Reply to Referee #2

We thank referee#2 for his/her comments. Below you find the detailed answers (normal font) to the issues raised by the reviewer (typewriter). Added text blocks for the revised version of the manuscript are written in italics, citations of the original manuscript are enclosed in brackets [].

This paper describes the results of model simulations that are supposed to tell us about the factors controlling the production of CH3I in the global surface ocean. The authors are using a model they developed previously to assess the controls on the production of CH3I in the water column. They link that model to a global ocean circulation model to extrapolate to global ocean and then compare to a newly released dataset of CH3I in the surface water from a number of cruises around the globe. The idea is good, but I am not sure that we know enough to accomplish it.

I am not sure these results actually move our understanding of the cycling of CH3I in the surface ocean forward beyond what was determined in the earlier paper describing the water column model. Also, there is far too much reliance on what was in the earlier paper. While I understand this is meant to be a continuation of that work, this paper cannot be read on its own in its current form. I have some concerns that the results from the earlier paper are not strong enough to support the global extrapolation described here

Specifically, how is Opt 3 different from Opt 1 except in the scaling factors? The SLDOC is linked to PP, and PAR would promote PP in regions with enough nutrients leading to higher SLDOC. To me, this is still about PP. Also, dont you need UV, not PAR, to react with the SLDOC to produce CH3I? What is the chemical mechanism proposed here?

It is true that SLDOC is ultimately a product of primary production. However, one difference between Opt1 and Opt3 lies in the depth-dependence of methyl iodide production. In Opt1 methyl iodide is directly produced during primary production. Primary production (and thus CH3I production) occurs where sufficient light (PAR) and nutrients are available, e.g. in the oligothropic ocean below 40m depth and in equatorial upwelling regions at the surface. In Opt3 methyl iodide production is tight to the DOC concentration and UV light. The model does not use different input fields for light at different frequencies, but its vertical absorption characteristics are used to differentiate between PAR and UV. Therefore, in Opt3 (as dependent on UV) CH3I production is limited to the surface level (similar to UV decay), which is 12 m deep. Furthermore, DOC and phytoplankton (PP) have different life times, i.e. the temporal behavior of methyl iodide production is different in Opt1 compared to Opt3. For example, after a short bloom, when CH3I drops in Opt1, CH3I production continues in Opt3, because DOC persists (or even still increases due to a time lag caused by zooplankton grazing).

There are also some language issues that make the paper difficult to follow. I feel that major revision is necessary to allow publication of this paper.

We will improve the English language in the revised version of manuscript.

I am including only a few other specific issues below (in no particular order):

1) I find eyeballing maps of calculated CH3I distributions and comparing them to a cruise track difficult. How do the results compare on a point by point basis? Correlation plots would help here.

We agree with the reviewer, that comparison of Figure 1 (observational data) and the respective simulated mean concentrations is difficult. Point to point comparison, however, is provided in the Supplemental Information, where for each data point of the ship cruises the corresponding model simulated concentrations are shown. We think, that correlation maps are not ideal to compare the model results to observations, here. Due to the model's relatively coarse horizontal resolution very often several observational data points fall into one grid cell. For a correlation plot either these point data would have to be averaged or arbitrary data points need to be excluded from the analysis. Instead we are going to show a Box-Whisker plot for the Atlantic Ocean (see below), that aggregates data into 10 degree latitudinal boxes and allows for an easy comparison of all experiments with observations over a large region in one figure. For these plots all observations within a 10 degree latitudinal zone (or mean model results within 1 degree of the respective locations) are plotted as boxes with size characteristics obtained from the statistics of the data (model results). The width of each box is determined by the 25 % and 75 % percentiles, furthermore it shows the median of the data, and outliers, i.e. any data smaller or larger than 1.5 times the difference of the 75 % and 25 % percentile.

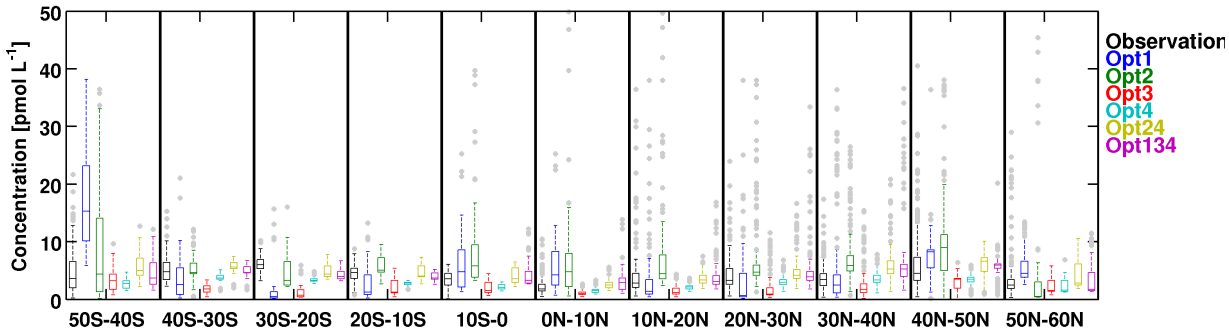

Figure 1: Box-Whisker plot of simulated and observed surface ocean CH3I concentrations [pmol L-1]. Box widths are determined by the 25% and 75% percentile of data within each 10 degree latitude box, outliers (gray) are located outside 1.5 times the differences of the percentiles, the middle line of each box shows the median. Simulated concentrations are averaged over 1 degree boxes around the location of observations.

In the revised version of the manuscript on P12L5ff this figure (there Fig.2) will be referred to:
[The simulated surface methyl iodide concentrations are compared with observations (Figs.1, *2,* 8, and S1-S25). Generally the model represents methyl iodide observations well (*Fig.2* and Supplemental Information Figs. S1-S25).]

`2) Figure 4. It looks like RDOC produces more CH3I than SLDOC. This doesnt make sense. Refractive DOC should be less reactive.`

The parametrization of the photochemical production of CH3I used does not intend to reflect reactivities of DOC. It rather uses large scale spatio-temporal characteristics of proxies (UV light, DOC) and a constant CH3I production rate to mimic the timing and location of CH3I production. The production rates used in the experiments are optimized to obtain best agreement with observed methyl iodide concentrations. The spatial inhomogeneity of DOC concentrations in Opt3 results in different amounts of CH3I produced depending on the focus region of the optimization. Therefore, it is not possible to conclude from the amount of methyl iodide produced in Opt3 vs. Opt4 on the assumed reactivity of DOC.

`3) Figures in general use the same color code for the opts in all figures. It is confusing in Figures 8, 9 and 10.`

We apologize for the confusion, in the revised version of the manuscript we will assure consistent color coding of the experiments.

`4) The statistics describing the comparison of model to observations is lacking.`

We agree with the reviewer that information on the statistics describing the comparison of simulated and observed surface concentrations is needed. To provide information on the sensitivity of simulated methyl iodide surface concentrations to the choice of production rates and (a)biotic variables we performed a set of additional experiments.
For each experiment that includes only one source process depending on a single production rate (ratio) (Opt1,Opt3,Opt4), we performed two additional experiments with the production rate (de-)increased by 10% (called Opt1,3,4m and Opt1,3,4p, where 'm' and 'p' stand for 'plus' and 'minus').
A fundamental assumption of the model is, that large scale features in the CH3I concentrations are unaffected by the interannual variability of environmental conditions, which allowed us to use the climatological OMIP (Ocean Model Intercomparison Project) forcing. To address the impact of different environmental conditions, we performed a model experiment in which the model is forced with NCEP reanalysis data in a transient experiment for the years 1959-1973 in contrast to the OMIP climatological forcing used in the previous experiments. Furthermore, this forcing is temporally higher resolved, as it includes a diurnal cycle based on 6h-ly values, in contrast to the daily mean data used in OMIP. Also here the 'standard' setup of rates used in HAMOCC (plankton grazing, mortality, growth) is used instead of the one presented in Stemmler et al. 2013. This introduces modifications of the relevant biogeochemical (e.g. phy, doc) and abiotic (radiation, temperature, wind speed) variables. Large scale features that are determined by characteristics of the physical model (circulation patterns and resulting limitations (e.g. nutrient trapping in the tropical Pacific) are unchanged as the identical model (MPIOM) was used to derive tracer advection and diffusion. This experiment includes only production of methyl iodide from photochemistry (Opt4), i.e. production depends only on incoming radiation, sinks (degradation and gas-exchange) depend on temperature and wind speed. We did not include biological production (Opt1) and photochemical production from SLDOC (Opt3) in the experiment, because analysis of the previous experiments already revealed that both of them show unrealistic gradients (from oligotrophic subtropical gyres towards more productive ocean regions). These features are inherent also in an NCEP simulation, as shaped by the large scale oceanic circulation (independent from forcing).

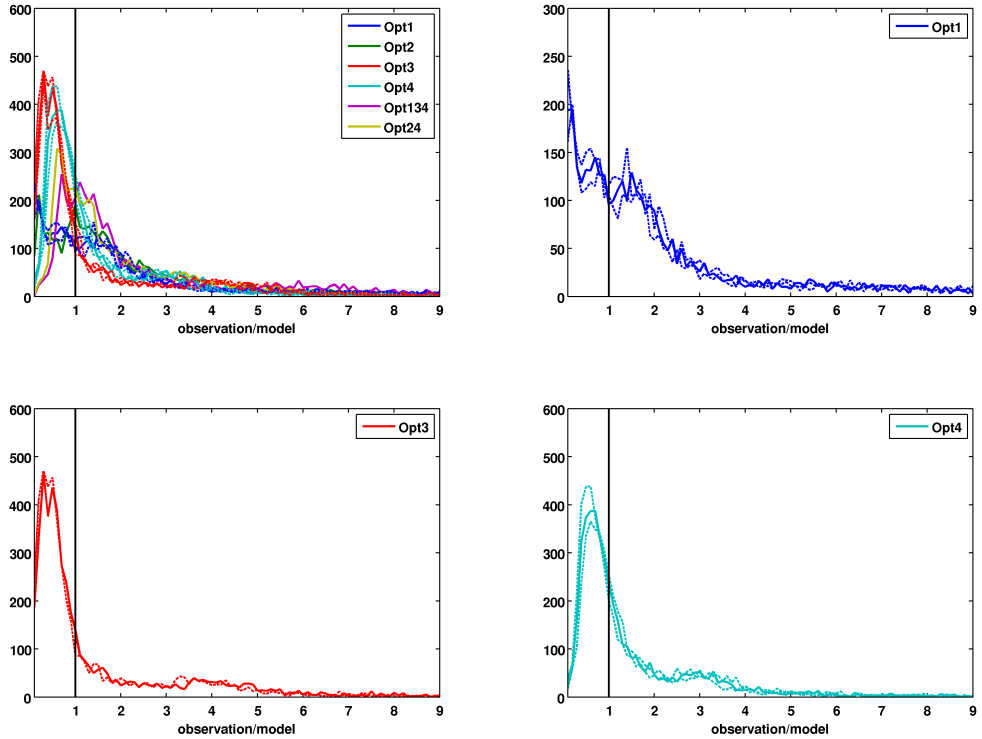

Figure 2: Histogram of the ratio between observed and simulated surface ocean methyl iodide concentrations (R=obs/model) for all original experiments and Opt{1,3,4}{p,m} (upper left), Opt1 and Opt1p & Opt1m (upper right), Opt3 & Opt3p & Opt3m (lower left), and Opt4 & Opt4p & Opt4m (lower right).

The spatial distribution is unaffected by the choice of input parameters (Fig 3&4), and differences among the experiments are larger than differences in the uncertainty experiments, i.e. when production rates are varied by 10 %(the p and m experiments (see Fig.3, 4)). Therefore, the shape of the PDF of the ratio observation/model is the same (Fig 2), which means the relative performance of the experiments is largely unaffected by the input parameters, as long as deviations from the optimum value are small (i.e. when production rates are e.g. 1000 times higher the performance will be lost even for the most successful experiment). Thus, the identification of Opt4 as the most successful experiment is robust and not by chance, though we can not give the exact measure of statistical significance, here. By using transient NCEP 6h-ly instead of a climatological daily mean OMIP forcing, and looking into individual years, we can assess the robustness of the model results towards driving variables (here radiation). Similar to the results of the p & m experiments

the spatial distribution and the PDF of the ratio observation/model do not change considerably (Fig.s 5,6). This again means the identification of Opt4 as the most successful experiment is robust. The reason for this is that the large scale features in the concentration distribution are more influenced by the choice of the source process rather than by the choice of the parameter values. More specifically, the experiment that are directly or indirectly driven by total primary production (Opt1, Opt3) are less successful because of the deviation arising from the spatial distribution patterns of primary production (low in subtropical gyres) and not from production ratios.

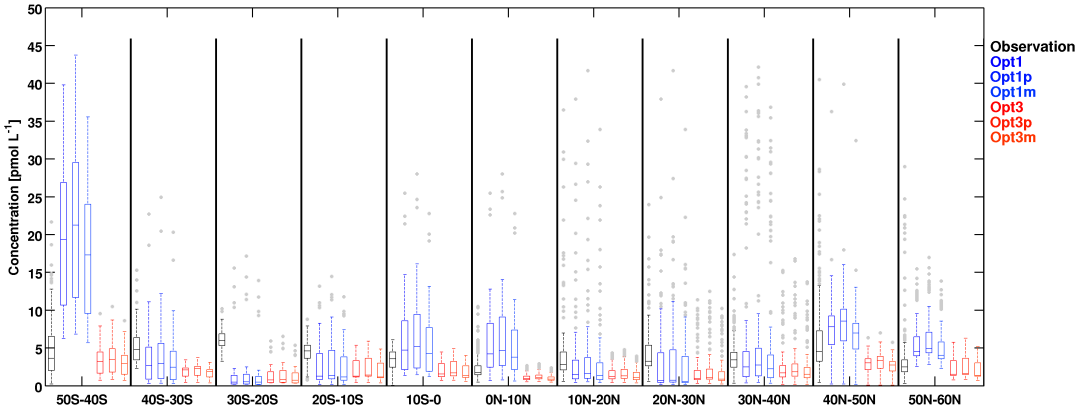

Figure 3: Box-Whisker plot of simulated and observed surface ocean CH3I concentrations [pmol L-1]. Box widths are determined by the 25% and 75% percentile of data within each 10 degree latitude box, outliers (gray) are located outside 1.5 times the differences of the percentiles, the middle line of each box shows the median. Simulated concentrations are averaged over 1 degree boxes around the location of observations.

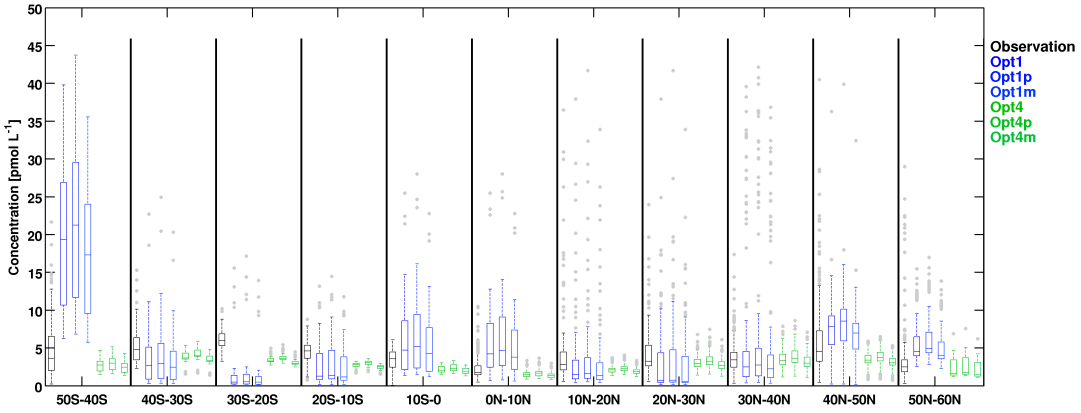

Figure 4: Box-Whisker plot of simulated and observed surface ocean CH3I concentrations [pmol L-1]. Box widths are determined by the 25% and 75% percentile of data within each 10 degree latitude box, outliers (gray) are located outside 1.5 times the differences of the percentiles, the middle line of each box shows the median. Simulated concentrations are averaged over 1 degree boxes around the location of observations.

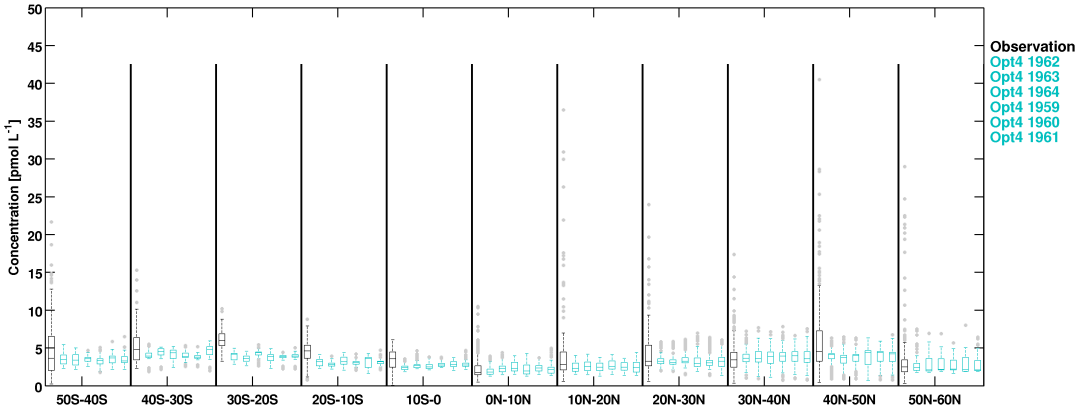

Figure 5: Box-Whisker plot of simulated and observed surface ocean CH3I concentrations [pmol L-1]. Box widths are determined by the 25% and 75% percentile of data within each 10 degree latitude box, outliers (gray) are located outside 1.5 times the differences of the percentiles, the middle line of each box shows the median. Simulated concentrations are averaged over 1 degree boxes around the location of observations.

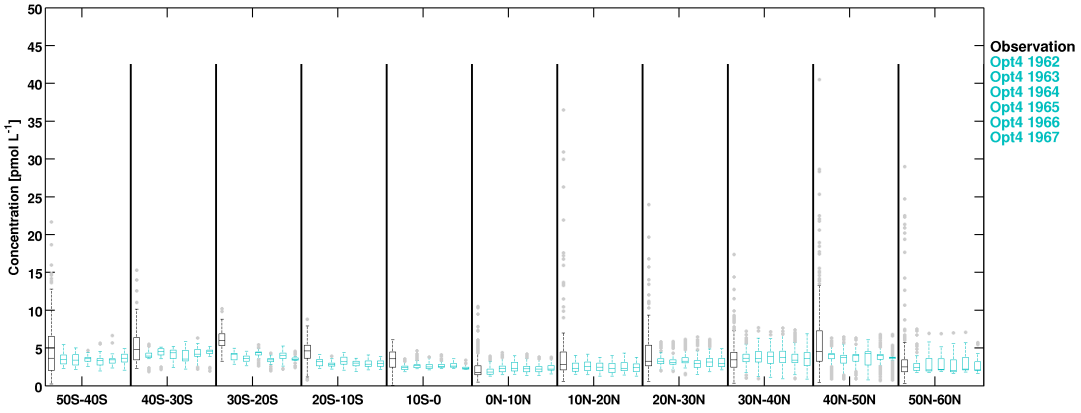

Figure 6: Box-Whisker plot of simulated and observed surface ocean CH3I concentrations [pmol L-1]. Box widths are determined by the 25% and 75% percentile of data within each 10 degree latitude box, outliers (gray) are located outside 1.5 times the differences of the percentiles, the middle line of each box shows the median. Simulated concentrations are averaged over 1 degree boxes around the location of observations.

We will add the following in the revised manuscript P16L11 (P1765L11):
[Opt3 furthermore underestimates observations more strongly than Opt4 and Opt2, indicated by the highest median ratio of observations and simulated concentration.] *A variation of the production ratios by 10% in Opt1, Opt3, Opt4 leads to the same spatial distribution (Fig 3,4) and the PDF (probability density function) of the ratio observation/model (Fig 2) is unchanged. This is also true when a different forcing (transient NCEP 6h data instead of climatological daily mean OMIP) is used in Opt4 (e.g Fig. 5). Thus, differences in the RMSD and the ranking (Tab 3) of the experiments are robust and driven by the spatial distribution of the concentrations rather than by the choice of production rates. In particular, Opt1 and Opt3 are least successful, because their spatial distribution is determined by primary production, which shows features that are not present in global patterns of observed methyl iodide. In contrast to model results, observations do not show low concentrations in oligotropic subtropical gyres and high concentrations in productive regions. But, one has to keep in mind, that halocarbon production rates are different for different phytoplankton species (Moore and Tokarczyk 1993, Hughes et al 2006, Smythe-Wright et al. 2006, Brownell et al 2010), hence community composition differences would lead to changes in the bulk CH3I production rate. This could lead to a different CH3I distribution pattern compared to bulk phytoplankton concentration. The inhomogeneity of the community composition and CH3I production rate implies that also chlorophyll-a may not be a good predictor of CH3I production (more on this in Section 3.2). The success of Opt4 over Opt3 shows that the representation of DOC indeed strongly influences the*

ability of the model to reproduce observed concentrations when considering photochemical production alone. Where Opt3 shows minima due to low DOC, Opt4 shows maxima due to high insolation. These differences are higher than differences that arise from variable insolation (i.e Opt4 with OMIP forcing compared to Opt4 with diurnal NCEP forcing in different years). In reality, most likely biological and photochemical production occur at the same time. In [the next step we consider the hypothesis ..] (P16 L12, i.e. P17565L12)

`5) As someone who has made measurements and used models, I dont fault data for lack of agreement to a model. I fault the model and an incomplete understanding of the processes being modeled.`

We agree with the reviewer that discrepancies between model results and observations arise from oversimplification or false implementation of processes in the model. However, we were not aware of and did not intent to fault the observational data by the phrasing we chose in the manuscript.

The reviewer does not point to the sentence where we used ambiguous phrasing. She/he might refer to:
[For the Atlantic some information on the seasonal cycle of CH3I concentrations is available from Wang et al.(2009). They find maxima in summer in the North East Atlantic south of Greenland (compare Figs. S21-S23). The model experiments Opt1 and Opt2 show maxima in spring, only the experiments that are dominated by photochemical production show maxima in summer, with a similar magnitude in and difference between the seasons as in the observations.]

Here we list first what observations tell us about the seasonal cycle and what different model experiments show. We do not include any conclusion here, but only state that it is only the photochemical experiments that are able to reproduce the observed seasonality. We do not indicate any fault in the data. In contrast the obvious conclusion from this statement is, that the experiments with photochemical methyl iodide production are more realistic than with biological production if temporal variability is considered.

References

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Moore, R. and Tokarczyk, R.: Volatile biogenic halocarbons in the northwest Atlantic, Glob. Biogeochem. Cyc., 7, 195–210, 1993.

Smythe-Wright, D., Boswell, S., Breithaupt, P., Davidson, R., Dimmer, C., and Eiras Diaz, L.: Methyl iodide production in the ocean: Implications for climate change, Global Biogeochem. Cy., 20, GB3003, doi:10.1029/2005GB002642, 2006.

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