Meteorological constraints on oceanic halocarbons above the Peruvian Upwelling

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Relevant changes made to the manuscript

- The whole manuscript has been revised according to the reviewer's suggestions, including a wider more balanced discussion of our key results.
- The text has been streamlined and re-checked for English, and redundant phrases were removed to improve the readability of the manuscript.
- Due to the reviewer suggestions, sections 3.4 and 3.5 were shortened and reorganized.
- The comparisons of the study's results to other oceanic regions are now summarized in the new section "3.6. Comparison to other oceanic regions".
- Discussions throughout the manuscript are now all summarized in Section "4. Discussion", which also led to a shortening and streamlining of Section "5. Summary".
- Several unnecessary subheadings were removed (2.2.1, 2.2.2, 2.4.1) and the corresponding paragraphs summarized according to the reviewer suggestion.
- Figure 1 is now Figure 2 and vice versa.
- The algebraic signs in Figure 2 and Section 2.6 were updated to make loss and source processes apparent. This did not affect the results.

Changes made to the manuscript are marked **blue (new)**, **red (deleted)** and **green (shifted)**.

Response 2 to Referee #2

We would like to thank the reviewer for his/her positive assessment of the manuscript as well as the large and careful effort and the very helpful comments. We now have significantly improved the manuscript to capture the essence of our findings according to the reviewer's annotations. Below you find our point-by-point answers to your comments (*highlighted in italic*).

Fuhlbrügge et al. have done a much better job of getting their main points across in this revised version of their manuscript, "Meteorological constraints on oceanic halocarbons above the Peruvian Upwelling". The paper is clearer and, as I mentioned in my earlier review, the data look to be good and the overall approach sound. The paper now addresses uncertainties, the authors have removed much of the unnecessary text and clarified portions of it, and they have looked at upstream sources. That being said, I still have some concerns about the manuscript that warrant additional revision. This paper has potential to be a significant contribution to our understanding of how upwelling areas contribute to these gases in the atmosphere, but it needs to be written in a way that captures the essence of their findings.

General Comments:

1) I'm having a hard time coming to terms with the authors' suggestion that the larger mixing ratios of these gases over upwelling areas are due to advection from somewhere else. Although they've shown some numbers using mean values and based on certain assumptions, they need to do more to convince me, and probably others, of whatever explanation they come up with in the end. Is the Peruvian upwelling all that different that it requires advection from somewhere else to elevate the mixing ratios? If so, how would one account for this in open-ocean upwelling areas? How much does the upwelling contribute to the excess, say, beyond what is found over the open ocean? The simple selection of advection for this area is not enough and I think the authors have enough information in their data and in the published literature to go further with this and draw out some generalities about air-sea flux and transport of short-lived halocarbons in the atmosphere.

We agree with the reviewer that advection alone cannot increase the VSLS mixing ratios above the upwelling. Taking your concerns into account and thoroughly revising our results, we interpret the situation over the Peruvian Upwelling as the following:

1) Relatively steady state atmospheric (southerly flow parallel to the coast) and oceanic conditions (Humboldt Current) prevail over a large area (approx. 5 S to 35 S) along the West coast of South America and the East Pacific lead to an accumulation below the two inversion layers of the VSLS from coastline and remote coastal areas leading to an accumulation of background concentrations.
2) Stable atmospheric conditions with a low and isolated MABL especially above the Peruvian Upwelling together with a pronounced trade inversion layer suppress vertical mixing of the emitted in-situ VSLS.
3) In addition to these background concentrations and low and stable conditions, maximum VSLS fluxes observed above the Peruvian Upwelling can explain the remaining part of the measured in-situ VMR at the Peruvian coast.
4) Coast lines can be elevated source regions (Ziska et al., 2013; Lennartz et al., 2015) and are assumed to lead or to contribute to the elevated atmospheric VSLS mixing ratios (this study), but those regions have not been sampled during the cruise.

We believe that these conditions together can largely explain the observed atmospheric VMR above the Peruvian Upwelling (see new Section 4. Discussion). However, the mean observed in-situ VSLS fluxes cannot explain 100% of the observed in-situ VSLS VMR, indicating that higher VSLS surface water concentrations and emissions may exist nearby at the coastlines. We tried to sharpen our argumentation in the manuscript along these basic points now specifically in the abstract and the revised discussion.

2) Although improved in many places, the text still seems to meander or jump around, especially in the Discussion, but also elsewhere. In my view, some text is still unnecessary. Along those lines, while I fully appreciate the difficulties in dealing with the nuances of a second language, and the authors are overall doing a very good job with it (far better than I would do in German or Norwegian), I still find a number of statements throughout the paper that are awkward and require additional effort of the reader to understand just exactly what is being said. Since one of the co-authors is native to the English language, I would strongly

recommend that he carefully go through the final version simply to ensure clarity and flow of the text before the manuscript is resubmitted.

We agree with the reviewer and have revised the whole manuscript according to the reviewer's suggestions again (comments above and below). In particular the Discussion was rewritten and restructured to give a clearer message. The native English co-author has also carefully re-checked the manuscript.

3) The authors need to do a little more work on demonstrating their approach clearly, as their assumptions are key to the validity of their conclusions. Some of the text remains disjointed and needs tuning (see points below). Their treatment of statistics and uncertainties is improved, but they've not addressed representativeness of their choices and that is a bigger part of the overall uncertainty analysis. There are several good points to be made as a result of this paper – things that will improve our understanding of the contribution of upwelling zones overall to short-lived halogens in the atmosphere. This paper can come across strongly if it is organized about making those few points and can justify them.

We agree with the reviewer and revised the manuscript according to the suggestions (above and below). See also our general answer to 1) stressing our main conclusions. According to this, we concentrated the discussion of the results into the new Discussion Section. Thus the key results are better highlighted and separated from our interpretations and method uncertainties. We especially addressed the representativeness of our study and an overall uncertainty analysis more clearly now as described below in the individual minor comments.

4) The repeated comparisons to the Mauritian upwelling during the parts of the paper are distracting and they are not handled well in the Discussion either. It would be best for the authors to convey their findings for this study overall in a way that is clear to the reader, and after that have a separate section to compare to characteristics the Mauritian upwelling and other zones (noted below), but only to underscore their main points.

We agree with the reviewer. All comparisons to characteristics of the Mauritanian upwelling and other oceanic regions are now handled and restructured in the new Subsection "3.6 Comparison to other oceanic regions".

5) Finally, the paper has too many subheadings. That's an easy fix.

We agree and removed the subheadings 2.2.1, 2.2.2 and 2.4.1.

Specific Comments:

1. *Abstract.*

In my mind, an abstract needs to say no more than "what we did, what we found, and what it means". Any more should be reserved for the introduction or elsewhere. In this light, the authors could improve their abstract by deleting the first two sentences. The third sentence states clearly, succinctly, and compellingly what they did. It also identifies why this might be important (in this case, unique) and is a very good lead sentence. I offer a few minor suggestions below to help strengthen the abstract overall.

We changed the abstract according to your comments.

a. *Lines 19-20. Awkward. Please rewrite, e.g., "oceanic emissions of dibromomethane and bromoform were relatively low, while those for methyl iodide were high . . ." or something to that effect. Also, "relatively" refers to what? Other parts of the ocean? Methyl iodide emissions? Etc.*

   We changed the sentence to: "Oceanic emissions of bromoform and dibromomethane were relatively low compared to other upwelling regions, while those for methyl iodide were very high."

b. *Line 21 delete "both".*

   Done.

c. *Lines 24-27. Awkward sentence? Perhaps simply state that the specific properties correlated well rather than "correlations were found"?*

   We changed the sentence to: "Observed atmospheric VSLS abundances, sea surface temperature, relative humidity and MABL height correlated well during the cruise."

d. *Lines 26-27. Insert "below the trade inversion" after "abundances".*

   Done.

e. *Is the last sentence of the abstract true? Does it really reflect the authors' findings or is it conjecture? They make a case for emissions in their study area not being all that significant in delivery of the brominated compounds to the MABL, which seems counter to what this sentence says.*

We agree with the reviewer and changed the sentence to: "This study confirms the importance of oceanic upwelling and trade wind systems on the atmospheric distribution of marine VSLS emissions."

2. *Introduction*

a. *Lines 34-37. This sentence seems to conflate tropospheric and stratospheric processes, e.g., the phrase "ozone depletion" normally is used to address a distinct phenomenon in the stratosphere. Try something like, "Oceanic fluxes of short-lived halocarbons contribute to reactive halogens in the atmosphere, where they are subsequently involved in ozone chemistry, aerosol formation, and other chemical cycles that influence the fate of pollutants and climate" or something to that effect.*

Thanks, done.

b. *Lines 43-46. Shouldn't this be a more general statement than one confined to the Mauritanian upwelling area? Isn't it generally understood that the composition of anything in the MABL is largely a function of oceanic sources and meteorology?*

We agree and changed the sentence to "Meteorological conditions strongly influenced the atmospheric mixing ratio of the marine compounds bromoform ($CHBr_3$), dibromomethane (CH_2Br_2) and also methyl iodide (CH_3I) (Fuhlbrügge et al., 2013; Hepach et al., 2014)."

c. *Line 46. Delete "Especially" at the beginning of the sentence. Since this sentence clearly is about Mauritanian upwelling, maybe there is probably a good way to make it a logical follow-up from a general statement in the (reformulated) previous sentence.*

Done.

d. *Line 49. Insert "high" before "atmospheric"; delete "also".*

Done.

e. *Line 55. Make "waters" singular.*

Done.

f. *Lines 56-59. The way this sentence is written makes one think that the referenced studies were conducted in the Peruvian upwelling. Perhaps rewriting the sentence would help, e.g., "Given that others have found elevated levels of short-lived halocarbons over upwelling regions, it is likely (or 'we would expect') that the Peruvian upwelling zone similarly is a source of these gases" . . . or something like that.*

Thanks, we changed the sentence to: "We therefore expect elevated levels of short-lived halocarbons in the Peruvian Upwelling zone as source for the atmosphere.

g. *Lines 62-63. Delete comma after "Although"; insert comma after " . . . Liu et al.2013)".*

Done.

h. *Replace "studies" with "have".*

Done.

i. *Line 69. Insert "calculated" before "emissions"*

Done.

j. *Lines 70-71. Delete sentence.*

Done.

k. *Lines 76-80. Delete. Not necessary.*

Done.

3. *Data and Methods*

a. *Lines 87-88. Delete "to collect . . . data". It's not necessary.*

Done.

b. *Somewhere in this short paragraph, the authors should refer to a figure of the cruise track. The best they have in this version is Figure 2a, which should suffice, but then Fig 2 would have to become Fig 1, should they choose that route.*

We agree and referred to Figure 2a in the first sentence. Thus Figure 2 becomes now Figure 1 and vice versa.

c. *Line 94. Insert "above sea level" or "above water level" after "height".*

Above sea level inserted, thanks.

d. *Line 96. Delete "UTC time"; it's internally redundant and also redundant with the parenthetic reference to UTC in the same sentence.*

Done.

e. *Lines 99-100. Is this sentence relevant to the paper? If not, I would delete it.*

Yes, we think it is relevant to the paper since we use the ERA-Interim meteorological fields for the Flexpart trajectories calculations and ERA-Interim assimilates the GTS data and thus our radiosonde measurements. Thus we'd like to keep it. However, we changed it to: "The collected radiosonde data was integrated in near real time into the Global Telecommunication System (GTS) to improve operational weather forecast models and meteorological reanalysis for this region, which were used as input parameters for our trajectory calculations."

f. *Line 107-108. Delete phrase beginning with "the convective . . . temperature". The explanations are clear in the following text.*

We changed the sentence to: "Two different kinds of MABL can be distinguished that are characterized by the gradient of the virtual potential temperature θ_v."

g. *Line 114. Replace "the determination" with "determining the height (thickness?)".*

Done. We changed the sentence to: "For determining the height of this stable layer above the convective MABL, we use the …"

h. *Line 116. Delete "during the ascent"; replace "whose" with "for which an".*

Done.

i. *Line 118. Replace "this stable layer" with "its"; replace "depth" with "thickness"(?). BTW, since "stable layer" is italicized in this discussion, shouldn't "convective layer", e.g., in line 109, also be italicized?*

We agree with the reviewer. “Convective layer” is now also italicized.

j. *Line 122. Since the section on relative humidity (2.2.1) is mainly about MABL height, I recommend deleting it as a separate sub-heading. Same thing for 2.2.2 on Line 135. Then combine the text logically.*

We agree with the reviewer, removed the sub-headings of 2.2 and combined the text logically.

k. *Line 124-127. Despite the authors' protest, I have a hard time thinking this statement is necessary, considering the likely readership. It's their call; just noting my disagreement.*

Although the reviewer is still disagreeing with the statement, we are confident that it will contribute to the readability in particular for readers with non-meteorological background.

l. *Line 127. Delete "therefore".*

Done.

m. *Line 131. Delete "An"*

Done.

n. *Line 132. Delete "therefore"; also does elevated humidity always require a low MABL?*

Done. Elevated absolute humidity does not always require a low MABL, but elevated relative humidity in this oceanic region likely indicates a low MABL. We changed the sentence accordingly to: “Elevated relative humidity in this oceanic region likely points to stable layers with suppressed mixing of surface air and to a low and stable MABL height.”

o. *Line 137. I think the authors mean "not" permitted here?*

The reviewer is right. We added “not”.

p. *Lines 135-142. What I gather from this section (which, as noted, does not need to be a separate section) is that either the same boundary layer height was used for all sampling areas that were in the coastal upwelling zone where sondes could not be launched, or*

(more likely?) that the equation was applied to the observed relative humidity and wind speed for each sampling site in the upwelling zone. Please rewrite to clarify.

In order to make clear that we use the observed MABL height, combined with the regressed MABL height close to the coast we added the following sentence after Eq. 1: "Missing MABL data close to the coast were then completed with the regressed MABL height (Eq. 1) at the VSLS sampling location."

4. *Atmospheric VSLS measurements*

a. *Line 144. Replace "were" with "was";("total" is singular). Insert "at" before "3"; replace "3" with "three" (typically done for single digit numbers); insert "intervals" after "hourly"; insert "above sea level" ("above water level"?) after "height".*

Thanks, done.

5. *Oceanic concentrations and sea-air flux*

a. *Line 154. Replace "3-hourly" with "every three hours".*

We changed it to: "at three hour intervals".

b. *Line 158-159. I presume "precision" is 1 sd? Of duplicate samples? Subsamples? Injections of calibration gas?*

The precision of one standard deviation is derived from multiple duplicate sample analyses. Standards have been injected as liquid standards (in methanol) in triplicates. We changed the sentence to: "The samples were then analysed for bromoform, dibromomethane and methyl iodide and other halogenated trace gases by a purge and trap system attached to a gas chromatograph combined with an ECD (electron capture detector). The analysis has a precision of 10 % (1σ) determined from multiple duplicate samples."

c. *Line 161. No need for subsection title.*

We agree and removed the subtitle.

6. *Trajectory calculations*

a. *Line 188. Replace "launched" with "initiated", here and elsewhere, when referring to trajectories.*

   Done.

7. *Oceanic contribution to MABL VSLS abundances –First, I want to thank the authors for making their approach much clearer. Figure 1, associated with this section, is very instructive and helps make clear the underlying assumptions and the acronyms used.*

a. *I do have one problem with the schematic. Typically, mass balance is written as "rate change in mass" = "rate in" minus "rate out". In that sense, if all terms are on one side of the equation, sources would be positive and sinks negative. The problem I have here is that, though advection is a source, it is being treated as positive on the wrong side of the equation. Were it on the same side as the other terms, it would be negative and the concept would not make sense. So I recommend that the authors show (and explain) this either with all terms on one side of the equation and zero (i.e., "rate change in mass" for steady state) on the other side, or sources on one side and sinks on the other. The authors have correctly done this in their calculations, since the numbers for ADR in Table 2 add up correctly, but it is not really correct for AD in this figure mainly because of the sign. At best, it's a little confusing as presented. (The colors help, however.)*

   We agree with the reviewer and adapted the equation in the schematic and in section 2.6. In the former equation (OD + COL + CL + AD = 0) the loss processes COL and CL were already kept as negative quantities and all processes were added up to equal zero. As this might be confusing, we changed the equation to OD – COL – CL + AD = 0 in order to make the loss processes visible. The new figure 2 is also changed accordingly.

b. *The primary conclusion of this paper depends heavily on computation of the convection term. (And there is some discussion of it in sections 3.4 and 3.5.) It provides a large number that has a large uncertainty. I note the fluxes shown for this term shown in Table 2 and hope they are representative. And I hope the uncertainties also are representative and include the various terms that go into their computation, as they are probably not normally distributed. It might be instructive to see the distribution of this term for some reassurance, or for the authors to examine how departures from the mean values shown here or variability of convection throughout the region might affect their main*

conclusion and share that with the reader. If this seems picky, I only focus on it because the ultimate sources of these gases being advected into this region are left to some degree of speculation that's a little hard to swallow. As mentioned in the general comments, it's hard for me to think why mixing ratios are elevated over areas of upwelling worldwide, if upwelling isn't contributing significantly or even predominantly to what is in the atmosphere. And I have a hard time thinking that Peru is all that special of a case as to warrant other sources. Although Peru is close to being coastal, there are other upwelling areas not close to the coast that still support high mixing ratios of these gases. So what's going on? The answer to that could be very useful for future investigations and I think they have it in their data and in analyses they have not shown.

See our answer for changing the main conclusions of the general comment 1). The "convection loss" (COL) term depends in general on the vertical transport derived from our Flexpart / ERA-Interim calculations. The probability density function of the MABL residence time (Fig. A) reveals a non-normally distribution (KS-Test) with a strongly decreasing probability for longer residence times. Below the trade inversion the highest probability is found for residence times between 10 and 60 hours (non-normally distributed). Since ODR is computed individually, elevated residence times for the MABL and trade inversion are considered in the mean ODR. Additionally, Fuhlbrügge et al. (2016) showed that differences in the MABL height of ERA-Interim and radiosonde observations affect the computed ODR only marginal. Testing the sensitivity of FLEXPART/ ERA-Interim calculations for surface to upper troposphere transport in the whole tropics and in the tropical East Pacific revealed a range of less than 5% in the percentage of transferred trajectories, when using different MABL heights, time steps and boundary layer parametrizations including turbulence in FLEXPART (Wærsted, 2015 Master thesis at University of Oslo; Wærsted and Krüger, 2016 poster presentation at SSiRC workshop). Thus, we believe that the COL term, although showing some variations, does not play the critical role in deriving our "*Oceanic contribution to MABL VSLS abundances"* estimates. We will add this consideration to the discussion as well.

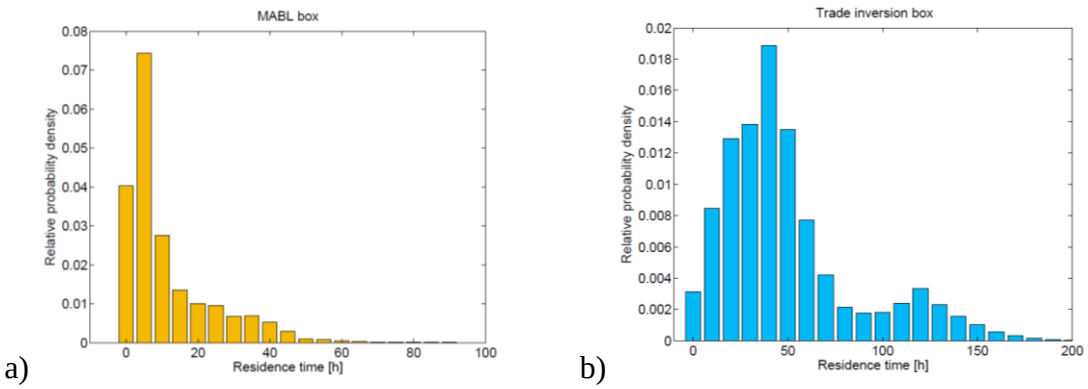

Figure A: Probability density functions of the residence time [h] for all 98 x 10.000 trajectories in a) MABL box (orange) and b) trade inversion box (blue).

c. *Line 195-196. Delete the second and third use of "to"; delete "the time scales of" before "air" and "the" before "chemical"; add "rates" after loss on line 196.*

Done.

d. *Line 206. Delete "process" after "this".*

Done.

e. *Line 211. Delete "acts as a loss process as well and".*

Done.

f. *Line 212. Reference to "steady state" should be at the beginning of this discussion. It is a necessary assumption underlying all of this section.*

Done.

g. *Lines 219-222. See "a" above. Be sure this is right.*

Done.

8. *Observations*

a. *Line 231. Change "backward trajectories" here and everywhere else to "back-trajectories".*

Done.

b. *Line 231-232. Awkward sentence. Try " . . .reveal a mix of open ocean and coastal air-masses".*

Done.

c. *Line 238. Change "is" to "was"; delete "for"*

Done.

d. *Line 242-243. Replace "The decreasing . . . upwelling" with "and indicating".*

Done.

e. *Line 248. Replace "for example . . . Figure 3c" with (e.g., Dec 9-11, 19; Figure 3c).*

Done.

9. *VSLS observations and oceanic emissions – remove reference throughout to Mauritian upwelling and focus on results from this study.*

Done. References to Mauritanian Upwelling are now summarized in Section "3.6 Comparison to other oceanic regions".

a. *Line 254 (and elsewhere). Spell out single digit numbers.*

Done.

b. *Line 258. It's a little unusual to rely to any degree on a paper that has only been submitted.*

The Hepach et al. 2016 paper is under revision (minor revisions requested by the editor); we added this information into the manuscript.

c. *Line 259. Change "are" to "were".*

Done.

d. *Line 260. "Low" compared to what? Focus on the temporal pattern. Stick with these results.*

Low meant in comparison to other upwelling regions. It has been removed, since the comparison to other oceanic regions is now summarized in section 3.6.

e. *Line 268. Replace "and" with "to".*

Done.

f. *Line 269. Delete "fresh".*

"Fresh" wind or breeze is a meteorological term for wind speed of 5 Beaufort which is between 8 and 10.7 m/s. Thus we would like to have it in.

g. *Line 270. Replace "are" with "have been".*

Done.

h. *Lines 271-272. The authors use different lifetimes earlier in the text. Decide which to use.*

The lifetimes earlier in the text (section 2.6) have been updated now.

i. *Line 271-274. Refer to Carpenter et al. parenthetically at the end of the sentence rather than the middle; insert "recently" before "enriched"; delete "with fresh".*

Done.

j. *Line 274-277. Delete "A general decrease of"; replace "the" before "concentration" with "This"; replace "is found" with "generally decreased"; delete "during the cruise". Last phrase of the sentence is not clear. Is the reader to presume south? Also, what do they mean by "remote" – do they mean "open ocean"?*

We agree with the changes suggested by the reviewer and changed the sentence to: "This concentration ratio generally decreased from the North to the South (Figure 3f), implying an intensification of fresh bromoform sources towards the southern part of the cruise track, which is also reflected by increasing water concentrations." In this case "remote" meant air masses that have not been enriched with bromoform. Nevertheless, we removed the phrase from the sentence.

k. *Line 280. Replace "synchronous" with "approximately simultaneous" or "approximately synchronous".*

Done.

l. *Line 283. Replace "are" with "were"; what is meant by "low"?*

Done. "Low" refers to other oceanic regions. We added this to the sentence: "… 245 ± 299 pmol m^{-2} hr^{-1} for dibromomethane compared to other oceanic regions (e.g. Fuhlbrügge et al., 2013; Hepach et al., 2015a) …"

m. *Line 286. Replace "are" with "were".*

Done.

10. *Lower atmosphere conditions*

a. *Line 291-293. Replace "The relative humidity shows a" with "A"; insert "positive" after "strong"; insert "of relative humidity" after gradient. Also where does the 75% refer to?" Delete "with height due to suppressed mixing.*

Done. Also the phrase "…from over 75 % to less than 50 %..." has been removed.

b. *Line 304-305. Delete "are good indicators . . . parameters".*

Done.

c. *Line 306-307. Delete sentence. This has been said already.*

Done.

d. *Line 316-318. Last phrase of sentence beginning with "before" is awkward. Revise.*

We agree with the reviewer. The paragraph (314-321) has been removed and rephrased in the new, revised discussion.

e. *Line 308-313. Beginning with "The regressed . . . ". The important point here is what? Hasn't it been made already? Is the range of the MABL heights something that could help explain their findings? Is it really correct to use the coefficients derived from open ocean radiosondes on something that yields a 10 m height?*

We agree and changed the sentence to: “The regressed MABL heights (Section 2.2) show a distinct decrease above the cold upwelling regions close to the coast with 158 ± 79 m on average.”

The MABL height coefficients derived from the regression are not only based on open ocean radiosonde data. Several observations e.g. on Dec 3, 4, 8 and 17, 2012 are either taken directly above the upwelling or influenced by air masses which recently passed upwelling areas.

f. Line 316-318. Last phrase in this sentence is awkward. This is a concluding paragraph, in that the authors state it as their interpretation. It needs to be clear.

Done, see also our answer to comment 10.d) above.

11. Contribution of oceanic emissions and meteorological constraints (sections 3.4 and 3.5). These sections still seem a little long and rambling. Perhaps they could be shortened. They certainly meander. Maybe a little reorganization focusing on the impacts of the uncertainties or variability would help? Also, move the comparisons to Mauritian upwelling to a separate section, as noted in my general comments.

According to the reviewers suggestions, we have shortened and revised both sections substantially.

a. Line 328-329. “a mean residence time for FLEXPART trajectories of 7 hours in the observed MABL during the cruise”. What exactly does that mean? At a velocity of 10m/s, which works out to 36 km/hour, it would seem these trajectories go back (or are stable within?) ~250 km or ~2-3 degrees latitude? I’m not sure why 7 hours was chosen and I’m sure others might be confused as well.

We agree that this sentence might be misleading. 7 hours is the mean residence time of the trajectories before leaving the MABL. The mean ODR is derived from the individual ODRs at each trajectory release points including the specific OD and COL at this location. Indeed, at some locations trajectories are up to 14 hours stable within the MABL. In order to make this clear we changed the sentence to: “The ratio of the individual OD of each compound and the individual COL at this location results in the particular ODR for each compound.”

b. *Line 331. Change "origins" to "originates".*

Done.

c. *Line 331-332. 3% + 99% = 102% . . . . . please fix or else explain.*

The chemical loss has to be considered (2%). We changed the sentence to: "The ODR reveals that on average only 3 % of the observed atmospheric bromoform in the MABL originates from nearby oceanic emissions and 99 % are advected including a chemical loss of 2 %."

d. *Line 335. The authors might consider putting comparisons with South China and Sulu Seas in with a Discussion section on Mauritanian upwelling, i.e., how results from this region compare with other parts of the ocean.*

We agree with the reviewer and included a new section (3.6. Comparison to other oceanic regions). This section now contains all comparisons between the Peruvian Upwelling and the Mauritanian Upwelling, respectively, the South China and Sulu seas.

e. *Line 337-339. Sentence fragment.*

According to our revised conclusions (answers to general comments 1)), the two sentences have been replaced by: "The numbers show that the observed mean atmospheric concentrations cannot be explained by the mean local oceanic emissions. While the surface air masses can leave the MABL within hours, they are suppressed from entering the free troposphere through the trade inversion. FLEXPART trajectories indicate an average residence time of air 48 h below the average trade inversion height of 1.1 km. During the 48 h and the prevailing southerly mean wind speed of 6.2 m/s oceanic VSLS emissions can accumulate over a fetch of 10° latitude."

f. *Line 342. "coastal" sources . . . I presume this means outside of the study area?*

Yes exactly. The computed averaged fluxes of the compounds which we measured during the cruise are generally not strong enough to explain the observed in-situ atmospheric mixing ratios of the compounds. Since atmospheric mixing ratios of the compounds were elevated above the upwelling we suppose stronger sources closer to the coast line, which has been observed in coastal studies (e.g. Leedham et al., 2013).

g. *Line 364-369. Has this been said already? I think much of it has.*

Actually, this hasn't been said before. We presented correlations between the meteorology and the MABL height earlier in the manuscript, but not between meteorology and the VSLS.

h. *Line 375. "co-correlated with each other" is redundant.*

We agree and removed "with each other".

i. *Lines 380 ff. M91? DRIVE? Readers might need a little help here.*

This paragraph has been rephrased and shifted to Section 3.6. Locations have been added to the cruise acronyms.

12. *Discussion and Summary – Sections 4 and 5*

a. *I think this section has much of what I'm asking, but it rambles a lot and inserts bits of speculation throughout. It's hard to walk away with a conclusion, or even any clear points in my head. What will help most is for the authors first to interpret the results that have been described, including the part addressing uncertainties in their data and assumptions, then go ahead and start making comparisons, but only where they are important and support the main conclusions. Support statements quantitatively where that can be done. The authors need to convince themselves about what points they want the reader to take away and then organize the discussion around them. It would make for a more enjoyable and more informative read.*

Thanks again for your very valuable comments and critics! We took them very seriously into account and intensively worked through the whole paper exactly following your advice to evaluate again what our main solid conclusions are we want to deliver. See also our detailed answer to your first general comment.

b. *The summary can be tightened up considerably following a reorganization and rewrite of the Discussion. If the discussion is well done, then a summary might not even be necessary.*

See also our comments before. We rewrote and reorganized the discussion thoroughly and kept a tightened up summary.

13. *Figures*

a. *Figure 1 – (see comment above). Also "summery" in the legend should be "summary".*

   Fixed.

b. *Figure 2 – this, too, is a very helpful figure*

   Thank you.

c. *Figure 3 – nicely done.*

   Thank you.

d. *Figure 4 – what is a "specific altitude" (line 570)?*

   Here "specific altitude" meant a trajectory height of 0 – 6 km. We changed the sentence to: "The black contour lines give the amount of trajectories in percentage reaching an altitude of 0 – 6 km height within the 10 days."

e. *Figure 5 – Line 587. Insert "near surface" in front of "atmospheric"*

   Done.

14. Tables

a. *Table 1 – Line 558. Uncertainty: which is it, s.d. or range? They are different.*

   We added to the legend of Table 1: "Values are given in mean ± 1σ. The range is given in []."

b. *Table 2 – aside from my previous concerns noted above about the representativeness of the values shown here, this table's OK*

   Thank you.

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Meteorological constraints on oceanic halocarbons above the Peruvian Upwelling

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Abstract

~~Halogenated very short lived substances (VSLS) are naturally produced in the ocean and emitted to the atmosphere. Recently, oceanic upwelling regions in the tropical East Atlantic were identified as strong sources of brominated halocarbons to the atmosphere.~~ During a cruise of R/V METEOR in December 2012 the oceanic sources and emissions of various halogenated trace gases and their mixing ratios in the marine atmospheric boundary layer (MABL) were investigated above the Peruvian Upwelling ~~for the first time~~. This study presents novel observations of the three very short lived substances (VSLS): bromoform, dibromomethane and methyl iodide, together with high resolution meteorological measurements, ~~and~~ Lagrangian transport ~~modelling~~and source-loss calculations. Oceanic emissions of bromoform and dibromomethane were relatively low compared to other upwelling ~~oceanic~~ regions, while those for methyl iodide were very high. ~~Although relatively low oceanic emissions were observed, except for methyl iodide, surface atmospheric abundances were elevated.~~ Radiosonde launches during the cruise revealed a low, stable MABL and a distinct trade inversion above acting ~~both~~ as strong barriers for convection and ~~trace gas~~ vertical transport of trace gases in this region. Observed atmospheric VSLS abundances, sea surface temperature, relative humidity and MABL height correlated well during the cruise. ~~Significant correlations between observed atmospheric VSLS abundances, sea surface temperature, relative humidity and MABL height were found.~~ We used a simple source-loss estimate to ~~identify~~ quantify the ~~in situ~~ contribution of oceanic emissions along

the cruise track to the observed atmospheric concentrations. This analysis showed that averaged, instantaneous emissions could not support the observed atmospheric mixing ratios of VSLS and that ~~which revealed that~~ the ~~observed~~ marine background ~~VSLS~~ abundances below the trade inversion were significantly influenced~~dominated~~ by ~~horizontal~~ advection of regional sources~~ below the trade inversion,~~. Adding to this background, the observed maximum emissions of halocarbons in the coastal upwelling could explain the high atmospheric VSLS concentrations~~variations can be explained by~~in combination ~~the low emissions combined~~ with their accumulation under the ~~different~~ distinct MABL and trade inversions. Stronger emissions along the near–shore coastline likely added to the elevated abundances under the steady atmospheric conditions. This study confirms the importance of oceanic upwelling and trade wind systems on the atmospheric distribution of marine VSLS emissions. ~~This study confirms the importance of oceanic upwelling and trade wind systems on creating effective transport barriers in the lower atmosphere controlling the distribution of VSLS abundances above ocean upwelling regions.~~

1. Introduction

Oceanic fluxes of short-lived halocarbons contribute to reactive halogens in the atmosphere, where they are subsequently involved in ozone chemistry, aerosol formation, and other chemical cycles that influence the fate of pollutants and climate~~Short-lived halocarbons from the oceans contribute to reactive atmospheric halogens, which are involved in tropospheric and stratospheric ozone depletion, aerosol formation, and other chemical cycles, influencing the fate of pollutants and climate~~ (McGivern et al., 2000; Saiz-Lopez and von Glasow, 2012; Simpson et al., 2015). Recent studies have identified open ocean upwelling areas in the Atlantic as large source regions for a number of brominated and iodinated oceanic trace gases (Quack et al., 2004; Quack et al., 2007; O'Brien et al., 2009; Raimund et al., 2011; Hepach et al., 2015b). Their sources are related to biological and chemical processes in the productive waters of the upwelling. The compounds are emitted from the ocean and are horizontally transported and vertically mixed in the marine atmospheric boundary layer (MABL) (Carpenter et al., 2010). ~~In the Mauritanian upwelling, it was found that besides oceanic sources,~~ M~~m~~eteorological conditions strongly influenced the atmospheric mixing ratio of the marine compounds bromoform ($CHBr_3$), dibromomethane (CH_2Br_2) and also methyl iodide (CH_3I) (e.g. Fuhlbrügge et al., 2013; Hepach et al., 2014). ~~Especially t~~The combination of a pronounced low MABL above cold upwelling waters with high concentrations and emissions

of the compounds causesd elevated atmospheric mixing ratios. In returnIn a negative feedback process, these high atmospheric mixing ratios also reduce the marine emissions through a decrease of the sea-air concentration gradient (Fuhlbrügge et al., 2013). Similar relationships would be expected for other oceanic upwelling areas, where not only the oceanic emissions, but also meteorological conditions in the lowermost atmosphere, i.e., the height, type and structure of the boundary layer and trade inversion, determine the VSLS contribution to atmospheric chemical processesabundance and atmospheric distribution. The intense oceanic upwelling in the Southeast Pacific off the coast of Peru transports large amounts of subsurface waters to the ocean surface and creates one of the highest most productive oceanic regions worldwide (Codispoti et al., 1982). We therefore expect elevated levels of short-lived halocarbons in the Peruvian Upwelling zone as potential source for the atmosphere. The Peruvian Upwelling is therefore a potentially intense source region for halogenated VSLS, e.g. bromoform, dibromomethane and methyl iodide. Indeed, Schönhardt et al. (2008) detected elevated IO columns during September and November 2005 along the Peruvian coast with the SCIAMACHY satellite instrument and implied elevated iodine source gases from the Peruvian Upwelling.

Although, recent studies investigated halocarbons in the East Pacific (Yokouchi et al., 2008; Mahajan et al., 2012; Saiz-Lopez et al., 2012; Gómez Martin et al., 2013; Liu et al., 2013), few studies have concentrated on the Peruvian Upwelling in the Southeast Pacific. Only measurements of methyl iodide exist in this region, revealing atmospheric abundances of 7 ppt (Rasmussen et al., 1982). Observations of bromocarbons above the Peruvian Upwelling are currently lacking.

In this study we present a novel high resolution dataset of meteorological parameters, oceanic concentrations, calculated emissions and atmospheric abundances of VSLS and calculated emissions along the Peruvian coast and in the Upwelling. Not much is known of the oceanic source strength of the VSLS and the meteorological influence on the marine trace gas distribution and abundances in this region. The goal of this study is to assess the influence of oceanic upwelling and meteorological conditions on the atmospheric VSLS abundances above the Peruvian Upwelling, and to determine the contribution of the local oceanic emissions to MABL and free tropospheric VSLS concentrations.

The paper is structured as following. Chapter 2 gives an overview of the data and methods we use in this study. Chapter 3 presents the results from our atmospheric and oceanic observations and analyses the contribution from oceanic VSLS emissions to the MABL, as

~~well as meteorological constrains on the observations. Chapter 4 discusses the results, before the study is summarized in Chapter 5.~~

2. Data and Methods

The cruise M91 on R/V METEOR from December 01 to 26, 2012 started and ended in Lima, Peru (Figure 1a). The ship reached the most northern position during the cruise on December 03, 2012 at 5° S. In the following three weeks the ship headed southward and reached its southern~~-~~most position at 16° S on December 21, 2012. During this time the track alternated between open ocean sections and sections ~~very~~ close to the Peruvian coast (up to 10 km distance) in the cold upwelling waters~~ to collect coastal as well as open ocean data~~. A focus on diurnal variations ~~were observed~~was accomplished by 24-hour sampling at ~~during 6~~ six stations along the cruise track.

2.1 Meteorological observations

Meteorological observations ~~measurements~~ of surface air temperature (SAT), sea surface temperature (SST), relative humidity, air pressure, wind speed and direction were taken every second at about 25 m height above sea level on R/V METEOR and averaged to 10 minute intervals for our investigations. Atmospheric profiles of temperature, wind, and humidity were obtained by 98 radiosonde launches ~~at standard UTC time~~ (0, 6, 12, 18 UTC) and additionally at ~~3~~ three ~~hourly~~ hour intervals during the diurnal stations along the cruise track, using Vaisala RS92 radiosondes. Due to permission limitations, radiosondes could not be launched within 12 nautical miles of the Peruvian coast. The collected radiosonde data was integrated in near real time into the Global Telecommunication System (GTS) to improve ~~the meteorological reanalysis (e.g. ERA Interim) and~~ operational ~~European Centre for Medium Range~~ w~~W~~eather f~~F~~orecast models and meteorological reanalysis ~~(op~~ECMWF~~)~~ for this region, which were used as input parameters for our trajectory~~model~~ calculations.

2.2 MABL ~~height~~

The radiosonde data are used to identify the height of the MABL, which is the atmospheric surface layer above the ocean in which trace gas emissions are mixed ~~horizontally~~ on a short time scale of an hour or less by convection and turbulence (Stull, 1988). Two different kinds of MABL can be distinguished~~,~~ that are ~~the convective and the stable MABL, which can be~~ characterized by the gradient of the virtual potential temperature θ_v. A negative or neutral gradient reveals an *unstable convective layer*, while a positive gradient reveals a *stable*

atmospheric layer. In case of an increase of the virtual potential temperature (positive gradient) near the surface, mixing in the MABL is suppressed. The upper limit of the convective MABL is set by a stable layer, e.g., a temperature inversion or a significant reduction in air moisture and is typically found above open ocean regions between 100 m and 3 km height (Stull, 1988; Seibert et al., 2000). For ~~the determination~~determining the height of this stable layer above the convective MABL, we use the practical approach described in Seibert et al. (2000) and compute the virtual potential temperature ~~during the radiosonde ascent whose~~ for which an increase with altitude indicates the base of a stable layer. In this study, ~~the~~its base ~~of this *stable layer*it is~~ is increased by half of ~~this *stable layer*~~its ~~depth~~ thickness ~~is~~, which is the definition for the MABL height. Over oceanic upwelling regions ~~this~~ the stable layer can even descend to the ocean surface (e.g. Höflich et al., 1972 and Fuhlbrügge et al., 2013).

~~2.2.1 Relative humidity~~

Estimates for atmospheric surface stability and MABL conditions ~~in oceanic upwelling regions~~ can be also obtained from variations of the surface humidity. While the absolute humidity determines the amount of water in a specific volume of air, the relative humidity is the ratio of the partial pressure of water vapour to the equilibrium vapour pressure at the observed temperature. Variations of the SAT ~~therefore~~ directly influence the relative humidity at the surface (Section 3.1). ~~A decrease of the SAT due to cold upwelling water leads to an increase of the relative humidity, while the absolute humidity stays constant or even decreases due to condensation of water vapour once the relative humidity reaches 100 % and the air is saturated with water vapour.~~ ~~An e~~Elevated relative humidity in this oceanic region ~~therefore~~ likely points to stable layers with suppressed mixing of surface air and to a low and stable MABL height. Relative humidity is also used to derive

~~2.2.2 Estimation of MABL height above the upwelling~~

~~To estimate~~ the MABL height above the upwelling areas close to the coast, where radiosonde launches were not permitted (Section 2.1). We applied a multiple linear regression (Eq. 1), ~~a multiple linear regression was applied.~~ using ~~observed~~ meteorological parameters along the cruise track that had~~revealing~~ significant correlations (see Section 3.5) with the observed MABL height ~~,~~(relative humidity (x_1), SAT (x_2), SST (x_3) and wind speed (x_4))~~, along the cruise we applied a multiple linear regression and obtained the following Eq. 1~~:

$$MABL\ height = b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 \quad \text{(Eq. 1)}$$

with $b_1 = -0.0117;\ b_2 = 0.0202;\ b_3 = 0.0467;\ b_4 = 0.0089$

Missing MABL data close to the coast were then completed with the regressed MABL height (Eq. 1) at the VSLS sampling location.

2.3 Atmospheric VSLS ~~measurements~~

A total of 198 air samples were~~as~~ collected at ~~3~~ three hourly intervals during the cruise at about 20 m height above sea level on the 5th superstructure deck of R/V METEOR using a portside jib of 5 – 6 m. The air samples were pressurized to 2 atm in pre-cleaned stainless steel canisters with a metal bellows pump and were analysed at the Rosenstiel School for Marine and Atmospheric Sciences (RSMAS, Miami, Florida) within ~~6~~ six months after the cruise. Details about the analysis, the instrumental precision and the preparation of the samples are described in Schauffler et al. (1999) and Fuhlbrügge et al. (2013). The VSLS atmospheric mixing ratios were calculated with a NOAA standard (SX3573) from GEOMAR.

2.4 Oceanic VSLS concentrations and sea – air flux

Starting after December 9, 2012, ~~total of~~ 102 water samples were taken ~~3 hourly~~every ~~at~~ three hour intervals at a depth of 6.8 m from a continuously working water pump in the hydrographic shaft, an opening in the base of the ship hull of R/V Meteor~~, after December 9, 2012~~. The samples were then analysed for bromoform, dibromomethane and methyl iodide and other halogenated trace gases by a purge and trap system~~,~~ attached to a gas chromatograph combined with an ECD (electron capture detector). The analysis has ~~with~~ a precision of 10 % (1σ) determined from duplicate samples. The approach is described in detail by Hepach et al. (2014).

~~2.4.1 Sea – air flux~~

The sea – air flux (F) of bromoform, dibromomethane and methyl iodide is calculated with k_w as transfer coefficient and Δc as concentration gradient between the water and equilibrium water concentration determined from the atmospheric concentrations (Eq. 2). The transfer coefficient was determined by the air – sea gas exchange parameterization of Nightingale et al. (2000) after a Schmidt number (Sc) correction for the three gases (Eq. 3).

$$F = k_w \cdot \Delta c \quad \text{(Eq. 2)}$$

196

$$k_w = k_{CO_2} \cdot \frac{Sc^{-\frac{1}{2}}}{600} \quad \text{(Eq. 3)}$$

197

198 Details on deriving the air – sea concentration gradient and emissions are further described in
199 Hepach et al. (2014) and references therein.

200

201 ## 2.5 Trajectory calculations

202 The Lagrangian Particle Dispersion Model FLEXPART of the Norwegian Institute for Air
203 Research in the Department of Atmospheric and Climate Research (Stohl et al., 2005) was
204 used for trajectory calculations to analyse the air mass origins and the transport of surface air
205 masses along the cruise track to the free troposphere (Stohl et al., 1998; Stohl and Trickl,
206 1999). The model includes moist convection and turbulence parameterizations in the
207 atmospheric boundary layer and free troposphere (Stohl and Thomson, 1999; Forster et al.,
208 2007). We use the ECMWF (European Centre for Medium-Range Weather Forecasts)
209 reanalysis product ERA-Interim (Dee et al., 2011) with a horizontal resolution of 1° x 1° and
210 60 vertical model levels as meteorological input fields, providing air temperature, horizontal
211 and vertical winds, boundary layer height, specific humidity, as well as convective and large
212 scale precipitation with a ~~6~~ six hourly temporal resolution. Trajectories were released three to
213 six hourly at the time and position of the VSLS measurements along the cruise track on R/V
214 METEOR. At each of these release points 10,000 forward- and 50 back-trajectories with a
215 total runtime of ~30 days were initiated from the ocean surface within ± 30 minutes and ~20
216 m distance of the measurements. In total 98 release points for the forward- and back-
217 trajectory calculations were analysed, determined by the spatial resolution of ERA-Interim
218 data along the Peruvian coast, defining the land-sea mask of our trajectory calculations.~~Due~~
219 ~~to the spatial resolution of ERA-Interim data along the Peruvian coast, defining the land-sea~~
220 ~~mask of our trajectory calculations, 98 out of 140 release points for the forward and backward~~
221 ~~trajectory calculations were analysed along the cruise track. At each these release points~~
222 ~~10,000 forward and 50 backward trajectories with a total runtime of 29 days were launched~~
223 ~~from the ocean surface within ± 30 minutes and ~20 m distance to the ship position. Time~~
224 ~~and position of the release events are synchronized with air samples taken on R/V METEOR~~
225 ~~(Section 2.32.3).~~

226

2.6 Oceanic contribution to MABL VSLS abundances

To ~~obtain an~~ estimate ~~of~~ the contribution of local oceanic sources to the atmospheric mixing ratios in the lowermost atmosphere above the Peruvian Upwelling, we apply a mass balance concept to the oceanic emissions, ~~to~~ the time scales of air mass transport and ~~to~~ the chemical loss (Fuhlbrügge et al., 2016). First we define a box above each release event with a size of ~400 m^2 around the measurement location and the height of the MABL and assume ~~a~~ steady-state ~~observed VSLS mixing ratio within~~in the box (Figure 2). During each trajectory release event we assume the specific sea-air flux to be constant and the emissions to be homogeneously mixed within the box. Then the contribution of the sea-air flux is computed as the ratio of the VSLS flux from the ocean into the MABL (in mol per day) and the total amount of VSLS in the box (in mol). This ratio ~~and~~ is defined as the Oceanic Delivery (OD) and ~~OD~~ is given in percentage per day. In addition to the delivery of oceanic VSLS to the box, the loss of VSLS out of the box into the free troposphere is defined as the Convective Loss (COL) and this quantity is derived from the mean residence time ~~derived from~~of the FLEXPART trajectories in the box during each release event. Note that the COL indicates the loss of surface air due to all kinds of vertical movement out of the box. Since this ~~process~~ is a loss process, COL is given as a negative quantity ~~and in~~expressed as percentage per day. The chemical degradation of VSLS by OH and photolysis in the MABL is ~~considered by the~~calculated from the chemical lifetime of each compound in the MABL. We use lifetimes of ~~16~~ 15 days for bromoform ~~and~~ , ~~60~~ 94 days for dibromomethane ~~(Hossaini et al., 2010)~~ and ~~3~~ 4 days for methyl iodide (Carpenter et al., 2014) ~~(R. Hossaini, personal communication)~~, representative for the tropical boundary layer. The Chemical Loss (CL) ~~acts as loss process as well and~~ is given as a negative quantity in percentage per day. ~~We further assume a steady state in the box.~~ OD, COL and CL must ~~therefore~~ be balanced by an advective transport of air masses in and out of the box. The change of the VSLS through advective transport is defined as Advective Delivery (AD) and also is given in percentage per day.

To estimate the relative importance of ocean emissions (OD) to the halocarbon loss through vertical mixing (COL) ~~By rationing OD to COL,~~ we ~~estimate~~ define an Oceanic Delivery Ratio (ODR) (Eq. 4) as the ratio between OD and COL:

$$ODR = \frac{OD\ [\%d^{-1}]}{-COL\ [\%d^{-1}]} = \frac{Sea{-}Air\ flux\ contribution\ [\%d^{-1}]}{Loss\ of\ box\ air\ to\ the\ FT\ [\%d^{-1}]} \quad \text{(Eq. 4)}$$

Similarly, the Chemical Loss in the box (CL) and the change in VSLS due to advection (AD) are related to COL to get the Chemical Loss Ratio (CLR) and the Advective Delivery Ratio (ADR). From mass balance considerations, ~~with A~~ODR ~~= 1 –~~ CLR ~~+ ODR~~ADR = 1. Since CL, OD and AD are divided by COL, ratios for source processes are positive and negative for loss processes (Fuhlbrügge et al., 2016).

3. Observations on R/V METEOR

3.1. Meteorology~~ical observations~~

The Peruvian coast is dominated by the southern hemisphere trade wind regime with predominantly south-easterly winds (Figure 1). The Andes, which are known to act as a barrier to zonal wind in this region, affect the horizontal air mass transport along the coast (Figure 1b-d). The steeply sloping mountains at the coast form strong winds parallel to the South American coastline (Garreaud and Munoz, 2005). ~~leading to distinct wind-driven oceanic upwelling of cold water along the coast.~~ The 10-day back~~ward~~ -trajectories reveal a mix of open ocean and coastal air-masses~~reveal predominantly near-shore air masses with coastal influence and marine air masses~~ (Figure 1). The average wind direction observed on R/V Meteor during the cruise is 160 ° ± 34 ° (mean ± σ) with a moderate average wind speed of 6.2 ± 2.2 ms^{-1} (Figure 3b). ERA-Interim reveals similar winds along the cruise track with a mean wind speed of 5.6 ± 1.8 ms^{-1} and a mean wind direction of 168 ° ± 21 ° (not shown here). The divergence of the wind driven Ekman transport along the Peruvian coast leads to the observed oceanic upwelling of cold waters. The most intense upwelling ~~is~~ was observed ~~for~~ several times near the coast where both~~,~~ SST and SAT rapidly drop from 19 – 22 °C to less than 18 °C (Figure 3a). The impact of the cold upwelling water on the ~~observed~~ air masses is also visible in the observed humidity fields (Figure 3c). Here, the decreasing SAT reduces the amount of water vapour that the surface air is able to contain, leading to an increase of the relative humidity ~~. The decreasing SAT and increasing relative humidity above the oceanic upwelling indicate~~and indicating a stable atmospheric surface layer with suppressed vertical mixing. The absolute humidity stays constant or even decreases above the oceanic upwelling due to condensation of water vapour when surface air cools and becomes saturated, coinciding with fog observations on the ship~~, which.~~. ~~coincides with fog observations on the ship above the upwelling regions.~~ A decrease of the absolute humidity outside the upwelling points to a change in advected air masses (e.g. ~~for example between~~ Dec~~ember~~ 9 ~~and~~, 11, ~~but also on December~~ 19, 2012; ~~(~~Figure 3c).

3.2. VSLS abundances ~~observations~~ and oceanic emissions

~~Surface bromoform concentrations in the Peruvian upwelling are generally lower during the cruise compared to the Mauritanian upwelling while dibromomethane surface water concentrations are comparable. However methyl iodide concentrations are almost 8 times higher than in the Mauritanian upwelling (Figure 3d, Table 1, Hepach et al., 2014). Samples taken in the S~~surface water samples of ~~in~~ the coastal upwelling areas show~~ed~~ elevated VSLS concentrations compared to the open ocean for all compounds~~. For further discussion on the distribution of the oceanic halocarbons, see~~ , especially for methyl iodide (Hepach et al., 2016, in review).

Atmospheric mixing ratios of bromoform ~~are~~ were on average 2.91 ± 0.68 ppt (Table 1). Dibromomethane mixing ratios (~~of~~ average 1.25 ± 0.26 ppt) ~~are low and~~ show a similar ~~temporal~~ pattern and good correlation with bromoform (Table 3). ~~Mixing ratios of both compounds are significantly lower above the Peruvian upwelling compared to observations above the Mauritanian upwelling, while methyl iodide mixing ratios are comparable (Fuhlbrügge et al., 2013).~~ Elevated mixing ratios for all three compounds are generally found above the intense cold oceanic upwelling regions close to the Peruvian coast (Figure 3e). While the bromocarbons double above the upwelling, methyl iodide mixing ratios increase up to 5-fold, demonstrat~~show~~ing its stronger accumulation in the low and stable boundary layer.

The concentration ratio of atmospheric dibromomethane ~~and~~ to bromoform can be used as an indicator of ~~fresh~~ bromocarbon sources along coastal areas. Low ratios of about 0.1 have been observed ~~at~~ in coastal source regions and ~~are~~ have been interpreted as the emission ratios of macro algae (Yokouchi et al., 2005; Carpenter et al., 2003). The ~~applied~~ shorter ~~mean~~ chemical lifetime of bromoform (15 days) in contrast to dibromomethane (94 days) in the boundary layer ~~after Carpenter et al. (2014)~~ leads to an increase of the ratio during transport as long as the air mass is not ~~recently~~ newly enriched with ~~fresh~~ bromoform (Carpenter et al., 2014). ~~A general decrease of the~~ This concentration ratio ~~is found~~generally decreased from the North to the South ~~during the cruise~~ (Figure 3f), implying ~~relatively remote air masses in the North and~~ an intensification of fresh bromoform sources towards ~~the~~ the southern part of the cruise track~~south~~, which is also reflected by ~~the elevated~~increasing water concentrations. Atmospheric methyl iodide measurements along the cruise track reveal a mean mixing ratio of 1.54 ± 0.49 ppt, which, similar to the two bromocarbons, maximizes over the coastal upwelling regions (Figure 3e).

Oceanic emissions during the cruise were calculated from the approximately synchronoussynchronized measurements of sea water concentrations and atmospheric mixing ratios, sea surface temperatures and wind speeds, measured on R/V METEOR. Oceanic concentrations and atmospheric mixing ratios of each compound are were weakly or not at all correlated ($R_{bromoform}$ = 0.00, $R_{dibromomethane}$ = 0.29 and $R_{methyl\ iodide}$ = 0.34). Mean sea-air fluxes of the bromocarbons during the cruise are very low with 117 ± 492 pmol m^{-2} hr^{-1} for bromoform and 245 ± 299 pmol m^{-2} hr^{-1} for dibromomethane compared to other oceanic regions (e.g. Fuhlbrügge et al., 2013; Hepach et al., 2015a), but for methyl iodide the fluxes are were elevated with 856 ± 623 pmol m^{-2} h^{-1} (Figure 3g, Table 1). Further investigations of the distributions and sources of iodinated compounds during this cruise are carried out by Hepach et al. (2016, in review).

3.3. Lower atmosphere conditions

The relative humidity shows aA strong positive vertical gradient of relative humidity from over 75 % to less than 50 % at ~1 km height (Figure 4a) which indicates an increase of the atmospheric stability with height due to suppressed mixing. This convective barrier, known as the trade inversion (Riehl, 1954, 1979; Höflich, 1972), is also reflected in the meridional wind (Figure 4b). Below ~1 km altitude the Southeast south-easterly trade winds create a strong positive meridional wind component, also visible in the forward trajectories (Figure 1c-d). The flow of air masses in the Hadley Cell back to the subtropics causes a predominantly northerly wind above ~1 km height. The intense increase of θ_v in combination with the relative humidity decrease and the wind shear at ~1 km height identifies this level as a strong vertical transport barrier (Figure 4c). Above the cold upwelling water, temperature inversions create additional stable layers above the surface, leading to very low MABL heights of < 100 m, e.g., on December 03, 08 or 17, 2012 and to a reduced vertical transport of surface air. The mean MABL height from the radiosonde observations is 370 ± 170 m (ERA-Interim 376 ± 169 m). The relative humidity, SAT, SST and wind speed are good indicators for the MABL conditions in this oceanic region and these meteorological parameters show significant correlations with the observed MABL height (Table 3). Thus, we use a multiple linear regression based on these parameters to estimate the MABL height above the coastal upwelling (Section 2.2.2). The regressed MABL heights (Section 2.2.2) show a distinct decrease above the cold upwelling regions close to the coast with are 158 ± 79 m on averageand go down to even 10 m as was previously observed above the Mauritanian Upwelling (Fuhlbrügge et al., 2013). TakingWith the regressed MABL heights

into account, the mean MABL height during the cruise decreases to 307 ± 177 m. The stable atmospheric conditions from the surface to the trade inversion lead to strong transport barriers also visible in the accumulation of below 2-day old air masses within the first kilometre of the atmosphere ~~and to a supressed transport of surface and MABL air into the free troposphere~~ (Figure 4d).

~~We interpret the observations as the following. In the region of the Peruvian Upwelling, compounds emitted from the ocean and observed at the marine surface are first homogeneously distributed within the MABL during a couple of hours before advection transport them further within the second transport barrier of the lowermost atmosphere the trade wind inversion. For air masses above or close to oceanic upwelling regions, the MABL height is the first weak transport barrier on short time scales (hours), while the trade inversions acts as the second more pronounced barrier for vertical transport on long time scales (days).~~

3.4. Contribution of oceanic emissions to ~~observed~~ VSLS abundances in the MABL

We estimate the contribution of oceanic emissions to mixing ratios within the MABL and below the trade inversion with a VSLS source-loss estimate (Table 2). The mean loss of VSLS out of the MABL box is -351.0 % d^{-1} and equal for all compounds, since it is computed from the loss of trajectories out of the box. The loss is based on a mean residence time of the FLEXPART trajectories of 7 hours in the observed in-situ MABL height during the cruise. The ratio of the individual OD of each compound and the COL at this location results in the particular ODR for each compound. The ODR reveals that on average only 3 % of the observed atmospheric bromoform in the MABL ~~origins~~ originates from ~~nearby~~ local oceanic emissions and 99 % are advected ~~that,~~ including a chemical loss of 2 %~~, 99 % are advected~~. ~~Local oceanic emissions of dibromomethane contribute about 10 % of the observed abundances in the MABL, while methyl iodide emissions contribute with 28 %, which is far less compared to observations in other source regions with high convection as in the South China and Sulu Seas (Fuhlbrügge et al., 2015).~~ ~~Generally, the low ODRs along the cruise track are caused by the relatively low oceanic emissions.~~ The numbers show that the observed mean atmospheric concentrations cannot be explained by the mean local oceanic emissions. While the surface air masses can leave the MABL within hours, they are suppressed from entering the free troposphere through the trade inversion. FLEXPART

trajectories indicate an average residence time of air 48 h below the average trade inversion height of 1.1 km. During the 48 h and the prevailing southerly mean wind speed of 6.2 m/s oceanic VSLS emissions can accumulate over a fetch of 10° latitude. ~~The elevations of the atmospheric mixing ratios above the cold coastal upwelling can partly be explained by accumulation of local oceanic emissions in the stable low MABL. However, as the emissions appear generally not strong enough, except for methyl iodide, to explain the mixing ratios, the contribution of coastal sources is very likely (Figure 1b). While the surface air masses can leave the MABL within hours, they are suppressed from entering the free troposphere through the trade inversion barrier. Adapting an average trade inversion height of 1.1 km as the transport barrier for surface air masses into the free troposphere reveals an average residence time of the FLEXPART trajectories of 48 hrs below this trade inversion height. The atmospheric VSLS below the trade inversion originate to 11 % from oceanic emissions (ODR) for bromoform, to 33 % for dibromomethane and to 92 % for methyl iodide. The increased residence time of air masses below the trade inversion, reflected by the FLEXPART trajectories, leads to a stronger enrichment of air masses with VSLS from the oceanic emissions, reflected by OD, compared to the MABL box. However, the low sea-air fluxes of bromoform and dibromomethane are by far not strong enough to lead to the observed mixing ratios. These numbers imply that observed VSLS concentrations are advected below the trade inversion in the more open ocean regions during the cruise. An overall discussion is given in~~The impact of these conditions on VSLS emissions is discussed in Section 4.

3.5. Meteorological constraints on atmospheric VSLS in the MABL

~~Fuhlbrügge et al. (2013) identified the influence of meteorological conditions, in particular of MABL height variations on VSLS abundances in the tropical Northeast Atlantic above the Mauritanian Upwelling, and suggested a general correlation of MABL conditions and VSLS abundances over oceanic upwelling regions. Indeed, we~~We ~~also~~ find significant high correlations between meteorological parameters and the abundances of bromoform, dibromomethane and methyl iodide (Table 3) along the Peruvian coast. The predominantly moderate winds during the cruise are negatively correlated with the atmospheric VSLS and positively correlated with the MABL height. This shows that VSLS abundances tend to be elevated during periods of lower wind speeds which ~~occur also~~ lead to reduced mixing of surface air and therefore to lower MABL heights, in particular above the coastal upwelling

events on December 11, 15-17 and 24, 2012~~,~~. No significant correlation is found between the oceanic emissions and the atmospheric VSLS (not shown) revealing a stronger influence of the wind speed on the atmospheric accumulation of the VSLS rather than the oceanic emissions. ~~where local sources could accumulate even more.~~ SAT and SST both are negatively correlated with atmospheric VSLS, since elevated atmospheric VSLS mixing ratios are generally found close to the oceanic upwelling regions with low SATs and SSTs. In these regions the decrease of the SATs leads to an increase of the relative humidity (Section 3.1), ~~resulting~~ which results in a significantly high correlation ~~between the surface relative humidity and~~ with the VSLS. Since SAT and SST impact the MABL, which affects the relative humidity, these correlation coefficients are co-correlated~~ with each other~~. Correlation~~s~~ coefficients between the MABL height and the VSLS are slightly lower (Table 3). A ~~principle~~ principal component analysis of the parameters in Table 3 ~~furthermore underlineds~~ also confirmed~~revealed a~~ the strong connection between SAT, SST, MABL height, relative humidity and atmospheric mixing ratios of bromoform and dibromomethane (not shown here).

~~The results reveal that the MABL properties (height and stability) during M91 influence the VSLS abundances at the marine surface, although not as distinct as above the Mauritanian Upwelling during the DRIVE campaign (Fuhlbrügge et al., 2013). A comparison between the observations from this campaign and DRIVE (Figure 5) shows that the lower variance of observations during M91 may explain the lower correlation. Generally higher emissions and occasional lower and even more stable MABL heights during DRIVE can explain up to 100% of the atmospheric abundances while during M91 the observed elevations could only partly be explained by the local oceanic emissions.~~

~~Mixing ratios of both compounds are significantly lower above the Peruvian upwelling compared to observations above the Mauritanian upwelling, while methyl iodide mixing ratios are comparable (Fuhlbrügge et al., 2013).Fuhlbrügge et al. (2013) identified the influence of meteorological conditions, in particular of MABL height variations on VSLS abundances in the tropical Northeast Atlantic above the Mauritanian Upwelling, and suggested a general correlation of MABL conditions and VSLS abundances over oceanic upwelling regions.~~

3.6. Comparison to other oceanic regions

Surface water concentrations of bromoform in the Peruvian Upwelling during the cruise were generally lower compared to observations in other coastal upwelling regions, e.g., the Mauritanian Upwelling (Carpenter et al., 2010; Fuhlbrügge et al., 2013; Hepach et al., 2014). While dibromomethane concentrations are comparable, methyl iodide concentrations are almost eight times higher than in the Mauritanian Upwelling (Figure 3d, Table 1, Hepach et al., 2014). Atmospheric mixing ratios of bromoform and dibromomethane are significantly lower above the Peruvian Upwelling compared to observations above the Mauritanian Upwelling, while methyl iodide mixing ratios are comparable (Fuhlbrügge et al., 2013).

MABL properties (height and stability) reveal a stronger influence on the VSLS abundances at the marine surface during the DRIVE cruise covering the Mauritanian Upwelling compared to this study (M91) covering the Peruvian Upwelling (Figure 5). Observed local oceanic bromocarbon emissions can only partly explain the atmospheric VSLS concentrations above the Peruvian Upwelling, while above the Mauritanian Upwelling, the generally higher emissions could occasionally explain up to 100% of the atmospheric abundances of VSLS in very low and stable MABL conditions (Fuhlbrügge et al., 2013; Hepach et al., 2014). The predominantly southerly winds along the western coast line of Peru allowed only minor continental influence on the offshore coastal atmosphere, while the Mauritanian Upwelling showed a larger variation of maritime and continental air masses. Although our investigations revealed low MABL heights close to the Peruvian coast, the maritime air mass origin led to less developed surface inversions compared to those observed above the Mauritanian Upwelling, where the higher emissions led to a stronger and more variable enrichment in the MABL. This can lead to the observed higher correlation coefficients between the MABL height and the VSLS abundances in the Mauritanian Upwelling (Figure 5).

Compared to the two eastern boundary upwelling systems, observed VSLS sources at the coasts of the South China and Sulu seas were significantly higher (Fuhlbrügge et al., 2016). Despite the elevated emissions there, the atmospheric VSLS abundances in the West Pacific were lower, due to the presence of a convective active, well ventilated MABL. The comparison between the different regions demonstrates that the atmospheric abundances of VSLS over the ocean are significantly controlled by prevailing meteorological conditions next to their oceanic sources and emissions.

4. Discussion

Compounds emitted from the Peruvian Upwelling are first homogeneously distributed within the MABL in only a few hours according to the observations during the M91 cruise. Afterwards the emitted compounds are distributed within and transported below the trade inversion. For air masses above or close to oceanic upwelling regions, the MABL height is the first transport barrier on short time scales, while the trade inversion acts as the second more pronounced barrier for vertical transport on longer time scales. ~~A~~ The residence time of air masses below the trade inversion of 48 h~~ours~~ leads to a stronger enrichment ~~with~~ of VSLS from the oceanic emissions, reflected in the OD (Table 2), compared to the enrichment in the MABL. For the mean wind speed of 6.2 ms^{-1} and wind direction of 160° observed during the cruise, air masses accumulate oceanic emissions from approx. 1.5° latitude distance during the residence time of 7 hours in the MABL and below the trade wind inversion from approx. 10° latitude during 48 hours, which covers the southern Peruvian as well as part of the Chilean coast.

Accumulation of background concentrations

~~*The increased residence time of air masses below the trade inversion, reflected by the FLEXPART trajectories, leads to a stronger enrichment of air masses with VSLS from the oceanic emissions, reflected by OD, compared to the MABL box.*~~The observed atmospheric mixing ratios suggest background concentrations of the compounds which were around 2 ppt for $CHBr_3$, 0.8 ppt of CH_2Br_2 and 1 ppt for CH_3I (Figure 3e and 5). The back-trajectories revealed air masses originating from the southern Peruvian and Chilean coast, which were transported along the coast for about 5 days. In combination with a stable MABL and a distinct trade inversion acting as strong barriers to the vertical mixing of trace gases, these air-masses travelled close to the surface where they could be enriched during 48 hours with regional emissions before they enter the free troposphere. Mean emissions of around 2000 pmol m^{-2} h^{-1} for $CHBr_3$ and for CH_3I and 800 pmol m^{-2} h^{-1} for CH_2Br_2 would have been needed during the residence time of 48 h of air below the trade wind inversion to reach the elevated background concentrations observed on-board the ship. These emissions are close to the maximum observed during the cruise and are frequently observed in other coastal oceanic regions (Quack et al., 2003, Carpenter et al., 2000, 2015, Ziska et al., 2013). Thus, although our measurements along the cruise track did not reflect conditions that produced an average ocean emission rate sufficient to support high background VSLS abundances, we propose~~,~~ that higher emissions may be present at other times and locations along the coast, which were passed by the air mass trajectories (Figure 1) and added additional VSLS to the MABL. We

suspect that waters very close to the coast, where generally elevated concentrations of the bromocarbons are found (Carpenter et al., 2005; Leedham et al., 2013; Ziska et al., 2013), might even be stronger source regions although these areas were not crossed by the cruise track.

Maximum mixing ratios in the coastal upwelling

In addition to the background concentrations, Figure 5 shows the good correlation of MABL height and the three atmospheric VSLS. The slopes reveal approximately 0.5 ppt per 100 m MABL height for $CHBr_3$, 0.2 ppt for CH_2Br_2 and 0.3 ppt for CH_3I, yielding mean maximum mixing ratios of around 4.5 ppt $CHBr_3$, 1.8 ppt for CH_2Br_2 and 2.4 ppt for CH_3I in the lowest observed MABL heights. The difference of 2.5 ppt $CHBr_3$, 1.0 ppt for CH_2Br_2 and 1.4 ppt for CH_3I to the accumulated background concentration requires mean source fluxes of 2500 pmol m^{-2} h^{-1} for $CHBr_3$, 1000 for CH_2Br_2 and 1400 for CH_3I into a stable MABL height of 100 m during 4 h accumulation. Although the mean fluxes during the cruise were lower, higher fluxes of 2000 pmol m^{-2} h^{-1} $CHBr_3$, 1000 for CH_2Br_2 and 4000 for CH_3I were occasionally observed especially near the coast line (Figure 3, Table 1), which plays an important role as source region for the trace gases. As an example, the same coastal upwelling region was crossed two times during the cruise (17 Dec and 25 Dec, 2012). While other conditions where similar, the wind direction on the second occasion was from the coast and the air showed elevated atmospheric mixing ratios compared to the first occasion. Thus, we strongly believe that major source regions for the accumulation of the VSLS below the stable MABL and the distinct trade wind inversion above the coastal upwelling are associated with the coastal upwelling waters and regions even closer to the coast lines, which are also under the influence of steady and stable meteorological conditions due to topography and the upwelling of cold waters along the Peruvian and Chilean coast. Overall, we suggest that the observed high atmospheric mixing ratios above the Peruvian Upwelling resulted from the close interaction between steady meteorological conditions, advection of elevated background air, increased atmospheric stability above the cold oceanic upwelling region, and VSLS sources in the coastal upwelling itself and even closer to the shore line, which we were not able to examine during our cruise.

Transport from the upwelling

After the air masses were observed on R/V METEOR, the 10 day forward trajectories revealed a near-surface transport towards the equator (Figure 1). These trajectories

predominantly stayed below 1 km altitude due to the horizontal extent of the trade inversion. 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 were transported into higher altitudes. Since the lifetime of methyl iodide is only four days in the MABL a significant contribution of methyl iodide from the Peruvian Upwelling to observations made by Yokouchi et al. (2008) at San Cristobal, Galapagos can not be expected. However, it can partly explain the elevated IO observed above the Peruvian Upwelling (Schönhardt et al., 2008), which is further investigated by the companion study of Hepach et al. (2016, in review). The low contribution of oceanic emissions and boundary layer air to the free troposphere in this region is representative for the prevalent neutral El Niño Southern Oscillation (ENSO) conditions as were observed during December 2012 (ENSO Diagnostic Discussion, NCEP/CPC issue, November 2012). Different ENSO conditions can be expected to influence VSLS air-sea interactions above the Peruvian Upwelling and should be investigated in future studies.

Uncertainties

Uncertainties of our study may result from the applied method, which takes in-situ observations during the cruise and close to the ships position into account. ~~accounts for a 400 m^2 box around a measurement point assuming steady stateThe~~ Although the cruise track covered a significant~~ly~~ large area of the Peruvian Upwelling between 5° S and 16° S, ~~but and while higher~~ elevated sea~~s~~ surface concentrations and emissions ~~are not to be expectedcan not be excluded and are~~ , especially closer to coast lines may have contributed to the observed VSLS abundances, which were not sampled during the cruise. In regions with low MABL heights very close to the coast, where the source-loss estimate could not be applied due to trajectory analysis gaps (Section 2.5), potentially high emissions in combination with the stable atmospheric stratification could significantly increase the oceanic contribution to the MABL. Different parameterizations for the wind-based transfer coefficient k_w, as discussed in Lennartz et al. (2015) and Fuhlbrügge et al. (2016), lead only to an overall difference of 34% in the calculated oceanic emissions during M91, due to the relatively low prevailing winds. Additional uncertainties in our source-loss estimate may arise from deficiencies in the meteorological input fields from ERA-Interim reanalysis as well as from the air mass transport simulated by FLEXPART, but these uncertainties are difficult to quantify. Both could lead to either a shorter or longer residence time of the surface air masses within the MABL or below the trade inversion ~~and thus influence the COL term.~~ . However, Fuhlbrügge

et al. (2016) showed that differences in the MABL height of ERA-Interim and radiosonde observations affect the computed ODR only marginal. ~~In particular very close to the coast, where the source-loss estimate could not be applied due to the trajectory analysis gaps (Section 2.5)), the ODRs of the compounds might be different. Here potential high coastal emissions in combination with stable atmospheric stratification. leading toslow vertical transport into the free troposphere, could significantly increase the oceanic contribution to the MABL and to the atmosphere below the trade inversion and explain the elevated atmospheric mixing ratios. DIn addition, different parameterizations for the wind-based transfer coefficient k_w, as discussed in Lennartz et al. (2015) and Fuhlbrügge et al. (2016) in more detail, can impact the air-sea gas exchange and thus the ODRsl. Applying the k_w parameterizations of Liss and Merlivat (1986) as well as Wanninkhof and McGillis (1999) lead both to mean ODRs in the MABL of 0.02 (bromoform), 0.07 (dibromomethane) and 0.21 (methyl iodide) and below the trade inversion of 0.08 / 0.08 (bromoform), 0.25 / 0.26 (dibromomethane) and 0.69 / 0.75 (methyl iodide) and thus an even lower oceanic contribution to the atmosphere in this region.~~ Further uncertainties may arise from spatial variations of the ~~MABL~~ VSLS lifetimes and thus the chemical degradation of the compounds we used in this study. These effects are expected to be small for bromoform and dibromomethane since the overall impact of photochemical loss rates is only a few % of the total budget. The uncertainty in chemical loss rates for methyl iodide is larger, and more detailed photolysis rate calculations and actinic flux measurements would be useful to better constrain this process for compounds, whose main loss is through photolysis. Finally, future studies need to investigate in particular the near coastal processes and sources to estimate their contribution to the air-sea gas exchange and lower atmospheric VSLS abundances above the Peruvian Upwelling.

~~This would affect the computed advection (ADR) and not the oceanic contribution. After the air masses are observed on R/V METEOR, the 10 day FLEXPART forward trajectories reveal a near-surface transport towards the equator (Figure 1Figure 1c-d). These trajectories predominantly stay below 1 km altitude due to the horizontal extent of the trade inversion. The contribution of oceanic VSLS emissions from the Peruvian Upwelling to the free troposphere above this region is therefore strongly suppressed by the trade inversion (Figure 4Figure 4d). 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 four4 days in the MABL a significant contribution of methyl iodide from the~~

~~Peruvian uUpwelling to 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 Upwelling (Schönhardt et al., 2008).The elevated mixing ratios of methyl iodide is further investigated by Hepach et al. (2016). It has to be noted that the determined low contribution of oceanic emissions and boundary layer air to the free troposphere in this region is only representative for normal El Niño Southern Oscillation conditions as it was observed in December 2012 (http://www.cpc.ncep.noaa.gov/products/analysis_monitoring/enso_disc_nov2012/ensodisc.pdf). Since the Walker Circulation is reversed during El Niño, upwelling along the Peruvian coast is known to be suppressed and convective activity enhanced (Philander, 1989).~~

~~This leads to lower correlation coefficients between the MABL height and the VSLS abundances compared to the Mauritanian Upwelling.~~

5. Summary

This study investigated the contribution of oceanic emissions to VSLS abundances in the lowermost atmosphere above~~,~~ coastal upwelling and open ocean regions along the Peruvian coast during December 2012. Meteorological data were obtained on R/V METEOR ~~near the ocean surface~~ and by radiosondes up to the stratosphere. Oceanic VSLS emissions along the cruise track were determined from air and surface water ~~data~~measurements. The transport of air masses was calculated~~determined~~ with FLEXPART trajectories using ERA-I reanalysis. All data was synthesized in a source-loss model, investigating the influences of VSLS emissions and atmospheric transport on the observed VSLS abundances.

Oceanic upwelling was observed close to the Peruvian coast, which strongly impacted meteorological conditions in this region. On average a low, stable MABL height of 307 ± 177 m was encountered during the cruise, decreasing to about 100 m above the upwelling. A distinct trade inversion at 1.1 ± 0.3 km height ~~evolved~~ was identified as the dominant transport barrier for MABL air into the free troposphere during the cruise. The halogenated VSLS bromoform and dibromomethane showed low average oceanic emissions of 117 ± 492 pmol m^{-2} h^{-1} for bromoform and 245 ± 299 pmol m^{-2} h^{-1} for dibromomethane, while methyl iodide emissions were elevated with 856 ± 623 pmol m^{-2} h^{-1}. In contrast, t~~T~~he atmospheric mixing ratios of the compounds were elevated compared to average open ocean regions with 2.9 ± 0.7 ppt (bromoform), 1.3 ± 0.3 ppt (dibromomethane) and 1.5 ± 0.5 ppt (methyl iodide). The mean oceanic emissions along the cruise track explained on average ~~only~~ 3 % (-8 to 33 %) of bromoform, 10 % (-5 to 45 %) of dibromomethane, and 28 % (3 to 80 %) of methyl

iodide abundances in the ~~mean~~ MABL. Thus, the ~~expected~~ significant contribution of local oceanic VSLS emissions ~~from the Peruvian upwelling~~ to the overlying atmosphere that we expected was not captured during the time and location of ~~the cruise~~ our sample collection, and showed the need for a separation of transported and local signals. The elevated atmospheric VSLS ~~mixing ratios~~background concentrations ~~above the Peruvian upwelling therefore~~in the region appear largely advected and enriched below the trade wind inversion during two days of transport from further south. The pronounced stable and steady atmospheric conditions close to the Peruvian and Chilean coast led during a few hours to an additional accumulation and increase of the atmospheric VSLS mixing ratios above the coastal upwelling, where ~~Additional potential~~ stronger source regions ~~must~~ are likely to exist ~~even~~ close~~r~~ to the coast line, which have not been sampled during the cruise. ~~and also further South of the cruise track along the coast line. Nevertheless, significant correlations between the MABL height and marine atmospheric abundances of the VSLS reveal an impact of the oceanic emissions on the atmospheric VSLS mixing ratio variations.~~

Our study confirms that elevated atmospheric VSLS abundances above oceanic coastal upwelling regions are generally related with stable and low MABLs ~~height and stability are generally related with atmospheric VSLS abundances above oceanic upwelling regions~~. Additionally, a pronounced ~~widespread~~ trade inversion can lead to a near-surface accumulation of the VSLS and thus also impacts oceanic emissions. ~~Despite the observed elevated atmospheric concentrations during the cruise, a significant contribution of oceanic emissions to the atmosphere, in particular of the bromocarbons bromoform and dibromomethane, was not identified in the observed area and during the time of the cruise.~~ Further studies are necessary to ~~clearly uncover~~investigate the coastal and near shore source regions of the elevated atmospheric VSLS in the Peruvian Upwelling during different seasons and ENSO conditions. ~~Also the double transport barrier phenomena should be investigated in future studies of other oceanic upwelling regions as well.~~

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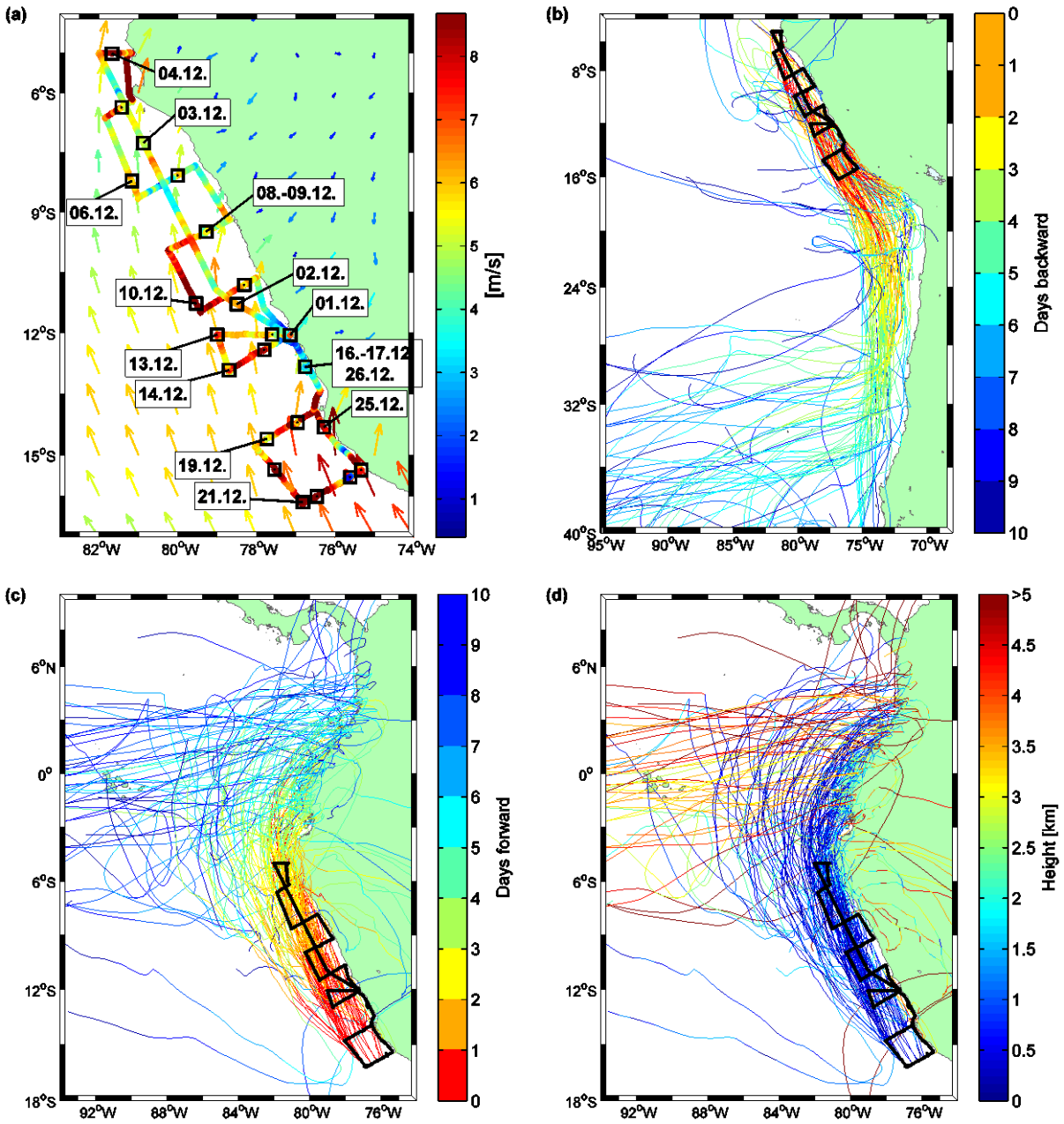
698 Figures

699



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701 Figure 1a-d: (a) 10 minute mean of wind speed observed on R/V METEOR displayed along
702 the cruise track; monthly mean (December 2012) of 10 m wind speed and direction from
703 ERA-Interim displayed as arrows. (b) Extract from 10-day FLEXPART back~~ward~~
704 trajectories coloured according to the time until they reach the specific ship position on the
705 cruise track of R/V METEOR (black). (c) Extract from 10-day FLEXPART forward

706 trajectories coloured according to the time since they were released. (d) same as c) coloured
707 according to the height (km) of the trajectories.

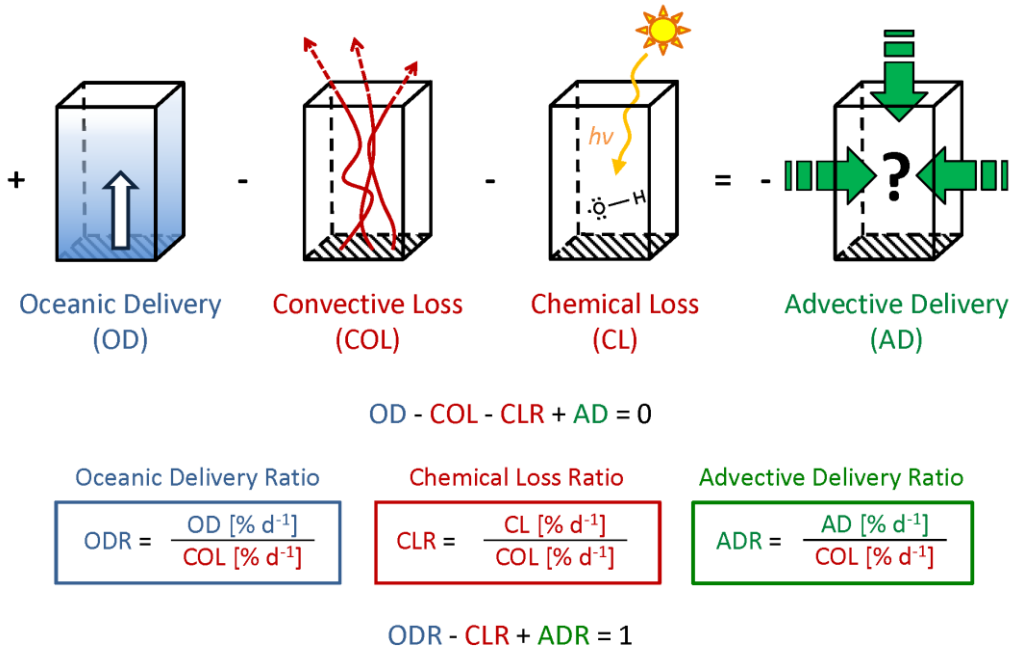


Figure 2: Schematic ~~summery~~ summary of the components of the applied mass-balance concept from Fuhlbrügge et al. (2016): Oceanic Delivery (OD), the Convective Loss (COL), the Chemical Loss (CL), the Advective Delivery (AD), the Oceanic Delivery Ratio (ODR), the Chemical Loss Ratio (CLR) and the Advective Delivery Ratio (ADR). The shaded area reflects an area of 400 m^2.

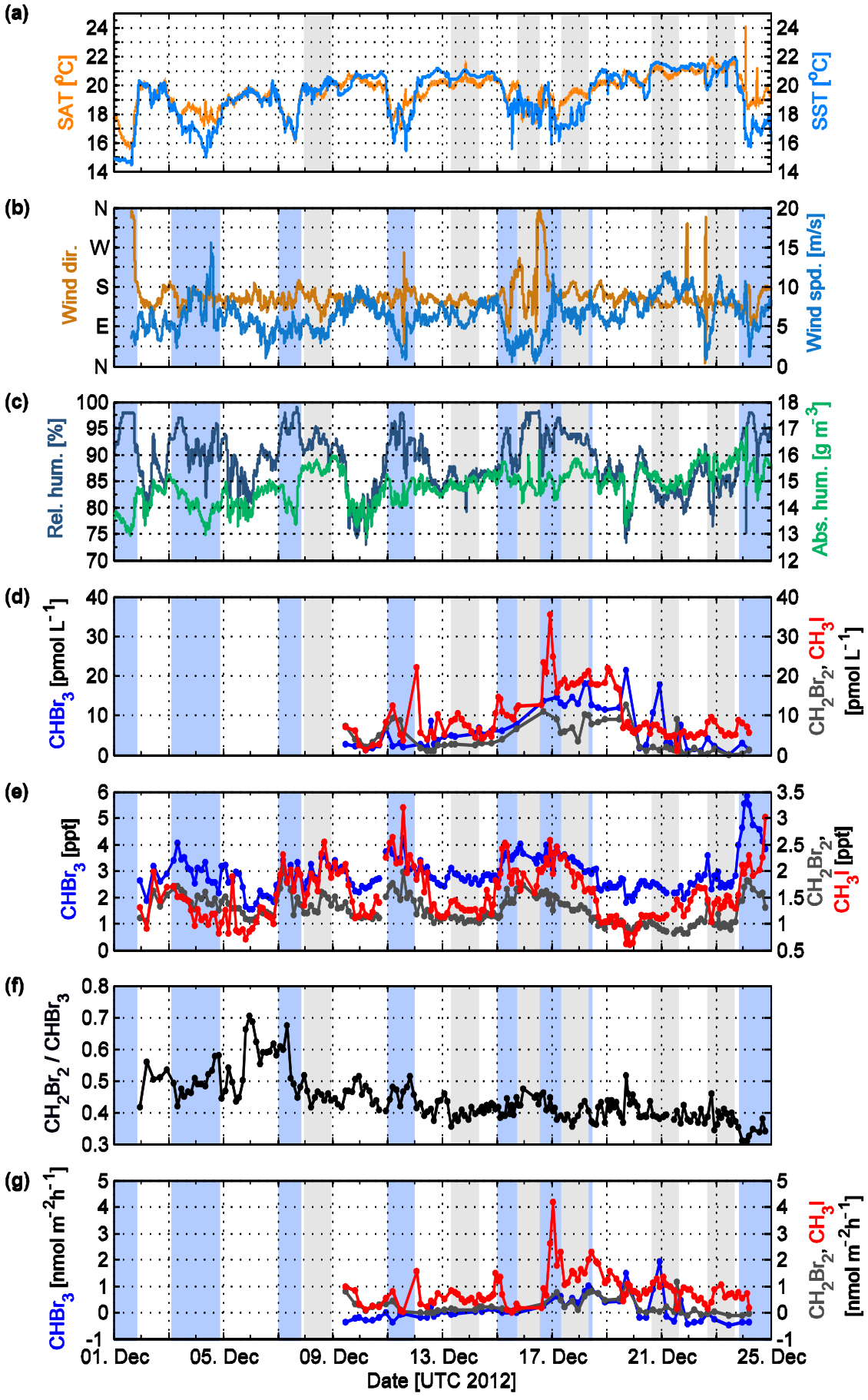

(a)
SAT [°C]
SST [°C]
(b)
Wind dir.
Wind spd. [m/s]
(c)
Rel. hum. [%]
Abs. hum. [g m-3]
(d)
CHBr3 [pmol L-1]
CH2Br2, CH3I [pmol L-1]
(e)
CHBr3 [ppt]
CH2Br2, CH3I [ppt]
(f)
CH2Br2 / CHBr3
(g)
CHBr3 [nmol m-2h-1]
CH2Br2, CH3I [nmol m-2h-1]
01. Dec
05. Dec
09. Dec
13. Dec
17. Dec
21. Dec
25. Dec
Date [UTC 2012]

Figure 3a-e: Observations during December 1 – 25, 2012 on R/V METEOR. Diurnal stations are indicated by grey background shades. (a) 10 minute mean of the SAT (orange) and the SST (blue) in °C. According to SST decrease, upwelling regions are marked with a light blue background shade in Figure 3b-e. (b) 10 minute mean of wind direction in cardinal directions (ocher) and wind speed in m/s (blue). (c) 10 minute mean of relative humidity in % (dark blue) and absolute humidity in gm^{-3} (green). (d) Oceanic surface concentrations of bromoform ($CHBr_3$, blue), dibromomethane (CH_2Br_2, dark grey) and methyl iodide (CH_3I, red) in pmol L^{-1}. (e) Atmospheric mixing ratios of bromoform, dibromomethane and methyl iodide in ppt. (f) Concentration ratio of dibromomethane and bromoform. (g) Sea-air flux for bromoform, dibromomethane and methyl iodide in npmol m^{-2} h^{-1}.

Table 1: Oceanic concentrations, atmospheric mixing ratios and sea-air fluxes of bromoform ($CHBr_3$), dibromomethane (CH_2Br_2), the concentration ratio of bromoform and dibromomethane and methyl iodide (CH_3I) observed during the cruise. Values are given in mean ± 1σ. The ~~[~~range ~~].~~is given in [].

	$CHBr_3$	CH_2Br_2	CH_2Br_2 / $CHBr_3$	CH_3I
Oceanic concentration [pmol L^{-1}]	6.6 ± 5.5 [0.2 – 21.5]	4.3 ± 3.4 [0.2 – 12.7]	0.9 ± 0.8 [0.1 – 4.2]	9.8 ± 6.3 [1.1 – 35.4]
Atmospheric mixing ratio [ppt]	2.9 ± 0.7 [1.5 – 5.9]	1.3 ± 0.3 [0.8 – 2.0]	0.4 ± 0.1 [0.3 – 0.7]	1.5 ± 0.5 [0.6 – 3.2]
Sea-air flux [pmol m^{-2} ~~r~~h^{-1}]	117 ± 492 [-477 – 1916]	245 ± 299 [-112 – 1169]	0.4 ± 8.6 [-24.5 – 48.9]	856 ± 623 [18 - 4179]

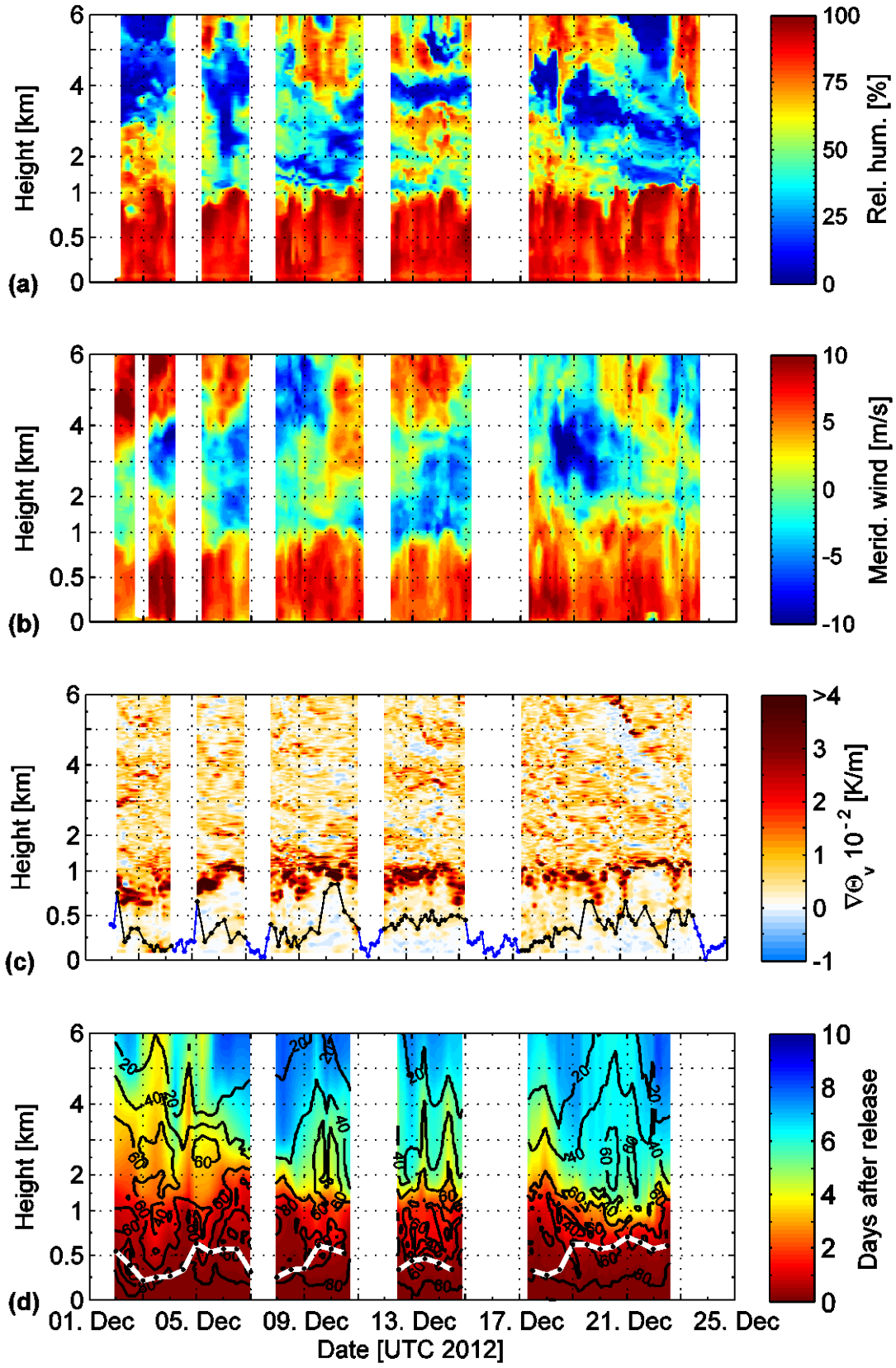


Figure 4: (a-c) Radiosonde observations of the lower 6 km of the atmosphere between December 2 and 24, 2012 on R/V Meteor. Shown are (a) the relative humidity in %, (b) the meridional wind in m/s and (c) the gradient of the virtual potential temperature in ~~E~~10^{-2} K/m

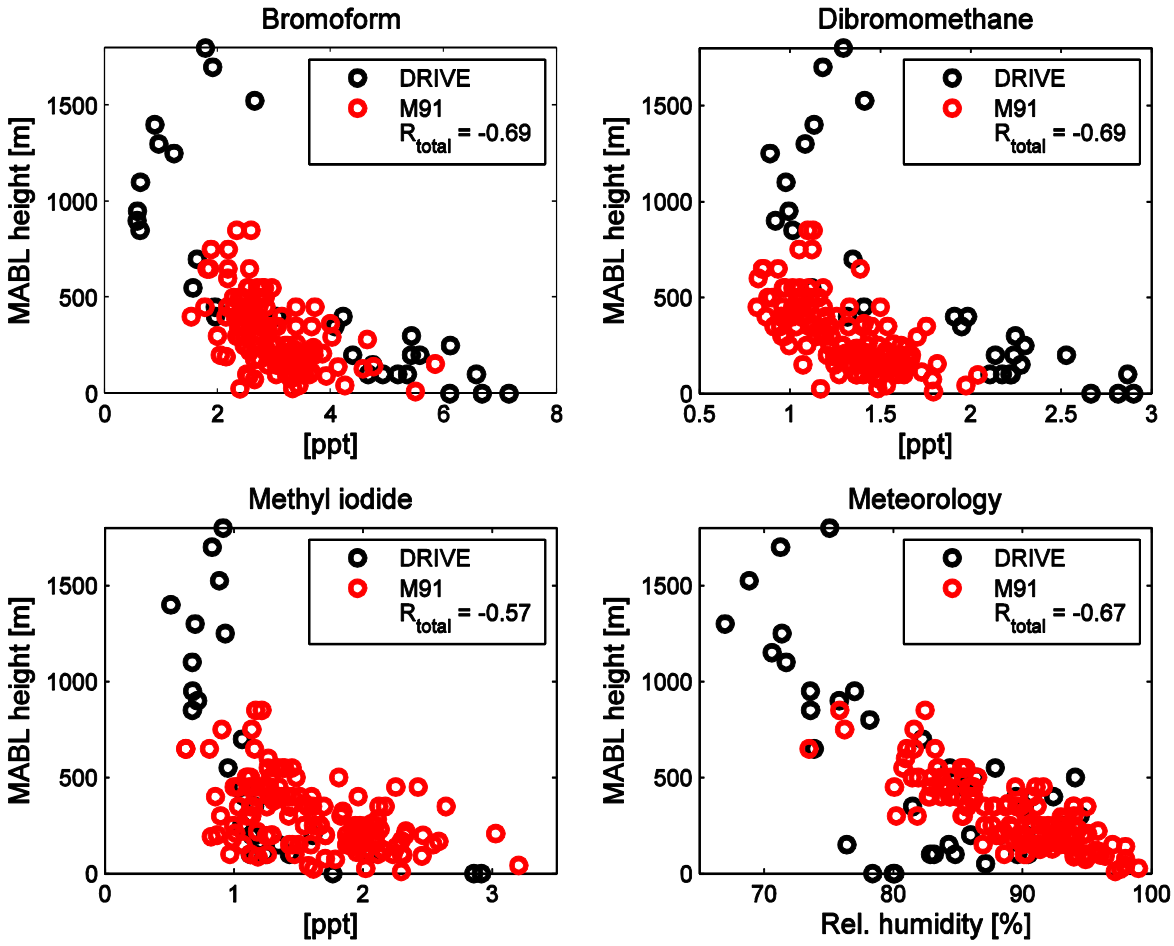
in combination with the determined MABL height (black) and the complimented MABL height above the oceanic upwelling from the multiple linear regressions (blue). (d) Distribution of 10-day FLEXPART forward trajectories. The black contour lines give the amount of trajectories in percentage ~~that reach~~reaching ~~a specific~~an altitude of 0 – 6 km height within the 10 days. The elapsed time in days until these trajectories reach this height is reflected by the colour shading. The white line shows the ERA-Interim MABL height at the ship position. Trajectory analyses gaps close to the coast are whitened (Section 2.5). The y-axes are non-linear.

Table 2: VSLS source-loss calculations: Mean ± 1σ of Oceanic Delivery (OD), Advective Delivery (AD), Chemical Loss (CL), Convective Loss (COL), Oceanic Delivery Ratio (ODR), Advective Delivery Ratio (ADR) and Chemical Loss Ratio (CLR) of bromoform ($CHBr_3$), dibromomethane (CH_2Br_2) and methyl iodide (CH_3I). Parameters have been computed for a box with the vertical extension of the in-situ MABL height (MABLH) and a mean trade inversion height (TIH) of 1.1 km. ~~(TIH).~~

		OD [% d^{-1}]	AD [% d^{-1}]	CL [% d^{-1}]	COL [% d^{-1}]	ODR	ADR	CLR
$CHBr_3$	MABLH	9.1 ± 28.0	349.0 ± 113.4	-7.1	-351.0 ± 109.4	0.03 ± 0.08	0.99 ± 0.08	-0.02 ± 0.01
	TIH	3.9 ± 12.0	53.2 ± 23.2	-7.1	-50.0 ± 18.4	0.11 ± 0.4	1.06 ± 0.39	-0.17 ± 0.07
CH_2Br_2	MABLH	32.1 ± 38.7	320.1 ± 115.6	-1.2	-351.0 ± 109.4	0.10 ± 0.11	0.90 ± 0.11	-0.00 ± 0.00
	TIH	13.8 ± 16.5	37.4 ± 25.9	-1.2	-50.0 ± 18.4	0.33 ± 0.54	0. 7 ± 0.54	-0.03 ± 0.01
CH_3I	MABLH	88.9 ± 48.1	286.1 ± 119.7	-24.0	-351.0 ± 109.4	0.28 ± 0.17	0.80 ± 0.16	-0.08 ± 0.03
	TIH	36.8 ± 20.5	37.2 ± 32.1	-24.0	-50.0 ± 18.4	0.92 ± 0.69	0.64 ± 0.55	-0.56 ± 0.24

Table 3: Spearman correlation coefficients (R) of meteorological parameters, MABL height and trade inversion height correlated with atmospheric bromoform ($CHBr_3$), dibromomethane (CH_2Br_2) and methyl iodide (CH_3I). MABL height* is the determined MABL height from the radiosonde launches, complimented by the regressed MABL height (Section 3.3). Bold coefficients are significant with ~~have~~ a p-value of < 0.05.

	MABL height	MABL height*	Trade inversion	$CHBr_3$	CH_2Br_2	CH_3I
Wind speed	**0.35**	**0.44**	-0.06	**-0.38**	**-0.53**	**-0.33**
SAT	**0.65**	**0.79**	**0.24**	**-0.50**	**-0.78**	**-0.37**
SST	**0.66**	**0.80**	**0.23**	**-0.57**	**-0.81**	**-0.42**
SAT – SST	**-0.39**	**-0.47**	-0.11	**0.38**	**0.48**	**0.30**
Rel. humidity	**-0.77**	**-0.81**	-0.06	**0.74**	**0.77**	**0.67**
MABL height*	-	-	0.08	**-0.55**	**-0.61**	**-0.45**
$CHBr_3$	**-0.55**	**-0.60**	-0.03	-	**0.79**	**0.79**
CH_2Br_2	**-0.61**	**-0.72**	-0.02	**0.79**	-	**0.66**
CH_3I	**-0.45**	**-0.50**	**0.30**	**0.79**	**0.66**	-



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761 Figure 5: Scatter plots of near surface atmospheric mixing ratios of bromoform,
762 dibromomethane, methyl iodide and relative humidity vs. MABL height. Black circles reflect
763 observations from the DRIVE campaign covering~~in~~ the Mauritanian Upwelling (Fuhlbrügge
764 et al., 2013) and red circles from this study (M91) covering the Peruvian Upwelling. R_{total}
765 gives the Spearman correlation coefficients for both data sets together.

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