Response to the referees for comments on "Enhanced dataset of global marine isoprene emission from biogenic and photochemical processes for the period 2001-2020"

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Response for comments and suggestions from referee#1

General comments:

The revised manuscript "Enhanced dataset of global marine isoprene emission from biogenic and photochemical processes for the period 2001-2020" by Cui et al. has been improved in content and structure by addressing the comments of the reviewers.

However, I have a few comments and questions which should addressed before publication.

Biological consumption term (α): In the response letter, the authors explain their recalculation of α using equation 1 in Simó et al., (2022) and the resulting changes in global isoprene emissions.

First. I still do not understand why $\alpha=0.373$, when [chla]=5.77 using $\alpha=0.1$ x [chla] +0.05. In this case $0.373=1-\alpha$. Why do the authors calculate $1-\alpha$ instead of α in ll. 124?

Second. Line 116 explains the calculation of the flux. However, multiplying α (h-1) with the production (g m-2 h-1) will not result in g m-2 h-1? Please check the provided equation, it's units and the calculations in the model.

Comparison BIO and SML module: I am still a little confused be the definition of the "BIO emissions" compared to the "SML emissions". For the SML emissions the authors state that the wind speed highly influences the emissions due to the cubic wind speed dependency - I totally agree. However, when it comes to the BIO emissions (assuming steady state isoprene concentrations?!) the authors state that those emissions are not influenced by wind speed as only the BIO production is accounted for. The authors say, due to the static assumption, production equals emission to the atmosphere. I am still struggling, if this assumption is valid, especially when talking about the wind speed. Why is the sea-to-air transfer coefficient k considered when calculating SML emissions but not when calculation BIO emissions? At high winds the SML emission sharply decrease due to a non-existing SML, however, at the same time, isoprene emissions should be very high due to high wind speed, but this is, to my

understanding not accounted for (as only production is taken into account). Perhaps the authors could give some info in the manuscript and state, why their assumption is valid enough in terms of error estimations. Furthermore, the sensitivity runs, using a pre-defined atmospheric mixing ratio of isoprene, show influence on the output of the BIO emission module. How is this even possible, when no gas exchange term is used (as discussed above) and the BIO emissions only depend on isoprene production and biological and chemical isoprene consumption?

<u>Response to **General comments:**</u>

Thank you for your latest comments and suggestions. We are grateful for your further concern of our response letter and updated manuscript. All the additions and corrections in the main text of our revised manuscript using red letters, while these updated paragraphs are quoted in *blue italics* in this response letter.

First, the form of Eq. 2 for the BIO emission model have been transformed with extended description of each term in case of misunderstanding. We updated the Eq. 2 and its description as following in Line 122: *"The value of α is calculated by the following equation based on previous observational study (Simo et al., 2022):*

$\alpha = (0.0042 \times C_{chl} + 0.0021)$ *(When $C_{chl} < 5.77\ mg\ m^{-3}$)*

$\alpha = (0.0042 \times 5.77 + 0.0021) = 0.026$ *(When $C_{chl} \geq 5.77\ mg\ m^{-3}$)* *(2)*

The term $0.1 \times C_{chl}$ represents the degradation and utilization of isoprene by heterotrophic bacteria (Simo et al., 2022). It accounts for the observed correlation between bacterial activity and chlorophyll concentrations in the mixed layer. The second term 0.0021 is empirical rate of chemical consumption of isoprene per hour in the ocean (Palmer and Shaw, 2005; Booge et al., 2018). It is important to note that when the chlorophyll concentration in the seawater exceeds $5.77\ mg·m^{-3}$, α is set to a constant value of 0.026 as a maximum stable biological and chemical consumption per hour. This approach was derived from observations when the chlorophyll concentration in the seawater was up to $5.77\ mg·m^{-3}$ (Simo et al., 2022). Therefore, the specific value of 0.026 is determined to account for biological and chemical consumption in nutrient-rich environments."

Second, the Eq. 1 was updated to make the units more reasonable according to the comments in Line 115: *"The BIO model can be expressed by the following equations:*

$F_b = (1 - \alpha) \cdot P \cdot S$ *(1)*

where F_b ($g·grid^{-1}·h^{-1}$) represents the isoprene emission flux from the air-sea interface to the MBL, P ($g·m^{-2}·h^{-1}$) is the isoprene production rate generated by phytoplankton. S ($m^2·grid^{-1}$) is the grid cell area and α is chlorophyll-based rate constant to determine the biological and

chemical consumption of isoprene per hour." In addition, the Eq. 1 only considers the biological and chemical loss of the incremental part by isoprene production.

Next, windspeed affects the BIO and SML emission process in totally different ways. The SML emission comes from photochemical processes in the sea micro-layer based on surfactant concentration there. Windspeed over the sea surface is applied to quantify the air-sea exchange velocity of isoprene from SML emission. The BIO emission is calculated according to biogenic production with the assumption that the net production rate equals the isoprene BIO emission flux since we assumed the isoprene mixing ratio is negligible in the marine boundary layer. As a result, windspeed was not used in the calculation of BIO emission as shown in Eq. 1. Actually, the isoprene in the marine boundary layer would suppress the air-sea exchange of isoprene from BIO emission, where air-sea exchange velocity is determined by windspeed and temperature (Eq. 11). To describe this suppress process, Eq. 13 has been added in Sect. 3.4, which was applied to test the sensitivity of isoprene in the MBL with various mixing ratios" (in Line 487). The discussion is added as follows: *"The BIO module is based on the assumption that isoprene in the MBL is of very short lifetime, as well as its low mixing ratio in most remote ocean areas. The isoprene presence in the MBL will inhibit the emission of marine isoprene to the MBL. Considering the atmospheric concentration of isoprene in the MBL (C_{air}), an emission suppression term is added into the Eq. (1):*

$$F_b = (1 - \alpha) \cdot P \cdot S - k_{ex} \cdot H \cdot C_{air} \tag{13}$$

In Eq. (13), the air-sea exchange velocity k_{ex} (m·h^{-1}) is determined by Eq. (11). H is a dimensionless Henry's law constant, which is calculated by Mochalski et al. (2011):

$$H = exp\left(-17.85 + \frac{4130}{T+273.16}\right) \tag{14}$$

Here T is water temperature in Celsius degree."

The last term in Eq. 13 accounts for the influence of atmospheric isoprene concentration on BIO emissions with the contribution of windspeed. Due to the lack of simulated isoprene concentration in the offline BIO emission calculation, we omitted this term in Eq. 1. It is very possible to calculate BIO emission using Eq. 13 instead of Eq. 1 in the future work when the BIO module is coupled into earth system model which is able to simulate the isoprene

concentration in the MBL.

Finally, the SML emission at high windspeed is strictly limited by the threshold of 13m·s^{-1}, when the SML no-longer exists. Previous study has pointed out that under the limit of 13m·s^{-1}, almost all ocean surface are covered by SML with different equivalent surfactant concentrations (Brüggemann et al., 2018). Moreover, we checked all windspeed date and found that windspeed larger than 13m·s^{-1} only occurred in about 3% grid cells with daily windspeed. Therefore, we think this windspeed limit is almost reasonable and makes very small uncertainty in the estimation of global SML emission.

<u>Response to **Specific comments**</u>

1.   Introduction: The last sentence of the abstract should be moved to the paragraph "data availability".

<u>Response:</u>

Thank you for your comments. It seems the DOI link at the end of the abstract is a common custom for this journal.

2.   Line 56: "Several enhancements…" This new sentence in the revised version does not belong to the introduction if the authors are talking about their own refinements. If this content reflects work from other people they should be cited here.

<u>Response:</u>

Thank you for your comment. Related citation *(Gantt et al., 2009)* have been added in Line 59.

3.   Line 315: Could the authors give some insights (references) why they included the SML emissions when calculating the oceanic isoprene concentrations in order to compare with observations? Is it likely that gases which are produced in the SML will diffuse to the underlying water instead of being emitted to the atmosphere? Observations, the authors compare their model results to, are normally made at ~5m. In most of the comparison studies (Figure 4) the simulated isoprene concentrations are at the higher end or even significantly higher than the range of observations. Might this be due to the fact that SML emissions are included in the calculation of the simulated oceanic isoprene concentrations?

<u>Response:</u>

Thank you for your comments and useful information. Indeed, the sampling depth of ~5m is not considered in our comparison of observed marine isoprene concentration and our dataset. As the referee commented, including SML emission may cause an overestimation of isoprene concentration in the sea water. However, we cannot quantify the isoprene diffused into seawater from SML emission in recent version module. As a result, we actually got a maximum isoprene

concentration in the seawater with assumption that all isoprene from SML emission enters the underlying seawater. We added related sentences in Line 310 to remind this tips: *"Note that here both BIO and SML emission are considered to have effects on the marine isoprene concentration with assumption that all isoprene from SML emission enters the underlying seawater. This may cause an overestimation of the isoprene concentration in the seawater compared to the actual situation."*

4.   Line 418: "The uncertainty…". It is not clear, which uncertainty is described here. Is it based on interannual variability? Is it 1sigma standard deviation? Or is this uncertainty only based on the phytoplankton sensitivity tests?

<u>Response:</u>

Thank you for your comments. The uncertainty mentioned here is based on the sensitivity tests. For BIO emission, the uncertainty here accounts for test of phytoplankton types. For SML emission, the uncertainty here accounts for the surfactant concentration test. We revised the related sentences for a more specific description in Line 412: *"From a series of sensitivity tests, the range of annual global BIO emission is 0.443 to 0.664 Tg·yr^{-1} and 0.583 to 0.655 Tg·yr^{-1} for SML emission."*

<u>References:</u>

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Gantt, B., Meskhidze, N., and Kamykowski, D.: A new physically-based quantification of marine isoprene and primary organic aerosol emissions, Atmos Chem Phys, 9, 4915-4927, https://doi.org/10.5194/acp-9-4915-2009, 2009.

Mochalski, P., King, J., Kupferthaler, A., Unterkofler, K., Hinterhuber, H., & Amann, A. (2011). Measurement of isoprene solubility in water, human blood and plasma by multiple headspace

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Palmer, P. I. and Shaw, S. L.: Quantifying global marine isoprene fluxes using MODIS chlorophyll observations, Geophys Res Lett, 32, https://doi.org/10.1029/2005gl022592, 2005.

Simo, R., Cortes-Greus, P., Rodriguez-Ros, P., and Masdeu-Navarro, M.: Substantial loss of isoprene in the surface ocean due to chemical and biological consumption, Commun Earth Environ, 3, ARTN 20 https://doi.org/10.1038/s43247-022-00352-6, 2022.

Response for comments and suggestions from referee#2

General comments:

This revised manuscript presents a global marine isoprene emission dataset at high spatial and temporal resolution spanning the period 2001 - 2020. Emissions are calculated using a combination of satellite chlorophyll and radiance measurements and meteorological reanalysis data with empirical parameterizations. Uncertainties in the emission estimate are quantified using a sensitivity analysis which shows how the emission estimate responds to changes in the input meteorology and satellite data as well as plankton distributions and empirical parameters. The estimated emissions are compared with a variety of observational records, and correlations with meteorological driving variables as well as climate modes of variability are explored. This manuscript has been significantly improved by the authors' revisions. All of my major concerns from the previous version have been addressed.

Specifically, the new sensitivity analysis described in Section 3.4 and summarized in Table 5 provides strong evidence that the emissions estimates are quite robust. This is extremely important for potential data users, and it also makes the comparisons with observations and previous emission estimates (Sections 3.1 and 3.2) more meaningful. Key assumptions are justified based on previous observations or modelling results, and these justifications are now clearly explained in the text. The multi-panel plots are much easier to interpret with the addition of descriptive labels, legends, and captions. Confusing terminology has also been largely fixed. The authors added their module code to the online database, which will be helpful for future modelling studies. I also appreciate that the authors have also expanded the discussion of the trends and variability of the data in Section 4, which makes the paper more interesting than a simple data description.

I believe this dataset will be highly valuable for the global atmospheric modelling community,

especially for anyone working on chemistry-climate interactions in the marine environment. I think the scientific content and overall structure of the revised manuscript is sound and does not need to be changed. The phrasing and grammar of the manuscript could be improved for clarity, but the paper is reasonably easy to understand as is.

I recommend accepting this manuscript for publication as is.

<u>Response to</u> **General comments:**

Thank you for your latest comments. We are pleased to have your suggestions and support during the review process of this work.