Biogeosciences Discuss.,
https://doi.org/10.5194/bg-2017-257-RC1, 2017

Biogeosciences Discussions

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 #1

Received and published: 21 July 2017

General Comments The authors report that there is a significant isoprene sink in the ocean, that needs to be accounted for to explain the observed concentrations of isoprene in the waters. In situ estimates of marine isoprene production is not made to the same extent of other biogenic hydrocarbons of global significance. Many of us still do not believe that marine isoprene is significant globally. It can be as little as 1 Tg per year if you accept conservative models, or some other more significant number, if you believe biologically meaningful assessment of empirical estimates. More studies such as the one by Booge et al will help us get closer to resolving this debate and help expand the research field of marine VOC-atmospheric interactions.

My biggest concern with this paper is the way in which the authors have assigned chlorophyll normalised isoprene emission rates to phytoplankton functional types *PFTs and also the emission factors derived from light response curves (tables 2 and 3, and the papers that are cited there). The authors themselves recognize clearly in the introduction and again in conclusion (L345-348, L480 onwards) that there are significant species-specific differences in isoprene emission capacities with respect to temperature (e.g. Exton et al. 2013) and light levels (e.g. Meskhidze et al 2015). Such studies are meaningful and important as individual studies. They may even provide a broad understanding of what a PFT does. There must be some caution while choosing species that are truly representative of a PFT while trying to derive an emission factor. Booge et al., have carefully left out species studied at subzero temperatures (which is a good thing as reflected in the table of Booge et al 2016 in ACPD (I have not read that paper fully). However, it is clear that they have included many species that are globally not relevant in terms of their abundance and those grown under different culture conditions. In those papers cited, cultures were grown at 16, 20 and 26 átŠC. SST is crucial for isoprene production. 10-degree increase can increase isoprene emission by 2 to 3 times over long term, and even higher levels over the short term in terrestrial ecosystems. E.g. In Table 3 of Exton et al (2013), they provide separate Pchloro for temperature and light response (irrespective of PFTs) and there are huge differences. Bonsang et al (2010) grew culture at a max light intensity of 100 umol/m2/s, Colomb et al (2008) did it at 250 umol/m2/s, Exton et al (2013), did measurements at 100 to 300 umol/m2/s. For all of these reasons I worry about the tenuous discussion on the Pchloro, and Pdirect presented in this paper.

Specific Comments L170 onwards and again L290 onwards: You say that haptophytes were the most dominant PFT in all three cruises (L330) and diatoms were dominant in coastal upwelling zone (figure s4). How do you explain fig s3, where haptophytes have very low emission response at light intensities <200 umol/m2/s, which is lower than that of diatoms. From your own figures (S1 and S2) light intensity below 10 m of the sea surface was less than 100 umol/m2/s. How can EF of haptophytes (L335)

be greater than that of diatoms at the working light intensities in the ocean? Why use single point light response curves (figure s3) for cryptophytes and dinoflagellates? What species were used to obtain those curves in figure s3? See figure 1 of Gantt et al (2009, ACP). They have a light response curve that is based on measurements made at 4 or 5 different light intensities for each PFT and responses are strikingly different to what you are proposing. Why wasn't their study considered in Table 2?

L185 and L288 onwards: The big difference between Pneeded and Pdirect is most likely due to the way you have calculated Pchloro, since Pdirect is largely dependent on EF (which is highly sensitive to temperature, light intensity, and species distribution). You rightly identify this as a potential reason (L300) but as highlighted earlier, the justification is difficult. In the equatorial region Pdirect is lower than Pneeded (figure 5) because of high SST and possibly also due to low emission factor you are assigning to cyanobacteria. The discrepancy in diatoms dominated coastal waters during ASTRA-OMZ is noteworthy. The spike in isoprene in site 14 and 15 correlates with diatom blooms in coastal upwelling zone. But, chlorophyll normalised emission suggests an overestimation of Pdirect in coastal sites. Isoprene is mixed quickly in MLD (as you rightly say in L265), hence no vertical trend above MLD. But, what about the relative contribution of phytoplankton below and above MLD to isoprene? Since the mixed layer is very shallow in coastal sites (figure 4d), is it possible that a large proportion of isoprene is locked below MLD? You do mention advective mixing in the thermocline being a slow process (L444). If you know phytoplankton abundances below and above MLD (likely also a function of plankton size), it is perhaps possible to understand this. Can this hold for the entire cruise, given that MLD generally was lower here compared to SPACES- OASIS? You also have a significant proportion of chlorophytes in these waters (figure S5) and they don't emit isoprene at high rates. What was their light response like?

L272-274: What you say in L280-284 is more appropriate than what you say here. Most of the previous studies have shown positive correlation between chl-a and isoprene

concentration (as Table 1 shows) in the oceans. The role of SST is also pretty well established.

L280-284: There is strong correlation between SST, chl-a, and isoprene concentration in cooler waters during both SPACES and ASTRA-OMZ cruises. (summarised in Table 1). Easy to see also in figures 3 and 7, but not mentioned. The relationship seems to breakdown at temperatures >25 deg C. Why? The discussion on relationships between chl-a, SST and isoprene is not satisfactory.

L379: "Higher temperatures caused a decrease in isoprene production rate [in diatoms]. . . .If this temperature dependence can be transferred from diatoms also to haptophytes. . ." Yes. surely to Emiliania but perhaps to not all haptophytes. Please cite Heurtas et al. 2011 (Proc B) and a more recent meta-analysis from Chen, 2015 (J Phyt Res). However, I must point out that the discussion on cyanobacteria and Prochlorococcus is not satisfactory. Together they are 40% of the total biomass during SPACES-OASIS. They emit isoprene at high rates and considering how abundant they are, how tolerant they are even to temperatures >30 degC, they are really important to this discussion.

L463-465 and Figure 9: Assuming that bacterial consumption/degradation of isoprene does occur (L435, 454), you say that bacterial count correlates well with isoprene concentration in waters not dominated by haptophytes. I am not sure how anyone can conclude that high bacterial counts with increasing isoprene in waters translates to bacterial metabolism of isoprene. On the contrary, bacterial emission of isoprene is demonstrated (papers from the 1990s) and we don't know if some marine bacteria produce isoprene. Are there any specific reasons why bacterial counts are less when haptophytes are dominant? Do you mean bacterial populations thrive in waters not dominated by haptophytes? Is it that haptophytes are producing isoprene but there are other biogenic inhibitors that checks bacterial colonies in their vicinity? please explain My suggestion to you/ a clue: Haptophytes are the biggest consumers of bacteria in the ocean (please cite Unrein et al. 2013, ISME J). Now, please reassess figure 9.

L487-490: “The results show that the isoprene production is influenced by light, ocean temperature, and salinity, with an indication that the nutrient regime might exert some influence”. The same point has been made more elaborately by others (please cite Loreto and Dani 2017, Trends Plant Sci), where PFTs, temperature, nutrients and their impact on isoprene is anticipated including the parallel you seem to draw between dimethylsulphoniopropionate and isoprene (L385).

Technical comments: L52-54: It is one thing finding extraordinary numbers and then it is quite another explaining how and why? Your own estimates are closer to what we know from other marine waters.

L170: “Isoprene production rates of different PFTs were determined in laboratory phytoplankton culture experiments (see Table 2 in Booge et al. (2016))”. The measurements listed in the original table are also sourced from literature. Please state the same.

Figure 6: Missing letters a, b, c, d in subfigures

Figure S4: In a few sites, the category of others is really big. ?

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