

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

Received and published: 6 May 2013

We are very grateful to Christoph Völker for his thoughtful comments. Below you will find our response (normal font) to the remarks (italic) and the suggested changes to the manuscript for a revised version.

General comments

The paper by Iris Stemmler et al. presents a one-dimensional model study on the production of methyl iodide in the ocean. CH_3I is a halogen compound that plays an important role in atmospheric chemistry. It is not known, however, whether the main production pathways in the ocean are more from direct production by phytoplankton, or from photochemical degradation of coloured dissolved organic matter. Stemmler

C1563

et al. approach this question by performing a number of different model runs using different literature-based assumptions on the generation of CH_3I , and comparing the results to ship-based profiles of CH_3I measured recently in the North East Atlantic. This approach then allows to assess which assumptions on the generation of CH_3I are compatible with the existing data and which are not, at least as long as the different source processes are themselves described correctly in the model. The central result I learned from the manuscript is that neither inherent biological production by phytoplankton nor photochemical production can be excluded given the model results, but that a production by phytoplankton only under stress is unlikely because it leads to a strong maximum of CH_3I near the surface while the observations show rather a subsurface maximum. I think this is an interesting result and in principle warrants publication of the manuscript in Biogeosciences.

Nevertheless I have some reservations remaining about the results: I find that the authors do not show clearly enough that the model describes the source and sink processes with enough confidence, so that a mismatch between model and data can be interpreted. There are several aspects to this:

Firstly, the model contains a term that describes a photochemical destruction of CH_3I , and this term is assumed to be proportional to UV radiation (it is never mentioned in which wave length band, neither is the attenuation constant given), based on results in the atmosphere. I would consider this a not so well known process. Unlike for the production terms, however, the authors have not performed sensitivity studies with respect this process, e.g. by varying k_{UV} or the attenuation constant a_{UV} (which is effectively assuming a different wavelength-dependent quantum yield). Here a small set of additional sensitivity studies could help.

Photolysis rates of CH_3I have been determined over the wavelength range 235–400

C1564

nm by Rattigan et al, 1997. An attenuation coefficient of 0.33 m^{-1} was adopted here. This value will be added to the revised manuscript. Photolysis is only effective in the uppermost model level, i.e. any variation of the attenuation coefficient would affect “only” the surface concentrations of CH_3I . The subsurface concentrations, however, would hardly be influenced since only slightly more degradation would occur. Generally, the CH_3I photolysis is much slower than losses through Cl substitution (Zika & Gidel, 1984). Modelled residence times (τ =inventory/sink) with regard to chlorine substitution and photolysis are ≈ 23 d and ≈ 536 d, respectively. As UV decay is only a minor sink for CH_3I in subsurface seawater, we believe that sensitivity studies on the impact of the attenuation coefficient on the decay rate are not needed.

Secondly I find, as the other reviewer, the evaluation of the biological state of the model (on p 1131) a bit weak. What is the vertically integrated net primary production and the vertical carbon flux in the model, and are there in-situ values to compare with?

Our main goal is to explain the vertical distribution patterns of methyl iodide and identify source and sink processes. Since CH_3I might be produced as a byproduct during photosynthesis, we agree that the model should reflect observed primary production rates. Unfortunately, there is no information about this quantity available for the cruise P399/2. However, previous measurements in this region show values in the range between 0.3 to $2.6\text{ g C d}^{-1}\text{ m}^{-2}$ (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 $1.4\text{ g C d}^{-1}\text{ m}^{-2}$. Thus, our model matches previously observed values well. In addition, the relatively good agreement between simulated and observed concentrations of phytoplankton indicate that our biogeochemical model provides reasonable results. HAMOCC has been designed and evaluated to fit well global export production, pCO₂, and nutrient distributions (e.g. Six and Maier-Reimer. 1996, Ilyina et al. 2013). Since the nutrient concentrations are well

C1565

reflected by the model (see Figure A2d, e) we are confident that export production is in the right order of magnitude.

Could you perhaps use satellite Chl and NPP data to compare with, too? If the model predicted biomass is off this would project onto the production rate of CH_3I as well.

Of course any model deficiency with regard to reproducing biological conditions during the cruise will cascade into the production rate and consequently the predicted CH_3I concentrations. There are in-situ chlorophyll-a data available from the Poseidon cruise P399/2, hence there is no need for using satellite-derived chlorophyll data. In appendix A1 of the manuscript we compared the modelled phytoplankton biomass with the in-situ observations of pigment concentrations. As chlorophyll-a is not a prognostic variable of the model chlorophyll was converted into phytoplankton biomass for the model evaluation. This was done by using a depth dependent C:Chl-ratio and assuming a P:C ratio of 1:106. The C:Chl-ratio was calculated as described in Hense and Beckmann (2008) using modelled radiation profiles, as these were not measured during the cruise. To clarify what was done and the corresponding consequences for CH_3I , appendix A and the discussion of modelled CH_3I concentrations will be refined in the revised version of the manuscript.

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 maximum during the cruise, however, can not be unambiguously assessed, as phytoplankton concentration in model units has to be diagnosed from an empirically

C1566

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.

I think this mainly needs some evaluation and validation of the model runs, although the authors might also consider re-running the model not with monthly climatological forcing, but with daily or 6-hourly reanalysis data; this might improve the match of the physical and biological model.

We tested whether an atmospheric forcing with higher temporal resolution would lead to a considerable model improvement by using daily mean NCEP reanalysis data for the u and v wind components, air pressure and temperature at 2m, dew point temperature and cloud cover instead of the previously used monthly mean data. Minor changes in the temperature and salinity profiles as expected (due to the restoring) appear only in the surface layers and do not lead to any clear model improvement (Fig.1, below).

Of course also model predicted CH_3I concentrations and fluxes are affected by the choice of the atmospheric forcing. The impact of daily mean versus monthly mean forcing on features of the CH_3I distribution was tested for Opt1, the experiment that considers biological production of methyl iodide at a constant rate. In particular the gas flux to the atmosphere shows additional high frequency variability following the one of the wind-speed-dependent gas transfer velocity (Fig.2, below). Furthermore, the absolute values of the gas exchange are modified in consequence of a changed saturation anomaly, which in turn is different due to modified sea surface temperatures. All these changes are minor and they do not impact the conclusions drawn in the

C1567

manuscript. Therefore we will not rerun all model experiments for the revised version of the manuscript. However, we will discuss the effect of short-term variability and possible deficiencies in the forcing fields in the revised version.

Thirdly, the ecosystem model used is relatively simple and does not include prochlorococcus (mentioned by the authors as the probable main producer of CH_3I) as a separate model variable. This is okay as long as the authors acknowledge this as a possible caveat and discuss whether this might contribute to model-data differences. Specifically, it is known that there are different groups of prochlorococcus that are adapted to different light regimes. As the focus of the paper is on producing the subsurface peak in CH_3I , this may be important. Perhaps the authors might have a look into the paper by Salihoglu and Hoffmann (2007), J. Marine Res. 65, 219-273 that discuss a model including an explicit description of different prochlorococcus and synechococcus subtypes.

We agree and seized this suggestion. In the revised version, we will discuss in more detail the pros and cons of omitting *Prochlorococcus* as a separate model variable:

The ecosystem model used is rather simple and biological production of methyl iodide is described to be coupled to primary production of the bulk phytoplankton. Since *Prochlorococcus* is assumed to be the main producer of methyl iodide an explicit description of this phytoplankton group in the model might improve the overall representation of phytoplankton biomass and methyl iodide concentration. Since different ecotypes of *Prochlorococcus* exist (e.g. Johnson et al. 2006), we can not exclude that depth-dependent niche separation might also affect methyl iodide production and vertical distribution patterns of CH_3I concentrations. However, since our simulated subsurface CH_3I concentrations are in the same order of magnitude compared to observations, we refrain from adding more complexity to the model system.

C1568

Generally the manuscript is well written but could be somewhat more to the point sometimes. The discussion is still weak and does not discuss possible caveats enough.

In the revised manuscript version the discussion will be extended with respect to the models' performance. In particular, the models' ability to reproduce observed chl-a concentrations, the consequences and relevance of not implementing a prognostic picocyanobacteria tracer, the impact of monthly mean vs daily mean atmospheric forcing, the consideration of radiation with different absorption characteristics in production/loss of CH_3I and the possible role of horizontal advection will be highlighted.

I recommend publication after revision as indicated above. Minor comments follow below.

Specific comments

p 1113, line 16: Was that an atmospheric global chemistry-transport model?

Yes, this was a global atmospheric CTM coupled to a mixed layer ocean model. 'atmospheric' will be added to the sentence:

Based on a very limited data set, best agreement between observations and model results from global atmospheric chemistry-transport model (Bell et al., 2002) have been obtained when considering only a photochemical source instead of biological production.

p 1113, line 25: 'observations'; you mean in the ocean here, don't you?

C1569

Yes, this will be added:

We compare simulated concentrations of CH_3I with observations in seawater in order to assess distribution and strength of natural CH_3I sources in the ocean.

p 1114, line 1012:

why mention that GOTM can use very different parameterizations of turbulent transport, but not which one you are using?

We agree and add the details in the revised version:

We use a so-called two equation model in which the turbulent kinetic energy (TKE) and the length scale of turbulence (l) are calculated from differential transport equations. They are described by a $k-\varepsilon$ type equation for TKE and a dynamic dissipation rate model for l (details in Umlauf et al. 2005). In line with Hense & Quack 2009 a minimum value of $10^{-5} \text{ m}^2 \text{ s}^{-2}$ for TKE is prescribed to parameterise the effects of double diffusion in the Cape Verde region.

p 1114, line 14: Which version of HAMOCC are you using? Are the standard parameter values for the model taken from one of the cited publications?

We are using HAMOCC5.2, which was also used within the MPI-ESM in the CMIP5 experiments. Parameters of the 'default setup' are equal to the ones listed in Tab2. of Ilyina et al. 2013. But, in that article only the phytoplankton mortality rate in the euphotic zone is mentioned (which is identical and unchanged, here), despite the one in the deep ocean being different from the above value and identical to the value listed

C1570

in Tab.1 here. A reference to the model version will be added:

Phytoplankton dynamics are simulated using a single column implementation of HAMOCC5.2 (Ilyina et al, 2013, Six and MaierReimer, 1996; Wetzel et al., 2006).

Tab1: Parameter setup of the NPZD model, default HAMOCC values (Ilyina et al 2013) and new values after tuning to fit observations close to Cape Verde.

p 1115, line 2: $\partial/\partial t(A_v \partial c/\partial z)$; the first derivative need to be with respect to z, not t.

This will be corrected in the revised version.

p 1115, line 1011: Are there indications that the production rate is linear in PAR and in DOC? Also, the unit for k_{photo} is such that the formula should rather be written as linear in DOP, not DOC. Implicitly it assumed here that DOC has a redfield-like composition, isn't it? This is very likely not the case, so it might make more sense to write the equation in DOC and to convert the unit of k_{photo} accordingly.

We agree that this formulation might be indeed misleading and have thus chosen to use a consistent description for the photochemical production, i.e. the units are given in phosphorous units. This is the models' internal 'currency' for organic matter. The exact functional dependence of light intensity and CH_3I production or DOC concentration has not been studied yet. Choosing a linear approach in this regard is the simplest assumption and was therefore adopted here.

p 1115, line 1415: This formulation sounds as if the model includes terrestrial produc-

C1571

tion of DOC, which I believe not to be the case.

This part will be rephrased (see below the next comment for details).

p 1116, line 2: It might be necessary to check whether the constancy of refractory DOC near the surface is still the state of knowledge. Perhaps check the overview paper by Hansell et al. (2009), Oceanography 22, pp. 202211.

Thank you for this hint, we are aware of this article. Hansell et al. 2009 show that the surface concentration of total DOC is inhomogeneous in particular due to accumulation of semi-labile (lifetime 3-10 years) DOC in the subtropical gyres. It is not easy to conclude about the refractory DOC from the figures shown in the article. The paragraph on the RDOC experiments will be modified. We still believe that our experimental setup is feasible:

We chose an experimental setup that includes the semi-labile DOC from HAMOCC and a constant DOC pool for the following reasons:

According to Moore & Zafirov 1994 photochemical production of CH_3I most likely occurs via radical recombination of CH_3 and I, whereby the methyl radicals may originate from photolysis of humic material. Incubation experiments with filtered seawater show production of methyl iodide when the samples were irradiated (e.g. Happel & Wallace 1996, Richter & Wallace 2004). But, speciation of dissolved carbon from these experiments is not available. From this information, it seems reasonable to build a parameterisation of the photochemical production pathway on radiation and dissolved organic carbon (DOC). In nature, there are numerous bioavailable and refractory dissolved organic carbon species with different characteristics. HAMOCC

C1572

only considers one DOC pool that has a life time of a couple of months. Thus, we decided to set up one additional experiment that does not use HAMOCC's description of DOC. As we can not implement a prognostic DOC tracer that has a long life time, as it would be strongly influenced by advective processes, which are impossible to resolve in a 1D water column model, we decided to compare the HAMOCC SLDOC to a constant DOC pool. We call it refractory here, as long life times would most likely result in an almost uniform distribution of DOC. In fact, the experiment just reflects an unlimited source of DOC. The result show, that these two experiments are sufficient, as the vertical profile of CH_3I is only sensitive to light availability and insensitive to changes in the DOC concentration. The meaning of the two experiments will be made more clear in the revised version:

In the second group of experiments the DOC concentration is set to a constant value of $40 \mu\text{mol C kg}^{-1}$. This mimics an unlimited supply of DOC and enables us to assess whether the spatiotemporal 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 vertical distribution in the ocean.

p 1116, line 16: Does inclusion of the respiration rate give more reliable results? I would think it is probably unimportant compared to the error in the calculation of the growth rate, and thus can be omitted.

Of course, the consideration of respiration will hardly affect the model results. However, there is a significant *conceptual* difference between the measured *net production* rates and the *gross production* rates needed as a model input parameter; this cannot be ignored in our opinion.

C1573

*p 1117, line 78: does it make sense to give the production rate to four digits of accuracy?
Probably at most the first two are significant.*

We agree; this will be adjusted in the revised version.

p 1118, line 1417: chloride concentration in seawater is linearly proportional to salinity to a very high precision. Why do you use a constant value instead of having it vary with S? Probably the effect is negligible.

The effect would be minor indeed. Changes in this degradation pathway are stronger influenced by temperature changes than through changes in chloride concentration. As one can see from Fig1 below (or Fig A1 in the manuscript) an increase of the salinity from 35 (at $\approx 700\text{m}$) to 36 psu ($\approx 200\text{m}$) is accompanied by a temperature increase of approx. 10K (from $\approx 10^\circ\text{C}$ to $\approx 20^\circ\text{C}$). The decay rate will be 5 times higher in the warm water levels due to temperature effects and only 3% higher due to salinity changes:

$$S_{cl} = k_{cl}(T) * C_{cl} * C_{CH_3I}$$

$$k_{cl}(T) = A \exp(-B/T), A = 7.78e13, B = 13158$$

salinity effect (linear): $36/35=1.03$

temperature effect ($B=13158$): $\exp(-B/295)/\exp(-B/285)= 4.99$

p 1119, line 35: I do not understand why photolysis is prescribed as proportional to UV, while the photoproduction is proportional to PAR. Probably for both processes the

C1574

maximum quantum yield is in the UV spectral range, but UV is attenuated much more strongly. Can you give arguments why one process is better described through PAR, and the other through UV? Which spectral band of UV, anyhow?

Photolysis of CH_3I has been shown to occur at wavelengths of 235-400 nm (Rattigan et al, 1997) and is hence implemented dependent on UV light (see above).

In contrast, the photochemical production pathway is not fully understood yet. Wang et al. 2009 found positive correlations of CH_3I concentrations with both PAR and UV light at 325 nm, Moore & Zafirov 1994 found methyl iodide production in laboratory studies when using light with a spectral distribution close to sunlight over the wavelength 280-1100 nm. Richter & Wallace, 2004 tested CH_3I production under different light conditions to study the qualitative effect of UV light on production. They found no significant differences in CH_3I production between the experiment with the full spectrum of light compared to the ones with reduced UV light. But, their experiments do not resolve the impact of vertical light transfer in water to vertical distributions of CH_3I . In surface waters the light intensity might not change much when dimming certain wavelength bands, but the difference will be large below e.g. 30m, to where UV light does not penetrate. Thus, the experiments show that photochemical production takes place under PAR light conditions. Nevertheless, additional experiments including the two proxies for methyl radicals (i.e. Opt3/Opt3) were performed, which use the same radiation attenuation (reflecting UV light) for production that is used in the photolytical decay of CH_3I . The parameter optimization was also repeated for these two experiments. The finding, that biological production reproduces observed concentration profiles best remains unchanged when comparing to those experiments with Opt1-4, Opt123. But, it turns out that the strong light absorption in the surface layers in the additional experiments inhibits the evolution of a subsurface CH_3I concentration maximum (see Fig.3& Fig4 below). Since there is no clear indication for a UV induced

C1575

photochemical production pathway we refrain from show the additional results in the revised version. We will, however, briefly mention that such a consideration will not improve the model results.

Following modifications are suggested for the revised version of the manuscript:

Discussion:

When produced via the photochemical production pathway simulated methyl iodide concentrations were found to be sensitive to the absorption properties of light. A subsurface maximum is only simulated during times of a shallow mixed layer and when using light that is penetrating deep enough to allow for production below the mixed layer. UV light gets absorbed readily in the water column, whereas other wavelength show significant intensities down to approx. 100m (e.g. PAR).

Richter & Wallace, 2004 tested CH_3I production under different light conditions to study the qualitative effect of UV light on production. They found no significant differences in CH_3I production between the experiment with the full spectrum of light compared to the ones with reduced UV light.

Conclusion:

The coupled biogeochemical water column model that includes a methyl iodide compartment is able to reproduce observed subsurface maxima of CH_3I concentrations. However, our model results are not unequivocal. Subsurface maxima can occur due to direct biological and photochemical production. But, for the photochemical production pathway subsurface maxima strongly depend on the chosen light properties. Subsurface maxima occur only if significant production occurs also below the mixed layer, which does not happen for UV light. Furthermore, the gradient, i.e. the difference between surface and subsurface methyl iodide concentration is, however, best reproduced if direct biological production is taken into account.

C1576

p 1119, line 14: Is the atmospheric concentration of methyl iodide roughly constant over a seasonal cycle (or very low)?

No, atmospheric concentrations were shown to vary seasonally but the variations are rather small (compared to the ones of seawater concentrations) with values between 1 and 2 ppt (Butler et al. 2007, O'Brien et al. 2009, Fuhlbrügge et al. 2012, see also our comment to Referee No.1).

p 1120, line 910: This is a very general statement. Is it needed? p 1120, line 13: If I got it right, GOTM assumes that the lower model boundary is at the sea floor and calculates a bottom boundary layer. Could this influence values in the mixed layer? Probably not, but check!

This will not affect the results; these differences are negligible.

p 1120, line 1820: Why do you use monthly values? Why a climatology and not a reanalysis? That might make the comparison to the in-situ profiles better.

First of all, we would like to point out that the agreement between model and observations is not too bad. The WOCE data set is the most comprehensive data set and there is no reason why data extracted for the Cape Verde region are error-prone. In addition, the use of climatological data is consistent with the use of climatological atmospheric data (we are generally more interested in understanding possible production mechanisms of CH_3I and not in reproducing a certain observed snapshot). Nevertheless, we also tried to use reanalysis data (i.e. NCEP global ocean data assimilation system (GODAS) (<http://www.esrl.noaa.gov/psd/data/gridded/data.godas.html>), Behringer, 2004) in 2010), but this has not led to an improvement of the model results, as the reanalysis data are even more different from the P399/2 data. Using measured

C1577

values from P399/2 in June, April as a replacement to the climatological values of course improves the model's performance in those months (Fig5) and also alters the predicted MLD (Fig6). But, it is inconsistent, as no data for other month are available and in-situ data are treated as monthly means. Therefore, we decided to keep on using the climatological data.

p 1121, line 1927: To me it is not obvious in which parameter space the optimization searches. It is also not clear to me why you present the cases with fixed (i.e. not optimized) parameter values at all, if you later also have a set of model runs with respect to the same parameter and could just present the best one.

E1 & E2 include production rates that were derived from lab studies. Only after testing them and realizing that none of these parameters are suitable, a parameter optimization is performed. The optimization searches in different parameter spaces depending on the experiment. It is either a single parameter that is varied until the optimum is found (Opt1-4) or it is a parameter space spanned up by the different production rates ($k_{photo_{Rdoc}}$, $k_{photo_{sldoc}}$, k_{PP}) in Opt123.

p 1122, line 2122: Why do you mention station 311 at all, if you later argue that you cannot model it because of strong upwelling?

We totally agree and omit this figure.

p 1131, line 1014: If that is the cause of the greatest mismatch, then why did you not use reanalysis data instead of a climatology?

C1578

Please see, our comment above. We will add in the discussion the role of horizontal advection.

p 1131, line 2022: If you use an empirical C:Chl-ratio to convert Chl observations to C biomass, why is it impossible to do the same in the other direction?

We are not sure if we understand this comment. Whether chlorophyll is converted into the model unit (here phosphorus) or vice versa we convert the simulated phytoplankton concentrations in chlorophyll will not change the results and conclusions.

p 1132, line 68: should that not be mentioned early in the main text? Table 1: 'Grazing rate' should be 'maximum grazing rate'. The 'phytoplankton half saturation rate' is not a rate. Also it would be good to mention for which process it is the halfsaturation constant. Nutrient uptake?

Corrected.

Table 2: It would make it simpler to grasp the differences between the different experiments if the parameters that are not applicable for a specific experiment were indicated by a dash instead a zero.

This will be done in the revised version.

Figure A2: Showing phytoplankton biomass in phosphorous units is somewhat uncommon and makes it hard to quickly grasp an order of magnitude. Would it not be better to show carbon units, or perhaps even Chl units (which is probably what the data werein, originally)?

C1579

In principle we prefer to be consistent and show all results in model units, but we agree that for phytoplankton we should additionally show the concentrations in chlorophyll units (see Fig.7).

Technical corrections

p 1123, line 21: comma after Opt3 can be deleted

p 1128, line 13: order of magnitude of -6? probably 10^{-6}

p 1128, line 23: Syneococcus ! Synechococcus

p 1128, line 28: Erros ! Errors

p 1130, line 2: 'the strength OF modelled sea-air fluxes'

p 1132, line 8: 'will not be' should be 'are not'

Thank you, all these issues will be corrected in the revised version.

References:

Bell, N., Hsu, L., Jacob, D., Schultz, M., Blake, D., Butler, J., King, D., Lobert, J., and MaierReimer, E. (2002): Methyl iodide: atmospheric budget and use as a tracer of marine convection in global models, J. Geophys. Res., 107, 4340, doi:10.1029/2001JD001151.

Behringer, D.W., and Y. Xue (2004): Evaluation of the global ocean data assimilation system at NCEP: The Pacific Ocean. Eighth Symposium on Integrated Observing and Assimilation Systems for Atmosphere, Oceans, and Land Surface, AMS 84th Annual Meeting, Washington State Convention and Trade Center, Seattle, Washington, 1115.

C1580

Butler, J. H., D. B. King, J. M. Lobert, S. A. Montzka, S. A. Yvon-Lewis, B. D. Hall, N. J. Warwick, D. J. Mondeel, M. Aydin, and J. W. Elkins (2007): Oceanic distributions and emissions of short-lived halocarbons, *Global Biogeochem. Cycles*, 21, GB1023, doi:10.1029/2006GB002732.

Fuhlbrügge, S., Krüger, K., Quack, B., Atlas, E., Hepach, H. and Ziska, F. (2012): Impact of the marine atmospheric boundary layer on VSLS abundances in the eastern tropical and subtropical North Atlantic Ocean, *Atmos. Chem. Phys. Discuss.*, 12, 31205-31245.

Happell, J. and Wallace, D. (1996): Methyl iodide in the Greenland/Norwegian Seas and the tropical Atlantic Ocean: evidence for photochemical production, *Geophys. Res. Lett.*, 23, 2105-2108.

Hense, I. and Beckmann, A. (2008): Revisiting subsurface chlorophyll and phytoplankton distributions, *Deep-Sea Res. Pt. I*, 55, 1193-1199, doi:10.1016/j.dsr.2008.04.009.

Ilyina, T., K. D. Six, J. Segschneider, E. Maier-Reimer, H. Li, I. Núñez-Riboni (2013): The global ocean biogeochemistry model HAMOCC: Model architecture and performance as component of the MPLeaRth system model in different CMIP5 experimental realizations, accepted for publication in *JAMES*, doi:10.1002/jame.20017.

Johnson, Z. I., Zinser, E. R., Coe, A., McNulty, N. P., Woodward, E. M. S., Chisholm, S. W. (2006): Niche partitioning among *Prochlorococcus* ecotypes along oceanscale environmental gradients. *Science*, 311, 1737-1740.

C1581

Moore, R. M. and Zafirou, O. C. (1994): Photochemical production of methyl iodide in seawater, *J. Geophys. Res.*, 99, 16,415-16,420.

Morel, A. Antoine, D., Babin, M., Dandonneau, Y. (1996): Measured and modeled primary production in the northeast Atlantic (EUMELI JGOFS program): the impact of natural variations in photosynthetic parameters on model predictive skill, *Deep-Sea Res. I*, 43, 1273-1304.

O'Brien, L. M., Harris, N. R. P., Robinson, A. D., Gostlow, B., Warwick, N., Yang, X. and J. A. Pyle (2009): Bromocarbons in the tropical marine boundary layer at the Cape Verde Observatory - measurements and modelling, *Atmos. Chem. Phys.*, 9, 9083-9099.

Rattigan, O., Shallcross, D., and Cox, R. (1997): UV absorption crosssections and atmospheric photolysis rates of CF_3I , CH_3I , C_2H_5I and CH_2ICl , *J. Chem. Soc. Faraday T.*, 93, 2839-2846.

Richter, U. and Wallace, D. (2004): Production of methyl iodide in the tropical Atlantic Ocean, *Geophys. Res. Lett.*, 31, 1-4.

Six, K. and Maier-Reimer, E. (1996): Effects of plankton dynamics on seasonal carbon fluxes in an ocean general circulation model, *Global Biogeochem. Cy.*, 10, 559-583.

Umlauf, L., Burchard, H., and Bolding, K. (2005): GOTM – scientific documentation: version 3.2, *Mar. Sci. Rep.*, 63, 1-3.

C1582

Wang, L., Moore, R., and Cullen, J. (2009): Methyl iodide in the NW Atlantic: spatial and seasonal variation, *J. Geophys. Res.Oceans*, 114, C07007, doi:10.1029/2007JC004626.

Zika, R.G., and Gidel, L.T. (1984): A comparison of photolysis and substitution decomposition rates of methyl iodide in the ocean, *Geophys. Res. Lett.* 11 (4), 353-356.

Figure captions:

Fig.1: Salinity [psu] (a,b) and temperature [°C] (c,d) profiles in April (a, c) and June (b, d), model predicted (solid lines, black-high frequency forcing, green- low frequency forcing) and observations (red markers P399 cruise data, blue markers WOA data).

Fig.2: Methyl iodide sea-air flux [$pmol\ m^{-2}\ h^{-1}$], wind speed [$m\ s^{-1}$], sea surface temperature [°C], CH_3I water and air concentration equilibrium ($c_w - c_a/H$, [$pmol\ L^{-1}$]), and gas transfer velocity [$cm\ h^{-1}$] using monthly mean atmospheric forcing (lf, blue/black) and daily mean forcing (hf, red).

Fig.3: Methyl iodide concentrations [$pmol\ L^{-1}$], production [$pmol\ L^{-1}\ h^{-1}$], degradation [$pmol\ L^{-1}\ h^{-1}$], gas exchange [$pmol\ m^{-2}\ h^{-1}$] for the photochemical production pathways using UV or PAR.

Fig.4: Methyl iodide concentration profiles [$pmol\ L^{-1}$] from stations TENATSO and St.308 in the Cape Verde region. Observed data were collected during Poseidon cruise P399/2 in 2010. For the Tenatso station only data from the upper 350m of the water column are shown.

C1583

Fig.5: Salinity [psu] (a,b) and temperature [°C] (c,d) profiles in April (a, c) and June (b, d), model predicted (solid lines, black-high frequency forcing, green- low frequency forcing) and observations (red markers P399 cruise data, blue markers WOA data).

Fig.6: Mixed layer depth [m] when using WOA restoring (black) or data from P399 in April and June (red).

Fig.7: Phytoplankton (a,b) and nutrient (c,d) concentrations in April (a,c) and June (b,d) [$ng\ Chla\ L^{-1}$], model predicted (black solid lines new and dashed lines default parameter setup) and observed (red markers) profiles. Observations were taken from the Poseidon Cruise P399 in 2010. For model data the chlorophyll content has been diagnosed using a vertically dependent C:Chl-ratio (e.g., Hense and Beckmann, 2008) and the Redfield ratio for conversion from phosphorous to carbon.

Interactive comment on Biogeosciences Discuss., 10, 1111, 2013.

C1584

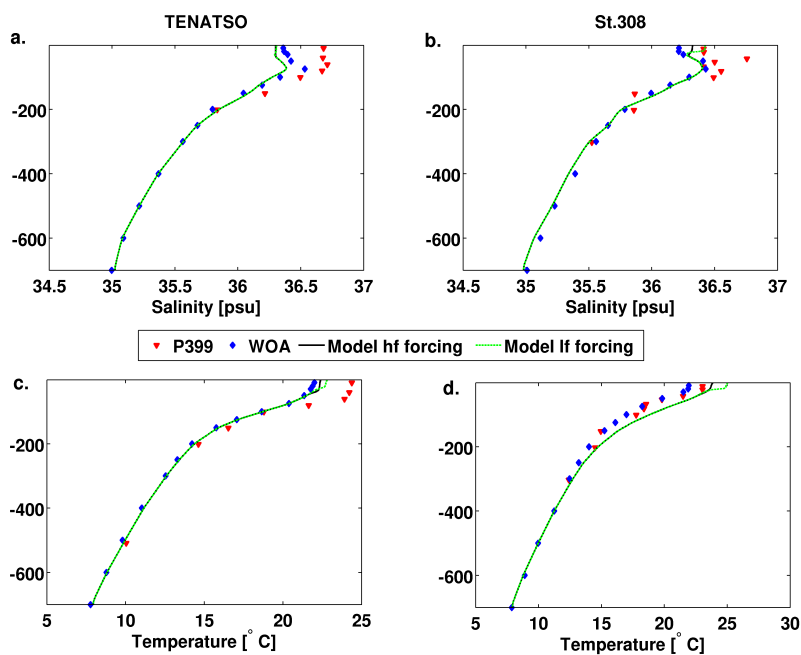


Fig. 1. Salinity [psu] (a,b) and temperature [C] (c,d) profiles in April (a, c) and June (b, d), model predicted (solid lines, black-high frequency forcing, green- low frequency forcing) and observations (red)

C1585

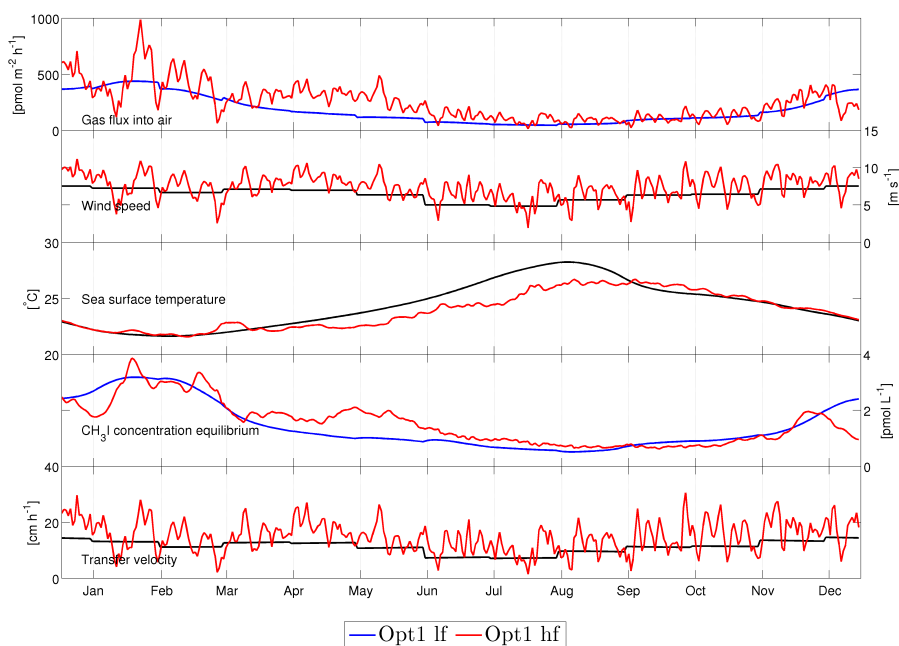


Fig. 2. Methyl iodide sea-air flux [$\text{pmol m}^{-2} \text{h}^{-1}$], wind speed [m s^{-1}], sea surface temperature [C], CH_3I water and air concentration equilibrium ($c_w - c_a$, [pmol L^{-1}]), and gas trans

C1586

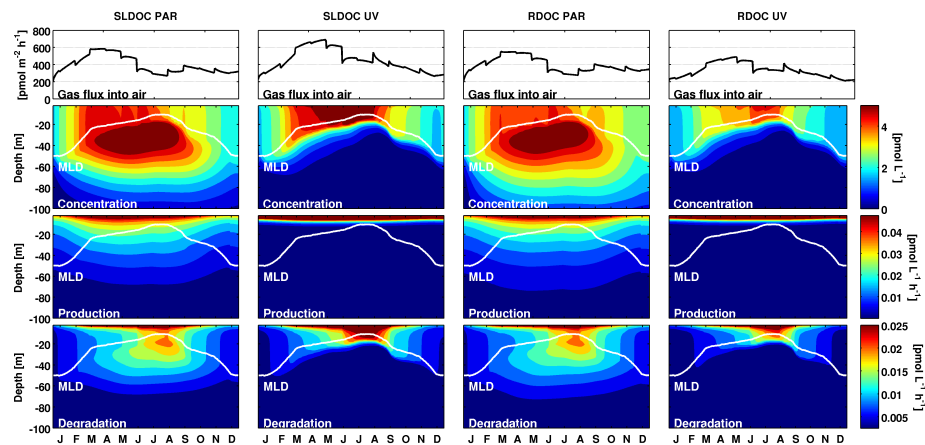


Fig. 3. Methyl iodide concentrations [pmol L⁻¹], production [pmol L⁻¹ h⁻¹], degradation [pmol L⁻¹ h⁻¹], gas exchange [pmol m⁻² h⁻¹] for the photochemical production pathways

C1587

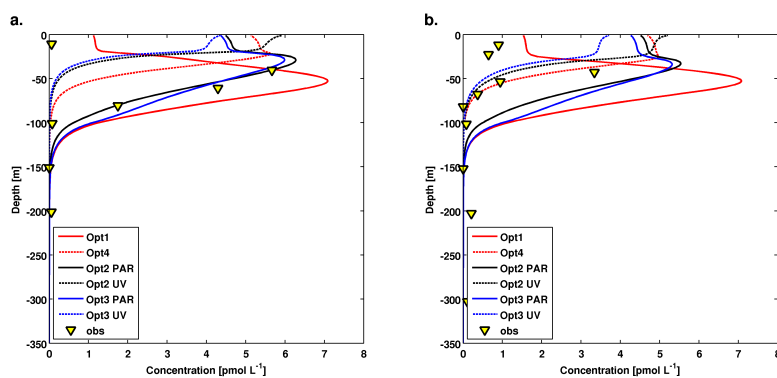


Fig. 4. Methyl iodide concentration profiles [pmol L⁻¹] from stations TENATSO and St.308 in the Cape Verde region. Observed data were collected during Poseidon cruise P399/2 in 2010. For the Tenatso station only

C1588

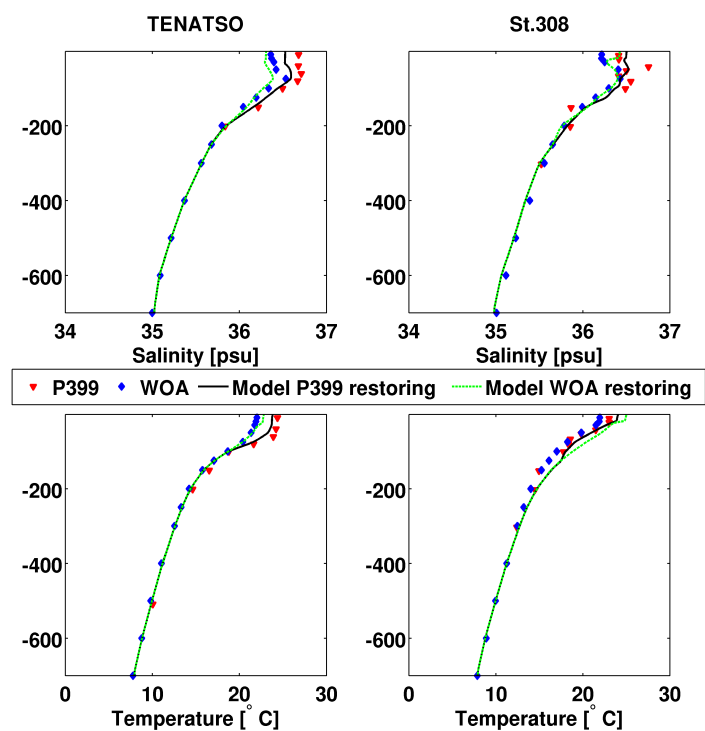


Fig. 5. Salinity [psu] (a,b) and temperature [C] (c,d) profiles in April (a, c) and June (b, d), model predicted (solid lines, black-high frequency forcing, green- low frequency forcing) and observations (red)

C1589

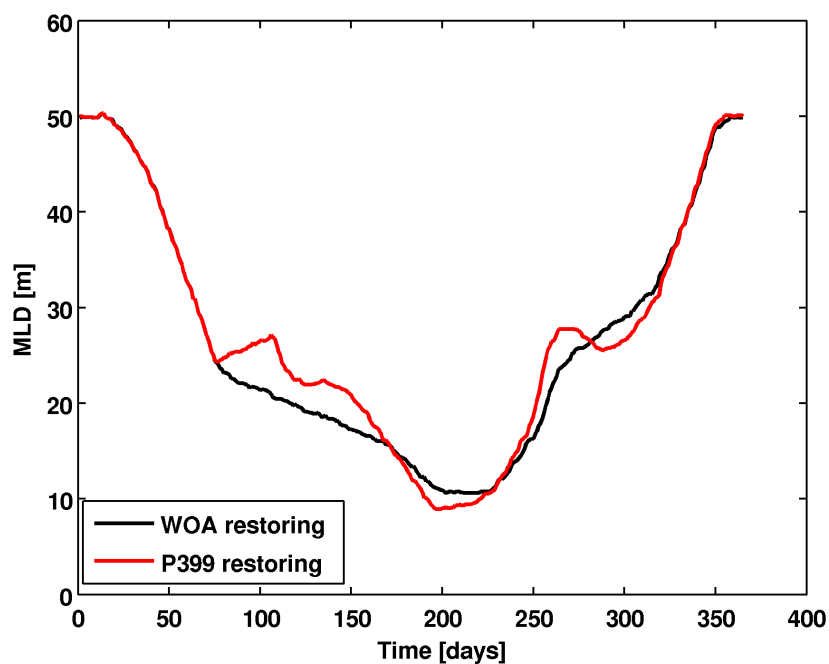


Fig. 6. Mixed layer depth [m] when using WOA restoring (black) or data from P399/2 in April and June (red).

C1590

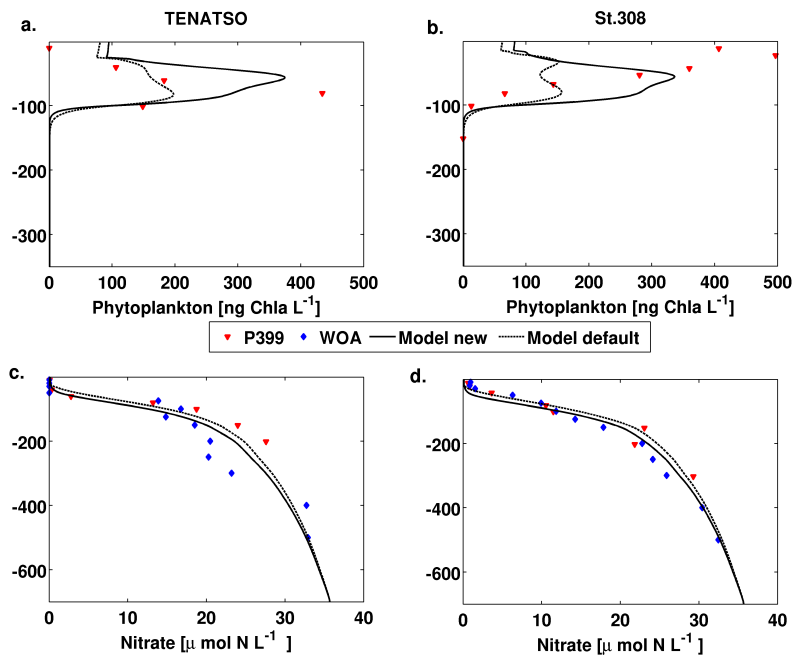


Fig. 7. Phytoplankton (a,b) and nutrient (c,d) concentrations in April (a,c) and June (b,d) [ng Chla L⁻¹], model predicted (black solid lines new and dashed lines default parameter setup) and observed (r