log-normal distribution does fit these data better. We will list the measures (mean and variance) based on a log-normal distribution in table 2. For the subset "open ocean" the use of arithmetic means is justified.

The section starting on page 22207, line 15 is edited as follows: "In table 2 a summary for the datasets from the IAU Frankfurt is shown. Due to the uneven distributions of sources and sinks along the track in the West Pacific the mixing ratio data tend to be better described by a log-normal rather than a normal distribution. Thus, the geometric values of mean and standard deviation were calculated for the overall summary of this data set. (The differences between geometric and arithmetic means are very small, only for CHBr3 a significantly higher arithmetic mean (+13%) was determined.) For the subset of open ocean samples discussed below, arithmetic means are given, as these have proven to be more appropriate for this case. CHBr$_3$ shows an overall mean mixing ratio of 0.91 ppt, with a range between 0.44 and 2.16 ppt. As noted above, the higher values were detected for samples with coastal influence, while the open ocean mixing ratios were considerably lower. When excluding all samples with trajectories passing through regions with larger islands, we find an average of only 0.62 ppt for CHBr$_3$. Considering the whole data set, CH$_2$Br$_2$ exhibits an average of 0.92 ppt and a range between 0.69 and 1.21 ppt. For the limited set of samples without coastal influence we obtain an average of 0.83 ppt for this substance. Thus, above the open ocean CH$_2$Br$_2$ had somewhat higher concentrations than CHBr$_3$, which can be explained by the combination of its relatively longer lifetime and the absence of significant emissions. The three polyhalogenated compounds show average mixing ratios of 0.10, 0.20 and 0.14 ppt (for CH$_2$BrCl, CHBrCl$_2$ and CHBr$_2$Cl respectively). The corresponding open ocean values of 0.09, 0.17 and 0.11 ppt (in the above order) are also lower compared to those with coastal influence."
In table 2 on page 22227 the values have been changed accordingly.

Question 2: Another issue relates to the importance of coastal emissions. I see from the data that levels are higher over coastal regions so I agree that the emissions must be higher. However, it is not clear to me that that means coastal emissions are important to the stratosphere. Is it not just as likely that coastal emissions are not important because the oceanic levels are lower? The coastal regions are very small in extent, so there needs to be some other argument made to show coastal fluxes are quantitatively important (perhaps based on modeling).

Reply: This is shown in former studies, e.g. Quack and Wallace, 2003 (based on available data from surface water and MBL air measurements). This study attributes 23% of total emissions to the narrow nearshore areas, 48% to continental shelf and the remaining 29% to the open oceans. In our study we rely on these quantitative findings. Furthermore, our measurements support these results qualitatively. But any quantitative investigations on this issue are beyond the scope of this paper.

Concerning the comments on the use of the English language: While the reviewer, in agreement with reviewer #4, is correct in pointing out that the wording is sometimes overly complicated, we believe that the criticism is exaggerated and that this is a not reason to reject this paper. The paper has been re-edited by a native speaker to correct for grammatical errors and in order to ensure a better readability. This has been done in a way not to change any statements or discussion presented in the original manuscript.

Questions Referee #3:

Question 1: List data: While I assume that further analyses of the West Pacific observations onboard Sonne will follow in forthcoming publications, the List data set will probably not discussed in more detail elsewhere? In this respect it may be appropriate to discuss the conditions during this campaign and the results of this campaign in somewhat greater detail. The current manuscript contains essentially only one paragraph on the results of this campaign. The most intriguing feature of the measurements is the increase of most of the bromocarbons by about a factor of 3 during one event on 25 June. This is explained by "a change in catchment area from the North Sea to the Baltic". To me this raises a number of questions: (a) how much are the measurements influenced by local emissions from the nearby tidal flats versus transport from more remote source regions? (b) why are bromocarbon mixing ratios so similar between the beginning and the end of the campaign although trajectories initially come from the North Sea and later from the Baltic? I would have expected this to be very different environments. (c) Why does the change on 25 June lead to enhanced bromocarbon mixing ratios? Is this related to increased wind speed? While you probably cannot answer all these issues, it would be useful to provide more information here.

Reply: These are valuable remarks and questions. It is indeed necessary to provide more information here. On page 22206 at line 10 a new section will be added:
“The similar levels of short-lived bromocarbons observed for air transported from both the North Sea and the Baltic Sea lead to two important conclusions. First, the mean emission fluxes of these species in the two environments apparently do not differ significantly. Second, we conclude that local sources of brominated VSLS are of minor importance, since local wind directions changing from West (open sea) to East (tidal flats) have no noticeable impact on the observed mixing ratios. This latter finding is also supported by the comparison of local wind speeds and bromocarbon mixing ratios. A correlation between these measures was observed in former studies for regions with strong nearby sources (Zhou et al., 2008), but such correlation is not found for our data from List. The elevated concentrations detected on 25 June suggest that the sampled air masses had crossed extended areas of coastal regimes in the transition zone between the North Sea and Baltic Sea. This would be consistent with the importance of bromocarbon emissions in coastal environments.”

Question 2: Emission ratios: There are a number of assumptions and inherent uncertainties in the estimated emission ratios. It would therefore be helpful if you could give some quantitative uncertainty for the estimated emission ratios. One point that did not come out so clear for me was if you have clear indications that the emission ratios are universal in the sense that you expect to find the same ratios in different regions and under different conditions, or if they represent only something like an average ratio with individual emissions differing?

Reply: Due to the limited number (and limited characteristics) of our measurements we can just give very rough estimates of these values. In the first step we derive lower bounds of the emission ratios. For this we indeed have to assume that the emission ratios are more or less universal. This assumption is justifiable considering that the results of our correlation analyses, the two- and the three-component analyses, indicate no significant discrepancies of these emission ratios in the different regions. The only exception is CHBr2Cl, for which we find several data points in the West Pacific that don't agree with the ratio values indicated by the other data. The determination of an uncertainty of these lower bounds (based on measurement precision and calibration scale uncertainties) would be possible, but given the missing knowledge about natural variations, the total uncertainty cannot be well estimated. In the second step we compare our findings with the results from former studies and find the value of 9 for CHBr3/CH2Br2 in a rough agreement with the overall information from our data. Based on this value and our observations we determine an estimate for the corresponding emission ratio of CHBr2Cl/ CH2Br2.

The passage starting at page 22214, line 17 is changed as follows: "To estimate emission ratios from a broad database containing samples of a range of characteristics (in terms of dilution and chemical decay processes), we combined the datasets from the two source regions under the assumption of (1) similar relative emission strengths and (2) similar lifetime ratios in both regions. (1) is supported by the above findings of the two-component analyses. (2) is also justified, given that only the ratios of the lifetimes must be similar. Hossaini et al. (2010) found altitude dependant ratios of the local tropical lifetimes for CHBr3 and the CH2Br2 ranging from 0.31 (16days/52days) near the surface to 0.09 (21days/237 days) in the upper troposphere (500-200 hPa region). For the lower troposphere (1000-500 hPa) Hossaini et al. (2010) report a ratio of 0.26 (17days:65 days). This compares rather well with the ratio of local lifetimes of 0.22 (26days/120days) given by Ko and Poulet (2003) for average tropospheric conditions at about 5 km altitude. While it is thus true that tropospheric local lifetime ratios vary significantly, it seems that the altitude variations are much stronger than the latitudinal variations."

page 22200, line 13: sentence edited:
"Using a combined dataset from the two campaigns and a comparison with the results from two former studies, rough estimates of the molar emission ratios between the correlated substances were: 9/1/0.35/0.35 for CHBr$_3$/CH$_2$Br$_2$/CHBrCl$_2$/CHBr$_2$Cl."

Question 3: page 22202, line 13: "free grass area": free of what? More generally it would be useful to provide more information on the local environment: I assume this is close to tidal flats? Do you see a signature of the tides in the bromocarbon data? This could provide some indications to discriminate local from remote emissions.

We will change this passage as follows:
"The sampling was carried out about 100 m from the eastern coast of Sylt Island. This eastern coastline is characterized by tidal flats, while the western coast is oriented to the open sea."

Concerning the signature of the tides: We don't find such a relationship (now mentioned in text, see reply to question 1 by the same referee). Instead, there seems to be a signature of the diurnal cycle during the last three days, which could be associated with the diurnal change of the vertical extension of the MBL. We have decided to leave out a discussion on this issue in the paper.

Question 4: page 22205, line 10: "Possible temporal drifts…were not considered": What will this mean for the uncertainty?

Reply: We will add the following sentence on page 22205, line 10:
"An estimate of this potential error is given in section 5.1."

Question 5: page 22207, line 7: "our measurements": IAU only?

Reply: "our measurements" changed to: "the IAU measurements"

Question 6: page 22207, line 25: Is this really the absence of emissions?

Reply: "absence of emissions" changed to: "absence of significant emissions"

Question 7: page 22209, line 15: What is the meaning of the phrase "typical quantitative ratios"?

Reply: This means that the molar emission rates of the correlated species have to show similar ratios. "typical quantitative ratios" changed to: "similar ratios"

Question 8: page 22211, line 20: I'm having some difficulties with the concept of an "initial concentration". To me this is a continuous process where in steady-state emission is balanced by in-mixing (and photochemical decay). Are these only two points of view leading to the same conclusions, or are there further assumptions involved that justify the concept of an initial concentration?

Reply: The relationships we derive for two species with constant emission ratios are based on the assumption of an air parcel that is photochemically aging or continuously mixed with background air of certain conditions. Other processes, mixing with non-background air (air parcels with relatively high bromocarbon mixing ratios) and new emissions along the pathway are not considered. This latter scenario of continuous emissions is theoretically described in Carpenter et al. (2003). It is shown for this case that the slopes of the resulting regression lines are approximately equal to the ratios of the emission rates. Our data clearly indicate that the scenario of measurements in some distance to the sources is the most likely, with the consequence of slopes that can deviate from the emission ratios. We need to introduce this "initial concentration" for the derivation of the theoretical two-component relationships (while the absolute values are not relevant for the conclusions with respect to emission ratios, as these are derived from the slopes). But eventually the concept of an "initial concentration ratio" is important, as this value can never be exceeded in theory, no matter if continuous emissions along the trajectory occur or not.

Question 9: page 22217, line 20: I don’t understand the reasoning for the relatively low potential temperature. Please elaborate or just remove.

sentence removed

Question 10: page 22218, line 15: “Given are the contributions of the different source gases to a virtual mixing ratio of bromine atoms.” Wouldn’t it be okay just to write "the mixing ratio of bromine atoms"?

This sentence has been deleted. Instead we phrase as follows:
“In Table 7 the budget of organic bromine for the air sample near the LZRH is listed. For molecules with multiple bromine atoms the initial source gas mixing ratio is multiplied with the number of bromine atoms in order to derive total bromine.”

Question 11: page 22218, line 26: How reasonable is it to assume a linear drift versus an exponential decay? How would this change the results? Do you have any possibility to estimate this?

Reply: The degradation of the samples occurs much faster at low sample pressures. It is therefore likely that the drift is not exponential (as would be expected for a first-order process) but depends on time and pressure in some unknown way. We have therefore chosen the linear decrease as the simplest possible assumption. This is supported by the outcomes of the four consecutive analyses on the two instruments (within five weeks) very soon after the sampling, in which no significant decay of the short-lived bromocarbons was observed. Thus, a calculation using an exponential decay would lead to a strong overestimation of this error. The sentences on page 22219, lines 1-6 are edited as follows:
“These values are assumed to represent best estimates of the maximum error caused by sample instabilities. The very high pressure (of around 30 bar) has certainly stabilised the conditions in the canisters prior to the first measurements, so that the presumption of an exponential decay (as indicated by the investigations of the two-liter canisters in section 2.2) would lead to a strong overestimation of this error. This assumption of relatively stable conditions at the beginning is supported by the outcomes of the four consecutive analyses on the two instruments (conducted within five weeks starting about one month after the sampling. During these measurements no significant decay of the brominated VSLS was observed.”

page 22203, line 29: sentence edited:
“The laboratory analyses were conducted in July and August of the same year on the Agilent-7890 GC-MSD system and another GC-MSD system (Sichromat1) using both detector modes EI and NCI for each system.”

Question 12: page 22219, line 25: Can you make at least a rough order of magnitude estimate by how much the 8 months storage time could have reduced bromocarbon measurements?

We will edit the sentence as follows:
“Nevertheless, in the specific case of the 2005 Teresina samples, we expect a considerable decay of the VSLS in the BONBON canisters during storage times of 8 months between

sampling and measurements. Considering the relative decreases as observed between initial and repeated measurement for Teresina 2008, the for the VSLS budget 2005 is expected to be underestimated by up to 0.3 ppt."

Questions Referee #4:

Question 1: The authors attempt to determine correlations and universal ratios between the different short-lived species that can then be used to assess emissions if only one or two of these gases is actually measured. Why should these ratios be constant? Also, given the differences in degradation rates in and out of the water as well as the need to cross the air-sea boundary, why should atmospheric concentration ratios relate to production or emission ratios? Production ratios may differ in coastal and open ocean waters. Degradation in the surface waters in coastal areas is important for bromoform, but it may not be in a different region. The exchange between the surface water and the atmosphere may impart changes in the ratios of the gases after production in the surface water and thus impact their atmospheric concentration ratios. While I think the data are important and these gases are significant sources of bromine to the stratosphere in regions with rapid transport, I don't think that the concentration ratios are ever going to be suitable for using one of the VSLS gases as a proxy for another VSLS gas.

Reply: Many previous studies have found good correlations (with common regression slopes) between the mixing ratios of, for example, CHBr3 and CH2Br2. These observations clearly indicate the presence of typical relative emission strengths. The estimates we give for the emission ratios are values for the fluxes into the atmosphere. With our measurements we can, of course, make no statements for the emission fluxes into the seawater. Differential degradation in the surface water leads to additional variations in the emission fluxes to the atmosphere. Nevertheless, the determination of mean emission ratios is reasonable and useful, if significant correlations are found and the results are comparable with other observations. In the case of CHBr2Cl, our measurements indicate inconsistencies (in the form of several outliers) leading to limitations of the use of this approach.

The following phrases have been edited to make the above remarks clearer in the text:

page 22216, line 20 and 22221, line 11: "initial concentration ratio" -> "initial atmospheric concentration ratio"

page 22216, line 23: "global flux estimates" -> "global sea-to-air flux estimates"

page 22216, line 24: sentence added: "As noted above, higher global fluxes of CHBr2Cl are likely considering the observation of several inconsistently high values near the coastlines of the West Pacific."

page 22209, line 14: passage changed as follows:
"The presence of high correlations implies that the related species are emitted from the same sources or source regions in relatively consistent and constant ratios. The determination of these emission ratios can help to predict the distributions of the related species, if the atmospheric levels of one substance are well characterised. It should be pointed out that only emission fluxes into the atmosphere are relevant to this study. During the initial emission

from the algae species into the ocean water deviating values are expected, due to differential degradation in the surface water prior to the emission through the sea surface. This however is not of relevance to our study as we only consider emissions into the atmosphere and make no assumptions or conclusions about the initial emissions from the biological processes”