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## ***Interactive comment on*** “Numerical modelling of methyl iodide in the Eastern Tropical Atlantic” **by I. Stemmler et al.**

**I. Stemmler et al.**

irene.stemmler@zmaw.de

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**We thank referee#1 for his/her comments. Below you find the detailed answers (normal font) to the issues raised by the reviewer (italic).**

*This paper describes a model analysis of methyl iodide in the tropical ocean. It is an issue that is important for the biogeochemical cycling of iodine and may have significant impact on atmospheric composition. Therefore it would be appropriate for publication in BGD. I do, however, have some deep concerns about the procedure, the data treatment and the conclusions. The main point of concern are: the concentration of CH<sub>3</sub>I in the atmosphere, the performance of the model, the measurements. In addition, discussion of the scenarios and of the model results is poorly organized*

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*and rather confusing. It seems to me that keeping the value of  $CH_3I$  constant means constraining the sea-air flux. This may lead to erroneous calculation of the concentration of  $CH_3I$  in the subsurface, which may or may not propagate to the lower levels of the water column. It is impossible to say whether this is an issue and how it affects the results and the conclusions. The authors seem to be aware of the potential problem (page 1130, lines 510) but make no attempt to deal with it or even discuss it.*

This is wrong, setting the atmospheric concentrations to a constant value does not imply constraining the air-sea flux, because seawater concentrations, temperature, and wind speed vary with time. In the model gas-exchange is calculated from the two-film model, hence it is determined by the saturation anomaly between air and sea water, and a wind-speed-dependent transfer coefficient. The saturation anomaly is defined as the methyl iodide concentration dissolved in sea water minus the atmospheric concentration that would dissolve in sea water at saturation, derived from the temperature dependent Henry coefficient. The saturation anomaly is mostly influenced by the oceanic values here, as the ocean is strongly oversaturated. This has been found previously based on observational data in air and seawater for both early summer months (May, June: O'Brien et al., 2009, Fuhlbrügge et al. 2012) and late fall (October, November, Butler et al. 2007). Furthermore, the mixing ratios in May-June and October-November over the open ocean close to Cape Verde were in the range of 1-2ppt (Butler et al. 2007, O'Brien et al. 2009, Fuhlbrügge et al. 2012). Hence, the expected seasonal variability of atmospheric concentrations will be much lower than the one of seawater concentrations (which show a factor of 6 between low summer and high winter values in the simulations).

*The information in the Appendix and the related figures are troubling. The model does not seem to be performing well, despite claims of the opposite (btw, those figures should be rescaled to the same yaxis as Fig 4, otherwise they give a wrong impression*

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to the reader).

In contrast to Fig4, the comparison of model results with observations is shown for the whole simulated water column. This is reasonable, since there are observations available for salinity, temperature and nutrients down to 700 m depth (in contrast to methyl iodide and chlorophyll concentrations). We do not see the reason to omit these data points, particularly since the physical and nutrient profiles show that the overall physical and biogeochemical conditions are well reflected by the model.

*Particularly in the upper layers of the water column, the model does a fairly bad job at predicting salinity and temperature (especially at the TENATSO site)*

Discrepancies between model and observed temperature and salinity profiles occur in the surface layers, where the model is not restored to observed profiles. We assume that the simulated too low salinities and too low temperatures are a result of the specific hydrographic and atmospheric conditions during the cruise P399/2. But, the model is capable of reproducing the hydrographical features at in the Eastern Tropical Atlantic. It shows intense mixing in winter and spring followed by a strong stratification of the water column in summer. We would also like to refer to the additional experiments we performed that are illustrated in the response to the 2nd reviewer. Generally, the use of different temperature and salinity profiles (NCEP global ocean data assimilation system (GODAS) (<http://www.esrl.noaa.gov/psd/data/gridded/data.godas.html>, Behringer, 2004) for 2010, WOA, or P399/2) would not impact the presented differences among CH<sub>3</sub>I sources and hence the conclusions drawn here, as they are arising from the nature of the source (radiation driven versus phytoplankton growth driven). For the experiments that include photochemical production from PAR (Opt2, Opt3) the actual location of the subsurface maximum will be influenced by the location of the mixed layer, which will change if the model is restored to the profiles observed during

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P399/2 instead of the climatological data (see Fig1). But, any usage of these data is inconsistent, as no data for other months are available and in-situ data are treated as monthly means.

*and terrible job at predicting phytoplankton concentration.*

We would like to point out that chlorophyll is not an indicator for phytoplankton biomass. In contrast, the model simulates phytoplankton biomass. To compare model results with observations, chlorophyll needs to be converted into model units (or the modelled phytoplankton concentration needs to be converted into chlorophyll units). Since there is no mechanistic understanding about the relationship between both quantities, there are large uncertainties. We would also like to refer to our response to reviewer No.2. Overall, the model does a good job in representing the conditions in the Eastern Tropical Atlantic, as it does show a pronounced subsurface maximum of similar strength as the observations. Furthermore, previous measurements in this region show integrated primary production is in the range of 0.3 to 2.6  $g C d^{-1} m^2$  (summer and fall for the oligotrophic/mesotrophic region; see Morel et al. 1996). Vertically integrated (0-100m) daily primary production derived from our model ranges between 0.7 and 1.4  $g C d^{-1} m^2$ . Thus, our model matches previously observed values well. We agree that the discussion about the mismatch between model and observations needs to be addressed in much more detail. Therefore we suggest the following changes/additions:

Discussion:

In the experiment that include biological production of  $CH_3I$  using a constant production ratio the depth of the maximum of primary production determines the depth of the maximum of  $CH_3I$  concentrations. The modelled phytoplankton concentration was compared to observed chlorophyll-a data. Both show a subsurface maximum and are in the same order of magnitude. The exact location of the biomass

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maximum during the cruise, however, can not be unambiguously assessed, as phytoplankton concentration in model units has to be diagnosed from an empirically derived depth-dependent relationship between chlorophyll and carbon. Although there is no doubt that the C:Chl ratio varies with depth (with higher values at surface than subsurface) there is no mechanistic understanding about the co-variation of carbon and chlorophyll with depth. Therefore, a match or mismatch of the exact location of the  $CH_3I$  maximum is not a good indicator for the model performance, here.

*These are key parameters for the whole study presented here. I would expect that both photochemical and biological processes are deeply affected by temperature and salinity, and obviously the model fails in predicting phytoplankton (and hence might be expected to fail in calculating  $CH_3I$  production). However I don't see anywhere in the paper any mention of these parameters as possible causes for the discrepancy between the model and the measurements. Before even looking at the optimization of the biological production parameters I would look into the basic model performance. If the authors don't think these affect the results, they should very clearly explain why.*

We agree with the referee#1 and would like to refer to our comments above.

*Regarding the measurements there is not a bit of information about them, not even a reference to another paper (except the cruise report). I don't think it is acceptable to present a model-measurement comparison without giving even the basic information about the measurements. It is impossible to determine how far off the model and the measurements are, without knowing the error, the detection limit and other information about the measurements (and also about the model, to be honest).*

We agree and thus will include this part in a revised version; we will add another

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co-author who conducted the measurements (H.Hepach, Geomar, Helmholtz Centre for Ocean Research Kiel). Measurements on board have been conducted using a purge and trap system attached to a GC-MS (the method description will be added to the manuscript). Information on the precision (16 % for  $CH_3I$  in sea water during P399/2) and the detection limit ( $0.05 \text{ pmol L}^{-1}$ ) will be added as well.

Suggested modifications to the paragraph on the observations:

To evaluate the simulated concentrations model results are compared to observations from a ship cruise in the tropical Northeast Atlantic close to Cape Verde, i.e. the Poseidon Cruise P399/2 in April-June 2010 (Bange et al., 2011). Generally, methyl iodide profiles are available from three stations located at  $18^\circ N 17^\circ W$  (St.311),  $17.6^\circ N 24.3^\circ W$  (St.307 - in the following called TENATSO, which stands for Tropical Eastern North Atlantic Time-Series Observatory), and  $18^\circ N 21^\circ W$  (St.308). But, as Stat.311 is influenced by wind-driven coastal upwelling, which the 1D water column model GOTM is not able to reproduce,  $CH_3I$  observations from that station are not included in the evaluation of the model. Dissolved  $CH_3I$  was measured in sea water sampled in 500 mL amber glass bottles from 10 depths from TENATSO and station 308 each from 10 L Niskin bottles attached to a 12-bottle-rosette with a CTD (Conductivity Temperature Depth). A purge and trap system attached to a gas chromatograph with mass spectrometer (GC-MS) and detection in single ion mode were used to analyze the samples. 80 mL of sampled water was heated up to  $70^\circ C$  while being purged with a stream of helium at  $30 \text{ mL min}^{-1}$  in a glass chamber. Volatilized trace gases were trapped on glass beads at  $-100^\circ C$  and were desorbed onto a deactivated capillary in liquid nitrogen as second trap at  $100^\circ C$  after one hour of purging. The trace gases were injected into the GC-MS after three minutes. Volumetrically prepared standards in methanol were used for quantification. Precision of the measurements lay within 16 % determined from duplicates with a detection limit of  $0.05 \text{ pmol L}^{-1}$  for  $CH_3I$ . [..]

*For all these reasons, it is hard to understand what are the conclusions of the paper,*

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*the message it tries to convey and its contribution to the literature. The paper shows potential, and is potentially interesting, but it requires a lot more work before it is considered for publication.*

*Minor Comments:*

*In the Introduction the authors should have done a literature search a little more thorough. there have been plenty of papers regarding the impact of iodine on the atmosphere and the potential sources of iodine from algae and nonorganic sources since the Chameides and Davis, 1980, and the Nightingale et al., 1995, papers. In particular with regard to the Cape Verde region, as well as other tropical oceanic regions, which is very relevant to this work. It will not only put the discussion in context but also provide some material to which the present study could be compared.*

In the revised version of the manuscript the introduction will be refined where necessary.

*The authors mention two type of DOC on page 1115, but do not say anything about the difference between them.*

The explanation of the two DOC types can be found in the same page: In one group of experiments the semi-labile DOC (SLDOC) pool of pure marine origin as provided by HAMOCC is used as a source for methyl groups. In the experiments that mimic a biologically refractory pool of DOC (RDOC) as the source of methyl groups, the DOC concentration is set to a constant value of  $40 \mu\text{molCkg}^{-1}$ .

To make it more clear what is meant by the two types we are going to rephrase this paragraph for the revised version of the manuscript:

To cover DOC pools of different lability two types of experiments with photochemical

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production of  $CH_3I$  are performed. In one group of experiments the semi-labile DOC (SLDOC) pool of pure marine origin as provided by HAMOCC is used as a source for methyl groups. In the second group of experiments the DOC concentration is set to a constant value of  $40 \mu\text{molCkg}^{-1}$ . This mimics an unlimited supply of DOC and enables us to assess whether the spatio-temporal behaviour of DOC affects  $CH_3I$  production in the model. In the following this production pathway is referred to as photochemical production from refractory DOC (RDOC), as a very long life time of DOC would lead to almost uniform distribution in the ocean.

*Also, regarding the values of  $k_{pp\ max}$  and  $k_{pp\ min}$ , it is not clear how they were chosen and what relation they have with the values mentioned on page 1117 (lines 78).*

$k_{PP_{min}}$  and  $K_{PP_{max}}$  are the lower and upper limit of the production rates derived from Moore et al. (1996) and Smythe-Wright et al. (2006). These parameters are used when considering enhanced biological production during stress (experiment E3). In experiment Opt4 these two values were derived from a numerical parameter optimization. To make this more clear in the revised version the following ( $k_{pp_{min}}$ ,  $k_{pp_{max}}$ ) will be added to p1121:

In experiment E3 the production rates by Moore et al. (1996) and Smythe-Wright et al. (2006) are used as the lower ( $k_{pp_{min}}$ ) and upper ( $k_{pp_{max}}$ ) boundaries of the variable biological production rate that mimics production by phytoplankton in dependence of stress.

*page 1115, line 11: "photochemical"*

Will be corrected.



*page 1120: where are these climatological data coming from?*

Information on the source of atmospheric input data will be added in the revised version: The coupled physical biogeochemical model is forced by climatological monthly mean data of 2m atmospheric air temperature, air pressure, dew point temperature, 10m zonal and meridional wind velocities, cloud cover and precipitation based on the the 40yr ECMWF Re-Analysis (ERA40) data (Uppala et al. 2005).

*page 1123, line 20: "exceeds"*

Will be corrected.

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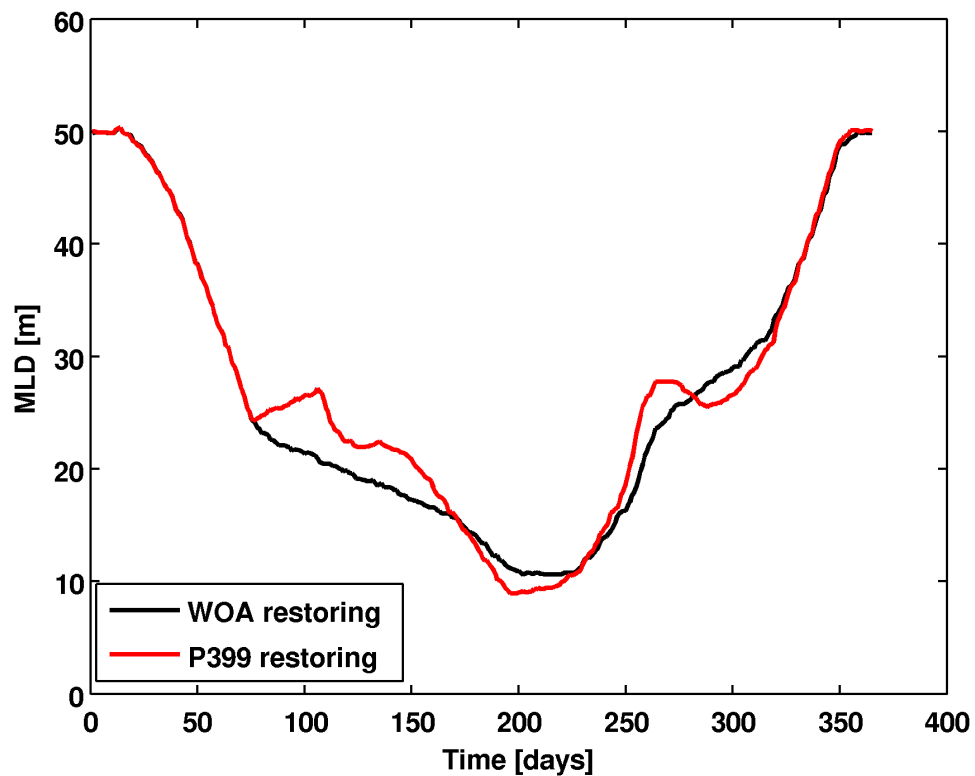
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**Fig. 1.** Mixed layer depth [m] when using WOA restoring (black) or data from P399/2 in April and June (red).

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