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Atmospheric Chemistry and Physics Discussions

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 #2

General Comments This manuscript by Hepach and co-authors presents gas-phase and oceanic observations of halogenated VOCs, including CHBr3, CH2Br2, CH2ClI, CH3I, and CH2I2 from a ship cruise in the eastern tropical Pacific Ocean. In addition to the concentrations and sea-air flux calculations, the analysis includes correlations to phytoplankton groups measured in the surface water along the cruise path. The paper is reasonably well written and the many of the data presented are new observations. The paper should be published in ACP after addressing the following minor corrections.

- We thank referee #2 for this review. We will address the specific comments in the following. All corrections with respect to the suggestions by referee #2 will be marked

in red in the manuscript. Further changes are marked in green.

Specific Comments Page 5, line 2 – Three hourly is not explicit – every three hours, or three samples per hour? And was this day and night? What were the samples taken in? I would like to see a little more detail, even though the system was described in another paper.

- Samples were taken every three hours throughout the whole day, hence both during day and night, adding up to in total eight samples. Water was sampled in amber glass bottles. We added respective details in the manuscript. See also our changes with respect to referee #1.

Page 5, line 7 – replace "lay" with "was".

- Done.

Page 5, line 9 – "set up problems" sounds odd. Perhaps "instrument issues?"

- We replace this with the suggestion of the referee.

Page 5, line 10 – 20 m "above sea level?" How were these samples stored? Stainless canisters? Glass flasks?

- We added "above sea level" to the section. For the second issue, please see our answer to referee #1.

Page 5, line 11 – "starting on December 1"

- Done.

Page 5, line 23 – replace "build up" with "comprise"

- Done.

Page 5, line 26 – "a" should be italicized.

- Agreed.

Page 7, line 20 – The authors explain that they do not include detailed tropospheric iodine chemistry, and specify what they, explicit removal of HOI, HI, IONO2, and IxOy through scavenging or 20 heterogeneous recycling of HOI, IONO2, and INO2 on aerosols, and then reference Saiz-Lopez et al., 2014. It should be made clear whether or not Saiz-Lopez did or did not omit iodine removal . I.e., "we didn't do x, y and z (reference)" - is the reference an example where x, y and z were omitted, or not omitted?

- Thanks for pointing this out. Since the Saiz-Lopez et al., 2014 study includes detailed tropospheric iodine chemistry and removal, it is not an appropriate reference in this sentence and has been removed in the current version of the manuscript.

Page 8 – section 2.6 and section 2.5 should be swapped (i.e., measurement methods before model description.)

- We agree. See changes according to referee #1.

Page 10, lines 1-4 – The suggestion that the observations from this work "compare well" with observations from Liu et al. (2013) needs to be backed up with something more quantitative. CHBr3 seems to have a similar range, but the CH2Br2 range from Liu et al. are about half the values from the current work. Can you be more specific about the region covered by Liu et al., i.e. where the observed maxima were located?

- The campaign covered a large region between Punta Arenas, Chile and Seattle, USA. The coastal region covered by Liu et al. (2013) was south of 40° S, while we investigated a region between 5° S and 16° S, where the data of Liu et al. (2013) only consist of open ocean data, which could explain the difference in the ranges between our study and theirs. Unfortunately, not much more data exist for the coastal tropical East Pacific. However, Liu et al. (2013) measured about 20 pmol L-1 of CHBr3 and around 6 pmol L-1 of CH2Br2, showing that also the more southern part of the South American coast is characterized by concentrations in our range. We will specify this in the manuscript.

Page 11, line 11 – "during a large part"

- Done.

Page 11, lines 18-21 – I have a bit of an issue with this interpretation. In Figure 4, we see that there were four subsurface measurements made between the surface and a depth of 25 m, and one single subsurface maxima is shown at a depth of about 20. First, it would be helpful to see the measurement uncertainties on this plot, as the data aren't super convincingly supportive of a maximum. Second, to suggest that there was "no subsurface maxima" in Figure 4(c) when only two measurements were made between the surface and the 25 m depth suggests that it is entirely possible that there is a subsurface maxima that just wasn't observed because no 20 m depth was measured. This needs to be included in the discussion.

- The measurement error is estimated to be around 10 % for all halocarbon measurements in seawater. The maximum concentrations shown are well outside of this 10 % range. We agree that there could be a maximum at 20 m. We do not preclude a subsurface maximum per se at this particular profile, we merely state that we observed it considerably often in the mentioned upwelling region. This profile was chosen, because the mentioned features could be observed for all iodocarbons. We clarify this in the manuscript.

Page 16, lines 18-20 – it would be nice to see a consideration of the daytime/nighttime differences in the correlations – if, as the authors are suggesting, there is atmospheric accumulation during the night, one might expect a better correlation during the night than during the day.

- Thank you for this suggestion. We tested this hypothesis by dividing the data into "day" and "night" by assuming "night" was when there was no radiation at all. Then, we correlated the data again. The shorter the lifetime of the compound, the better is the correlations between the oceanic and atmospheric halocarbons. Considering only data points when there is light, oceanic and atmospheric CH2ClI correlate significantly

with r = 0.5, during the night, this correlation is stronger with r = 0.68. This observation is even clearer for CH2I2, which correlates not significantly during the “day” with r = 0.4, owing to the very few data points during light hours, and very strongly during the night with r = 0.92. This supports our hypothesis that atmospheric CH2ClI and CH2I2 build up during the night, and are degraded during the day. We include this separation in the discussion, and add a figure depicting this (new Fig. 7).

Page 17, line 29 – “in the latter case.”

- Done.

Page 21, line 21 – are there really no units for salinity?

- Salinity measurements here are based on the conductivity ratio, which is dimensionless. The use of the commonly applied unit “PSU” (Practical Salinity Unit) is not recommended anymore, hence, no units are used here. For more information see Millero (2010).

Page 29, line 2 – “note the colorbar in”

- Changed.

Page 29, line 5 – I don’t think “Global” is necessarily the right adjective of the observed radiation. Also, for this plot (Figure 3) and Figure 6, it would be better to change either the black or blue dots to a slightly different color, because they look very similar. Perhaps change the symbols, too, so that they’re not all circles.

- “Global radiation” is a parameter measured onboard by a pyranometer and refers to the total short-wave radiation, which includes both the direct solar radiation and the diffuse radiation. Hence, the adjective hereby is part of the parameter name. This is made clearer in the figure description now. The blue symbols were changed to a lighter color and the line style was changed for better distinction.

References Liu, Y. N., Yvon-Lewis, S. A., Thornton, D. C. O., Campbell, L., and

Bianchi, T. S.: Spatial distribution of brominated very short-lived substances in the eastern pacific, J. Geophys. Res.-Oceans, 118, 2318-2328, 10.1002/jgrc.20183, 2013.
Millero, F. J.: History of the equation of state of seawater, Oceanography, 23, 18-33, 10.5670/oceanog.2010.21, 2010.

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