

## ***Interactive comment on “Marine isoprene production and consumption in the mixed layer of the surface ocean — A field study over 2 oceanic regions” by Dennis Booge et al.***

### **Anonymous Referee #2**

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#### General comments

This manuscript reports a new data set of isoprene depth profiles alongside supporting data from the Pacific and Indian Oceans, which is subsequently analysed for production and loss rates in the mixed layer. On the whole, the data presented in this work is a valuable addition to the existing global isoprene data set, along with the analysis of the results in a novel approach, with relevant supporting data to investigate suggested relationships, and fits into the scope of the journal.

A comparison with available literature parameterisations is made, with the valid conclusion that none are currently adequate for global predictions. To consolidate essentially

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bottom-up and top-down production rates based on literature, the authors calculate a new field-based production rate, and subsequently suggest that a further adjustment from a significant and variable biological loss is needed to explain their isoprene observations. The analysis of the new data does not produce significant, quantitative correlations, but some interesting qualitative comparisons to several environmental variables appear to support the assignments to stress-related production and to losses to heterotrophic respiration.

The conclusions suggest investigation of different avenues which would add new insights into processes at various levels (semi-qualitative for heterotrophic respiration with large natural variability, quantitative for air-sea gas exchange losses) as well as repeating existing hypotheses supported by the new data analysis (environmental factors affect isoprene production).

Specific comments (major)

Line 113: Did you test for matrix effect/purge efficiency differences between MilliQ and seawater?

Line 177: Were detailed light intensities (and light cycle timings) available and comparable for all literature values? How did the authors account for potential effects of temperature variations (and growth stage) between studies?

Line 336-341/Table 3: Double-check literature values for Prochlorococcus and diatoms are correct (should exclude Arnold et al., 2009, as described in Hackenberg et al., 2017). The difference between diatom Pcalc and literature is rather large, but both are described as "low". Prochlorococcus are in fact within a similar low range, using Shaw et al. (2003) production rates.

Line 372: Are mean radiation values for ASTRA-OMZ equator, as opposed to the lower mean values described for open ocean and coastal regimes in the next sentence (Fig 6 suggests yes)? Also, the global radiation for those two is lower than SPACES, but

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Pchloronew is higher for both, which is qualitatively consistent within ASTRA-OMZ, but not with the previous description across all cruises - this could perhaps be worded more clearly, e.g. line 373 "production rate was lower than around the equator".

Line 381: A caveat (transfer of dependence from diatoms to haptophytes) has already been noted by the authors, but it may also be worth considering that temperature effects may be just as variable as light effects between different species and hence also PFTs (cf. reference to Srikanta Dani, 2017, line 353).

Line 430: Would stations where a loss term was not needed not still represent part of the range of required potential additional loss terms, so that they should be included in the averages? Line 443: Both OASIS and ASTRA-OMZ open ocean kAS are 0.1 day<sup>-1</sup>, while the loss rates are 0.05 day<sup>-1</sup> for SPACES and 0.15 day<sup>-1</sup> for ASTRA-OMZ - why are SPACES and OASIS considered more comparable to kconsumption than the others?

Line 486: Has the effect of salinity been shown before? Could describe that stress (from light and temperature) has also been shown to be a factor.

Line 497: It is (almost?) impossible to exactly know all the different processes, as there are so many different factors and variations, e.g. just the number of phytoplankton and bacteria species and their exact distribution in the ocean at any one time. Our understanding of global marine isoprene cycling depends on a better knowledge of the involved systems and processes, but I hope that we can make significant progress even without exact knowledge... (The statement also suggests that knowing processes for PFTs in general may not be sufficient, as large variations within PFTs do occur - in contrast to the use of average rates in this manuscript.)

Line 495 etc: What is the authors' view on the relative importance of uncertainty due to variations within PFTs compared to air-sea gas exchange? The large variation for haptophytes, for example, is much larger than differences in kAS . As a result, could the suggested missing sink not also be explained at least partially by the presence of

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a much lower-producing species of haptophytes?

Specific comments (clarifications/additions needed)

Line 56: Please also cite Moore and Wang 2006 and Hackenberg et al. 2017; both also show depth profiles.

Line 57/Table 1: The correlation shown in Kurihara et al. 2010 is for isoprene between 5 and 100 m depth, not only surface waters.

Line 100: Can you give more details for the vials used? (e.g. custom-made/manufacturer, how is the headspace achieved)

Line 139: Can you re-word " to relate... diagnostic pigments" to clarify the sentence? I can't follow what it means.

Line 140: Specify that [PFT] in the remaining text refers to the chl-a concs of each PFT. Lines 150-153: Can it be made clearer which steps were a separate step and which were a more detailed description of a previously mentioned step? Also, line 153-155: could clarify by deleting "last" and changing to "... profile, the C<sub>tot</sub> and Z<sub>eu</sub> values from this last integration" (it was not immediately clear whether the last or second to last set of values was referred to). Line 152: How was determined which equation needed to be used?

Line 157-163: Is EdPAR(0-) in W m<sup>-2</sup> before conversion to PAR<sub>surface</sub> ? If so, please explain the unit conversion more clearly. The text changes from using subsurface irradiation to surface irradiation without giving details of why these are equivalent. Also, why was the measurement used in those units if it was also available in  $\mu\text{mol m}^{-2} \text{s}^{-1}$  (line 146)?

Line 163: Does EdPAR(0+) refer to surface irradiance as initially defined? If so, why is it used in a depth profile, while a correction is necessary for subsurface radiation EdPAR(0-)?

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Lines 172 and 484 and Table 3: This suggests that Booge et al. 2016 contains new laboratory data; please specify that it is a collection of literature values, also in Table 3.

Line 181-187: This paragraph was slightly difficult to follow. Which depth does "each depth" refer to (isoprene sampling depth? 1-m bins)? If pigment data and hence [PFT] was only available at a variable, small number of depths within the MLD at each station, how does this affect Pdirect given that it is calculated as the "sum of all products", which presumably means at all measured depths? Would a sum of two depths not result in higher production than a single depth, if all depths display similar [PFT] and production rates? Please clarify the paragraphs on these calculations, including how they relate to the introduction to section 2.7 (one production rate per station vs. different numbers of depths used).

Line 198: Mean wind speed/temperature taken from satellite in situ or from 24h of shipboard observations (not at the same site as CTD)?

Line 305 etc: Please specify if these calculations (and any others in the manuscript) were performed only for MLD data. This is not always clear where results are referred to after the initial presentation of the profiles.

Line 425: Can you re-word "these cruises" to be more specific? OASIS is mentioned separately due to a higher kAS (Wanninkof and McGillis, 1999), so it can't mean all three cruises in this work?

Line 449-451: While the statement that rates should be evaluated in water (and possibly in seawater, due to matrix effects?) is valid, the singlet oxygen reaction rate in Palmer and Shaw (2005) is in fact for chloroform (from Monroe, 1981).

Line 464: Should this be "isoprene concentration is no longer correlated to bacteria abundance", rather than referring to the isoprene production rate?

Line 467: Please clarify "it is important to scale the loss" - why is it important/in order to do what?

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Line 468: Caused by the presence of different bacteria or by differences in their ability to use isoprene (or both)?

Lines 473-475: This point has effectively been previously made in other studies. Environmental factors/stresses such as temperature and light are already known to influence biological activity, and that in turn is already known to influence isoprene production.

Line 489: Ideally, use a different word instead of "show" - the results support existing theories/knowledge that these influences exist (described just before this), as opposed to showing something new. The salinity and nutrient relationships specifically do appear to support the hypothesis of stress-related isoprene production.

Lines 499-502: What exactly do you mean by this? Do the parameterisations need to be assessed, i.e. are specific factors for isoprene needed? Generally agreed values are not even available for the most common gases studied. It is worth pointing out that the parameterisation chosen will affect each study, so that perhaps it is useful to present different results if possible/relevant in a study.

Line 502: Could "The evaluation [...] should be examined" be worded differently?

Line 694 (Table 1): bold/italic is defined, but what are the R<sup>2</sup> values that are neither?

Fig 1: Why are not all station numbers shown? Where they are shown, it is often difficult to assign them to a particular dot. There also seem to be stations omitted or not visible? If they cannot be shown (same location as another one) or were not sampled (as suggested by Fig 3), please add this information to the caption. It may also be useful to add station numbers to Fig 3 to connect the two pieces of information.

Fig 5: Can you please show  $n$  in this figure for each set of data and add some details to the caption about the left vs. right part of the graph or refer to the main text (especially 5b) to clarify? Also, why are most of the whiskers for SPACES and OASIS in 5a different once the outliers have been excluded (other values should not be affected if one point

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is removed)? (For 5b, the new calculations can explain the changed whiskers, but are only mentioned in the main text.)

Fig 6, 7, 8, 10: What do the error bars show? Error on measurement or standard deviation of the average? Please add this information to the caption.

Fig S2: Why was EdPAR(0+) calculated if there were also measurements available (binned data implies measured)?

Fig S3: Why are chlorophytes and cyanobacteria functions not shown (EFs are listed in Table 2)? Please add to plot or add reason to caption.

Technical comments

Line 49: Change to "the concentrations generally range", as the following sentence presents different concentrations.

Lines 76 and 454: reference should be Acuña Alvarez

Line 131: Use "Phytoplankton functional types..." as heading for consistency

Lines 133, 146 and 150: Change to "same stations as isoprene was sampled"; "sub-surface irradiation", to define EdPAR(0-); and to "...the total chl-a concentration integrated..."

Line 139/140: Replace "By that" with something like "This was used to derive..." or "The chl-a concs... were derived that way"

Line 143 etc: Can PAR stand for both photosynthetically active radiation and photosynthetic available radiation? The latter does not seem commonly used.

Line 163: EdPAR(0+) should have superscript and be in italics? (also in Fig S2?)

Line 167: Suggest changing to "...due to a shallow mixed layer depth (MLD) resulting in only one..."

Line 254-256: Either the numbers or the description appears to be the wrong way

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round; dividing the mean by the concentration at a certain depth would give  $>1$  for a smaller specific concentration.

Lines 300, 318, 453: punctuation before "2)" is almost invisible; remove comma after "which"; add comma after halocarbons

Line 308/318: Is there a difference between  $>80\%$  of "total PFTs" and "total phytoplankton chl-a"? If not, this statement is only needed once.

Line 334, 357, 487: change "than" to "from"; "stations"; "in-field production rates"

Line 388: "more saline" or "higher salinity"

Line 441: Add "Here, [the loss rate constant...]" to start of the sentence to clarify.

Line 499: must be further assessed? Furthermore, air-sea [...] has to be assessed?

Line 504: evaluate "their" impact (of the isoprene concentrations - if this refers in fact to the evaluation of the processes, the sentence is not very clear and should be reworded)

Line 507: A link to the database would be useful.

Lines 704 and 738: (Table 3 and Fig 5 captions): remove the first "that"

Fig 1: x-axis values partially obscured for OASIS/SPACES

Fig 4 and Line 252 / Fig 8 and Lines 417-434: A darker shade of green would be easier to see (Fig 4); dotted lines are quite faint and legend covers error bar (Fig 8). Legend and description duplicate the information needed, details are also not needed in main text. ASTRA-OMZ details are also already given above the plot; check (c/d/e) (Fig 4).

Fig 6 caption: Pchloronew , not Pchloro , according to main text?

Fig S1: y-axis is  $\mu\text{mol m}^{-2} \text{ s}^{-1}$ , while caption refers to  $\text{W m}^{-2}$ . If a conversion was made, please specify.

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