Atmospheric Chemistry and Physics Discussions

Interactive comment on "Evaluation of the global oceanic isoprene source and its impacts on marine organic carbon aerosol" *by* S. R. Arnold et al.

S. R. Arnold et al.

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We thank the 2 anonymous reviewers and Dr Shaw for their positive and helpful comments, and address their specific points below.

Reply to comments from Anonymous Reviewer 1

One aspect, however, was not dealt with although it is vital in establishing isoprene abundance over the ocean, i.e., the chemical oxidation rate. This is an important factor: when oxidation of isoprene is more efficient, a larger emission flux is needed to establish a specific concentration. The authors mention that degradation of isoprene may enhance the source of radicals (p 16460, l4-5). This then would speed up the isoprene oxidation by OH, a sort of positive feedback maybe. I missed some information

on the reactivity and reaction scheme of isoprene: what reactions are considered in GEOS-CHEM?

The isoprene oxidation scheme in GEOS-chem is based on the chemical mechanism of Horowitz et al. (1998). This scheme treats the dominant sinks for isoprene which are reaction with OH, O_3 and NO_3. The GEOS-chem model is described in Bey et al. (2001) and Park et al. (2003) which we cite in our paper.

Can it be expected that the isoprene chemistry scheme, probably developed for continental conditions (relatively high isoprene and low OH), is also representative for marine conditions?

To our knowledge, there is no indication that isoprene oxidation in the marine atmosphere may proceed differently from that in continental environments. The model may be missing small oceanic sources of other VOCs, which would also act as OH sinks, however these cannot be expected to impact OH to a significant extent (Lewis et al., (2001) showed oceanic alkenes to be 1% of the OH sink at Cape Grim) - the chief OH sinks are CO and methane. While we are not able to evaluate the model's CO and methane in the remote marine atmosphere, our recent study on organic carbon aerosol in these regions using the same model (Spracklen et al., 2008) demonstrated that the model does a good job at transporting continental sourced pollutants (e.g. black carbon) to these regions.

How does isoprene oxidation feed back to oxidant/radical concentrations in the model? However, I do not expect that the main conclusion of the paper, i.e., that isoprene does not contribute significantly to marine OC, will be different because of this.

Isoprene acts as an OH sink, and is oxidised rapidly to produce a suite of organic radical species that impact local oxidant chemistry. The parameterised isoprene oxidation scheme in the model attempts to capture these impacts. A recent study over the South American tropical forest has demonstrated the possibility that extra radical recycling in the isoprene oxidation mechanism may be occurring that is not included in

current models, which increases the abundance of OH expected for a given burden of isoprene (Lelieveld et al., 2008). However, while uncertainties in the isoprene oxidation mechanism certainly exist, we agree that these would not explain the order of magnitude increase in isoprene concentration required to produce significant amounts of OC aerosol.

One small comment: Table 2: the ITOP isoprene concentration is missing (-).

This has been corrected.

Reply to comments from Anonymous Reviewer 2

Page 16450, lines 15-17: Could you provide the uncertainty associated with the PFT distributions?

The PHYSAT PFT distributions give the dominant PFT in a given grid-cell of ocean based on satellite-observed ocean colour and a database of in-situ ship observations. Hence, they are a non-numerical product derived from an empirical method. It is therefore not possible to assign a quantitative uncertainty. A large effort has been made to evaluate the method using in-situ observations (Alvain et al., 2008). Situations where problems are more likely with the product (e.g. large aerosol column, poor representation of the in-situ community in the database) have been mentioned in the text.

Page 16451, lines 14-16: Could you comment on how truncating affects the final results, i.e. in addition to the negative values, how unrealistic the result would be if the tails were not restricted to the min and max observations?

We have tested the effects of removing truncation from the PDFs of isoprene production rate. The mean value is unaffected to 2 significant figures (remains 0.31 Tg/yr). The standard deviation increases slightly from 0.08 to 0.09 Tg/yr. This has no effect on our conclusions.

Page 16453, lines 16-17: Short lived chemical reactive compounds like isoprene experience large diurnal variability, do you account for this when comparing with observa-

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tions? And how?

Unfortunately we do not have information on the time of day at which the majority of the individual isoprene observations we are using were taken. This means it is not possible to compare directly the isoprene in the model with the observations over a diurnal cycle. If we assume a constant isoprene source we would expect the diurnal cycle in OH to result in a daytime minimum and nighttime maximum in isoprene (this may also be impacted by any diurnal variation in the marine boundary layer height, which would result in the same phase of cycle in isoprene, assuming a deeper - and hence more dilute - BL during the day). There is some evidence that there may be a photochemical dependency for the isoprene source (a dependence on photosynthetically active radiation has been observed (Shaw et al., 2003)), which may result in maximum diurnal emission and concentrations during daylight hours, however there are not sufficient data on this to parameterise a light-dependent source term across the PFTs of interest. With this limited information and in the absence of direct observations of the isoprene diurnal cycle over phytoplankton blooms, it is not possible to determine the expected diurnal profile of marine boundary layer isoprene over ocean source regions. This leads to further uncertainty in our 'top-down' emission estimates. We have acknowledged this point with the addition of the following text:

"Further uncertainty results from our model-observation comparisons. Information is not available on the time of day at which most of these observations were taken. It is therefore not possible to account for the isoprene diurnal cycle in comparisons of the model with the observations. In addition, it is not known if there is a diurnal cycle in the phytoplankton isoprene source. This leads to an uncertainty in our derivation of the source strength that best reproduces the observed isoprene abundance, since this is based on a diurnally constant emission and diurnal mean model output."

Page 16456, section 4: Please make clear differentiation between Tg-C and Tgcompound.

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We have used units of Tg(isoprene) for our isoprene source estimate and Tg(C) for OC aerosol. These units have been made clearer in this section - we always state TgC where this is intended.

Page 16457, lines 25-26 and next page discussion: Consideration of isoprene chemistry forming secondary organic aerosol instead of a flat 2% yield will affect the seasonal patterns, since it will alter the timing of maxima and thus the whole discussion that follows. In the present study secondary organic aerosol formation is uncoupled from chemistry

We have removed our discussion of the seasonality in the OC contribution from isoprene, as we recognise (as pointed out) that our 2% flat yield is not representative of expected seasonal variation in SOA production due to photochemistry. Relevant text has also been removed from the conclusions. In addition, the following text has been removed from the abstract: "In addition, we find the seasonal cycle of the isoprene SOA source is out of phase with the observed cycle in OC in the remote Southern Ocean."

Page 16458, lines 10 and 24, also page 16460 lines 22-24: Explain how decoupling is done and why this is needed. See also comment above that is relevant.

This aspect of the discussion has been removed.

Page 16456, lines 1 and 2: there are typos to the exponentials.

These have been corrected.

Reply to comments from S. Shaw

A variable relationship between isoprene production and chlorophyll-a is a reasonable possibility, as few phytoplankton species have as yet been tested for their production rates. I look forward to seeing the upcoming manuscript which reports these experiments and additional data. Despite their inclusion in a separate manuscript, it is important that the number of replicates and experimental series are reported in the

current manuscript so the reader can evaluate their repeatability. (Perhaps as additional columns in Table 1?) This is particularly important here as the production rates are statistically combined into PDFs for further use.

The aim of the PFT emissions study was to screen as many phytoplankton species as possible and therefore there are no replicates for the various species. However, since most species was monitored up to two days, the data presented here are a mean of several measurements (approx. 60 for diatoms). An additional column has been added to Table 1 containing this information.

A listing of other common PFT that are not included in the estimates due to the available satellite products could be included for those readers not familiar with phytoplankton types. Mention of any of these whose production rates have been measured would also be helpful.

We have added the following text to the description of our method:

"The PHYSAT product limits our analysis to the four PFTs that it considers. However, isoprene has also been observed to have been produced by *Trichodesmium* belonging to the nitrogen-fixation phytoplankton types. Our measured rates of isoprene production for *Trichodesmium* lie within one standard deviation of our mean rate for 'unclassified' species (Table 1)."

P16449, L24: How are the isoprene production rates related to chlorophyll-a concentration (e.g. linear, otherwise)? Please state briefly in advance of the separate manuscript.

The relationship between isoprene production rate and Chl-a is linear. The text has been modified to include this: "The rate of seawater isoprene production is **linearly** related to the chlorophyll-a concentration present in the sample."

Combining the measured production rates into PDFs is a creative idea, and one that should be used in future work as additional production rate data becomes available. An interesting possibility would be to include additional published production rate data into

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a second set of PDFs for each PFT as a comparison case to what is already reported here. Several papers have been published in the last few years which may or may not be useful for this purpose depending on the units of the reported production rates. This could be useful as a sensitivity study for the ensemble simulation and flux calculation. It would also be a simple way to increase the robustness of the values within each PFT.

We agree that it would be interesting to carry out the PDF and Monte-Carlo analysis using existing isoprene production data, however the production of new emission estimate and model simulations for these would take a fair amount of time. The advantage of using the new datasets that we have is that they were all taken under the same controlled conditions for each PFT. Inclusion of other datasets into the analysis would require careful screening to ensure they were truly comparable. We have compared production rates for specific haptophytes and diatoms with some previous published rates (Shaw et al., 2003) and find good agreement (Page 16450, Line 1) - values are certainly within the range of those used in our PDF analysis. We would not expect the magnitude of the emissions to be affected greatly by the inclusion of other data and hence the conclusions of the paper would remain unchanged.

Please mention if the general shapes (e.g. half-width) of the PDFs within each PFT are dramatically different from each other.

All PDFs are defined to be normally distributed. The relative magnitudes of the PDF widths can be quantified from the mean and standard deviation information available in Table 1. The standard deviations are in the range 40-70% of the mean for all PDFs.

In my opinion, the factor of 6 between the bottom-up and top-down estimates is not a large difference given the lack of species tested for isoprene production, and could easily be due to that reason alone. For example, the differences between reported production rates from cyanobacteria for different growth conditions are of that same order (P16450, L2). It is not clear which type of laboratory growth conditions, if any, best estimate in situ production rates. Production rates from same species at different

light and temperature levels varied by a factor of 4 at least (Shaw et al 2003), and that was just in one of several types of culturing apparatus that could be used. Factors of more than 10 would not be surprising as we do not yet know the biological reason for isoprene production by phytoplankton, and thus we can not be sure we are measuring what and how we should be measuring. The additional reasons mentioned in the manuscript (e.g. limited ambient data, difficulties with satellite data) are also possible very important contributors.

Our discussion of the factor 6 difference has been modified to take these comments into account.

We have also added some text to the abstract: "We suggest our reliance on limited atmospheric isoprene data, **difficulties in simulating in-situ production rates in the lab**, and limited knowledge of isoprene production mechanisms across the broad range of phytoplankton communities in the oceans **under different environmental conditions** as contributors to this difference between the two estimates."

Capitalize and italicize proper species names (e.g. Skeletonema sp., Emiliania huxleyi)

These have been corrected.

P16461, L5: Why is the secondary formation of OC from other precursors (volatile or semi-volatile) not a possibility?

This is a valid point, and this last sentence of the paper has been changed accordingly:

"These findings suggest a nondominant role for isoprene in driving OC abundances in the remote Southern Ocean, implying an alternative source from primary OC aerosol emission or oxidation of other ocean-emitted volatile organics."

References

Alvain, S., et al., (2008), Seasonal distribution and succession of dominant phytoplankton groups in the global ocean: A satellite view, Global Biogeochemical Cycles, 22,

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Bey, I., et al., (2001), Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation, J. Geophys. Res., 106(D19), 23073-23096, 10.1029/2001JD000807.

Horowitz, L., J. Liang, G. Gardner, and D. Jacob (1998), Export of reactive nitrogen from North America during summertime: Sensitivity to hydrocarbon chemistry, J. Geophys. Res., 103(D11), 13451-13476.

Lelieveld, J., et al., (2008), Atmospheric oxidation capacity sustained by a tropical forest, Nature, 452, 737-740.

Lewis, A.C., L. Carpenter, and M.J. Pilling (2001), Nonmethane hydrocarbons in Southern Ocean boundary layer air, J. Geophys. Res., 106, 4987-4994.

Park R. J., D. J. Jacob, M. Chin, R. V. Martin, (2003), Sources of carbonaceous aerosols over the United States and implications for natural visibility, *J. Geophys. Res., 108*, 4355, doi:10.1029/2002JD003190.

Shaw, S. L., S. W. Chisholm, and R. G. Prinn (2003), Isoprene production by Prochlorococcus, a marine cyanobacterium, and other phytoplankton, *Mar. Chem., 80*, 227?245.

Spracklen, D. V., S. R. Arnold, J. Sciare, K. S. Carslaw, and C. Pio, (2008), Globally significant oceanic source of organic carbon aerosol, Geophys. Res. Lett., 35, L12811, doi:10.1029/2008GL033359.

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