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Interactive comment on "Biogenic halocarbons from the Peruvian upwelling region as tropospheric halogen source" *by* H. Hepach et al.

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Anonymous Referee #1

General comments: This manuscript by Hepach et al. reported their observations on a series of bromo- and iodocarbons from surface ocean as well as subsurface waters in the Peruvian upwelling zone. The authors further investigated into possible sources of the halocarbons and the contribution of organoiodine to stratosphere iodine loading. This manuscript is relatively well written and discussed drivers for the production of the halocarbons and transport of iodinated species, in addition to reporting data. I believe it is a new contribution to the scientific community. The authors also proposed directions for future studies for addressing the halocarbon budgets. I believe this manuscript is suitable for publication in ACP with minor revisions. Please see specific comments

suggested below.

- We thank referee #1 for the review. We will address the specific comments in the following. All corrections according to referee #1 will be marked in blue in the manuscript. Further changes are marked in green.

Specific comments Page 2 Line 2: delete "halogenated short-chained hydrocarbons" for "halocarbons" is clear enough for this definition.

- Done.

Page 2 Line 6: should read "Peruvian upwelling zone (or regions)".

- We added "zone".

Page 2 Line 23: perhaps use "very short-lived substances (VLS)" following the WMO terminology?

- Since we use "halocarbons" as terminology throughout the manuscript, we decide to keep it. The terminology is used in the oceanographic and lower troposphere community, while VLS also include compounds without halogens, thus we decided to be more specific with this term. To avoid confusion, we delete "organic compounds" and write "halocarbons" instead.

Page 3 Line 16: please clarify this sentence by adding "in seawater" after "for both compounds".

- We added "in the surface ocean" to clarify the location for which this is valid.

Page 3 Line 29: should read "the main sinks for both CH2I2 and CH2ClI are"

- Since it is only one sink, this should be singular. But we agree that it may be written a bit confusing, so we rewrite it as "The main sink for both CH2I2 and CH2ClI is photolytical breakdown [. . .]".

Page 4 Line 14: replace "the latter two compounds" with "CH2ClI and CH2I2" to avoid

confusion.

- Done.

Page 5 Line 2: it is a bit confusing here, is it “every 3 hours”?

- Yes, we clarified this sentence. See also changes with respect to referee #2.

Page 5 Line 6 and 7: were purge efficiency measured for these gases?

- Purge efficiencies were determined in previous laboratory experiments. We purge 50 mL of water at 70 °C with a stream of helium of 30 mL min-1 for 50 min. With these conditions, we achieve a purge efficiency of larger than 98 % for all five compounds. We add a short sentence with these specifications.

Page 5 Line 11: please specified how the gas samples were stored – stainless steel canisters?

- Yes, the gas samples were taken in pre-cleaned stainless steel canisters. This is described in Fuhlbrügge et al. (2015) in more detail, but we also add this to this part of the manuscript.

Page 5 Line 25: Cyanobacteria may pass through the GF/F filters at the initial filtering (i.e. before the filter pore size decreased as materials accumulated), which may affect the quantification of the cyanobacteria marker pigments. Did the authors estimate such a biomass lost?

- The referee is correct that concern has been raised that filtering through GF/F filters may sometimes cause very small cyanobacteria, mainly prochlorophytes, to pass through the filter. The smallest prokaryotic algae are probably not measured with the same accuracy as all other phytoplankton cells above 0.7 μm by this technique (Dickson and Wheeler 1993). However, Chavez et al. (1995) compared HPLC results from GF/F 0.7 μm and membrane 0.2 μm filters, and clearly showed that GF/F filters can be used to accurately measure pigments also from very small phytoplankton. Less

than 1 % of prochlorophytes pass through the GF/F filters. We believe that the error caused by some of the smallest prokaryotic algae passing through the filter and not being accurately accounted for, is very low for our cruise.

Page 5 Lines 28 to Page 6 Lines 1 to 7: The DOM samples were collected from 20 cm and the gases were collected from about 6 to 7 m, which were not exactly parallel samples. Some DOM can be recycled relatively fast. In addition, DOM at surface ocean may be degraded via photolysis. I suggest the authors to also report the mix layer depth and possible residence times for the DOM compounds they measured, such that a valid argument can be made about those DOM were well mixed within the mixed layer and hence the depth difference would not affect the data analysis and interpretation.

- The mixed layer depths during M91 were rather shallow, usually between 6 and 25 m. We assume that this very upper layer was well mixed, so samples for both components were taken from the same water masses. Unpublished data from a recent cruise (ASTRA-OMZ, SO243 onboard the RV Sonne) show that our halocarbon measurements from the first meter are in good agreement with measurements from the hydrographic shaft if the mixed layer is not shallower than the shaft depth. High molecular weight dissolved combined carbohydrates, such as determined during this study, have been considered as labile to semi-labile with turn-over times of several days to months (Engel et al. 2011; Hansell, 2013), suggesting that the mixing time in the upper water is faster than the turn-over of the combined sugars, which will also be added to the manuscript. We add in the methods section: “Very-well mixed layers at these measurement locations reach down to between 6 and 25 m, and DOM turn-over times for the respective compounds has been reported to be several days to months (Engel et al., 2011; Hansell, 2013).”

Page 8 Lines 1 to 15: I suggest move this to before the FLEXPART model simulation.

- Done.

Page 9 Line 2: change “correlated very well” to “significantly correlated”.

- Done.

Page 11 Line 11: I suggest the authors also include the depth profile of the bromocarbons.

- We added the bromocarbons to Fig. 4. The text in the manuscript is changed accordingly (section 4.2 and the figure caption).

Page 11 Lines 22 to 24: this sentence is a bit confusing, please rephrase.

- We agree and rewrite as “CH2I2 was hardly detected in deeper water in the northern part of our measurements (Figure 4, upper panel).”

Page 12 Line 22: Liu et al., 2015 tested a series of carbohydrates, and found that these DOM moieties were not fast reacting substrates for CHBr3, which seems to be consistent with findings in this study. In addition, bromocarbon formations via HOBr reaction are potentially DOM moiety specific. In Liu et al., 2013, no correlations were observed between the bromocarbons and total dissolved organic carbon.

- Thank you for this suggestion. We include this hypothesis in the manuscript and write: “Bromocarbon production from DOM has also been suggested to be slow (Liu et al. 2015), which could shift larger bromocarbon concentrations to later times after our cruise.”

Page 13 Line 12: the bulk DOM may correlate better with total biomass (estimated from TChla).

- This is certainly a reasonable assumption. However, we tested the data and correlations are not much better. This may be due to the fact that the main part of the total biomass is made up of diatoms. Hence, the correlations between the total biomass and DOM are mainly regulated by diatom abundance, which leads to similar correlations for biomass and DOM vs diatoms and DOM.

Page 13 Lines13 to 15: I suggest change “is determined by the phytoplankton species” to “is determined by ecosystem compositions”, because DOM contribution is not governed by phytoplankton species alone.

- Done.

Page 13 Line 21: Please also cite Lin and Manley 2012, who also tested bromocarbon formations using different molecular weight natural DOM as substrates.

- Done.

Page 13 Lines 24 to 27: The authors depicted possible abiotic sources of HOI and HOBr in Fig 5. I would suggest the authors also put the abiotic sources of HOI and HOBr into this context (see Carpenter et al., 2005).

- We included this in the figure, but only schematically, since we focus on the biotic formation in our manuscript.

Page 14 Line 6: I suggest remove “In conclusion” here.

- Done.

Page 31 Fig 5: The conception model figure is a bit confusing on the CH3I part via methyltransferase, for it is an intracellular enzyme. Thus the reaction is likely occurring inside the cell. However, figure seems to depict an extracellular reaction.

- We agree, and it was actually intended as such. Thus, we make this clearer in the figure now.

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