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Interactive comment on “Investigating organic aerosol loading in the remote marine environment” by K. Lapina et al.

K. Lapina et al.

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Received and published: 15 July 2011

The authors thank both Referees for their reviews and insightful comments on our paper. Our responses are inserted as point by point replies to the comments below.

We would first like to note that following submission of this manuscript, we found a minor error in our GEOS-Chem simulations (related to the met product) which slightly increased simulated AOD over the oceans, leading to a more modest disagreement with observations. This does not change any of the conclusions of the manuscript, and we have modified text and figures throughout to reflect new values.

Anonymous Referee #1

In this paper the authors evaluate different organic aerosol parameterizations in the

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GEOS-Chem model against comparison to ship observations. The authors find that the observations are consistent with a marine OM source of 9 Tg/yr or smaller. The authors also find that the model underestimate AOD by 13-30% but that this is not due to organic aerosols. This is a generally well-written study with interesting results. My main concern with the manuscript is that the authors do not place the 30% model underestimate of MODIS AOD within the context of uncertainties of the satellite retrievals, which are at least as large as the difference between model and observations. I also have a number of minor comments that are listed below.

Main concern:

The authors insist at length on the 30% model underestimate of the MODIS AOD, without any satisfactory explanation. The difference corresponds to a mean underestimate of 0.03 in AOD (page 10985, line 1). Such attention doesn't seem warranted given that this difference is within the accuracy of the MODIS retrieval over Oceans which is $\pm 0.03 \pm 0.05$ AOD (see any MODIS retrieval paper). For AOD > 0.1 this corresponds to an uncertainty of 0.035 in AOD. Thus the difference between model and observations is within the reported uncertainty. In addition, as noted by Remer et al. (2008) the TERRA AOD is biased high by 0.015 (which accounts for half of the difference between model and observations). Finally, when the authors compare the model AOD to AERONET MAN AOD, they find only a 13% underestimate. Clearly a small difference. I recommend that the authors discuss these AOD differences with more attention to the AOD uncertainty in both MODIS and MAN.

A: We agree with the reviewer that it is important to view the MODIS AOD in the context of the expected uncertainty. However, the conclusions presented in this work are based on the MODIS data which are averaged over large spatial (globally, over remote oceanic regions) and temporal (i.e. one year) scales, and, thus, we expect the resulting uncertainty to be lower than the one expected for individual retrievals. Also, we use only high-quality AOD data which we further screened for potential cloud contamination, known to cause a positive bias in AOD data [Remer et al 2008]. Hence, a

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persistent, albeit small, AOD bias between MODIS and the model is, we believe, worth discussing. As noted above, the model bias is in fact reduced with updated simulations, and with this in mind, we have reduced our emphasis on this conclusion in the manuscript. We have also added text on satellite retrieval uncertainty as raised by the reviewer here.

R: In addition, many uncertainties are associated with the model calculation of AOD, from estimate of the burden of the different aerosols (related to sources and sinks) to the optical properties used. The authors have clearly demonstrated that whatever the scenario used, OM accounts for a tiny fraction of the AOD. However the model AOD over these remote regions is dominated by sea salt and sulfate. It seems that small changes in the assumed optical properties of either one of these components could easily account for the 30% difference in AOD. A discussion of this would be useful.

A: This is a good point, particularly in light of the reduced bias between model & satellite AOD in our updated manuscript. We have added text to discuss this.

Minor comments:

R: Abstract, line 14 “mean OM concentrations. . . , are largely underestimated”. Please be more quantitative. By how much are the observations underestimated? Also, the authors should note that OM concentrations are underestimated if a marine OM is not included. This isn’t clear in the abstract.

A: Changed as suggested.

R: Page 10979, lines 1-5. It seems that the authors use SeaWiFS chlorophyll for 2006 and 2007, but MODIS chlorophyll for 2008. For consistency why not use MODIS chlorophyll for the entire 3 years? Are the 2 datasets identical? It would be useful if the authors compared MODIS and SeaWiFS chlorophyll in 2006 and 2007 and the resulting OM emissions. This would help evaluate uncertainties in OM source associated with the chlorophyll dataset used.

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A: We aim to first reproduce the work of Spracklen et al., hence our consistent use of SeaWiFS fields. We calculated the total annual OM emissions (as based on Spracklen et al. (2008) scheme) and found that the 2008 emissions (9.0Tg C, computed using MODIS chlorophyll-a) are not significantly different than the emissions computed using SeaWiFS (2006: 7.7 tgC, and 2007: 8.9 Tg C) . We have added references indicating that these two products are consistent.

R: Page 10979, line 5. “. . . re-gridded to 1 degree resolution”. I thought the model was run at 2x2.5 resolution (page 10977, line 4). Please clarify.

A: We clarified the wording.

R: Equation 1. What are the units of [Chl]?

A: We added the units.

R: Page 10980, line 22-28. It appears that even though the authors are using the same OM parameterization as in Langmann et al. (2008) and in Vignati et al. (2010), the resulting OM sources are very different in these 3 studies: 8.2 TgC/yr, 2.8 TgC/yr, 5.8 TgC/yr. Nearly a factor of 3 difference! The authors mention different sea salt parameterization as the culprit. Could they elaborate? What are the assumed accumulation mode sea salt emissions used for each study? What parameterizations are used?

A: The differences could be the result of many parameters, including the true inter-annual variability in emissions, difference in meteorological fields used in the models, as well as the difference in sea salt parameterization schemes. For example, Vignati et al [2010] report global emissions of fine sea salt to be 24 Tg, which is twice less than what was obtained in the current work (55 Tg), which partially explains a larger OM source presented here. Sea salt emissions were not reported in Langmann et al (2008). We have added text to this effect in the manuscript.

R: Figure 1. I am confused as to the difference between the central and left panels in Figure 1. They both used the Langmann et al. (2008) parameterization for chlorophyll,

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correct? Then I assume that the sea salt must be difference. It seems that the sea salt on the right is based on Jaegle et al. (2011). What sea salt is used for the central panel? What are the total OM sources for each panel? Which one is referred to as Langmann et al. in the text (8.2 TgC/yr)? Which one is referred to as GCL in Table 1?

A: We clarified the caption for this Figure.

R: Page 10985. Line 22. “Comparing model AOD to the MAN data, separately for the fine and coarse components. . .” It would be useful to the reader if the authors clarified this statement a bit. What is the model underestimate for fine AOD? Coarse AOD?

A: We have removed this statement in the updated draft.

R: Page 10986 line 1-3. “anticorrelated with sea salt AOD simulated in the model”. How does the difference correlate with sulfate AOD simulated by the model? How about total AOD? Simply looking at the figures it would seem that there is an anticorrelation with total AOD, indicating that the percent difference is largest at the lowest AOD where the retrievals are most uncertain (see main comment above).

A: The difference is also anti-correlated with the model sulfate.

R: Page 10986 line 15. “ICEALOT is the only campaign where GC is biased low”. It appears that the model is also biased low during RHAMBLE (Table 1).

A: The reviewer is correct. However the RHAMBLE underestimate is well within the variability of the observations. We have modified the text to clarify our statement.

R: Page 10988 line 20-22. “Measurements of the sea salt component of sea spray (not detected by AMS) would be required to verify this relationship”. I know that measurements of submicron Na⁺ mass concentrations were conducted for ICEALOT and VOCALS using cascade impactors. I believe that Russell et al. (2010) discuss the correlation between Na and OM. It could well be that Na mass concentration measurements are also available for the other campaigns discussed by the authors, as it is a fairly standard measurement.

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A: We agree that this would be a useful analysis, but were unable to investigate this, as the abovementioned measurements were not available across all analyzed campaigns.

Anonymous Referee #2

General Comments:

This is an interesting analysis and the topic is appropriate for publication in ACP. I commend the authors for integrating a very large body of information into a comprehensive analysis. From my perspective, however, the authors do not adequately address several important sources of uncertainty in their model. Comparisons between simulated and measured results are interpreted primarily in terms of processes in the surface ocean and lower atmosphere. As detailed below, however, the source function for primary submicron sea-salt aerosol in the model may not be representative; it appears – though not stated explicitly - that all OM and inorganic sea salt in the model are assumed to be emitted as externally mixed, chemically distinct particles, which is not representative; the assumed size distribution of particulate OM is based on measurements in continental air, which are probably not representative; and important secondary sources and sinks for particulate organic carbon over the ocean are not considered. These limitations render the simulated results highly uncertain, though they are not adequately considered in text or data interpretation. To recommend publication, I feel that two major issues must be addressed: (1) The authors should describe in explicit detail the sources, mixing state, particle sizes, and microphysical processes that are assumed, included and/or neglected using the chosen configuration. (2) The associated uncertainties should be considered in more detail.

A: We thank the reviewer for this comment. We certainly did not intend to minimize the limitations of our model treatment of aerosol processes, however, as discussed in the paper, we do not feel that these limitations translate to critical uncertainties related to our conclusions related to the mass budget of marine OM. We addressed the uncertainties associated with mixing state and associated size differences in our discussion

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of the comparison with Vignati et al. 2010 results and in the discussion of Spracklen et al.'s previous work on hydrophobic/hydrophilic conversion. Sub-micron aerosol deposition is relatively insensitive to size/mixing state, and as we have focused in this analysis on the mass concentrations and budget, as discussed in the paper, we felt this was not a limiting issue. Of course size distribution is critical to the AOD calculations. We addressed this in Section 3, but have expanded this discussion to address both the concerns raised here and those of Reviewer #1. Finally, we state at the end of Section 2.2 that we do not include marine SOA, and that our comparisons thus implicitly constrain the total OA budget. We have added some additional minor clarifications to the text.

Specific Comments:

R: Page 10975, line 19. The marine atmosphere is polluted to variable degrees everywhere. "Clean" should be characterized quantitatively and in terms of specific constituents.

A: We modified the sentence as suggested.

R: Page 10976, lines 20-24. This statement is misleading. Some of the reported estimates correspond to OM associated with only submicron size fractions whereas others correspond to OM associated with both supermicron and submicron fractions. In addition, some are specific to primary sources whereas others include both primary and secondary sources. The text should be clarified.

A: Text has been clarified.

R: Page 10977, line 13. The lower end of the Gong (2003) source function was "tuned" to match measurements of ambient marine aerosols reported by O'Dowd and Smith [1993, JGR]. The lower detectable limit for those measured size distributions was $0.2 \mu\text{m}$ -dry diameter. More recent measurements (many of which are cited in this manuscript) indicate that submicron size fractions smaller than $2\text{-}\mu\text{m}$ dry diameter typi-

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cally dominate the number production flux of marine aerosol. In addition, as discussed in the manuscript and cited literature, the lower ends of the volume and mass size distributions of marine aerosol are typically dominated by organic matter. The O'Dowd and Smith measurement technique would likely have volatilized some, probably most, of the organics resulting in biased distributions. The authors should discuss these important limitations in the Gong function in the context of the reliability of their simulated results.

A: We agree that this is a key issue for simulating aerosol size distributions. Given that we do not focus on size here (but mass), we rely on the validation of the sea salt Gong et al. scheme (including size) by Jaegle et al., 2011. The impact of uncertainties in size distribution of organics on our mass/AOD-based analysis is addressed in Section 3.

R: Page 10978, lines 24-25. Relative to smaller size fractions, supermicron marine aerosols have much shorter atmospheric lifetimes against deposition and, consequently, larger aerosols typically dominate the net flux of OM despite the fact that they account for only about 30% of the mass burden [e.g, Turekian et al., 2003, JGR]. What are the associated implications for data interpretation?

A: This is an interesting point. While coarse OA is not likely to impact AOD (as stated in the text), a shorter lifetime would imply a more significant coarse fraction of the emission than burden. We provide information on the PM10 filter data for OA that was available, suggesting that coarse OA may be important in some locations, however, we are clear to indicate throughout the text that we have only constrained the sub-micron fraction of marine OM, so ultimately this issue is outside the scope of our investigation.

R: Page 10978-10979. The authors should discuss uncertainties associated with the assumption that chl a is a reasonable proxy for surfactant organics that are emitted to the atmosphere in association with marine aerosol production.

A: We have added appropriate references to the literature on this topic.

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R: Page 10978-10981, Section 2.2. It appears that that the authors approach is based on the assumption that inorganic sea salt and primary marine aerosol are externally mixed as chemically distinct particles. This key assumption should be stated explicitly. Available evidence indicates that some primary marine OM may be externally mixed but most is probably not. What are the associated implications for data interpretation?

A: We have added a statement to this effect. The only issue that arises from our external treatment is that fine mode sea salt and marine organics differ in size distribution in our simulation. We chose to keep the size distribution of organics consistent with Spracklen et al., 2008 for direct comparison. Given that our analysis is mass-based and that the solubilities, optical properties and deposition efficiencies of these particles are similar, there are no significant implications of this treatment, other than for the size-dependence of the AOD calculation (as discussed in Section 3). This would be more critical to address in the case of examining aerosol number (which is not our focus).

R: Page 10979, lines 6-8. Why do the authors assume that primary marine OM is emitted “with the same sub-micron size distribution as existing continental OM?” The filtering procedure that they employed is intended to identify the subset of conditions that reflect minimal continental influences. Size distributions of OM associated with fresh marine aerosol have been measured (see several of the cited papers). Why are the assumed distributions not based on those measurements?

A: As discussed above, this was done to allow for consistency with Spracklen et al., 2008. Simulated mass concentrations are not sensitive to the assumed sub-micron size and we have characterized the uncertainty in AOD associated with this in Section 3.

R: Page 10979, eq 1. Is there any evidence that supports the assumed linear relationship between the organic mass fraction in aerosols and chl a? Some available data cited in the manuscript suggest that the organic mass fraction of fresh marine aerosols

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exhibits relatively little variability over wide ranges in chl a.

A: The approach used here was developed and previously applied by O'Dowd 2004. It was based on the observations that exhibited a linear relationship between OM fraction and Chl-a. We do not attempt to develop or refine a marine OA emission scheme, but rather apply two schemes published in the literature.

R: Also, “[Chl]” in the equation should be changed to “[Chl a]” and the units of the terms should be specified.

A: Changed as suggested.

R: Page 10980, lines 4-5. This statement is not clear. Do the authors intend to say that the approach of Vignati et al. is size-resolved?

A: Our statement refers to the previous sentence (lines 2-5, same page) regarding the change in modal diameter based on season. To clarify this, we added word “modal” to “diameter”.

R: Page 10980, lines 10 and 11. In contrast to this statement, the authors' analysis is sensitive to simulation of both mass and number concentrations. For example, the assumed mixing state (external versus internal) of OM and the corresponding number size distributions will have a much greater influence on AOD (discussed later in the manuscript) than the mass size distributions. The text should be clarified.

A: We have modified the text.

R: Page 10981, lines 1-16. Secondary organic compounds including for example oxalic and methansulfonic acids that originate from marine derive-precursors are important components of submicron marine aerosols. In addition, some OM emitted in association with marine aerosol is not conservative and reacts to form products [e.g., see papers by Anastasio et al. and Zhou et al.] some of which are probably volatile. The authors should discuss the associated implications in the context of comparing observations of ambient aerosols with simulated results based on a model that does not

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consider these important sources and sinks for particulate OM over the ocean.

A: We agree that these are compelling issues. We have added some text in Section 3 to address the general implications of our omission of SOA sources in the model.

R: Page 10982, line 6. Were the size cuts for particles analyzed by the AMSs during all cruises the same? Some papers report upper limits in the range of $2.5 \mu\text{m}$. In addition, are these size cuts comparable to the upper limits for particles simulated in the model and, if not, what are the implications?

A: We have added text to indicate that all measurements were performed with AMS instruments, with a standard size cut (estimated to be approximately 800 nm), with transmission of larger sub-micron particles at reduced efficiency. These are indeed comparable to the simulated OA.

R: Page 10982, lines 9-10. Did the authors perform additional analyses of the data from the ICEALOT campaign? If so, could the conclusion that OM in the coarse mode contributed little to the OM mass flux/burden be elaborated upon?

A: During ICEALOT campaign 80% of OM mass, on average, was present in submicron form.

R: Page 10985, line 27. The authors should clarify that “less than 2%” refers to mass (as opposed to number or surface area).

A: Clarified as suggested.

R: In addition, these differences between the measured and simulated AOD may also reflect the large (several orders of magnitude) negative bias in production fluxes of submicron marine aerosol based on the Gong [2003] function.

A: While we agree that there can be large uncertainties in simulated sea salt, the scheme employed here was based on Gong but with additional SST dependence. This scheme was developed, implemented in GEOS-Chem and evaluated against observa-

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tions in Jaegle et al., 2011, both in terms of size and mass. While additional evaluation for fine-mode sea salt is needed (and under exploration by Lyatt Jaegle) we feel the uncertainties are not as large as suggested by the reviewer. We have however added to the text that uncertainties in sub-micron sea salt size could indeed contribute to uncertainties in AOD, as raised by Reviewer #1.

R: It appears that the relatively large simulated influence of OM on AOD resulted from its assumed mixing state (external versus internal). If the model mixed the OM internally, the influence would be much smaller. This important point should be stated explicitly.

A: We do not believe that this would be the case. Given that OM and sea salt are both highly scattering aerosols, their optical properties are similar. Internal mixing would only modify the optical efficiency of OM insofar as it would imply a shift in the size distribution. The uncertainty associated with size distribution is discussed.

R: Page 10986, line 29 & Figure 6. A more detailed analysis of the data depicted Fig. 6 would be useful in evaluating the nature of differences between observed vs. modeled results. Can this be improved? Does GEOS-Chem provide an inorganic sea-salt tracer as well (e.g. an Na⁺ analog).

A: The modeled OM surface concentrations shown in Fig. 6 were obtained using the scheme by Spracklen et al [2008]. OM is driven solely by Chl-a concentrations in this approach, it is not related to sea salt production. As a result, the largest differences between the modeled and measured OM are often observed near the high Chl-a regions (e.g. in the coastal zones).

R: Page 10987, lines 4-18. In this context, the authors may also wish to consider and discuss the possibility that the organic mass fraction is not linearly related to of chl a [e.g., Long et al., 2010]. Saturation of the bubble-plume surface area by surfactant organics may constrain organic enrichment of marine aerosol in biologically active areas, which could contribute to overestimates in particulate organic matter based on a model

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that assumes a linear functional relationship.

A: We have added this point to our discussion.

R: Page 10987, lines 12-14. The authors should cite the “recent study” mentioned here.

A: We thank reviewer for noting this. We added the missing reference.

R: Page 10988, lines 23-25. This statement vaguely alludes to an important point. Given that lifetimes for submicron marine aerosol typically range from about 4 to 10 days, chl a at the measurement site may be unrelated to chl a in the region far upwind where the aerosol was produced. The implications of such spatial disconnects in these data should be mentioned explicitly as another potentially important source of variability.

A: We modified text to address this point.

R: Page 10989, line 3. I would suggest that “nutrients” should be replaced with “nutrient” for consistency with common usage.

A: Changed as suggested.

R: Page 10989, starting on line 24. I don’t understand the rationale here. Both the source function and the OM measurements correspond to submicron size fractions. In addition, simulated OM produced in association with marine aerosol is the only source of marine derived OM in the model (i.e., secondary sources are not considered) and this OM is assumed to be chemically inert. As such, OM associated with supermicron fractions is completely decoupled from the analysis. If the authors wish to consider the fraction of OM associated with supermicron aerosol, they would have to modify the source function to produce much more (by many factors) total OM in order to sustain measured concentrations of OM associated with ambient supermicron size fractions.

A: The OM measurements we have used are indeed sub-micron, but the AOD is not.

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Our statement here indicates that precluding this coarse OM (if indeed it is important) may be critical for mass budgets, but is negligible for AOD.

R: Page 10990, line 20. It is not necessarily the case that this study addresses the issues of satellite chl a products or plankton speciation sufficient to isolate them as potential sources of uncertainty above others. While satellite observations of chl a may not capture its spatial variability in comparison to ship-based sampling methods, OM in submicron aerosol will inevitably constitute a mixture of OM from primary, secondary, natural, and anthropogenic sources far upwind. As such, the spatial variability of local OM production would not be reflected in the observed ambient submicron aerosol population. Such a signal would only be marginally discernible in the larger, shorter lived particles which are not considered in either the observations or simulated results. As well, the admitted absence of a sufficient online microphysical scheme would prohibit such conclusions. Lastly, little is known about the character of OM in the surface ocean either combined with or absent the effects of biological processes associated with plankton growth, grazing and senescence. Experiments such as those performed by Fuentes et al. [2010], cited in this manuscript, were done under conditions far from those seen in ambient environment. e.g. DOC concentrations used in that study were several times greater than any reported DOC concentrations that I know of, and perhaps as much as an order of magnitude higher than typical DOC concentrations in the surface ocean. The potential impact of such high levels of surfactants on fundamental fluid properties (e.g. dynamic viscosity & surface tension – both fundamental to OM particle association, and particle formation) was not reported and, to my knowledge, not addressed in current literature.

A: We have expanded our discussion here to include the possibility that not accounting for a secondary source in the model could explain some of the disagreement. As previously discussed, we do not think that the lack of a microphysical simulation is in any way limiting when comparing to sub-micron mass concentrations. While we certainly don't comment on which uncertainty is dominant, we think it is critical to indicate

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the possible reasons that satellite chlorophyll-a may not be a useful proxy. The other concerns raised by the reviewer all fall under “other unknown drivers for OM production not accounted for here”.

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ACPD

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