Anonymous Referee #1

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.

We thank referee #1 for reviewing this manuscript and for providing helpful comments. We will address the comments in the following (bold). The lines refer to the originally uploaded manuscript.

*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 á¸tŠC. 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.*

- **We absolutely understand the concerns of referee #1. The production rates of different PFTs vary depending on temperature and light intensity, which is also stated in the manuscript (l.61, l.376), and, in every case there will surely remain uncertainty when averaging over different species of one PFT. In the following we would like to respond to the points stated by referee #1.**

  (1) Palmer and Shaw (2005) used bulk chl-a concentrations and a globally averaged production rate of 1.8 µmol (g chl-a)$^{-1}$ day^{-1} in order to calculate the isoprene production in their model. In Booge et al. (2016) we could use actual isoprene field measurements in order to improve this model by a factor of ~10, using actual averaged PFT concentrations, rather than using bulk chl-a concentrations. The next step is now, as we tried in this paper,

to include the light dependency of the different PFTs to test if these rates from laboratory tests are somehow suitable for calculating isoprene concentrations in the ocean.

(2) We set our focus on the light dependency due to the natural cycle of light, which is applicable to the entire ocean. Laboratory studies (e.g. Exton et al., 2013;Shaw et al., 2003) could show that almost all isoprene is produced during daytime with higher production during higher light levels. This is also applicable to a depth profile in the ocean with higher light levels at the surface and lower light levels with depth in the mixed layer, if we assume the temperature constant.

(3) You correctly mentioned the different temperatures at which the laboratory studies were carried out, and referring to Table 3 of Exton et al. (2013), that the temperature, averaged over all different PFTs, has an influence on the isoprene production rate. But as these production rates are chl-a normalized rates it is worth to look at the rates dependent on chl-a, which is shown in Figure 3 in Exton et al. (2013):

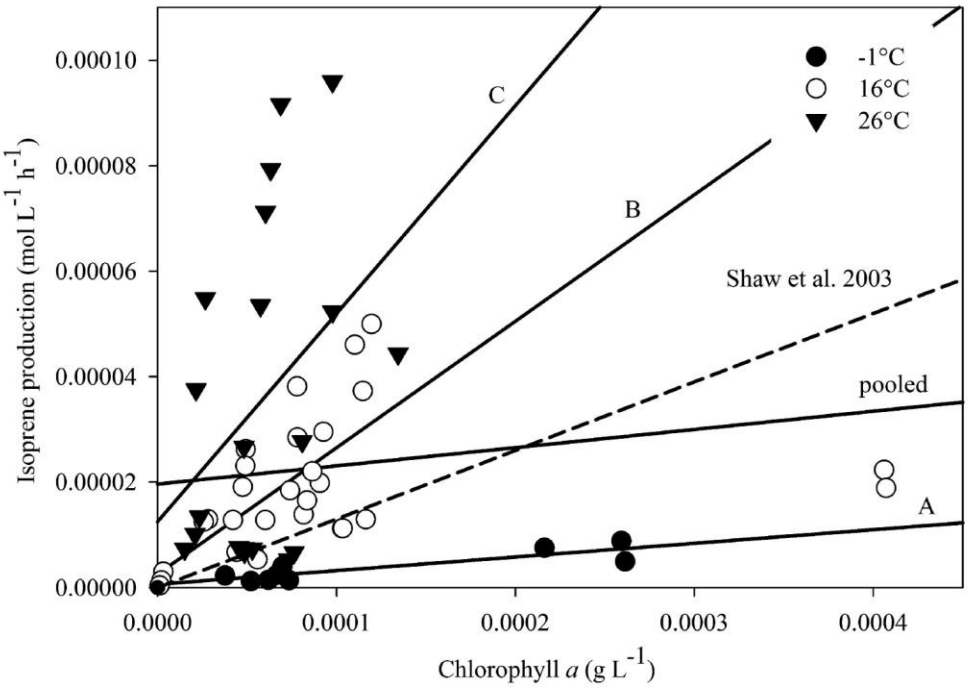

Fig. 3. The relationship between Chl *a* concentration and isoprene production rate in laboratory phytoplankton cultures grown at three different temperatures, showing regressions for (A) strains grown at −1°C (filled circles), (B) strains grown at 16°C (open circles), and (C) strains grown at 26°C (filled triangles; regression equation values are shown in Table 3). Also shown is an overall regression for all strains at all temperatures ("pooled"), and the SST-independent relationship used in previous global models of marine isoprene identified by Shaw et al. (2003; 0.13 μmol isoprene [g Chl *a*]$^{-1}$ h^{-1}). Outlying results for *Dunaliella tertiolecta* are omitted from the regression equations displayed here.

During our studies the chl-a concentration ranged from 0.1 up to 8 µg L^{-1}, which is at the very low end of the chl-a concentration range shown in Exton et al. (2013), (see where the black triangles (experiments at 26°C) and open circles (experiments at 16°C) are overlapping each other (note: their x-axis unit is g L^{-1})). The highest measured isoprene production rates were obtained at 26°C (top black triangles) which were in a chl-a regime that does not represent our study areas.

(4) By including the influence of light intensities only in this study, we were able to examine the temperature influence independently. We had the opportunity to corroborate the temperature-dependence found during laboratory studies directly in the field, since we did not include it from the beginning of our analysis.

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?

- **We agree that the isoprene production rates of haptophytes at 45 µmol m^{-2} s^{-1} and 75 µmol m^{-2} s^{-1} (data from Shaw et al. (2003) and Bonsang et al. (2010)) are lower than the production rates for diatoms at the same light levels (data also from Shaw et al. (2003) and Bonsang et al. (2010)). At higher light levels (300 µmol m^{-2} s^{-1}) the production rate of haptophytes is higher than for diatoms. In order to calculate the emission factor (EF) of each PFT, we applied a log squared relationship (following the approach of Gantt et al. (2009)). Therefore, in comparison to the individual measurements, the log squared curve is overestimating the production rate at lower light levels, but also underestimation the production rate at higher light levels. However, it is the best fit for all three data. The same is true for every PFT when applying the log squared fit. Even though this fit is associated with uncertainties depending on the individual data, the isoprene production rate for each PFT is still an average value of all investigated species within one PFT (as applied in Booge et al. (2016)), but now has a light dependency implemented, with significant influence on production rates.**

  To caution the reader, that there are uncertainties using a log squared fit, we added a sentence to line 300: "….2) uncertainty of using a light dependent log squared fit. Measurements from different laboratory studies used different species within one group of PFTs. All species within one PFT group were combined to produce a light dependent isoprene production rate (Figure S3), although the isoprene production variability of different species within one PFT group is quite high. This will certainly influence P_{direct}, but cannot explain the 70% difference between P_{direct} and P_{need} measured at SPACES/OASIS and ASTRA-OMZ (equator) (Figure 5);"

  Figure S1 actually can lead to the conclusion that the light intensity below 10 m of the surface was less than 200 µmol m^{-2} s^{-1}, but this is not true for most of the data. This data shown is an example from the SPACES cruise at approximately 25°S, which was the cruise operating in the highest latitudes of all three cruises. The mean light intensity was higher for all other data at lower latitudes near the equator (shown in updated Figure S1). The depth profiles of the stations chosen in Figure S2 from ASTRA-OMZ were performed during sunrise and sunset, resulting in lower light intensities.

  We understand that this figure might lead to confusion as referee #1 stated, therefore, we changed figure S1 as follows: Instead of using one single day as an example, we calculated the total mean of all cruises of the hourly radiation measurements from the ship (Figure

S1a) and a total mean calculated PAR over the course of the day, depending on depth (Figure S1b). We also included the mean MLD of each cruise for a better understanding of the light levels present when sampling different depths.

We followed the approach of Gantt et al. (2009) to determine our light dependent production rates in the original publication (and continue to do so here). Only one production rate was available in the literature for cryptophytes, dinoflagellates, and *Prochlorococcus.* For haptophytes and diatoms, we used 3 and 6 light dependent isoprene production rates, respectively, and assuming a similar log squared dependence, as Gantt et al. (2009) did for *Prochlorococcus* and *Synecchococcus* in their study.

We added a footnote to Table 2 stating that the specific species of tested PFTs can be found in the cited literature.

We did not add the laboratory derived production rates of Gantt et al. (2009) to our calculation because they only provide the EF and not the actual rates. Moreover, we do n ot understand how Gantt et al. (2009) calculated their emission rates (y-axis, Figure 1 in Gantt et al. (2009)). It seems they calculated the EF of *Prochlorococcus* by converting an isoprene production rate of 1.5 µmol (g chl-a)$^{-1}$ day^{-1} derived by Shaw et al. (2003) at 90 µmol m^{-2} s^{-1} to an hourly rate, and applied a similar log squared fit as observed for diatoms and coccolithophores. Shaw et al. (2003) used a 14 hours light cycle resulting in an hourly production rate of 0.11 µmol (g chl-a)$^{-1}$. When using their fit, you should expect a production rate of 0.11 µmol (g chl-a)$^{-1}$ h^{-1}, when using a light intensity of 90 µmol m^{-2} s^{-1}. However, according to the figure 1 in Gantt et al. (2009), a production rate of 0.7 µmol (g chl-a)$^{-1}$ h^{-1} is obtained at a light level of 90 µmol m^{-2} s^{-1}. Gantt et al. (2009) report similarly high rates for al measured PFTs in their study. As an example, their measured isoprene production rates for diatoms (see blue line, Fig. 1 in Gantt et al. (2009)) are in the range of 1.3 and 1.8 µmol (g chl-a)$^{-1}$ h^{-1} at light levels of about 350 and 750 µmol m^{-2} s^{-1}, respectively. In comparison, the isoprene production rates from literature values we used for diatoms at light levels of 300-900 µmol m^{-2} s^{-1} were in the range of ~0.22 µmol (g chl-a)$^{-1}$ h^{-1} (see Figure S3). Due to these big discrepancies, the EF of Gantt et al. (2009) is also strikingly higher than ours. We do not know how to resolve these differences, however we checked our calculations and cannot find an error. Therefore, we only used the approach, but not the data from Gantt et al. (2009) in our study.

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 ASTRAOMZ 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?

- **Yes, the referee is absolutely right, in equatorial regions P_{direct} is lower than P_{need} due to high SST. The temperature dependence of isoprene production rates is not included in the calculation of P_{direct}. As stated in our first comment (point (4)), this was exactly what we wanted to test, if the temperature dependence can be seen in field studies.**
  Also, the initial production rate of cyanobacteria might be a reason that P_{direct} is significantly smaller than P_{need}. This is what we could prove, when using our data to calculate new production rates ($P_{chloronew}$) using the multiple linear regression. As shown in Table 3, the new $P_{chloronew}$ values for cyanobacteria are 2 to 7 times higher for OASIS and SPACES, respectively.
  Yes, the referee is right, in contrast to the equatorial and open ocean regions, P_{direct} is overestimated compared to P_{need}. In these coastal upwelling areas, diatom concentrations are highly elevated and are accounting for ~80% of all PFTs. We attributed this either to a missing sink in this upwelling area or to incorrect literature derived P_{chloro} values of diatoms (lines 293-304). The newly calculated $P_{chloronew}$ values for diatoms show that only a production rate of 0.5-0.6 instead of 2.5 µmol (g chl-a)$^{-1}$ day^{-1} (Table 3) is needed to be in better agreement with P_{need} (Figure 5b).
  Advective mixing in the thermocline is a very slow process. If there is a strong concentration gradient with high concentrations of isoprene slightly below the mixed layer, this process might contribute to some point to these concentrations in the MLD. We checked the individual stations but concentrations are not higher below the MLD. This can also be seen in Figure 4, looking at the mean depth profiles.
  Light responses of all PFTs are shown in updated Figure S3. Thank you for pointing out this missing information.

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.

- **Yes, again we agree with the referee that many previous studies could show a positive correlation between chl-a and isoprene. The trend is clear: the more chl-a, the higher the isoprene concentration; the higher the SST, the higher the isoprene concentration (to some extent). However, we wanted to point out that, despite this large scale trend, the relationships between chl-a (or SST) and isoprene for each study or subset of a study are not consistent (i.e. no unique regression equation which can adequately describe the correlation between chl-a and isoprene globally, shown in Figure A). For clarification we changed the sentence in line 272 to: "…it can be seen that, even if the correlations for most of the datasets are significant, there is no globally unique regression factor to adequately describe the relationship between chl-a (and SST) and isoprene."**

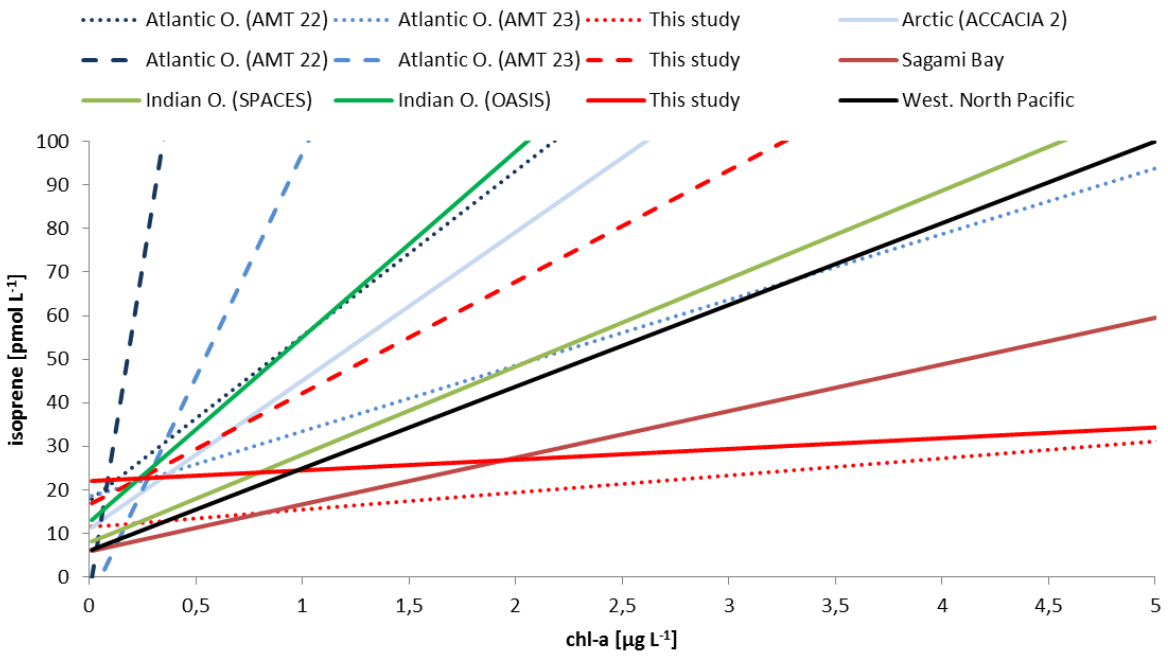

Figure A: Visualization of all significant regression equations of relationships between isoprene and chl-a in different oceanic regions (data taken from Table 1 in the manuscript). Dotted line: SST<20°C, dashed line: SST>20°C, solid line: no SST bin.

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.

- **The lowest SST measured during SPACES was higher than 18°C, meaning that data from SPACES is not included in the regression equation with the strong correlation (R^2=0.89, Table 1) which we think you are referring to. We mention the correlation of P_{norm} and ocean temperature during ASTRA-OMZ (shown in Figure 7) in lines 401 and 402: "…the P_{norm} values were lower (< 8 pmol (µg PFT)$^{-1}$ day^{-1}) correlating with lower ocean temperatures." However this is a correlation between isoprene and P_{norm} and not chl-a. If we look at temperatures lower than 25°C, Figure 3 might suggest, that there is a strong correlation (especially for SPACES) between chl-a, SST and isoprene but in fact the correlation coefficient of R^2=0.42 is not as high as one would expect from looking at the figure. Using the data from all 3 cruises the correlation is significant for both cases, >25°C and <25°C, but the correlation using temperatures <25°C (R^2=0.37) is not significantly higher than using temperatures >25°C (R^2=0.32). Therefore, a possible breakdown of a suggested relationship between chl-a, SST, and isoprene at temperatures >25°C is mathematically not proven. A breakdown of isoprene production rates of diatoms (and haptophytes) at temperatures >26°C is discussed in paragraph 3.4, lines 377-382.**

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.

- **We added the references in the updated sentence starting in line 380: "Increasing ocean temperatures influence the growth rate of phytoplankton generally, but also differently within a group of PFTs. For haptophytes, Huertas et al. (2011) show that two strains of *Emiliania huxleyi* were not tolerant to a temperature increase from 22°C to 30°C, whereas *Isochrysis galbana* could adapt to the increased temperature. In general, the optimal growth rate temperature decreases with higher latitude (Chen, 2015), but the link between growth rate of phytoplankton and isoprene production rate is still not known. Assuming this temperature dependence can be transferred…"**
  We concentrated on the discussion of haptophytes, because this was the only PFT of the three most abundant PFTS that recurred during all three campaigns. Nonetheless, we can see the referee's point that we have to add the results for cyanobacteria and *Prochlorococcus* to the discussion. Therefore, we added a paragraph starting at line 368: "*Prochlorococcus* was one of the three most abundant PFTs during SPACES and OASIS, but concentrations decrease to almost zero in the colder open ocean and upwelling regions of ASTRA-OMZ (Figure 1), which confirms the general knowledge that *Prochlorococcus* is absent at temperatures <15°C (Johnson et al., 2006). Our newly derived production rates confirm the actual laboratory derived rates, demonstrating *Prochlorococcus* as a minor contributor to isoprene concentration. However, *Prochlorococcus* is especially abundant at high ocean temperatures, where isoprene production rates from the other PFTs show evidence of decreasing. Cyanobacteria concentrations (excluding *Prochlorococcus*) were also related to temperature, but in contrast to *Prochlorococcus*, cyanobacteria were still abundant in colder waters during ASTRA-OMZ. The different derived isoprene productions rates for SPACES and OASIS might be related to the different mean ocean temperature and light levels during these cruises. During SPACES, with lower ocean temperatures and lower light levels, compared to OASIS, the production rate is higher. This relationship would confirm the findings of two independent laboratory studies of Bonsang et al. (2010) and Shaw et al. (2003). Bonsang et al. (2010) tested two species of cyanobacteria of at 20°C and found higher isoprene production rates than a different species tested by Shaw et al. (2003) at 23°C and even stronger light intensities. However, Exton et al. (2013) measured the same rate as Shaw et al. (2003) at 26°C for one species, but a 5-times higher production rate for another species at the same temperature. This leads to the conclusion that the production rate is not dependent on one environmental parameter and varies from species to species within the group of cyanobacteria."

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.

- **Figure 9 shows that at stations where isoprene concentrations are elevated, bacteria cell counts are elevated, too. We do not know if these two parameters are linked primarily to each other but we considered that there might be a correlation of bacterial cell counts and isoprene concentration due to the abundance of isoprene attracting bacteria to feed and thrive. If there is a lot of isoprene to eat (e.g. energy source), the bacteria abundance could increase, independent of any phytoplankton influence. This would support the findings from Acuña Alvarez et al. (2009) who showed that isoprene production by phytoplankton could facilitate the amount of hydrocarbon-degrading bacteria. However, due to the relatively high production rate of haptophytes in comparison to the rate of bacterial consumption of isoprene, we hypothesized that this correlation could not be seen anymore when haptophytes were dominant (>33%).**

  We gratefully acknowledge the information that haptophytes are important grazers of bacteria. This helps to explain our results (Figure 9) in a more reasonable way. We added the explanation for Figure 9 starting at line 459: " This is a high isoprene production rate and we could assume higher isoprene concentrations with higher concentrations of haptophytes. This relationship, however, is not evident (data not shown), which may be attributable to other processes masking this relationship. Multiplying the chl-a normalized isoprene production rate of 17.9 µmol (g chl-*a*)$^{-1}$ day^{-1} with the chl-a concentration of haptophytes results in a mean isoprene production rate of ~ 3 pmol L^{-1} day^{-1}, which is about 4 times higher than the mean calculated loss rate due to bacterial degradation over all cruises (~ 0.8 pmol L^{-1} day^{-1}). This could hide the correlation of isoprene concentrations with bacteria when haptophytes are dominant (>33%). In addition, haptophytes themselves are suggested to be the main marine bacterial grazers, compared to other PFTs (Unrein et al., 2014). This leads to the hypothesis that, if there is a lot of isoprene that can be used (e.g. as energy source) by bacteria, also the bacteria abundance will increase, independent of any PFT. However, if the phytoplankton community is dominated (>33%) by haptophytes, the isoprene concentration is no longer correlated to the bacteria abundance, due to the grazing of bacteria by haptophytes (Fehler! Verweisquelle konnte nicht gefunden werden.**, total bacteria cell counts of black points are lower than of the red points at similar isoprene concentrations)."**

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).

- **We thank the referee for pointing out this additional reference. We would like to make sure, however, that within our manuscript we focus on the production rate of isoprene. We changed the sentence starting line at 488 and added a second statement focussing on the actual rate of isoprene production: "The results confirm findings from previous laboratory studies that the isoprene production is influenced by light and ocean temperature, due to stress, and nutrients, due to their effect on changing phytoplankton communities and their abundances (e.g. Dani and Loreto, 2017;Shaw et al., 2010).**

Moreover, our data leads to the conclusion that isoprene production rates in the field, irrespective of phytoplankton communities and their abundance, are influenced by salinity and nutrient levels, which has never been shown before."

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.

- **We absolutely agree. However, in the introduction section of the manuscript we tried to give an overview about the current knowledge/findings related to the biogeochemical cycling of isoprene. As there are not many oceanic isoprene studies published, it is worth to give an overview about the concentration range of marine isoprene concentration, which also includes those publications with extraordinary numbers. We do not try to explain why those numbers are so high, but rather just present them as published results.**

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.

- **We changed the sentence to: "…were determined in laboratory phytoplankton culture experiments (see a collection of literature values: Table 2 in Booge et al. (2016)) and…"**

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

- **Done. Thank you for pointing that out.**

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

- **We think that the referee is referring to Figure S5, not S4. Yes, we agree that the proportion of "others" of the total phytoplankton chl-a concentration e.g. at station 1 during ASTRA-OMZ is 50%. Firstly, this is an exception and, secondly, "others" consists of several PFTs (i.e. 5 different PFTs). We tested and found that using the whole community for the calculations does not lead to different results in production rate and, furthermore, in some cases, to highly unlikely production rates for the less abundant PFTs. Therefore, we would like to keep our evaluation with the most abundant 3 PFTs.**

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Anonymous Referee #2

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 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).

We thank referee #2 for the helpful suggestions and comments. We will address the comments in the following (bold). The lines refer to the originally uploaded manuscript.

Specific comments (major)

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

- **Yes, we did purge efficiency tests with seawater and MilliQ and can confirm that the purge time and purge flow rate we used are sufficient to remove total amount of dissolved isoprene from our samples.**

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?

- **All references for the values we used provided a detailed light intensity description, as well as a light cycle timing, which we used to convert daily rates into hourly rates or vice versa. Shaw et al. (2003) and Exton et al. (2013) used a 14 h light and 10 h dark-cycle, whereas Bonsang et al. (2010) used a 12 h light and 12 h dark-cycle. The phytoplankton cultures from the different studies were reported as being in exponential growth stage. The potential effect of temperature variations was not considered and is discussed in answer #1 in response to referee #1.**

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.

- **In fact, we did not use the isoprene production rate for *Prochlorococcus* from Arnold et al. (2009) in our calculations (see reference for *Prochlorococcus* in Table 2) but forgot to exclude this value for comparison in Table 3. We changed the value in Table 3 from 9.66 to 1.5 µmol (g chl-a)$^{-1}$ day^{-1}, which is in a good agreement with our field derived calculated isoprene production rates for SPACES and OASIS. Accordingly, we changed the sentence starting on line 336 to: "During SPACES/OASIS the $P_{chloronew}$ values of *Prochlorococcus* (both 0.5 µmol (g chl-a)$^{-1}$ day^{-1}) are slightly lower but in a good agreement with the mean literature value (1.5 µmol (g chl-a)$^{-1}$ day^{-1}, Table 3), whereas…"**
  The literature value for diatoms is also changed (in Table 3 and line 340) from 2.54 to 2.51 µmol (g chl-a)$^{-1}$ day^{-1} by excluding Arnold et al. (2009) from average literature isoprene production rate of diatoms.

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 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".

- **We changed the sentences to: "Highest mean values were measured during ASTRA-OMZ (at equator, ~508 W m^{-2})…the isoprene production rate was lower than around the equator (mean global radiation decreased to ~310 W m^{-2})."**

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).

- **We added the following sentence at line 382 etc.: "Additionally, as mentioned before, the temperature, as well as the light dependence of isoprene production might vary between different species of haptophytes when comparing different ocean regimes."**

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-1, while the loss rates are 0.05 day-1 for SPACES and 0.15 day-1 for ASTRA-OMZ - why are SPACES and OASIS considered more comparable to kconsumption than the others?

- **We assume that isoprene production by phytoplankton is the only source for isoprene in the water column. To date, we do not exactly know all different processes of isoprene production/consumption, so there could be other production and loss processes that are not included yet, but would balance each other out. We only used those stations where a loss was needed mathematically, in order to assess loss processes where we expected a large signal. We realize a more thorough assessment would need an iterative approach**

between sources and sinks. However, we focused here on getting a more basic understanding of the important loss processes in the field and we hope to investigate these loss processes in more detail in the future.
We thank the referee for pointing out this mistake in comparing k values and we changed the sentence starting at line 441 to: "…resulting in a lifetime of isoprene of only 10 days, which is comparable to the lifetime due to air sea gas exchange during ASTRA-OMZ (open ocean) and OASIS."

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.

- **To our knowledge, the possible salinity stress of phytoplankton to produce isoprene has not been shown before. In addition we changed the sentence starting at line 488:" The results confirm findings from previous laboratory studies that the isoprene production is influenced by light and ocean temperature, due to stress, and nutrients, due to their effect on changing phytoplankton communities and their abundances (e.g. Dani and Loreto, 2017;Shaw et al., 2010). Moreover, our data leads to the conclusion that isoprene production rates in the field, irrespective of phytoplankton communities and their abundance, are influenced by salinity and nutrient levels, which has never been shown before."**

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.)

- **We absolutely agree with this statement. However, in this study we could show in the field that, even using average rates, temperature has an effect on the production rates. This is also partially discussed in our answer #1 in response to referee #1. We often caution the reader about possible uncertainties, like large variations of isoprene production within the PFTs (e.g. lines 64, 346, 392), which we still are not able to implement correctly when modelling oceanic isoprene concentration. However, trends and qualitative correlations in the field can already be concluded (and support laboratory studies), without knowing every rate exactly, which will hopefully help to further understand global marine isoprene cycling.**

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 a much lower-producing species of haptophytes?

- **The calculated emission factor for haptophytes was derived from three different laboratory studies, using with four different species within the group of haptophytes cultivated under three different light levels and temperatures (Figure S3, Table 2). We think that is a good example for the variation of isoprene production under different environmental conditions**

within one group of PFT. The uncertainty of this emission factor (error of log squared fit) is ~56%, hence also for the P_{direct} value. The uncertainty (standard deviation) of k_{AS} using three different parameterizations is dependent on the wind speed and is 10-15% in a wind speed regime of 8-12 m s^{-1} and can be 30% and higher at wind speed >15 m s^{-1}. Applying 15% uncertainty to the loss due to air-sea-gas-exchange (average: 2.88 pmol L^{-1} day^{-1}) and 56% uncertainty the production by haptophytes (average: 0.89 pmol L^{-1} day^{-1}) yields in an absolute error of 0.43 pmol L^{-1} day^{-1} and 0.50 pmol L^{-1} day^{-1} for the loss due to air-sea-gas-exchange and the production by haptophytes, respectively. As these two losses are both in the same range and following this approach and assuming that 56% uncertainty can be applied to all PFTs (and not only haptophytes) by using P_{direct} it may be possible that the large variations within one PFT could account for the missing sink.

However, we computed P_{need} values based on isoprene measurements, which allows us to disregard the uncertainties on P_{direct}. The resulting chl-a normalized isoprene production rates ($P_{chloronew}$) where highly variable among PFT (e.g. haptophytes) depending on the ocean region (Table 3). We hypothesize that these variations already reflect the influence of light, temperature, salinity, and nutrients. Hence, the uncertainty of the newly derived rates should be less than 56% (error of light dependent log squared fits from different laboratory studies using different temperatures and species), because these natural variations are already included. For this reason, we think that there has to be at least one missing sink, which accounts for the difference in P_{calc} and P_{need}.

Specific comments (clarifications/additions needed)

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

- **Thank you for pointing that out. We added Hackenberg et al. (2017), but not Moore and Wang (2006), as the sentence is about the comparison of chl-a and isoprene in a depth profile and they do not provide any chl-a data.**

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.

- **Sentence changed to: "…and furthermore, Broadgate et al. (1997) and Kurihara et al. (2010) show a direct correlation between isoprene and chl-a concentrations in surface waters and between 5 and 100 m depth, respectively."**

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

- **The sentence has been changed to: "10 mL of helium were pushed into each transparent glass vial (Chromatographie Handel Müller, Fridolfing, Germany) replacing the same amount of sea water and providing a headspace for the upcoming analysis."**

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

- **In the following we have explained in more detail this method. However, we think all this information can be easily obtained from the given citations in this text, so we would prefer to only slightly change the text (by adding only "to the concentration of monovinyl chlorophyll *a* concentration. The latter is an ubiquitous pigment in all PFT except *Prochlorococcus* sp. which contains divinyl chlorophyll *a* instead.." to the text) in order to keep the paper focused: "PFT was calculated using the diagnostic pigment analysis developed by Vidussi et al. (2001) and adapted in Uitz et al. (2006). This method uses specific phytoplankton pigments which are (mostly) common only in one specific PFT. These pigments are called marker or diagnostic pigments (DP) and the method relates for each measurement point the weighted sum of the concentration of seven, for each PFT representative DP to the concentration of monovinyl chlorophyll *a* concentration and by that PFT group specific coefficients are derived which enable to derive the PFT chlorophyll *a* (chl-a) concentration. The latter is an ubiquitous pigment in all PFT except *Prochlorococcus* sp. which contains divinyl chlorophyll *a* instead. In general, the chl-a is a valid proxy for the overall phytoplankton biomass. In the DP analysis as DP concentrations of fucoxanthin, peridinin, 19'hexanoyloxy-fucoxanthin, 19'butanoyloxy-fucoxanthin, alloxanthin, and chlorophyll *b* indicative for diatoms, dinoflagellates, haptophytes, chrysophytes, cryptophytes, cyanobacteria (excluding *Prochlorococcus* sp.), and chlorophytes, respectively, are used. With the DP analysis then finally the chl-a of these PFTs were derived. The chl-a concentration of *Prochlorococcus* sp. was directly derived from the concentration of divinyl chlorophyll *a*."**

Line 140: Specify that [PFT] in the remaining text refers to the chl-a concs of each PFT.

- **Every time we talk about the actual chl-a concentration of a PFT in the manuscript we now changed "PFT concentration" to "PFT chl-a concentration" to be more specific.**

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 Ctot and Zeu 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?

- **We have rephrased the whole paragraph and hope to have improved what exactly done. This should also clarify the two points mentioned below.**
  For clarification which equation was used: You first apply Equation 2. When your Z_{eu} is larger than 102 m you start again with the calculation using Equation 3 and taking the outcome of Z_{eu} from there.

Line 157-163: Is EdPAR(0-) in W m-2 before conversion to PARsurface ? 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 umol m-2 s-1 (line 146)?

- **Please see above.**

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-)?

- **Please see above**

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.

- **Done. Thanks for pointing that out.**

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).

- **"Sum of all products" does not mean "sum over all depths". Following Equation 7 we multiplied for every sampled depth z the concentration of each PFT (PFT_i) with its (light-depth-dependent) $P_{chloro,i}$ value resulting in a production rate for PFT_i at sampled depth z. To calculate the total isoprene production P_{direct} at sampled depth z we summed up all individual production rates of all PFTs measured. In order to use only one production rate per station, we integrated the derived production rates of all measured depths z for each station over the total MLD. Scaling with the MLD gives us the total "mean" isoprene production within the mixed layer.**
  We agree with referee #2 that these calculations are not described clearly in the text. For clarification, we changed the text, starting at line 180:"In order to calculate the isoprene production at each sampled depth (z) at each station, we used the scalar photosynthetic available radiation in the water column, PAR(z), (see section 2.6) as input for I, which was used with the respective, calculated EF of each PFT using Equation 6. The product was integrated over the course of the day, resulting in a P_{chloro} value (µmol isoprene (g chl-a)$^{-1}$ day^{-1}) for each PFT and day depending on the depth in the water column (Figure S4). The light and depth dependent individual $P_{chloro,i}$ values of each PFT at the sampled depth z were multiplied with the corresponding, measured PFT concentration ($[PFT]_i$). The sum of all products gives the directly calculated isoprene production rate at each sampled depth z:

$$\mathbf{P_{direct}(z)} = \sum\left(\mathbf{P_{chloro_i}} \times \mathbf{[PFT]_i}\right). \quad (1)$$

  Integrating over all measurements within the mixed layer and scaling with the MLD results in a "mean" direct isoprene production rate (P_{direct}) for each station."

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

- **For clarification we changed the sentence to: "…, we used the mean wind speed and the mean sea surface temperature of the last 24 h of shipboard observations before taking…"**

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.

- **In paragraph 2.7, lines 166 etc. we state: "For all calculations made we came up with one production rate per station within the mixed layer. This was either due to…" We give this information right in the beginning of the method section to make clear that this is valid for the whole paper. For clarification we added this information again at line 305: "Therefore, we calculated new individual chl-a normalized production rates of each PFT ($P_{chloronew}$) within the MLD."**

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?

- **We changed the sentence to: "However, during SPACES and ASTRA-OMZ the wind speed was…"**

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).

- **Correct, we changed the sentence to: "It must be noted that the loss rate due to the reaction with OH is a gas phase reaction rate (Atkinson et al., 2004) and the used rate for reaction with singlet oxygen derives from measurements in chloroform (Monroe, 1981), meaning that these rates might not be suitable for isoprene reactions in the water phase."**

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

- **Yes, we changed the sentence to: "…, the isoprene production rate is much higher than the degradation rate by bacteria and, therefore, the isoprene concentration is no longer correlated to the bacteria abundance."**

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

- **The loss rate constant of bacterial degradation is variable looking at the different regions (cruises). This means that this loss is not just a static number and therefore is dependent on something, such as environmental parameters or bacterial cell counts. For clarification, we changed the sentence starting in line 465: "Due to the different loss rate constants of bacterial degradation […] in the different regions it is important to identify their dependence on environmental parameters. "**

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

- **For clarification we changed the sentence to: "…, which may be caused by different heterotrophic bacteria, each with a different ability to use isoprene as an energy source."**

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.

- **Yes, the referee is absolutely right, it is known that environmental factors influence the isoprene production. The point we wanted to make is that the trend of higher loss rate**

constant and higher AOU values might be a hint that also isoprene loss/consumption is actually influenced by biological activity and not only by air sea gas exchange or chemical loss.

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.

- **Changed to "The results confirm findings from previous studies…".**

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.

- **As isoprene is a very insoluble gas, like CO_2, we think the existing parameterisations are applicable to isoprene. We wanted to point out that there are different commonly used wind speed based k-parameterisations (i.e. Nightingale et al. (2000) or Wanninkhof and McGillis (1999)), which lead to different emissions, especially in a high wind speed regime (>10 m s^{-1}), which we discussed in lines 420-429. To clarify this point in the conclusion we changed the sentence to: "Furthermore, the most appropriate wind speed based k parameterization to compute air sea gas exchange, the main loss process for isoprene in the ocean, must be used in future studies."**

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

- **We changed the sentence starting at line 502 to: "Isoprene loss processes, in conjunction with the complexity of isoprene production, should be further examined in order to predict marine isoprene concentrations and evaluate the impact of isoprene on SOA formation over the remote open ocean."**

Line 694 (Table 1): bold/italic is defined, but what are the R2 values that are neither?

- **The authors do not state in their publications if these correlations are significant or not. We added this additional information to the table caption.**

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.

- **For a better readability we added not all but almost all station numbers to Figure 1 and added the following sentence to the figure caption: "Numbers indicate stations where a CTD depth profile was performed. Stations 6 & 8 (SPACES) as well as stations 4 & 6 and 13 & 14 (OASIS) have almost the same geographical coordinates. If a station number is omitted (SPACES: stations 5 & 7; OASIS: station 3, 5 & 12; ASTRA-OMZ: stations 4 & 9) no CTD cast was performed."**
  Station numbers are added to Figure 3.

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

- **We updated Figure 5 by showing the number of stations that were included for each set of data in the boxplot and provided some information in the figure caption: "Percent differences […] for the different cruises / cruise regions. Left of the vertical black line data is divided into the three different cruises, right of the vertical black line data is shown for the three cruises where outliers from left part are excluded. Additionally, ASTRA-OMZ was split into three regions (equator, coast, open ocean). Number of stations (n) used for each set of data is shown in italics. The red line represents the median, the boxes show the first to third quartile and the whiskers illustrate the highest and lowest values that are not outliers. The red plus signs represent outliers. The number indicated after \ denotes a station that has been excluded from the analysis."**
  The referee is absolutely right, the whiskers should not be affected for SPACES and OASIS in Figure 5a when excluding the outliers. Accidently, the data for SPACES\1 and OASIS\10 in Figure 5a were interchanged. We have now fixed the figure.

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.

- **Error bars show the standard deviation of the average. This information was added to the figure captions.**

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

- **Measurements were not available for all stations, therefore EdPAR(0+) was calculated and verified with stations where measurements were available.**

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.

- **We added chlorophytes and cyanobacteria to figure S3.**

Technical comments

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

- **Done.**

Lines 76 and 454: reference should be Acuña Alvarez

- **Done.**

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

- **Done.**

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

- **Done.**

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

- **Done.**

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

- **Yes, it can. In our manuscript we use "photosynthetic available radiation" consistently.**

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

- **Done.**

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

- **Done.**

Line 254-256: Either the numbers or the description appears to be the wrong way round; dividing the mean by the concentration at a certain depth would give >1 for a smaller specific concentration.

- **Fixed the description to "…we normalized the measured values by dividing the concentration of each depth of each station by the mean concentration in the mixed layer from the same station profile."**

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

- **Done.**

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.

- **There is no difference and the second statement (line 318) was deleted.**

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

- **Done.**

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

- **Done.**

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

- **Done.**

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

- **Done.**

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)

- **We changed the sentence to: "Isoprene loss processes, in conjunction with the complexity of isoprene production, should be further examined in order to predict marine isoprene concentrations and evaluate the impact of isoprene on SOA formation over the remote open ocean."**

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

- **As there is no data uploaded yet, we cannot provide a link, unfortunately. We will update as soon as possible.**

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

- **Done.**

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

- **Done.**

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).

- **Done.**

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

- **Done.**

Fig S1: y-axis is umol m-2 s-1, while caption refers to W m-2. If a conversion was made, please specify.

- **Done.**

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Marine isoprene production and consumption in the mixed layer of the surface ocean – A field study over 2 oceanic regions

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Abstract

Parameterizations of surface ocean isoprene concentrations are numerous, despite the lack of source/sink process understanding. Here we present isoprene and related field measurements in the mixed layer from the Indian Ocean and the East Pacific Ocean to investigate the production and consumption rates in two contrasting regions, namely oligotrophic open ocean and coastal upwelling region. Our data show that the ability of different phytoplankton functional types (PFTs) to produce isoprene seems to be mainly influenced by light, ocean temperature, and salinity. Our field measurements also demonstrate that nutrient availability seems to have a direct influence on the isoprene production. With the help of pigment data, we calculate in-field isoprene production rates for different PFTs under varying biogeochemical and physical conditions. Using these new calculated production rates we demonstrate that an additional, significant and variable loss, besides a known chemical loss and a loss due to air sea gas exchange, is needed to explain the measured isoprene concentration. We hypothesize that this loss, with a lifetime for isoprene between 10 and 100 days depending on the ocean region, is attributed to heterotrophic respiration mainly due to bacteria.

1 Introduction

Isoprene (2-methyl-1,3-butadiene, C_5H_8), a biogenic volatile organic compound (VOC), accounts for half of the total global biogenic VOCs in the atmosphere (Guenther et al., 2012). 400-600 Tg C yr^{-1} are emitted globally from terrestrial vegetation (Guenther et al., 2006;Arneth et al., 2008). Emitted isoprene influences the oxidative capacity of the atmosphere and acts as a source for secondary organic aerosols (SOA)(Carlton et al., 2009). It reacts with hydroxyl radicals (OH), as well as ozone and nitrate radicals (Atkinson and Arey, 2003;Lelieveld et al., 2008), forming low-volatility species, such as methacrolein or methyl vinyl ketone, which are then further photooxidized to SOA via more semi-volatile intermediate products (Carlton et al., 2009). Model studies suggest that isoprene accounts for 27% (Hoyle et al., 2007), 48% (Henze and Seinfeld, 2006) or up to 79% (Heald et al., 2008) of the total SOA production globally.

Whereas the terrestrial isoprene emissions are well known to act as a source for SOA, the oceanic source strength is highly discussed (Carlton et al., 2009). Marine derived isoprene emissions only account for a few percent of the total emissions and are suggested, based on model studies, to be generally lower than 1 Tg C yr^{-1}

(Palmer and Shaw, 2005;Arnold et al., 2009;Gantt et al., 2009;Booge et al., 2016). Some model studies suggest that these low emissions are not enough to control the formation of SOA over the ocean (Spracklen et al., 2008;Arnold et al., 2009;Gantt et al., 2009;Anttila et al., 2010;Myriokefalitakis et al., 2010). However, due to its short atmospheric lifetime of minutes to a few hours, terrestrial isoprene is not reaching the atmosphere over remote regions of the oceans. In these regions, oceanic emissions of isoprene could play an important role in SOA formation on regional and seasonal scales, especially in association with increased emissions during phytoplankton blooms (Hu et al., 2013). In addition, the isoprene SOA yield could be up to 29% under acid-catalyzed particle phase reactions during low-NO_x conditions, which occur over the open oceans (Surratt et al., 2010). This SOA yield is significantly higher than a SOA burden of 2% during neutral aerosol experiments calculated by Henze and Seinfeld (2006).

Marine isoprene is produced by phytoplankton in the euphotic zone of the oceans, but only a few studies have directly measured the concentration of isoprene to date and the exact mechanism of isoprene production is not known. The concentrations generally range between < 1 and 200 pmol L^{-1} (Bonsang et al., 1992;Milne et al., 1995;Broadgate et al., 1997;Baker et al., 2000;Matsunaga et al., 2002;Broadgate et al., 2004;Kurihara et al., 2010;Zindler et al., 2014;Ooki et al., 2015;Hackenberg et al., 2017). Depending on region and season, concentrations of isoprene in surface waters can reach up to 395 and 541 pmol L^{-1} during phytoplankton blooms in the highly productive Southern Ocean and Arctic waters, respectively (Kameyama et al., 2014;Tran et al., 2013).

Studies have shown that the depth profile of isoprene mainly follows the chlorophyll-a (chl-a) profile suggesting phytoplankton as an important source (Bonsang et al., 1992;Milne et al., 1995;Tran et al., 2013;Hackenberg et al., 2017) and furthermore, Broadgate et al. (1997) and Kurihara et al. (2010) ~~could~~ show a direct correlation between isoprene and chl-a concentrations in surface waters and between 5 and 100 m depth, respectively. However, this link is not consistent enough on global scales to predict marine isoprene concentrations using chl-a (Table 1). Laboratory studies with different monocultures illustrate that the isoprene production rate varies widely depending on the phytoplankton functional type (PFT) (Booge et al., 2016 and references therein). In addition, environmental parameters, such as temperature and light, have been shown to influence isoprene production (Shaw et al., 2003;Exton et al., 2013;Meskhidze et al., 2015). In general, the production rates increase with increasing light levels and higher temperature, similar to the terrestrial vegetation (Guenther et al., 1991). However, this trend cannot easily be generalized to all species, because each species-specific growth requirement is linked differently to the environmental conditions. For example, Srikanta Dani et al. (2017) showed that two diatom species, *Chaetoceros calcitrans* and *Phaeodyctylum tricornutum,* have their maximum isoprene production rate at light levels of 600 and 200 µmol m^{-2} s^{-1}, respectively, which decreases at even higher light levels. Furthermore, Meskhidze et al. (2015) measured the isoprene production rates of different diatoms at different temperature and light levels on two consecutive days. Their results showed a less variable, but higher emission on day two, suggesting that phytoplankton must acclimate physiologically to the environment. This should also hold true for dynamic regions of the ocean and has to be taken into account when using field data to model isoprene production.

The main loss of isoprene in seawater is air-sea gas exchange, with a minor physical loss due to advective mixing and chemical loss by reaction with OH and singlet oxygen (Palmer and Shaw, 2005). The existence of biological losses still remains an open question, as almost no studies were conducted concerning this issue. Shaw et al. (2003) assumed the biological loss by bacterial degradation to be very small. However, Acuña Alvarez et

al. (2009) showed that isoprene consumption in culture experiments from marine and coastal environments did not exhibit first order dependency on isoprene concentration. They observed faster isoprene consumption with lower initial isoprene concentration.

This study significantly increases the small dataset of marine isoprene measurements in the world oceans with new observations of the distribution of isoprene in the surface mixed layer of the oligotrophic subtropical Indian Ocean and in the nutrient rich upwelling area of the East Pacific Ocean along the Peruvian coast. These two contrasting and, in terms of isoprene measurements, highly undersampled ocean basins are interesting regions to compare the diversity of isoprene producing species. With the help of concurrently measured physical (temperature, salinity, radiation), chemical (nutrients, oxygen), and biological (pigments, bacteria) parameters, we aim to improve the understanding of isoprene production and consumption processes in the surface ocean under different environmental conditions.

2 Methods

2.1 Sampling sites

Measurements of oceanic isoprene were performed during three separate cruises, the SPACES (Science Partnerships for the Assessment of Complex Earth System Processes) and OASIS (Organic very short-lived substances and their air-sea exchange from the Indian Ocean to the stratosphere) cruises in the Indian Ocean and the ASTRA-OMZ (Air sea interaction of trace elements in oxygen minimum zones) cruise in the eastern Pacific Ocean. The SPACES/OASIS cruises took place in July/August 2014 on board the R/V Sonne I from Durban, South Africa via Port Louis, Mauritius to Malé, Maldives and the ASTRA-OMZ cruise took place in October 2015 on board the R/V Sonne II from Guayaquil, Ecuador to Antofagasta, Chile (Figure 1~~Figure 1~~).

2.2 Isoprene measurements

During all cruises, up to 7 samples (50 mL) from 5 to 150 m depth for each depth profile were taken bubble-free from a 24 L-Niskin bottle rosette equipped with a CTD (conductivity-temperature-depth; described in Stramma et al. (2016)). 10 mL of helium were pushed into ~~E~~each transparent glass vial (Chromatographie Handel Müller, Fridolfing, Germany) replacing the same amount of sea water and providing a~~contained 10 mL of helium~~ headspace for the upcoming analysis~~purging~~. The water samples were, if necessary, stored in the fridge and analyzed on board, within 1 h of collection, using a purge and trap system attached to a gas chromatograph/mass spectrometer (GC/MS; Agilent 7890A/Agilent 5975C; inert XL MSD with triple axis detector) (Figure 2~~Figure 2~~). Isoprene was purged for 15 minutes from the water sample with helium (70 mL min^{-1}) containing 500 µL of gaseous deuterated isoprene (isoprene-d5) as an internal standard to account for possible sensitivity drift (Figure 2~~Figure 2~~: purge unit, load position). The gas stream was dried using potassium carbonate (SPACES/OASIS) or a Nafion® membrane dryer (Perma Pure; ASTRA-OMZ). CO_2- and hydrocarbon-free dry, pressurized air with a flow of 180 mL min^{-1} was used as counter flow in the Nafion® membrane dryer (Figure 2~~Figure 2~~: water removal). Before being injected into the GC (Figure 2~~Figure 2~~: trap unit, inject position), isoprene was preconcentrated in a Sulfinert® stainless steel trap (1/16'' O.D.) cooled with liquid nitrogen (Figure 2~~Figure 2~~: trap unit, load position). The mass spectrometer was operated in single ion mode quantifying isoprene and d5-isoprene using m/z - ratios of 67, 68 and 72, 73, respectively. In order to perform daily calibrations for

quantification, gravimetrically prepared liquid isoprene standards in ethylene glycol were diluted in Milli-Q water and measured in the same way as the samples. The precision for isoprene measurements was ± 8%.

2.3 Nutrient measurements

Micronutrient samples were taken on every cruise from the CTD bottles (covering all sampled depths). The samples from SPACES were stored in the fridge at -20°C and measured during OASIS. Samples from OASIS and ASTRA-OMZ were directly measured on-board with a QuAAtro auto-analyzer (Seal Analytical). Nitrate was measured as nitrite following reduction on a cadmium coil. The precision of nitrate measurements was calculated to be ±0.13 µmol L^{-1}.

2.4 Bacteria measurements

For bacterial cell counts, 4 mL samples were preserved with 200 µL glutaraldehyde (1% v/v final concentration) and stored at -20°C for up to three months until measurement. A stock solution of SybrGreen I (Invitrogen) was prepared by mixing 5 µL of the dye with 245 µL dimethyl sulfoxide (DMSO, Sigma Aldrich). 10 µL of the dye stock solution and 10 µL fluoresbrite YG microspheres beads (diameter 0.94 µm, Polysciences) were added to 400 µL of the thawed sample and incubated for 30 min in the dark. The samples were then analyzed at low flow rate using a flow cytometer (FACS Calibur, Becton Dickinson) (Gasol and Del Giorgio, 2000). TruCount beads (Becton Dickinson) were used for calibration and in combination with Fluoresbrite YG microsphere beads (0.5-1 µm, Polysciences) for absolute volume calculation. Calculations were done using the software program "Cell Quest Pro".

2.5 Phytoplankton ~~groups~~ functional types from marker pigment measurements

Different PFTs were derived from marker phytoplankton pigment concentrations and chlorophyll concentrations. To determine PFT chl-a, 0.5 to 6 L of sea water were filtered through Whatman GF/F filters at the same stations as isoprene was sampled. The soluble organic pigment concentrations were determined using high-pressure liquid chromatography (HPLC) according to the method of Barlow et al. (1997) adjusted to our temperature-controlled instruments as detailed in Taylor et al. (2011). We determined the list of pigments shown in Table 2 of Taylor et al. (2011) and applied the method by Aiken et al. (2009) for quality control of the pigment data. PFT chl-a was calculated using the diagnostic pigment analysis developed by Vidussi et al. (2001) and adapted in Uitz et al. (2006). This method uses specific phytoplankton pigments which are (mostly) common only in one specific PFT. These pigments are called marker or diagnostic pigments (DP) and the method relates for each measurement point the weighted sum of the concentration of seven, for each PFT representative DP to the concentration of monovinyl chlorophyll *a* concentration and by that PFT group specific coefficients are derived which enable to derive the PFT chl-a concentration. The latter is an ubiquitous pigment in all PFT except *Prochlorococcus* sp. which contains divinyl chlorophyll *a* instead. In general, chl-a is a valid proxy for the overall phytoplankton biomass. In the DP analysis as DP concentrations of fucoxanthin, peridinin, 19'hexanoyloxy-fucoxanthin, 19'butanoyloxy-fucoxanthin, alloxanthin, and chlorophyll *b* indicative for diatoms, dinoflagellates, haptophytes, chrysophytes, cryptophytes, cyanobacteria (excluding *Prochlorococcus* sp.), and chlorophytes, respectively, are used. With the DP analysis then finally the chl-a concentration of these PFTs were derived. The chl-a concentration of *Prochlorococcus* sp. was directly derived from the concentration of divinyl chlorophyll *a*. ~~to relate the weighted sum of seven, for each PFT representative diagnostic pigments~~

~~(DP). to the concentration of monovinyl chlorophyll *a* concentration. The later is an ubiquitous pigment in all PFT except *Prochlorococcus* sp. which contains divinyl chlorophyll *a* instead. By that the chl a concentration for diatoms, dinoflagellates, haptophytes, chrysophytes, cryptophytes, cyanobacteria (excluding *Prochlorococcus* sp.), and chlorophytes were derived. The chl a concentration of *Prochlorococcus* sp. was derived from the divinyl chl a concentration (marker pigment for this group) directly.~~

2.6 Photosynthetic available radiation within the water column measurements

~~Surface plane irradiance ($E_d(0^+,\lambda)$) data were taken from a RAMSES spectrometer and integrated from 400 to 700 nm to receive the downwelling photosynthetic available plane irradiance ($E_dPAR(0^+)$,in both units: W m^{-2} and µmol m^{-2} s^{-1}).~~ Since no underwater light data were available for all cruises, we used global radiation data from the ship's meteorological station together with the light attenuation coefficients (determined from the chl-a concentration profiles) to calculate the photosynthetic available radiation) within the water column during a day. In detail we processed these data the following way:

We fitted the hourly resolved global radiation data with a sine function to account for the light variation during the day and converted into PAR just above surface, PAR(0^+) in µmol m^{-2} s^{-1} during the course of a day, by multiplying these daily global radiation values with a factor of 2 (Jacovides et al., 2004) (Figure S1a).

The subsurface PAR (~~E_d~~*PAR*(0^-)) was calculated using the refractive index of water (n=1.34) and 0.98 for transmission assuming incident light angles <49°:

$$\text{~~E}_\text{d}\text{~~PAR}(0^-) = \text{E}_\text{d}\text{PAR}(0^+) \times 1.34^2 \text{~~\times~~}/0.98 \quad (1)$$

In order to derive the diffuse attenuation coefficient for PAR (K_dPAR) we calculated the euphotic depth (Z_{eu}) from the chl-a profile for all stations using the approximation by Morel and Berthon (1989) further refined by Morel and Maritorena (2001). In detail the following was done: From the chl-a profiles at each station the total chl-a integrated for Z_{eu} (C_{tot}) was determined. A given profile was progressively integrated with respect to increasing depth (z). The successive integrated chl-a values were introduced in Equation 2 or 3 accordingly, thus providing successive Z_{eu} values that were progressively decreasing. Once the last Z_{eu} value, as obtained, became lower than the actual depth z used when integrating the profile, these C_{tot} and Z_{eu} values from the last integration were taken. Profiles which did not reach Z_{eu} were excluded.

$$\text{Z}_\text{eu} = 912.5 \times \text{C}_\text{tot}^{-0.839} \text{ ; if } 10\text{m} < \text{Z}_\text{eu} < 102\text{m} \quad (2)$$

$$\text{Z}_\text{eu} = 426.3 \times \text{C}_\text{tot}^{-0.547} \text{ ; if } \text{Z}_\text{eu} > 102\text{m} \quad (3)$$

K_dPAR of each station was then calculated from Z_{eu} as follows:

$$\text{K}_\text{d}\text{PAR} = \frac{4.6}{\text{Z}_\text{eu}} \quad (4)$$

~~In order to derive the scalar photosynthetic available radiation at the surface ($PAR_{surface}$, µmol m^{-2} s^{-1}) over the course of one day, $E_dPAR(0^-)$ one hourly averages were fitted with a sine function to account for the light variation during the day and converted into $PAR_{surface}$ by multiplying $E_dPAR(0^-)$ values with a factor of 2 (Jacovides et al., 2004) (Figure S1a shows an example for one day).~~ The plane photosynthetic available irradiance at each depth (z) in the water column, $PAR(z)$, is then calculated applying Beer-Lambert's law (Figure S1b):

$$PAR(z) = PAR_{surface} \times e^{-K_d z}. \quad (5)$$

An example of two ~~E_d*PAR*(0+)~~ fitted depth profiles for the time of the two specific stations is shown in the supplement (Figure S2)~~.~~, which have been compared to directly measured downwelling photosynthetic available radiation (*E_dPAR*) profiles. The comparison shows that the fitted PAR profiles obtained from ship's global radiation data and chlorophyll profiles were reliable.

E_dPAR profiles were only measured during ASTRA daytime stations with a hyperspectral radiometer (RAMSES, TriOS GmbH, Germany) covering a wavelength range of 320 nm to 950 nm with an optical resolution of 3.3 nm and a spectral accuracy of 0.3 nm (for more details on the measurements see Taylor et al. (2011)). The downwelling irradiance *$E_d(z,\lambda)$* RAMSES data were interpolated to 1 nm resolution and then the *$E_d(z)$* given in W m^{-2} at each nm wavelength step between 400 to 700 nm was converted to µmol quanta m^{-2} s^{-1} by following the principle that one photon contains the energy $E_p=(h*c) / \lambda$ (with the Planck's constant $h=6.6266*10^{-34}$ Js and the speed of light c=299792458 m s^{-1}). Finally, the *$E_d(z, \lambda)$* were integrated from 400 to 700 nm to receive the downwelling photosynthetic available plane irradiance (*E_dPAR(z)*).

2.7 Calculation of isoprene production

We calculated the isoprene production rate (*P*) in two different ways: a direct and an indirect calculation, which will be explained in the following paragraphs. For all calculations made we came up with one production rate per station within the mixed layer. This was either due to the shallow mixed layer depth (MLD) ~~coming along with~~resulting in only one measurement within the mixed layer (coastal stations ASTRA-OMZ) or due to well mixed isoprene concentrations showing almost no gradient within the mixed layer (data explained in section 3.2).

2.7.1 Direct calculation of isoprene production rates

Isoprene production rates of different PFTs were determined in laboratory phytoplankton culture experiments (see a collection of literature values: Table 2 in Booge et al. (2016)) and were used here to calculate isoprene production from measured PFTs in the field. These literature studies showed that isoprene production rates are light dependent, with increasing production rates at higher light levels (Shaw et al., 2003;Gantt et al., 2009;Bonsang et al., 2010;Meskhidze et al., 2015). To include the light dependency in our calculations, we followed the approach of ~~–~~Gantt et al. (2009) for each PFT by applying a log squared fit between all single literature laboratory chl-a normalized isoprene production rates P_{chloro} (µmol isoprene (g chl-a)$^{-1}$ h^{-1}) (references in Table 2) and their measured light intensity *I* (µmol m^{-2} s^{-1}) during individual experiments to determine an emission factor (*EF*) for each PFT (Figure S3):

$$P_{chloro} = EF \times \ln(I)^2 . \quad (6)$$

The resulting *EF* from this log squared fit is unique for each PFT and is listed in Table 2: The higher the *EF* of a PFT, the higher its P_{chloro} value at a specific light intensity. In order to calculate the isoprene production at each sampled depth (*z*) at each station, we used the scalar photosynthetic available radiation ~~at each depth~~in the water column, *PAR(z)*, (see section 2.6) as input for *I*, which was used with the respective, calculated *EF* of each PFT using Equation 6. The product was integrated over the course of the day, resulting in a P_{chloro} value (µmol isoprene (g chl-a)$^{-1}$ day^{-1}) for each PFT and day depending on the depth in the water column (Figure S4). The light and depth dependent individual $P_{chloro,i}$ values of each~~all~~ PFT~~s~~ at the sampled depth *z* were multiplied with

the corresponding, measured PFT chl-a concentration ($[PFT]_i$). The sum of all products gives the directly calculated isoprene production rate ~~(P_{direct}) for each station~~at each sampled depth z:

$$P_{direct}(z) = \sum\left(P_{chloro_i} \times [PFT]_i\right) \text{~~} P_{chloro_i} \times [PFT]_i \text{~~} . \quad (7)$$

Integrating over all measurements within the mixed layer and scaling with the MLD results in a "mean" direct isoprene production rate (P_{direct}) for each station.

2.7.2 Indirect calculation of isoprene production rates

The indirect calculation of the isoprene production rate is dependent on our measured isoprene concentrations ($C_{Wmeasured}$). We used the simple model concept of Palmer and Shaw (2005), assuming that the measured isoprene concentration is in steady state, meaning that the production (P) is balanced by all loss processes:

$$P - C_{Wmeasured}\left(\sum k_{CHEM,i} C_{Xi} + k_{BIOL} + \frac{k_{AS}}{MLD}\right) - L_{MIX} = 0, \quad (8)$$

where k_{CHEM} is the chemical loss rate constant for all possible loss pathways (i) with the concentrations of the reactants (C_X = OH and O_2), k_{BIOL} is the biological loss rate constant due to biological degradation, and L_{MIX} is the loss due to physical mixing. These constants are further described in Palmer and Shaw (2005). k_{AS} is the loss rate constant due to air-sea gas exchange scaled with the MLD. The MLD at each station was calculated from CTD profile measurements applying the temperature threshold criterion (±0.2°C) of de Boyer Montégut et al. (2004). k_{AS} was computed using the Schmidt number (S_C) of isoprene (Palmer and Shaw, 2005) and the quadratic wind-speed-based (U_{10}) parameterization of Wanninkhof (1992):

$$k_{AS} = 0.31\, U_{10}^2 \left(\frac{S_C}{660}\right)^{-0.5} . \quad (9)$$

As we assume steady state isoprene concentration, we used the mean wind speed and the mean sea surface temperature of the last 24 h of shipboard observations before taking the isoprene sample to calculate U_{10} and S_C, respectively.

We modified equation 8 to calculate the needed production rate (P_{need}) by multiplying $C_{Wmeasured}$ with the sum of k_{CHEM} (0.0527 day^{-1}) and k_{AS} scaled with the MLD:

$$P_{need} = C_{Wmeasured}\left(k_{CHEM} + \frac{k_{AS}}{MLD}\right). \quad (10)$$

We neglected the loss rates of isoprene due to biological degradation and physical mixing because they are low compared to k_{CHEM} and k_{AS} (Palmer and Shaw, 2005;Booge et al., 2016), meaning that the resulting P_{need} value can be seen as a minimum needed production rate.

3 Results and discussion

3.1 Cruise settings

The first part of the Indian Ocean cruise, SPACES, started in Durban, travelled eastwards while passing the Agulhas current and the southern tip of Madagascar (Toliara reef) with relatively warm water masses (mean: 23.4°C) and southerly winds. Southeast of Madagascar wind direction changed to easterly winds and we encountered the Antarctic circumpolar current with significantly lower mean sea surface temperatures of 19.7°C before heading north to Mauritius. Mean wind speed during the cruise was 8.2±3.7 m s^{-1} and mean salinity was 35.5±0.2. Global radiation over the course of the day was on average ~360±70 W m^{-2}. As shown in Figure 3,

within the mixed layer, chl-a concentrations were very low (average value < 0.3 µg L^{-1}) during the whole cruise, coinciding with generally low nutrient levels in the mixed layer (mean values for nitrate and phosphate were 0.14 and 0.15 µmol L^{-1}, respectively).

The second part of Indian ocean cruise, OASIS, covered open ocean regimes, upwelling regions, such as the equatorial overturning cell as described in Schott et al. (2009) and the shallow Mascarene Plateau (8°-12°S, 59°-62°E). Constant south easterly winds (mean: 10.3±4.2 m s^{-1}) were observed that were characteristic for the season of the southwest monsoon. During the cruise, sea surface temperature was constantly increasing with latitude from 24.4°C (Port Louis) to 29.7°C (southern tip of the Maldives) with mean daily light levels of ~457±64 W m^{-2}. Salinity ranged from 34.4 to 35.4. As for the SPACES cruise, the chl-a concentration in the western tropical Indian Ocean was low (0.2-0.5 µg L^{-1} on average, Figure 3). Nitrate levels (mean: 0.42 µmol L^{-1}) in the mixed layer were higher than during SPACES, but not phosphate (mean: 0.17 µmol L^{-1}).

The ASTRA-OMZ cruise took place in the coastal, wind driven Peruvian upwelling system (16°S - 6°S). This area is a part of one of the four major eastern boundary upwelling systems (Chavez and Messié, 2009) and is highly influenced by the El Niño-Southern Oscillation. We observed constant southeasterly winds (8.2±2.5 m s^{-1}) travelling parallel to the Peruvian coast. During neutral surface conditions or La Niña conditions, cold, nutrient rich water is being upwelled at the shelf of Peru resulting in high biological productivity. However, in early 2015 a strong El Niño developed, which brought warmer, low salinity waters from the western Pacific to the coast of Peru, resulting in suppressed upwelling with lower biological activity due to the presence of nutrient-poor water masses. The cruise started with a section passing the equator from north to south at 85.5°W east of the Galapagos Islands with mean sea surface temperatures of 25.0°C and low salinity waters (mean for profiles: 34.2), as well as low chl-a concentrations (mean for profiles: 0.5 µg L^{-1}). Levels of incoming shortwave radiation were ~508±67 W m^{-2}. Afterwards, we performed 4 onshore-offshore transects at about 9, 12, 14, and 16°S off the coast of Peru (Figure 1~~Figure 1~~) where the incoming shortwave radiation was significantly decreased by clouds (~300 W m^{-2}). Upwelled waters identified by higher salinity (mean: 35.2) and lower sea surface temperatures (mean: 18.9°C) were found during the second part of the cruise. Chl-a values were highest directly at the coast (max: 13.1 µg L^{-1}), coinciding with lower sea surface temperatures (Figure 3) showing that some upwelling was still present.

3.2 Isoprene distribution in the mixed layer

The isoprene concentrations during the SPACES cruise were generally very low, ranging from 6.1 pmol L^{-1} to 27.1 pmol L^{-1} in the mixed layer (mean for the average of a profile: 12.3 pmol L^{-1}) in the southern Indian Ocean, mainly due to very low biological productivity. During the OASIS cruise, the isoprene concentrations south of 10°S were comparable to the concentrations of the SPACES cruise. North of 10°S, the isoprene values in the mixed layer were significantly higher (mean: 35.9 pmol L^{-1}) (Figure 3). These results are in good agreement with the sea surface isoprene concentrations of Ooki et al. (2015) in the same area east of 60°E, who measured concentrations lower than 20 pmol L^{-1} south of 12°S and concentrations of ~40 pmol L^{-1} north of 12°S during a campaign between November 2009 and January 2010. During ASTRA-OMZ the concentrations ranged from 12.7 pmol L^{-1} to 53.2 pmol L^{-1} with a mean isoprene concentration of 29.5 pmol L^{-1} in the mixed layer. Although the chl-a concentrations at the coastal stations (3.8 µg L^{-1}) were significantly higher than open ocean values (0.7 µg L^{-1}), the isoprene values did not show the same trend (Figure 3).

A mean normalized depth profile of each cruise for isoprene (blue), water temperature (black), oxygen (red), and chl-a (green) is shown in Figure 4. In order to compare the depth profiles of each cruise with respect to the different concentration regimes, we normalized the measured values by dividing the ~~mean~~ concentration of each depth ~~in the mixed layer~~ of each station by the mean concentration in the mixed layer ~~of each depth~~ from the same station profile. A normalized value >1 means that the value at a certain depth is higher than the mean value in the mixed layer, a value <1 means less than in the mixed layer. As the sampled depths at each station were not the same at every cruise, we binned the data into seven equally spaced depth intervals (15 m) and averaged each data of an interval over each of the three cruises. The calculated mean mixed layer depths of the SPACES and OASIS cruises, using the temperature threshold criterion (±0.2°C) of de Boyer Montégut et al. (2004), were about 60 m, the mean mixed layer depth of the ASTRA-OMZ cruise was 30 m excluding the four coastal stations, which had only a MLD of 20 m resulting in only one bin interval in the MLD. Figure 4 shows, that during all three cruises almost no gradient of isoprene in the mixed layer was detectable. In contrast to the isoprene concentration, the highest chl-a concentration was measured slightly above or below the MLD during SPACES/OASIS, whereas during ASTRA-OMZ chl-a showed the same trend as isoprene. These results suggest a very fast mixing of isoprene after it is produced by phytoplankton and released to the water column above the MLD.

As isoprene is produced biologically by phytoplankton, many studies attempted to find a correlation between chl-a and isoprene, but found very different results. Bonsang et al. (1992), Milne et al. (1995) and Zindler et al. (2014) did not find a significant correlation, whereas other studies could show a significant correlation and, therefore, attempted a linear regression to show a relationship between isoprene and chl-a, as well as SST (Broadgate et al., 1997;Kurihara et al., 2010;Kurihara et al., 2012;Ooki et al., 2015;Hackenberg et al., 2017). Comparing the different factors of each regression equation (Table 1), it can be seen that, even if the correlations for most of the datasets are significant, there is no globally unique regression factor to adequately describe the relationship between chl-a (and SST) and isoprene. As shown in Table 1, during ASTRA-OMZ there was no significant correlation between chl-a and isoprene, whereas during SPACES and OASIS the correlation was significant but with low R^2-values (SPACES: R^2=0.30, OASIS: R^2=0.10) and different regression coefficients. Hackenberg et al. (2017) split their data from three different cruises into two SST bins with SST values higher and lower than 20°C, resulting in significant correlations with R^2-values from 0.37 to 0.82 depending on the cruise (Table 1). Ooki et al. (2015) described a multiple linear relationship between isoprene, chl-a and SST when using three different SST regimes (Table 1). Our correlations, using the approaches of Ooki et al. (2015) and Hackenberg et al. (2017), were significant, except for SST values higher than 27°C, but the regression coefficients were also significantly different to those found by Ooki et al. (2015) and Hackenberg et al. (2017). These varying equations demonstrate that bulk chl-a concentrations, or linear combinations of chl-a concentration and SST, do not adequately predict the variability of isoprene in the global surface ocean, but do point to these variables as among the main controls on isoprene concentration in the euphotic zone.

3.3 Modeling chl-a normalized isoprene production rates

The directly calculated production rate (P_{direct}) using Equation 7 and the indirectly calculated production rate (P_{need}) using Equation 10 were compared and were found to be significantly different (Figure 5a, difference in percent: $(P_{direct} - P_{need})/P_{need}*100$). The difference of more than -~~60~~70% between P_{direct} and P_{need} during SPACES/OASIS means that P_{direct} is too low to account for the measured isoprene concentrations, which is also

true for the equatorial region of ASTRA-OMZ. In the open ocean region of ASTRA-OMZ, the average difference between P_{direct} and P_{need} is the lowest but still highly variable from station to station. However, in the coastal region of ASTRA-OMZ the directly calculated isoprene production rate is highly overestimating the needed production by 75% on average. There are ~~two~~ three possible explanations for this difference: 1) the presence of a missing sink, which is not accounted for in the calculation of P_{need}. Adding an additional loss term to equation 10 would increase the needed production to reach the measured isoprene concentration. This sink would only be valid for this specific coastal region, but would increase the discrepancy between P_{direct} and P_{need} for all other performed cruises. Furthermore, this possible loss rate constant would have to be on average 0.22 day^{-1} and, therefore, higher than the main loss due to air sea gas exchange in the coastal region (see section 3.5 and Figure 8). Thus, it is highly unlikely that this additional loss term is the only reason for the discrepancy between P_{direct} and P_{need}; 2) uncertainty of using a light dependent log squared fit. Measurements from different laboratory studies used different species within one group of PFTs. All species within one PFT group were combined to produce a light dependent isoprene production rate (Figure S3), although the isoprene production variability of different species within one PFT group is quite high. This will certainly influence Pdirect, but cannot explain the 70% difference between Pdirect and Pneed measured at SPACES/OASIS and ASTRA-OMZ (equator) (Figure 5); ~~2~~3) incorrect literature derived chl-a normalized isoprene production rate (P_{chloro}) for one or more groups of PFTs. For example, the high P_{direct} values, compared to the P_{need} values, during ASTRA-OMZ coincided with high chl-a concentrations in the coastal area. These coastal stations were, in contrast to all other measured stations, highly dominated by diatoms (up to 7.67 µg L^{-1}, Figure S5). This might point to a possibly incorrect P_{chloro} value (too high) for diatoms (and other PFTs).

Therefore, we calculated new individual chl-a normalized production rates of each PFT ($P_{chloronew}$) within the MLD. We used the concentrations of haptophytes, cyanobacteria and *Prochlorococcus* for SPACES/OASIS and the concentrations of haptophytes, chlorophytes and diatoms for ASTRA-OMZ, as these PFT were the three most abundant PFTs of each cruise, accounting on average for ≥80% of total PFTs. We performed a multiple linear regression by fitting a linear equation between the P_{need} values for each station and the corresponding PFT chl-a concentrations (analogous to equation 7) to derive one new calculated $P_{chloronew}$ value for each PFT and cruise, which is listed in Table 3. The lower and upper limit of the $P_{chloronew}$ value was set to 0.5 and 50 µmol (g chl-*a*)$^{-1}$ day^{-1}, respectively, when performing the multiple linear regression, to avoid mathematically possible but biologically unreasonable negative chl-a normalized isoprene production rates. The upper limit was chosen in relation to the maximum published chl-a normalized isoprene production rate of *Prasinococcus capsulatus* by Exton et al. (2013) (32.16±5.76 µmol (g chl-a)$^{-1}$ day^{-1}). This rate was measured during common light levels of 300 µmol m^{-2} s^{-1}. Applying a same log squared relationship between light levels and the isoprene production rate as for the other PFTs would increase this value up to 50 µmol (g chl-*a*)$^{-1}$ day^{-1} at light levels of ~1000 µmol m^{-2} s^{-1}. ~~We only used the three most abundant PFTs for each cruise, which, contribute on average ≥80% to the total phytoplankton chl-a concentration.~~ Our tests using the whole PFT community for the multiple linear regression did not change our results and, in some cases, led to highly unlikely production rates for the less abundant PFTs.

With the help of the multiple linear regression derived $P_{chloronew}$ values, we calculated the new direct isoprene production rate (P_{calc}) in the same way as P_{direct} in equation 7. We compared our calculated P_{calc} values with the P_{need} values, which are shown in Figure 5b (difference in percent between P_{calc} and P_{need}). We found one outlier station for each cruise (SPACES: Station 1, OASIS: Station 10, ASTRA-OMZ: Station 17), when using the new

$P_{chloronew}$ values for each PFT for each whole cruise (Figure 5b, left part). We excluded these stations from every following calculation and redid the multiple linear regression. Furthermore, we split the ASTRA-OMZ into three different regions (equator, coast and open ocean), due to their contrasting biomass to isoprene concentration ratio, and calculated new $P_{chloronew}$ values for each of the three most abundant PFTs for SPACES, OASIS, and each part of ASTRA-OMZ.

Haptophytes were one of the three most abundant PFTs during all three cruises (Figure S5) and their $P_{chloronew}$ values range from 0.5 to 47.9 µmol (g chl-*a*)$^{-1}$ day^{-1} with a mean value of 17.9 ± 18.3 µmol (g chl-*a*)$^{-1}$ day^{-1} for all cruises. The haptophyte production rates exhibited two interesting features. First, this range is highly variable depending on the oceanic region (tropical ocean (SPACES), subtropical ocean (OASIS)) and different ocean regimes (coastal, open ocean). Second, the average value is different ~~than~~from the mean value of all laboratory study derived isoprene production rates of haptophytes (6.92±5.78 µmol (g chl-*a*)$^{-1}$ day^{-1}, Table 3). During SPACES/OASIS the $P_{chloronew}$ values of *Prochlorococcus* (both 0.5 µmol (g chl-*a*)$^{-1}$ day^{-1}) are slightly lower but in good agreement with ~~than~~ the mean literature value (~~9.66~~1.5 µmol (g chl-*a*)$^{-1}$ day^{-1}, Table 3), whereas the cyanobacteria values are higher (44.7 and 13.9 µmol (g chl-*a*)$^{-1}$ day^{-1}) than the literature value (6.04 µmol (g chl-*a*)$^{-1}$ day^{-1}, Table 3). Chlorophytes, as well as diatoms, are known to be low isoprene producers with mean P_{chloro} values of 1.47 µmol (g chl-*a*)$^{-1}$ day^{-1} and 2.5~~14~~ µmol (g chl-*a*)$^{-1}$ day^{-1}, respectively (Table 3). For diatoms, this is verified with our calculated rates during ASTRA-OMZ (all values ≤ 0.6 µmol (g chl-*a*)$^{-1}$ day^{-1}), whereas the rate for chlorophytes in the coastal regions (6.1 µmol (g chl-*a*)$^{-1}$ day^{-1}) is significantly higher than in the open ocean and equatorial region during ASTRA-OMZ (0.5 µmol (g chl-*a*)$^{-1}$ day^{-1}). Over all three cruises no significant correlations were found between the new multiple linear regression derived $P_{chloronew}$ values of each PFT and any other parameter measured on the cruise. This may be caused by the high variability of the chl-a normalized production rates of different PFTs (Table 3). Another explanation could be the high variability of isoprene production of different species within one PFT group. For instance, in the PFT group of haptophytes, the isoprene production rates of two different strains of *Emiliania huxleyi* measured by Exton et al. (2013) were 11.28 ± 0.96 and 2.88 ± 0.48 µmol (g chl-*a*)$^{-1}$ day^{-1} for strain CCMP 1516 and CCMP 373, respectively. Laboratory culture experiments show that stress factors, like temperature and light, also influence the emission rate within one species (Shaw et al., 2003;Exton et al., 2013;Meskhidze et al., 2015). Srikanta Dani et al. (2017) showed that in a light regime of 100-600 µmol m^{-2} s^{-1} the isoprene emission rate was constantly increasing with higher light levels for the diatom *Chaetoceros calcitrans*, whereas the diatom *Phaeodyctylum tricornutum* was highest at 200 µmol m^{-2} s^{-1} and decreased at higher light levels. Furthermore, health conditions (Shaw et al., 2003), as well as the growth stage of the phytoplankton species (Milne et al., 1995), can also influence the isoprene emission rate.

With the new P_{calc} values, we slightly overestimate the needed production P_{need} by up to 20% on average (Figure 5b, right part). For SPACES and OASIS, except for stations 1 and 10, using one $P_{chloronew}$ value for each PFT for the whole cruise is reasonable because the biogeochemistry in these regions did not differ much within one cruise. This was not true for ASTRA-OMZ, due to the biogeochemically contrasting open ocean region and the coastal upwelling region. Using just one $P_{chloronew}$ value for each PFT for the whole cruise resulted in a highly overestimated and variable P_{calc} value (Figure 5b, "ASTRA-OMZ"). Therefore splitting this cruise into three different parts (equator, coast, open ocean), due to their different chl-*a* concentration and nutrient availability, resulted in less variable P_{calc} values. However, in the coastal region, the variability is still the highest, but with the new derived P_{calc} the agreement with P_{need} is significantly better than with P_{direct} (compare Figure 5a and b).

3.4 Drivers of isoprene production

As mentioned above, no significant correlations between each calculated $P_{chloronew}$ value and any other parameter during the three cruises were found. *Prochlorococcus* was one of the three most abundant PFTs during SPACES and OASIS, but concentrations decrease to almost zero in the colder open ocean and upwelling regions of ASTRA-OMZ (Figure 1), which confirms the general knowledge that *Prochlorococcus* is absent at temperatures <15°C (Johnson et al., 2006). Our newly derived production rates confirm the actual laboratory derived rates, demonstrating *Prochlorococcus* as a minor contributor to isoprene concentration. However, *Prochlorococcus* is especially abundant at high ocean temperatures, where isoprene production rates from the other PFTs show evidence of decreasing. Cyanobacteria concentrations (excluding *Prochlorococcus*) were also related to temperature, but, in contrast to *Prochlorococcus*, other cyanobacteria taxa can be abundant in colder waters during ASTRA-OMZ. The different derived isoprene productions rates for SPACES and OASIS might be related to the different mean ocean temperature and light levels during these cruises. During SPACES, with lower ocean temperatures and lower light levels, compared to OASIS, the production rate is higher. This relationship would confirm the findings of two independent laboratory studies of Bonsang et al. (2010) and Shaw et al. (2003). Bonsang et al. (2010) tested two species of cyanobacteria at 20°C and found higher isoprene production rates than a different species tested by Shaw et al. (2003) at 23°C and even stronger light intensities. However, Exton et al. (2013) measured the same rate as Shaw et al. (2003) at 26°C for one species, but a 5-times higher production rate for another species at the same temperature. This leads to the conclusion that the production rate is not dependent on one environmental parameter and varies from species to species within the group of cyanobacteria.

~~However, c~~Comparing the calculated isoprene production rates of the haptophytes with global radiation, ocean temperature, salinity and nitrate results in some interesting qualitative trends (Figure 6). Mean global radiation during SPACES (~360 W m^{-2}) was lower than during OASIS (~457 W m^{-2}). Highest mean values were measured during ASTRA-OMZ (at equator, ~508 W m^{-2}). The same trend can be seen in the $P_{chloronew}$ values of the haptophytes. Within the open ocean and coastal regimes of ASTRA-OMZ, the isoprene production rate was lower than around the equator~~low, again showing the same trend as the~~ (mean global radiation ~~(~~decreased to ~310 W m^{-2}). A similar trend can be seen with the mean ocean temperature and the $P_{chloronew}$ values of the haptophytes. These results are similar to several laboratory experiments with monocultures: Higher light intensities and water temperatures enhance phytoplankton ability to produce isoprene (Shaw et al., 2003;Exton et al., 2013;Meskhidze et al., 2015). However, Meskhidze et al. (2015) showed in laboratory experiments that isoprene production rates from two diatoms species were highest when incubated in water temperatures of 22 to 26°C. Higher temperatures caused a decrease in isoprene production rate. During OASIS, mean water temperatures were 27.3°C with up to 29.2°C near the Maldives. Increasing ocean temperatures influence the growth rate of phytoplankton generally, but also differently within one group of PFTs. For haptophytes, Huertas et al. (2011) show that two strains of *Emiliania huxleyi* were not tolerant to a temperature increase from 22°C to 30°C, whereas *Isochrysis galbana* could adapt to the increased temperature. In general, the optimal growth rate temperature decreases with higher latitude (Chen, 2015), but the link between growth rate of phytoplankton and isoprene production rate is still not known. Assuming~~If~~ this temperature dependence can be transferred from diatoms also to haptophytes, the high seawater temperatures during OASIS could explain why the calculated

isoprene production rate is lower than in the ASTRA-OMZ-equatorial regi ***Prochlorococcus* was one of the three** me. Additionally, as mentioned before, the temperature as well as the light dependence of isoprene production might vary between different species of haptophytes when comparing different ocean regimes. Another reason for the very high isoprene production rate of haptophytes in the equatorial regime during ASTRA-OMZ, apart from temperature and light intensity, could be stress-induced production caused by low saline waters, which was already shown for dimethylsulphoniopropionate, a precursor for the climate relevant trace gas dimethyl sulphide, produced by phytoplankton (Shenoy et al., 2000). The salinity is considerably lower at the equator during ASTRA-OMZ than for all other cruise regions, with values down to 33.4. We observed that the $P_{chloronew}$ values decrease again in regions with ~~higher~~ more saline waters, where phytoplankton likely experience less stress due to salinity, temperature or light levels (Figure 6).

In order to identify parameters that influence not only the chl-a normalized isoprene production rate of haptophytes, but the rate of all PFTs together, we calculated a normalized isoprene production rate (P_{norm}) independent from the absolute amount of each PFT. Hence, we divided each P_{calc} value at every station by the amount of the three most abundant PFTs:

$$P_{norm} = \frac{\sum_{i=1}^{3} P_{chloronew_i} \times [PFT]_i}{\sum_{i=1}^{3} [PFT]_i} = \frac{P_{calc}}{\sum_{i=1}^{3} [PFT]_i} \quad (11)$$

i = three most abundant PFTs during each cruise.

The P_{norm} value helps us to obtain more insight about the influencing factors at each station, rather than only one mean data point for each cruise. We plotted the P_{norm} values of each station versus the ocean temperature and ~~color~~ color-coded them by nitrate concentration as a marker for the nutrient availability (Figure 7). During SPACES (squares) and OASIS (triangles), the normalized production rate is on average 12.8±2.2 pmol (µg PFT)$^{-1}$ day^{-1} and independent from the ocean temperature, while the nitrate concentration is very low (0.33±0.53 µmol L^{-1}). During ASTRA-OMZ (circles) in the coastal and open ocean region, the nitrate concentrations were significantly higher (16.4±5.5 µmol L^{-1}), but the P_{norm} values were lower (< 8 pmol (µg PFT)$^{-1}$ day^{-1}) correlating with lower ocean temperatures. In the equatorial region of ASTRA-OMZ, the production rates are significantly higher than during SPACES and OASIS, with up to 36.4 pmol (µg PFT)$^{-1}$ day^{-1}. On the right panel of Figure 7, the mean salinity for each P_{norm} dependent box (separated by the dashed lines) is shown. ASTRA-OMZ (equator) and SPACES and OASIS do not differ in ocean temperature or in nitrate concentration. However, the normalized production is significantly higher at the ASTRA-OMZ equatorial region, which may be caused by the low salinity there. In summary: 1) During ASTRA-OMZ (coast, open ocean) P_{norm} is comparably lower (< 8 pmol (µg PFT)$^{-1}$ day^{-1}) under "biogeochemically active" conditions (high nitrate concentration) but increases with increasing ocean temperature, 2) Under limited nutrient conditions P_{norm} is significantly increased likely due to nutrient stress 3) If the phytoplankton are additionally stressed due to lower salinity, P_{norm} is furthermore increased. These results show that there is no main parameter driving the isoprene production rate, resulting in a more complex interaction of physical and biological parameters influencing the phytoplankton to produce isoprene.

3.5 Loss processes

The comparison between P_{calc} and P_{need} in Figure 5b shows a mean overestimation of 10-20%. This is likely due to a missing loss term in the calculation, which would balance out the needed and calculated isoprene production. Chemical loss (red dashed line) and loss due to air sea gas exchange (black solid line) using the gas

transfer parameterization of Wanninkhof (1992) were already included in the calculation (Equation 10) and their loss rate constants are shown in Figure 8. For comparison, we added the k_{AS} values using the parameterizations of Wanninkhof and McGillis (1999) (black dotted line) and Nightingale et al. (2000) (black dashed line). They have different wind speed dependencies of gas transfer, which could influence the computed isoprene loss at high wind speeds. The parameterization of Wanninkhof and McGillis (1999) is cubic and will increase the loss rate constant of isoprene due to air sea gas exchange at high winds compared to the other parameterizations (Figure 8, OASIS). Nightingale et al. (2000) is a combined linear and quadratic parameterization, which would decrease the isoprene loss due to air sea gas exchange. However, during ~~these cruises~~SPACES and ASTRA-OMZ the wind speed was between 8 and 10 m s^{-1} where the parameterization of Wanninkhof (1992) is higher than both Wanninkhof and McGillis (1999) and Nightingale et al. (2000). Therefore the use of these alternative parameterizations would even lower the loss rate constant due to air sea gas exchange, leading to the need of an additional loss rate in order to balance the isoprene production.

To calculate the additionally required consumption rate ($k_{consumption}$), we only used stations where a loss term was actually needed to balance the calculated and needed production ($P_{calc} > P_{need}$). Those values were averaged within each cruise and are shown in Figure 8. For comparison, we added the loss rate constants due to bacterial consumption from Palmer and Shaw (2005) (blue dashed line; 0.06 day^{-1}) and an updated value from Booge et al. (2016) (blue dotted line; 0.01 day^{-1}). Comparable to the chemical loss rate, the k_{BIOL} values were assumed to be constant (following the assumption of Palmer and Shaw (2005)), because no data about bacterial isoprene consumption in surface waters is available. Figure 8 clearly shows that the needed loss rate constant is not a constant factor. During SPACES and OASIS the loss rate constant is roughly in the middle of the assumed k_{BIOL} values of Palmer and Shaw (2005) and Booge et al. (2016), whereas during ASTRA-OMZ (equator and open ocean) the calculated loss rate constant fits quite well with the assumed value of Booge et al. (2016). In all four regions, the additional calculated sink is lower than the chemical loss and the loss due to air sea gas exchange, which is not true for the coastal region of ASTRA-OMZ. Here, ~~T~~the loss rate constant (0.1 day^{-1}) is about 10 times higher than in the open ocean region, resulting in a lifetime of isoprene of only 10 days, which is comparable to the lifetime due to air sea gas exchange during ~~SPACES~~ ASTRA-OMZ (open ocean) and OASIS. Physical loss, like advective mixing through the thermocline, cannot account for this sink, as this lifetime is assumed to be several years (Palmer and Shaw, 2005) and, therefore, negligible. Even a change in the chemical loss rate would only change the absolute value of the calculated loss rate constant, but not its variability. We tested a temperature dependent rate for the reaction with OH, but the mean difference of the temperature dependent k_{CHEM} to the non-temperature dependent k_{CHEM} was less than 2% for all temperature regimes during the cruises and, therefore, negligible. It must be noted that the loss rate~~s~~ due to the reaction~~s~~ with OH is a gas phase reaction rate (Atkinson et al., 2004) and the used rate for reaction with singlet oxygen derives from measurements in chloroform (Monroe, 1981)~~are gas phase reaction rates~~, meaning that ~~they~~ these rates might not be suitable for isoprene reactions in the water phase. These rates, involving possible temperature and pressure dependencies, have to be evaluated in seawater in order to determine the chemical loss in the water column.

Marine produced halocarbons, like dibromomethane and methyl bromide, are known to undergo bacterial degradation (Goodwin et al., 1998). Compared to halocarbons, isoprene is not toxic and has two energy-rich double bonds and, therefore, may be even favored to be oxidized by heterotrophic marine bacteria (Acuña Alvarez et al., 2009). Figure 9~~Figure 9~~ shows a comparison of total bacteria counts and isoprene concentration from each station in the MLD. The correlation between bacteria and the concentration of isoprene is only

significant when haptophytes are less than 33% of the total phytoplankton chl-a concentration (R^2=0.80, p=2.34*10^{-7}). Haptophytes were one of the three dominant PFTs during all cruises and had a mean calculated isoprene production rate of 17.9 µmol (g chl-*a*)$^{-1}$ day^{-1} (Table 3). ~~Compared to literature values of other PFTs t~~This is a high isoprene production rate and we could assume higher isoprene concentrations higher concentrations of haptophytes. This relationship, however, is not evident (data not shown), which may be attributable to other processes masking this relationship. Multiplying the chl-a normalized isoprene production rate of 17.9 µmol (g chl-*a*)$^{-1}$ day^{-1} with the chl-a concentration of haptophytes results in a mean isoprene production rate of ~ 3 pmol L^{-1} day^{-1} which is about 4 times higher than the mean calculated loss rate due to bacterial degradation over all cruises (~ 0.8 pmol L^{-1} day^{-1}). This could hide the correlation of isoprene concentrations with bacteria when haptophytes are dominant (>33%). In addition, haptophytes themselves are suggested to be the main marine bacterial grazers, compared to other PFTs (Unrein et al., 2014). This leads to the hypothesis that, if there is a lot of isoprene abundant which can be used (e.g. as energy source) by bacteria, also the bacteria abundance will increase, independent of any PFT. However, if the phytoplankton community is dominated (>33%) by haptophytes, the isoprene concentration is no longer correlated to the bacteria abundance, due to the grazing of bacteria by haptophytes (Figure 9, total bacteria cell counts of black points are lower than of the red points at similar isoprene concentrations). ~~This leads to the hypothesis that, if the phytoplankton community is dominated (>33%) by haptophytes, the isoprene production rate is much higher than the degradation rate by bacteria and, therefore, no longer correlated to the bacteria abundance.~~

Due to the different loss rate constants of bacterial degradation (~0.01 day^{-1} during ASTRA-OMZ (equator) compared to ~0.1 day^{-1} in the coastal region of ASTRA-OMZ, Figure 8) in the different regions it is important to identify their dependence ~~scale the loss~~on environmental parameters. Unfortunately, the absolute amount of bacteria does not have a significant influence on $k_{consumption}$ (Figure 10a,b), which may be caused by different heterotrophic bacteria, each with a different ability to use isoprene as an energy source. However, we find a similar qualitative trend for $k_{consumption}$ and the apparent oxygen utilization (AOU) (difference of equilibrium oxygen saturation concentration and the actual measured dissolved oxygen concentration) during the three cruises (Figure 10c). The higher loss rate constant of isoprene due to possible bacterial consumption coincides with considerably higher AOU values in the coastal regime of ASTRA-OMZ, which may be caused by heterotrophic respiration. Even if this correlation is not significant, this trend points to the influence of environmental conditions on biological activity, which in turn influences the isoprene consumption.

4 Conclusions

For the first time, marine isoprene measurements were performed in the eastern Pacific Ocean. In addition, our isoprene measurements in the highly undersampled Indian Ocean further increase the small dataset of oceanic isoprene measurements in this region. The results from both oceans show that isoprene is well mixed in the MLD. Despite the known biogenic origin of isoprene, the marine isoprene concentrations cannot be described globally with a simple parameterization including chl-a concentration or SST or a combination of both. On regional scales this relationship might be sometimes significant (Ooki et al., 2015;Hackenberg et al., 2017), but laboratory monoculture experiments show that isoprene production rates range widely over all different PFTs, as well as within one PFT (collection of literature values in Booge et al. (2016)). The production rates from laboratory experiments have to be evaluated in the field, as different PFTs are not distributed equally over the

world ocean and are also influenced by temperature and salinity, as well as changing light levels. Therefore we used isoprene measurements as well as different phytoplankton marker pigment measurements to derive in-field production~~s~~ rates for haptophytes, cyanobacteria, *Prochlorococcus*, chlorophytes, and diatoms in different regions. The results ~~show~~ confirm findings from previous laboratory studies that the isoprene production is influenced by light and~~,~~ ocean temperature, due to stress, and ~~salinity~~nutrients, due to their effect on changing phytoplankton communities and their abundances (e.g. Dani and Loreto, 2017;Shaw et al., 2010). Moreover, our data leads to the conclusion that isoprene production rates in the field, irrespective of phytoplankton communities and their abundance, are influenced by salinity and nutrient levels, which has never been shown before. ~~with an indication that the nutrient regime might exert some influence.~~ Our calculations also show that, besides chemical loss and the loss due to air sea gas exchange, another non-static isoprene consumption process has to be taken into account to understand isoprene concentrations in the surface ocean. This loss may be attributed to bacterial degradation, or more generally, to heterotrophic respiration, as we could show a similar qualitative trend between the additional loss rate constant and the AOU. These results clearly indicate that further experiments are needed to evaluate isoprene production rates for every PFT in general, but additionally under different biogeochemical conditions (light, salinity, temperature, nutrients). With the help of incubation experiments under different conditions, the additional loss process can be investigated. The exact knowledge of the different production and loss processes, as well as their interaction, is crucial in understanding global marine isoprene cycling. Furthermore, the most appropriate wind speed based k parameterization to compute ~~A~~air sea gas exchange, the main loss process for isoprene in the ocean, must be used in future studies.~~has further to be assessed due to the variability and the uncertainty of the different k parameterizations.~~ Different parameterizations under different wind levels highly influence the loss term, which is additionally influenced by surface films at low or bubble generation at high wind speeds. ~~The evaluation of these~~ Isoprene loss processes, in conjunction with the complexity ~~variability~~ of isoprene production ~~by phytoplankton~~, should be further examined in order to predict marine isoprene concentrations and evaluate ~~its~~the impact of isoprene on SOA formation over the remote open ocean.

5 Data availability

All isoprene data and bacterial cell counts are available from the corresponding author. Pigment and nutrient data from SPACES/OASIS and ASTRA-OMZ will be available from PANGAEA, but for now can be obtained through the corresponding author.

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Table 1: Factors of different regression equations ([isoprene]=u*[chl-a]+v*SST+intercept) from different studies compared to factors from this study. Bold/*italic*/regular R^2 value: correlation significant/not significant/significance not known (significant: p<0.05). [chl-a] in µg L^{-1}, SST in °C, [isoprene] in pmol L^{-1}.

reference	cruise/region	SST bins	u	v	intercept	R^2
Hackenberg et al. (2017)	AMT 22 (Atlantic O.)	<20°C	37.9	---	17.5	**0.37** (n=39)
	AMT 23 (Atlantic O.)		15.1	---	18.4	**0.55** (n=11)

	ACCACIA 2 (Arctic)		34.1	---	11.1	**0.61** (n=34)
	AMT 22 (Atlantic O.)	≥20°C	300	---	-3.35	**0.60** (n=93)
	AMT 23 (Atlantic O.)		103	---	5.58	**0.82** (n=22)
Ooki et al. (2015)	Southern Ocean, Indian Ocean, Northwest Pacific Ocean, Bering Sea, western Arctic Ocean	3.3-17°C	14.3	2.27	2.83	**0.64**
		17-27°C	20.9	-1.92	63.1	**0.77**
		>27°C	319	8.55	-244	**0.75**
Kurihara et al. (2012)	Sagami Bay	no bin	10.7	---	5.9	**0.49** (n=8)
Kurihara et al. (2010)	Western North Pacific	no bin	18.8	---	6.1	**0.79** (n=60)
Broadgate et al. (1997)	North Sea	no bin	6.4	---	1.2	0.62
This study	whole study	no bin	2.45	---	22.1	**0.07** (n=138)
	SPACES (Indian Ocean)		20.2	---	8.01	**0.30** (n=37)
	OASIS (Indian Ocean)		42.6	---	12.6	**0.10** (n=59)
	ASTRA-OMZ (Southeast Pacific O.)		1.26	---	26.5	*0.07* (n=42)
		<20°C	3.92	---	11.5	**0.59** (n=46)
		≥20°C	25.6	---	16.6	**0.14** (n=92)
		3.3-17°C	1.30	10.0	-144	**0.84** (n=10)
		17-27°C	10.4	0.76	-3.70	**0.41** (n=97)
		>27°C	40.4	-0.58	39.7	*0.17* (n=31)

Table 2: Emission factor (*EF*) of each PFT determined by applying a log squared relationship between light intensity and isoprene production rates resulting from published phytoplankton cultures experiments.

~~Species~~PFT	emission factor	references of literature values used for fitting*
Diatoms	0.0064	Shaw et al. (2003), Bonsang et al. (2010), Exton et al. (2013), Meskhidze et al. (2015)
Chlorophytes	0.0168	Shaw et al. (2003), Bonsang et al. (2010), Exton et al. (2013)
Dinoflagellates	0.0176	Exton et al. (2013)
Haptophytes	0.0099	Shaw et al. (2003), Bonsang et al. (2010), Exton et al. (2013)
Cyanobacteria	0.0097	Shaw et al. (2003), Bonsang et al. (2010), Exton et al. (2013)
Cryptophytes	0.0120	Exton et al. (2013)
Prochlorococcus	0.0053	Shaw et al. (2003)

***exact species within a PFT tested for calculation production rates can be found in the references cited for each PFT**

Table 3: Calculated chl-a normalized isoprene production rates ($P_{chloronew}$, µmol (g chl-*a*)$^{-1}$ day^{-1}) of the three most abundant PFTs during SPACES/OASIS (haptophytes, cyanobacteria, *Prochlorococcus*) and ASTRA-OMZ (haptophytes, chlorophytes, diatoms). Number indicated after \ denotes ~~that~~ a station that has been excluded from the analysis. For explanation of the omission, please refer to paragraph 3.3.

cruise		haptophytes	cyanobacteria	*Prochlorococcus*	chlorophytes	diatoms
SPACES\1		0.5	44.7	0.5	--	--
OASIS\10		21.2	13.9	0.5	--	--
ASTRA-OMZ	equator	47.9	--	--	0.5	0.5
	coast\17	9.6	--	--	6.1	0.6
	open ocean	10.3	--	--	0.5	0.5
Collection of literature values in Booge et al. (2016)		6.92	6.04	~~9.66~~1.5*	1.47	~~2.54~~2.51*

*production rates from Arnold et al. (2009) were excluded from literature values listed in Booge et al. (2016)

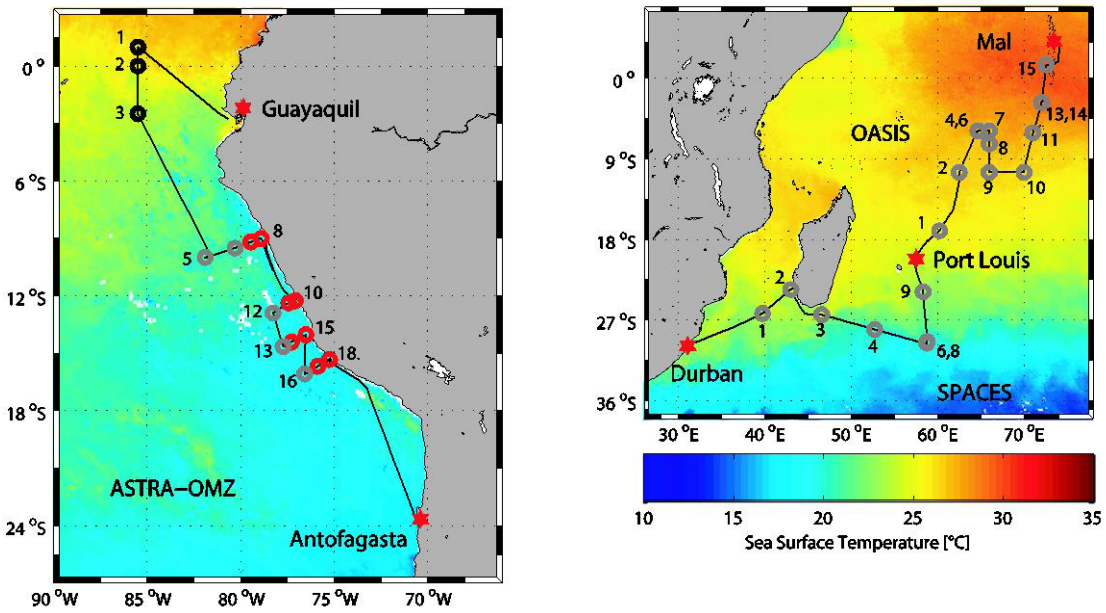

Figure 1: Cruise tracks (black) of ASTRA-OMZ (October 2015, East Pacific Ocean) and SPACES/OASIS (July/August 2014, Indian Ocean) plotted on top of monthly mean sea surface temperature detected by the Moderate Resolution Imaging Spectroradiometer (MODIS) instrument on board the Aqua satellite. Circles indicate CTD stations (grey: SPACES/OASIS and open ocean stations during ASTRA-OMZ, black: equatorial stations during ASTRA-OMZ, red: coastal stations during ASTRA-OMZ). Numbers indicate stations ~~number~~, where a CTD depth profile was performed. Stations 6 & 8 (SPACES) as well as stations 4 & 6 and 13 & 14 (OASIS) have almost the same geographical coordinates. If a station number is omitted (SPACES: stations 5 & 7; OASIS: stations 3, 5 & 12; ASTRA-OMZ: stations 4 & 9) no CTD cast was performed.

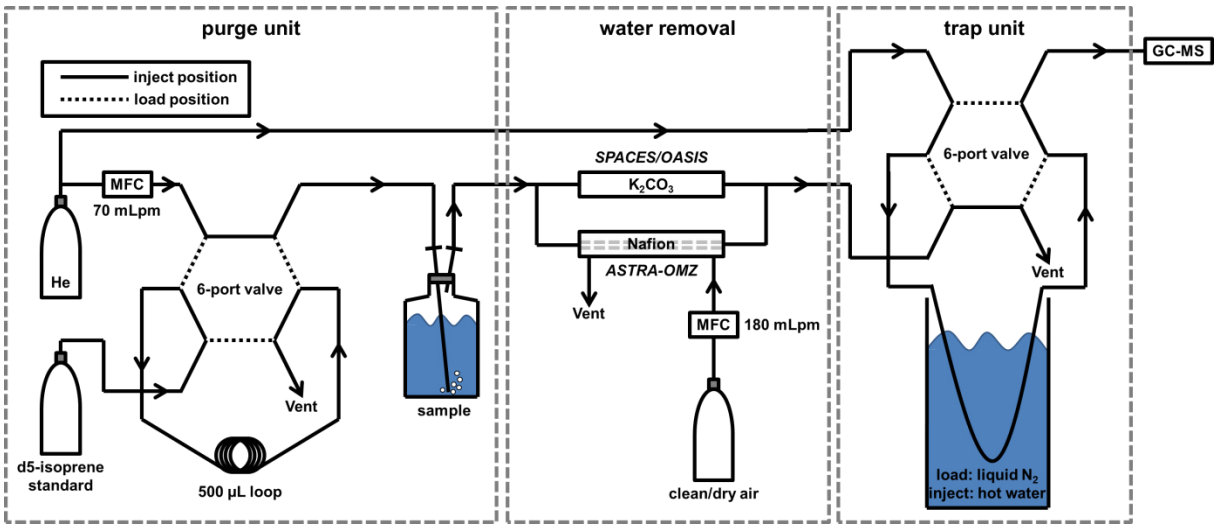

Figure 2: Schematic overview of the analytical purge-and-trap-system, divided into three parts: purge unit (left), water removal (middle) and trap unit (right). He: helium, MFC: Mass flow controller, K_2CO_3: potassium carbonate, GC-MS: gas chromatograph/mass spectrometer.

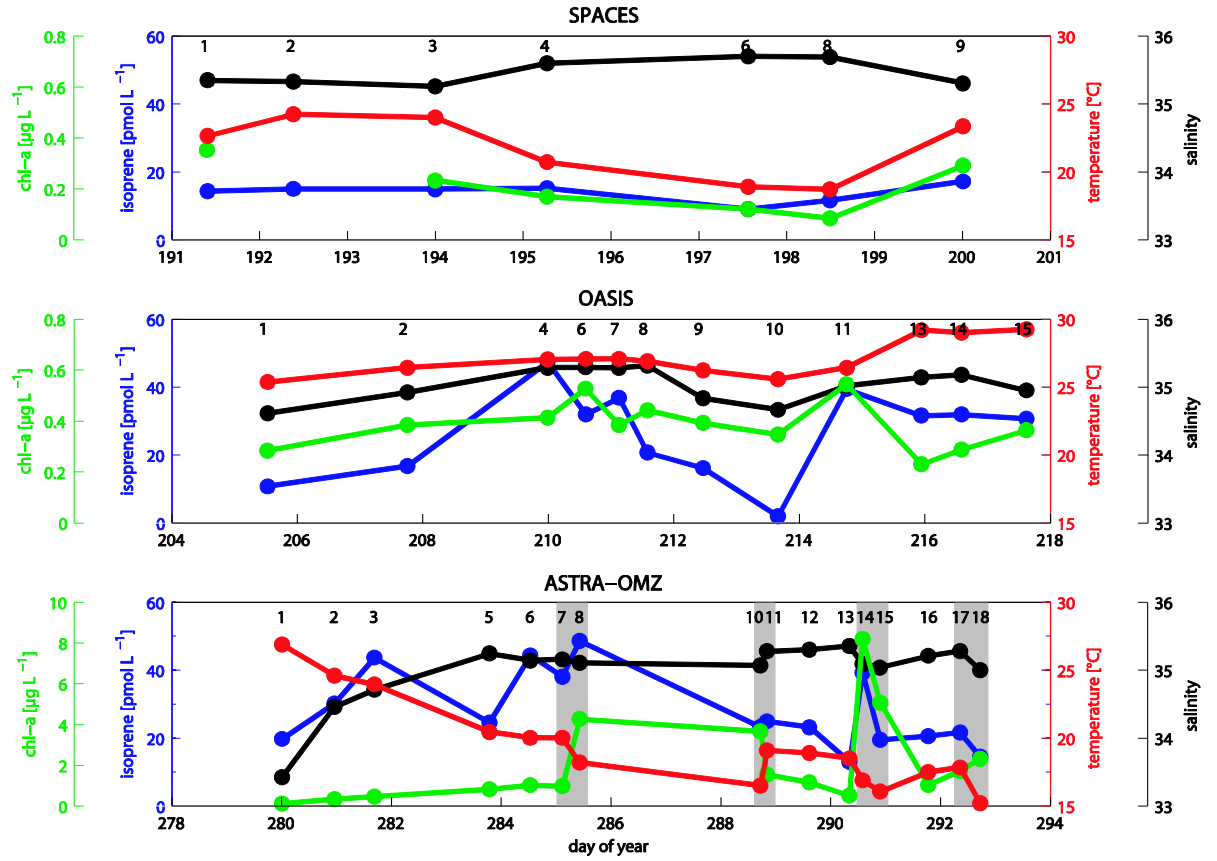

Figure 3: Mean salinity (black), isoprene concentration (blue), temperature (red), and chl-a concentration (green) in the MLD at each station during SPACES (upper panel), OASIS (middle panel), and ASTRA-OMZ (bottom panel). Grey rectangles highlight the 8 coastal stations during ASTRA-OMZ. Numbers in each panel refer to corresponding number of station.

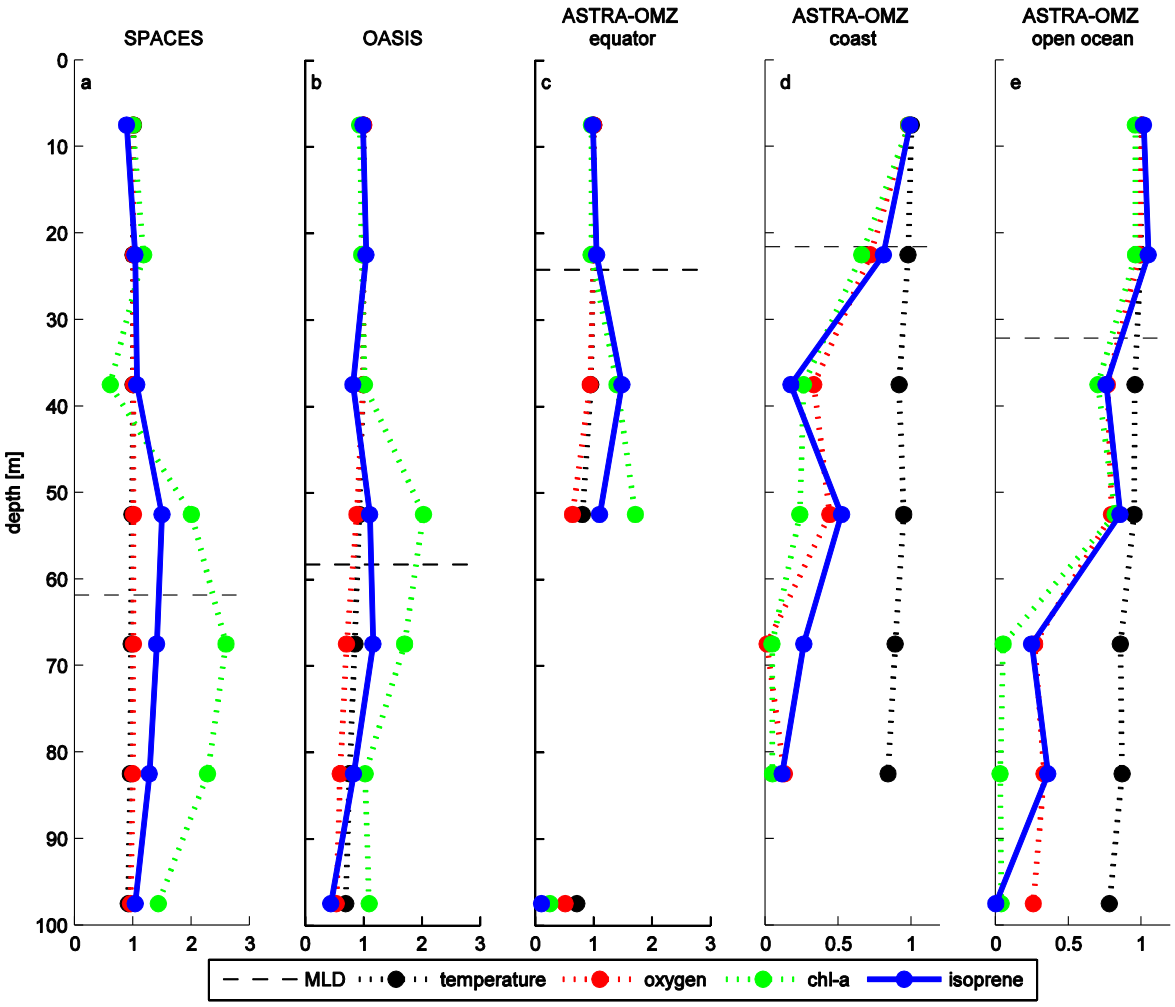

Figure 4: Mean normalized depth profiles of temperature (black), oxygen (red), chl-a (green) and isoprene (blue) during (a) SPACES, (b) OASIS, and (c,d,e) ASTRA-OMZ ~~(c: open ocean, d: coast)~~. The black dashed line represents the mean MLD for each cruise.

845

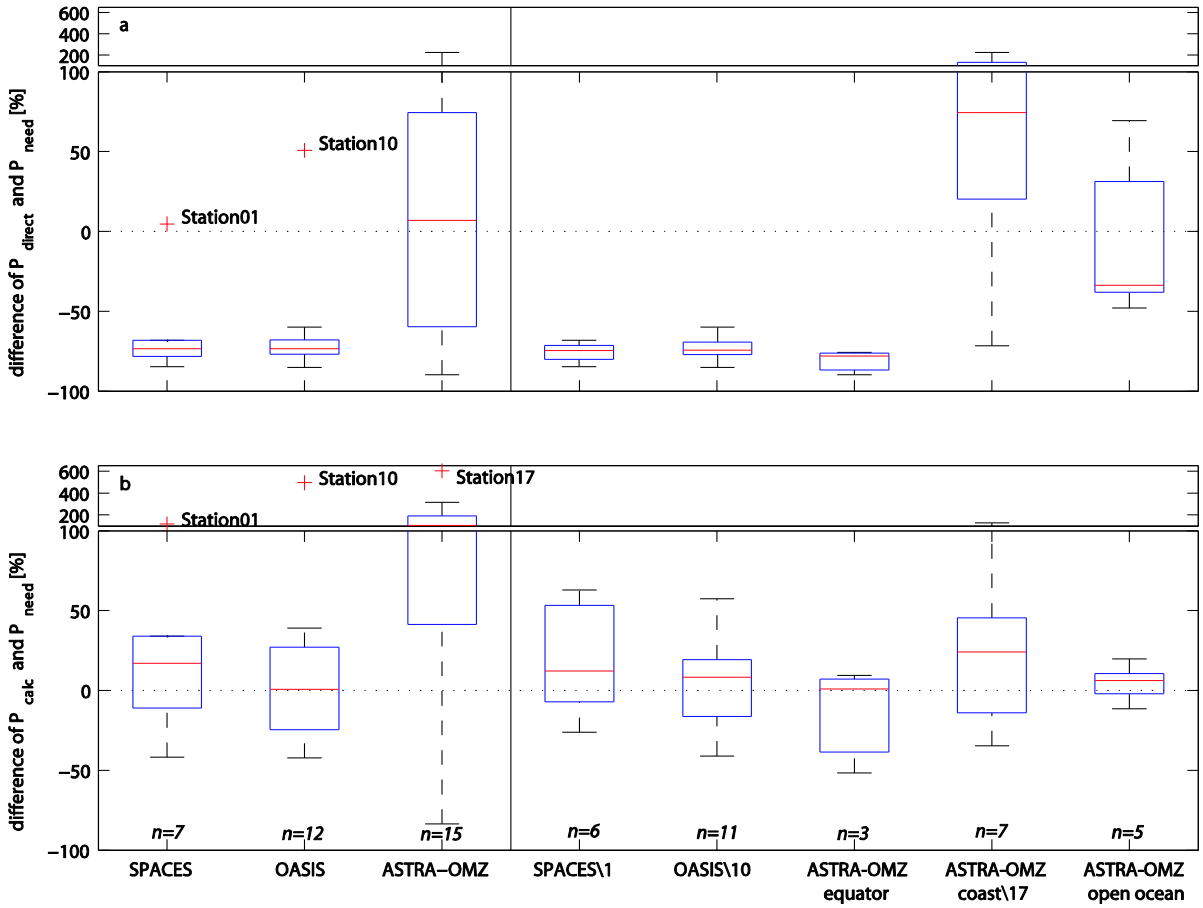

Figure 5: Percent differences between (a) P_{direct} and P_{need} ($(P_{direct}-P_{need})/P_{need}$) and (b) P_{calc} and P_{need} ($(P_{calc}-P_{need})/P_{need}$) for the different cruises / cruise regions. Left of the vertical black line data is divided into the three different cruises, right of the vertical black line data is shown for the three cruises where outliers from left part are excluded. Additionally, ASTRA-OMZ was split into three regions (equator, coast, open ocean). Number of stations (n) used for each set of data is shown in italics. The red line represents the median, the boxes show the first to third quartile and the whiskers illustrate the highest and lowest values that are not outliers. The red plus signs represent outliers. The number indicated after \ denotes ~~that~~ a station that has been excluded from the analysis.

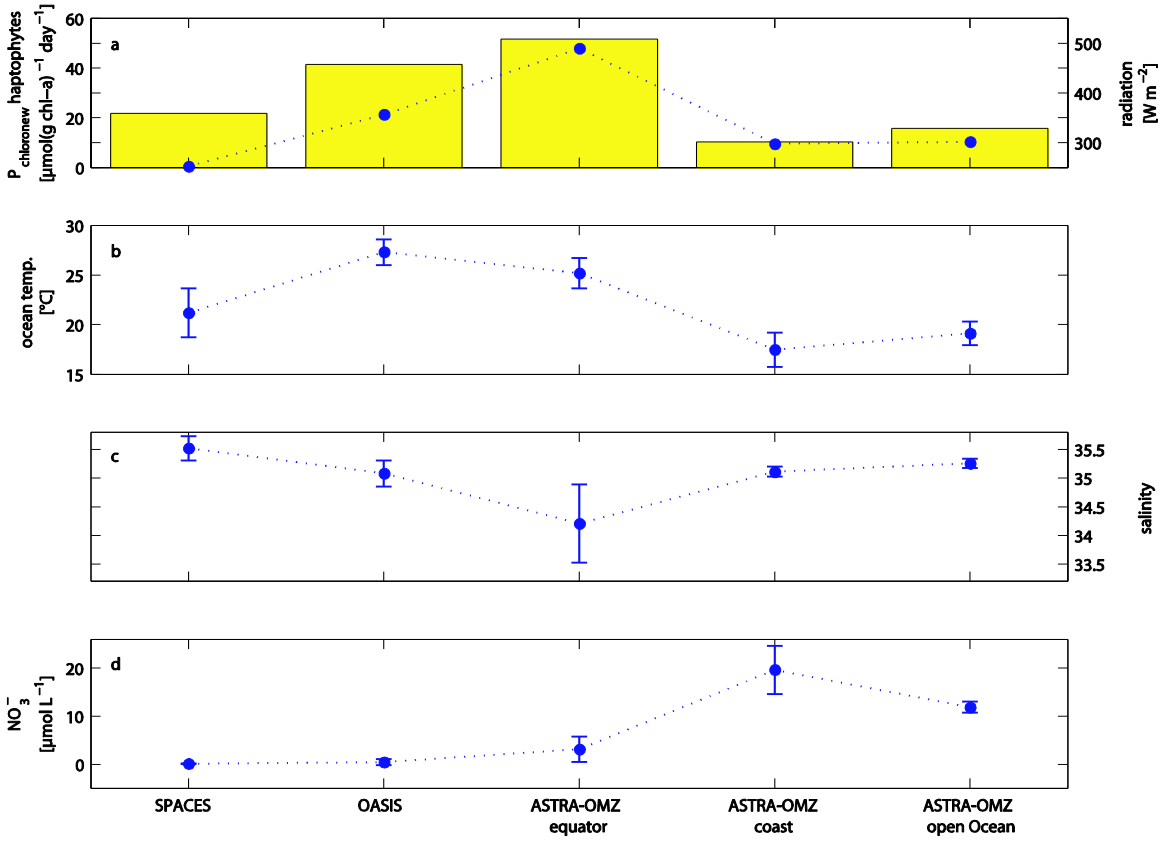

Figure 6: Mean values (± standard deviation) for (a) calculated $P_{chloronew}$ haptophytes (blue line) and global radiation (yellow bars), (b) ocean temperature, (c) salinity and (d) nitrate during SPACES/OASIS and ASTRA-OMZ (split into 3 different parts: equator, coast and open ocean).

860

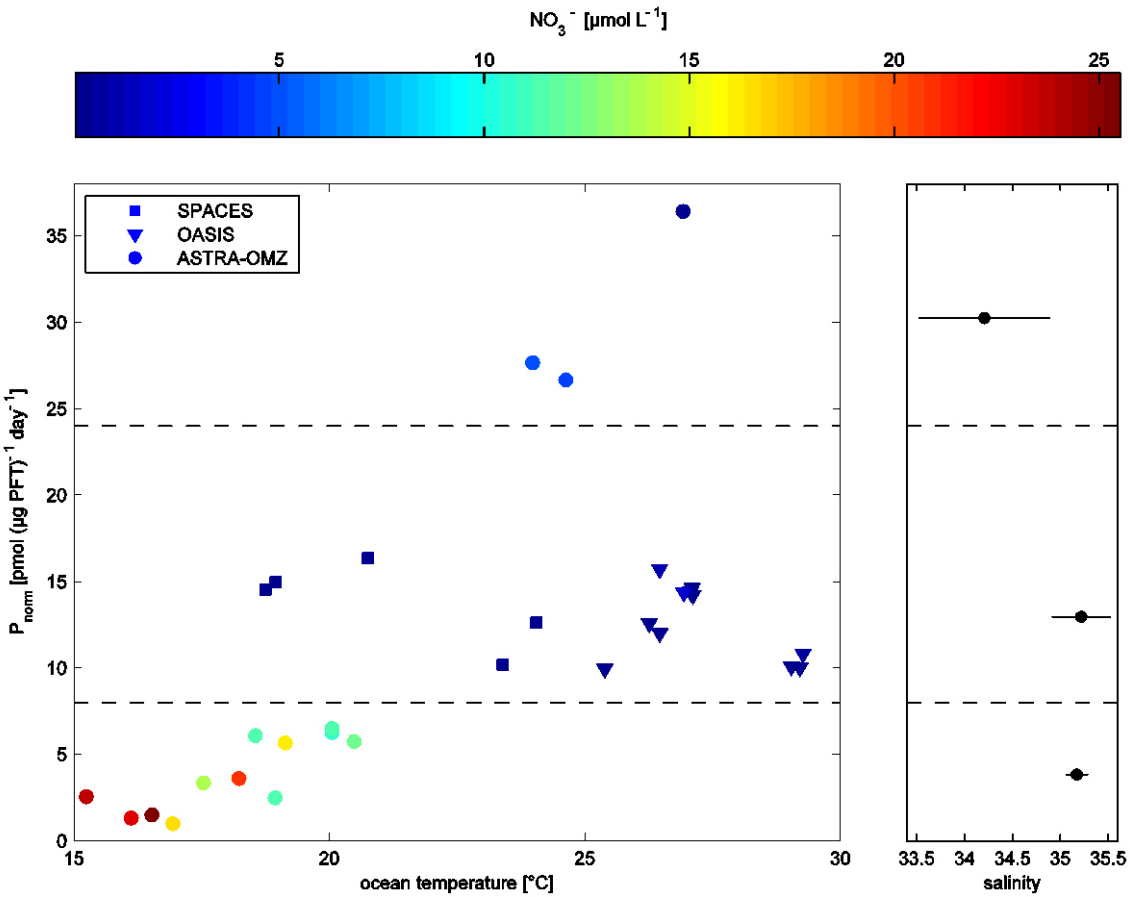

Figure 7: Left panel: Relationship between P_{norm} in pmol (µg PFT)$^{-1}$ day^{-1} and ocean temperature in °C during SPACES (squares), OASIS (triangles), and ASTRA-OMZ (circles) color-coded by NO_3^- in µmol L^{-1}. Right panel: mean salinity (± standard deviation) of samples from left side plot in each box divided by dashed lines.

865

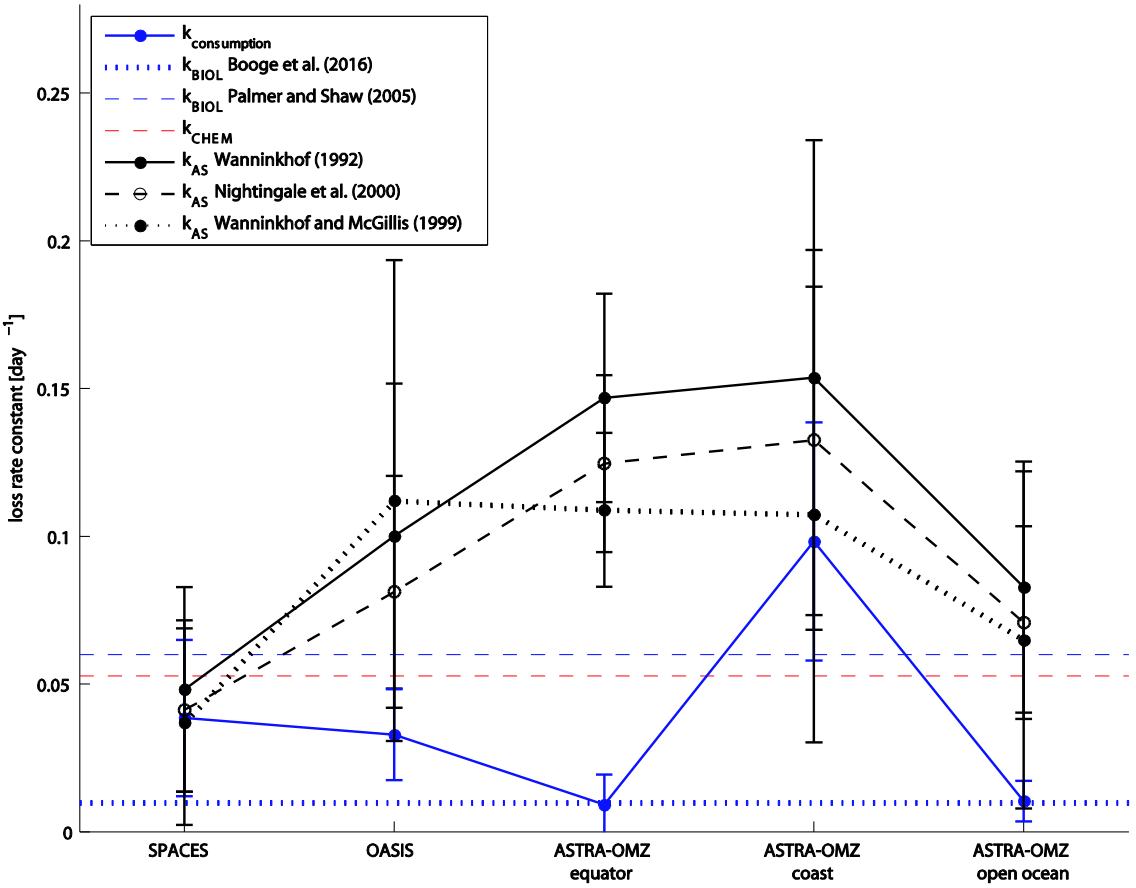

Figure 8: Different mean loss rate constants (± standard deviation) during SPACES, OASIS und ASTRA-OMZ. Blue points: calculated loss rate ($k_{consumption}$), blue dotted line: k_{BIOL} from Booge et al. (2016), blue dashed line: k_{BIOL} from Palmer and Shaw (2005), red dashed line: k_{CHEM}, black points: calculated loss rate constants due to air-sea-gas exchange.

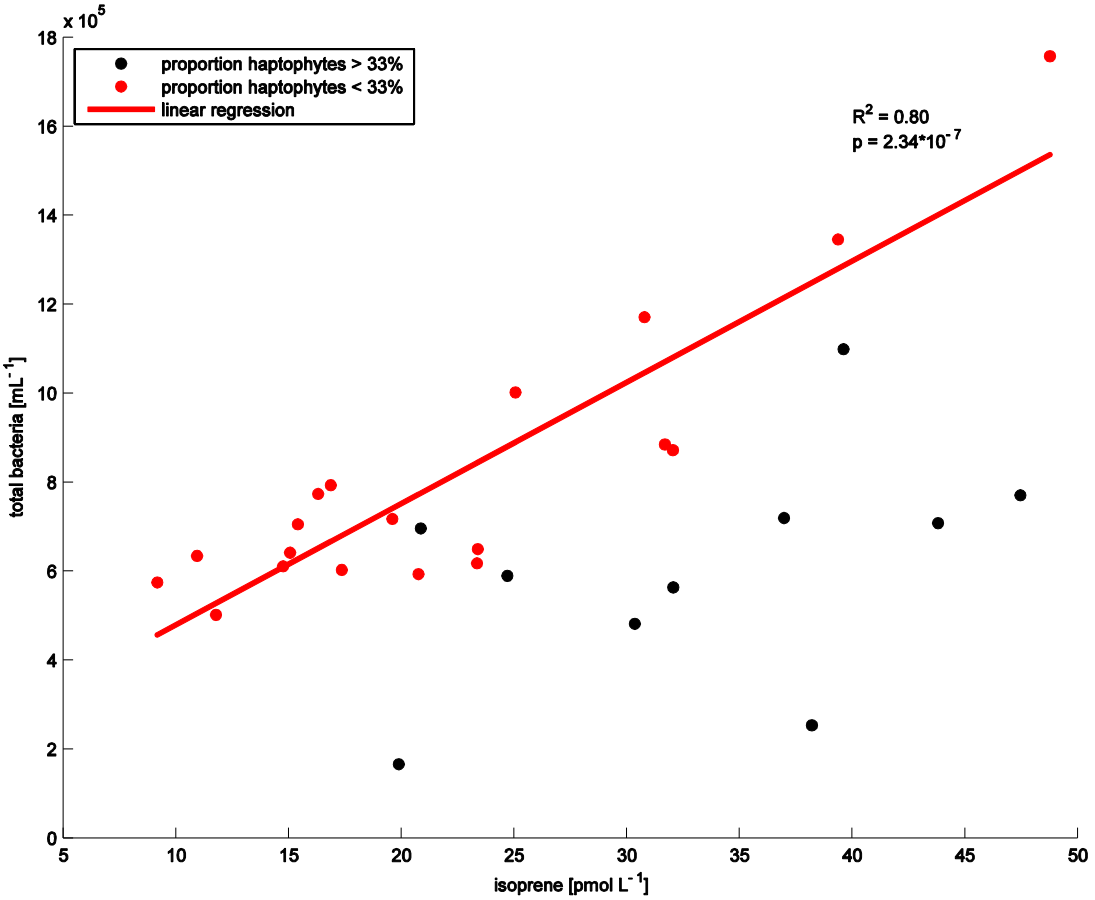

Figure 9: Relationship between isoprene concentration [pmol L^{-1}] and total bacteria counts [mL^{-1}] during SPACES/OASIS and ASTRA-OMZ. Black and red points represent samples where the contribution of haptophytes to the total phytoplankton chl-a concentration is higher and lower than 33%, respectively. Linear regression (R^2=0.80, p=2.34*10^{-7}) for red points only.

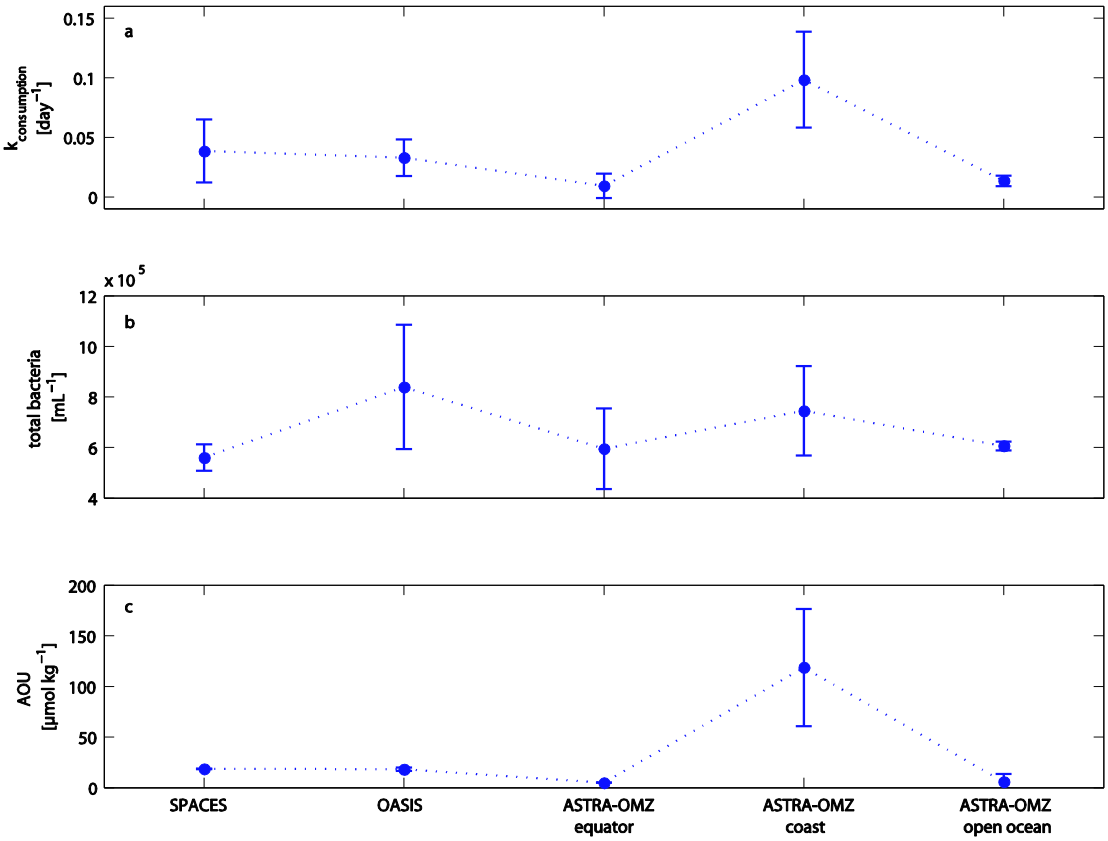

Figure 10: Mean values (± standard deviation) for (a) $k_{consumption}$ [day^{-1}], (b) total bacteria counts [mL^{-1}] and (c) AOU [µmol L^{-1}] during SPACES/OASIS and ASTRA-OMZ (split into 3 different parts: equator, coast and open ocean).

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Supplement

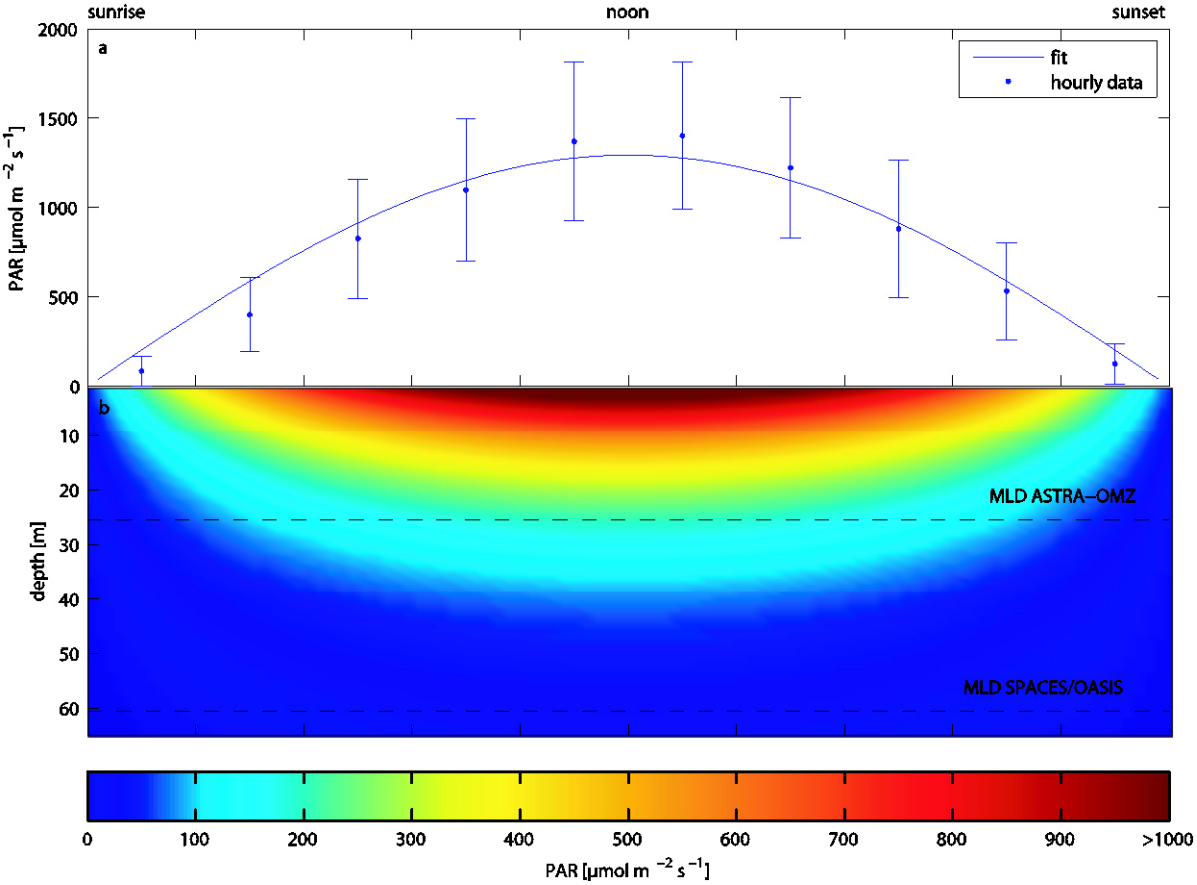

Figure S1: Example for above and in-water radiation. **(a) Data points represent hourly radiation measurements (converted from W m^{-2} into photosynthetic active radiation (PAR, µmol m^{-2} s^{-1}) as described in paragraph 2.6) from the ship (~~DOY 193.1 – 193.6 during SPACES~~mean values ± standard deviation from all cruises) ~~converted into photosynthetic active radiation (PAR, µmol m^{-2} s^{-1})~~, blue line is the fitted data using a sine function. (b) Underwater mean ~~C~~calculated PAR over the course of a day depending on depth by applying the attenuation coefficient K_dPAR and Beer-Lambert's law. Dashed line represents mean mixed layer depth (MLD) for each cruise.**

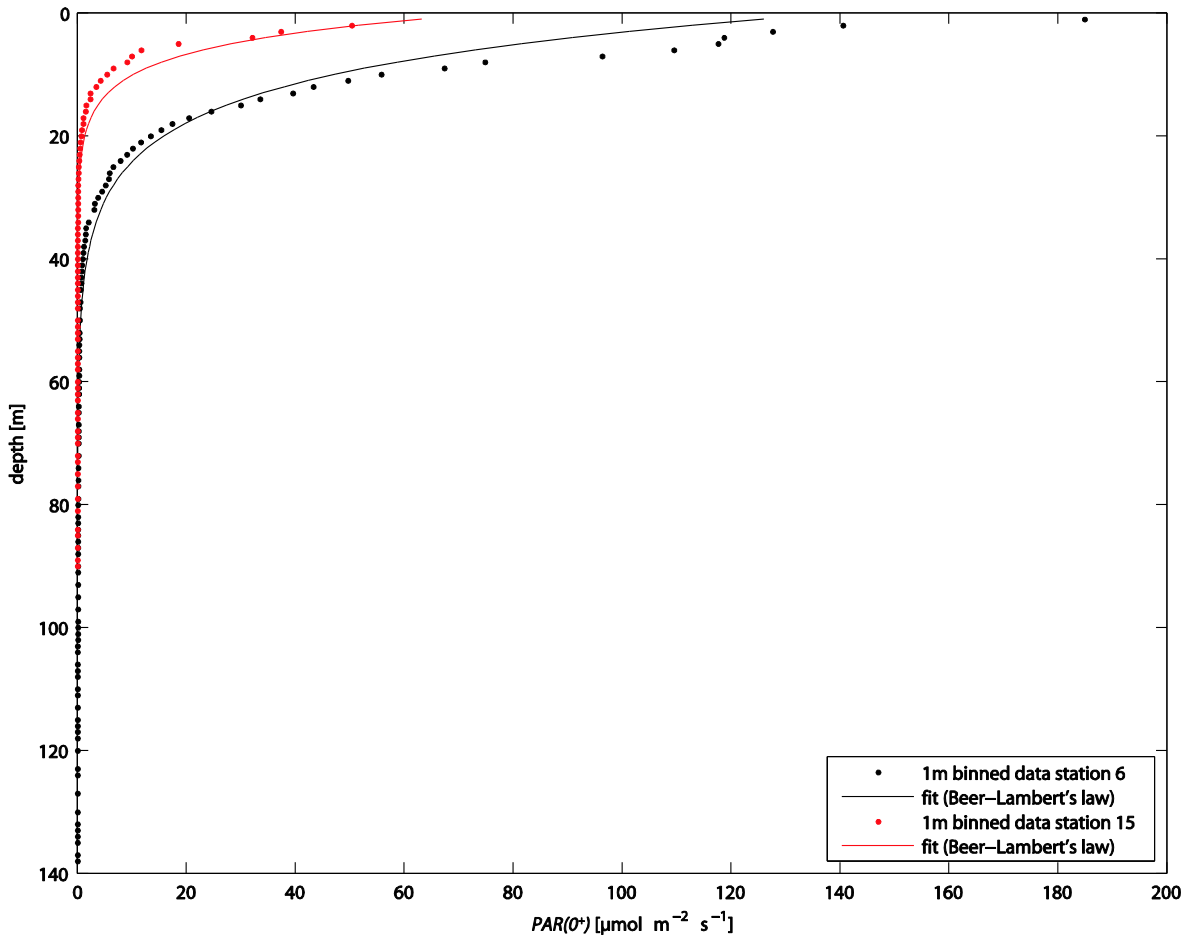

Figure S2: Example of two ~~E_d~~*PAR*(0^+) depth profile measurements during ASTRA-OMZ. Data points are 1m binned data of station 6 (black) and station 15 (red). The line is calculated from ~~E_d~~*PAR*(0^+) ~~profile~~ by applying Beer-Lambert's law using a mean~~station specific~~ attenuation coefficient K_d*PAR* obtained from ~~the~~ all E_d*PAR*(0^+) depth profile measurement~~s at the corresponding station~~ during OASIS and ASTRA-OMZ.

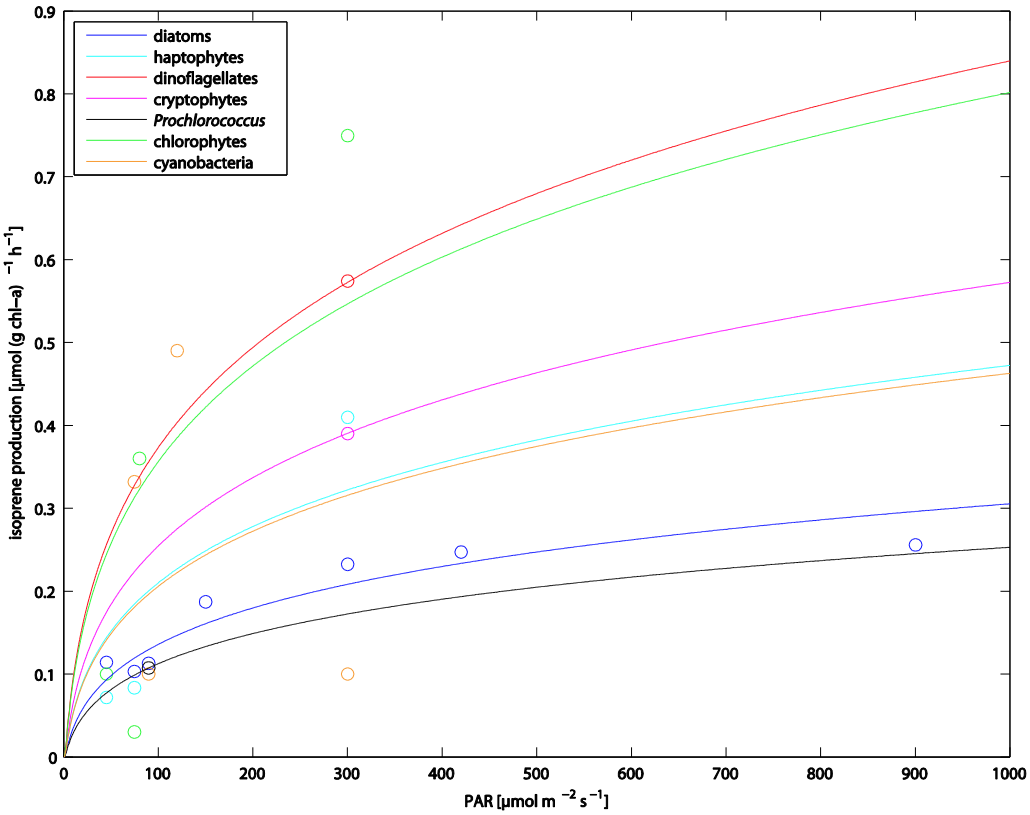

Figure S3: Single literature laboratory chl-a normalized isoprene production rates P_{chloro} (µmol isoprene (g chl-a)$^{-1}$ h^{-1}) (Table 2) as a log squared function of light intensity I (µmol m^{-2} s^{-1}).

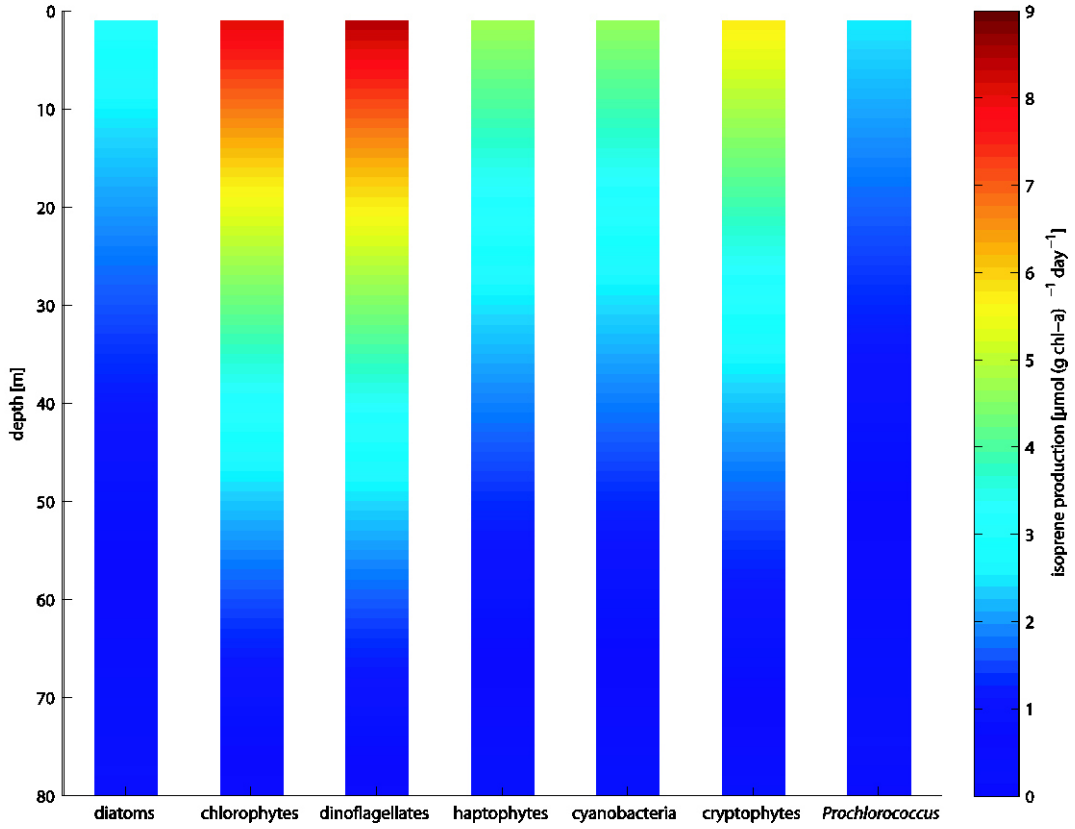

Figure S4: Example of calculated P_{chloro} values (µmol isoprene (g chl-a)$^{-1}$ day^{-1}) for each PFT at station 9 during SPACES depending on the depth in the water column.

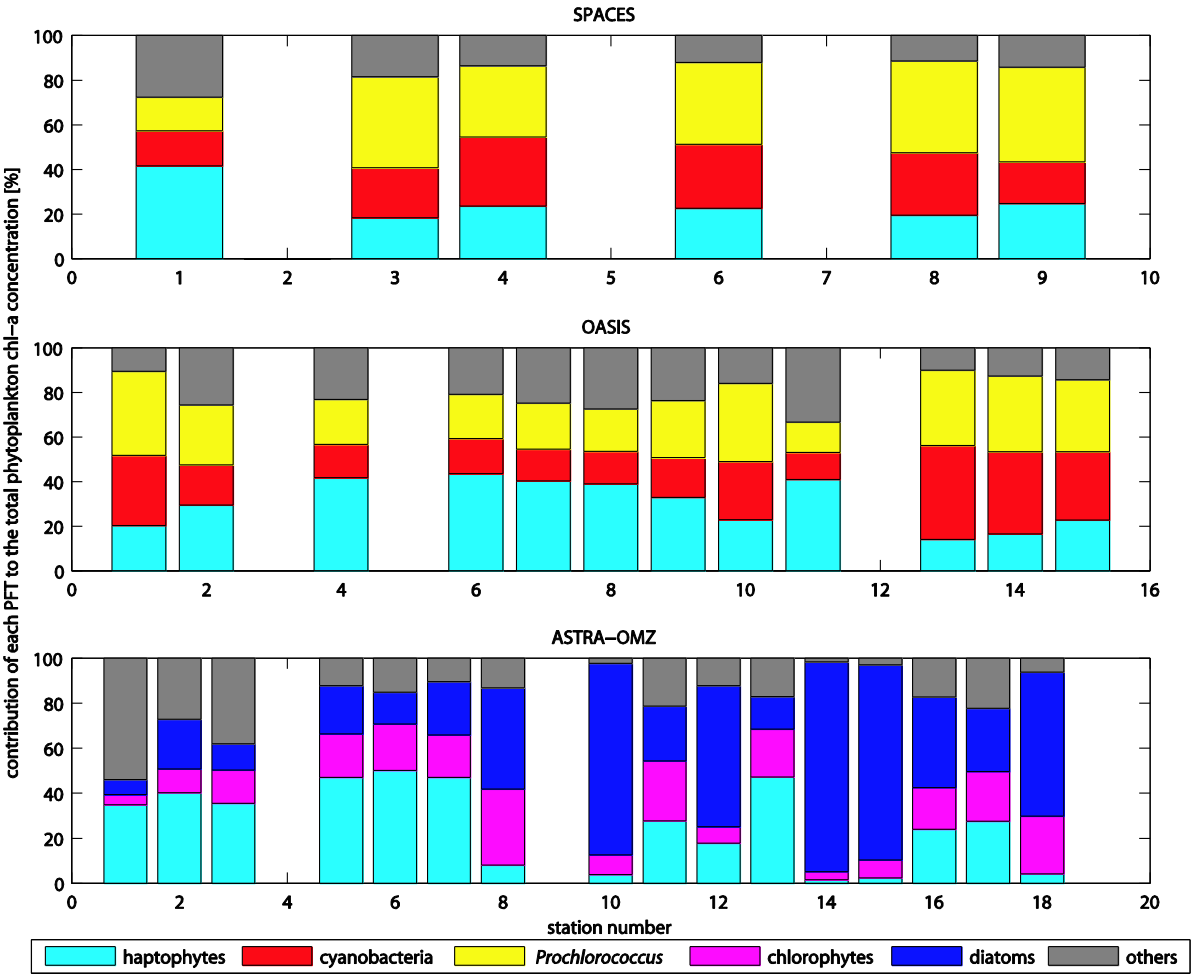

Figure S5: Contribution of each of the three most abundant PFTs to the total phytoplankton chl-a concentration at each station during SPACES (upper panel), OASIS (middle panel), and ASTRA-OMZ (bottom panel).