

RESPONSE TO REVIEWERS

We would like to thank Anonymous Referee #1 for his/her comments. We have done our best to address each of the points as detailed below.

Note: All reviewer comments in *italics*; all responses by the authors in normal font.

I am glad to have been given the opportunity to review this article. I did so because I have a strong interest in the field, and as such, it is important to me that the literature be clear, comprehensive, and considered critically. This review gave me the opportunity to delve deeply into some recent research with a much more critical eye than my recent work has permitted. Through this, I have learned much, and am appreciative. As such, though, I spend a considerable amount of time in this review. There are parts towards the end where I just was unable to put the effort into it that was put into earlier sections. Forgive me for this. This review addresses an important albeit poorly understood area of atmospheric chemistry and physics. The research community has actively investigated the production of marine aerosols for many decades and recent comprehensive reviews have emerged [Lewis and Schwartz, 2004; de Leeuw et al., 2012]. The author's manuscript attempts to contribute to this body work through additional synthesis of recent work. The obvious question arises, does this review manuscript represent a substantive contribution that provides new insight beyond that which is already available through these other efforts?

General Comments

This review addresses an important albeit poorly understood area of atmospheric chemistry and physics. The research community has actively investigated the production of marine aerosols for many decades and recent comprehensive reviews have emerged [Lewis and Schwartz, 2004; de Leeuw et al., 2012]. The author's manuscript attempts to contribute to this body work through additional synthesis of recent work. The obvious question arises, does this review manuscript represent a substantive contribution that provides new insight beyond that which is already available through these other efforts? I will return to this point below.

My review is based on what I consider to be the essential elements of a credible review paper. These elements and my overall evaluation of the manuscript in light of each are itemized below. Specific comments on the manuscript follow.

1. Covers the scope of topics relevant to the review. Fair: There were several topics that I thought could benefit from more in-depth attention, and several that should be added. These are addressed below. In my view, this review has a relatively narrow focus that is a bit too similar to the authors' recent work.

2. Synthesizes results across all research groups working in a field. Good: Overall, the authors incorporate results from a broad range of research within the context of the current draft's scope (see (1) above). That being said, were the scope expanded, the breadth of reviewed research would follow. Further, some of the incorporated research is only 'name-dropped' and not presented in a sufficiently comprehensive manner appropriate for a useful review article.

3. Summarizes major recent advances and discoveries. Fair: Much of the emphasis is on a small subset of published work (much of which corresponds to research at Mace Head, Ireland) with only minimal attention given to other relevant efforts.

4. Identifies significant gaps in current understanding. Poor/Fair: While synthesizing results is useful, the current draft does not adequately assess what needs to be done, where weaknesses lie, or how well the field overall and its associated facets are understood. While over-arching statements of what can be done to improve upon a given set of work are presented in a few cases, there is relatively little critical analysis.

5. Summarizes current debates. Poor: Within the field investigating marine organic aerosol there are several fundamental outstanding debates regarding the source, production, character, processing, measurement technique, theory, and even validity of data that are barely acknowledged here. Several are addressed below.

6. Proposes future research to address outstanding questions. Poor: There is little in the way of future research efforts that are needed to resolve outstanding uncertainties.

Overall, this manuscript tries to cover an area of research associated with major open questions that reflect challenging issues involving both theory and experimental design. As such, a review of the current understanding requires not only an overview of what the current science tells us, but also why the work done to date has been unable to fully resolve open questions and what can be done to address this both in experimental as well as theoretical contexts. This is only marginally done here. In addition, the presentation is often unclear and/or overly superficial with little critical analysis. My overall evaluation of this review manuscript is that it is far from complete, requires extensive revision, expansion, and consideration of the full scope of research in the current literature. I cannot recommend publication.

Major Concerns that should be addressed:

Remote Marine Boundary Layer: The term “remote” is qualitative and not applied consistently by different research groups. The authors should explicitly define their definition of ‘Remote Marine’? Can observations made in the NE Atlantic be considered representative of ‘remote marine’? More generally, are results summarized in Table 1 comparable? Since this issue is controversial yet central to how the available data are interpreted, the definition of Remote Marine may deserve a dedicated section.

In the updated manuscript, the following discussion was added: “This was the first of many measurements of organic aerosol concentrations in “clean marine” (defined by Clarke (1989) as having anthropogenic-source black carbon (BC) concentrations $< 0.05 \mu\text{g m}^{-3}$) conditions averaging $\sim 0.5 \mu\text{g m}^{-3}$ and is summarized in Table 1 and Figure 1.”

Mace Head: Irrefutable evidence challenges the assumption that on-shore flow from the ‘clean’ marine sector at Mace Head is devoid of significant anthropogenic influence. Time series measurements in sectored-on-shore flow at Mace Head under the AEROCE program revealed significant concentrations of combustion-derived species including Sb, NO₃⁻, and nss SO₄²⁻-that were highly correlated [Savoie et al., 2002]. On average, 85% to 90% of nss SO₄²⁻ sampled in the “clean” marine sector at Mace Head originates from anthropogenic sources. Although not

measured by Savoie et al, it is entirely reasonable to expect that particulate organic carbon from combustion-derived and terrestrial biogenic precursors was also present in on-shore flow. In addition, the black carbon threshold that is applied in some studies at Mace Head [Ceburnis et al., 2011] to filter out samples impacted by combustion sources is much higher (factor of 10) than background levels in remote marine regions of the southern hemisphere [e.g., see papers by A. Clarke and co-workers]. Finally, as discussed in more detail below, isotopic analyses of ^{13}C at other locations in the North Atlantic undermine studies at Mace Head that attempt to characterize Mace Head observations as 'clean'. This review, which relies so heavily on results and interpretation of observations made at Mace Head, should address this issue.

The updated manuscript now includes the following discussion concerning Mace Head measurements: “At Mace Head, Ireland, the criteria for clean marine conditions include onshore wind direction, BC concentration $< 0.05 \mu\text{g m}^{-3}$, and total particle number concentration below 700 cm^{-3} (Rinaldi et al., 2009). Such strict conditions insure that sampling does not occur during occasional incursions of European pollution (Savoie et al., 2002).”

Surface microlayer hypothesis: Do the authors contend that the surface microlayer is the source of all marine organic aerosol? This would suggest the review be expanded to discuss this. From my view, this is still an open question. Evidence presented is circumstantial at best, and neglects a wide range of literature on organic processing at water surfaces. I would understand if the authors point out that this is a review of research into marine organic aerosol, not marine organic matter in general; though, their invocation of the surface microlayer opens this issue.

We agree with the reviewer. Considering the uncertainty regarding the interaction between the surface microlayer and marine primary organic aerosol, the updated manuscript does not differentiate the chemistry of the microlayer and subsurface seawater.

What do we know about OC? Speciation? Physical properties?

What about the production mechanism?

What about the fractionation of OC across size distributions?

What about chemical processing of marine derived OC? There is some literature that addresses this issue.

We agree with the reviewer. Manuscript has been expanded to include discussion of speciation, size-dependent fractionation, photochemical oxidation, production mechanism, and ice nucleating properties of ocean-derived primary organic aerosol.

Uncertainty: This would seem to be an important set of information that should be addressed in this review.

The updated manuscript now includes additional discussion of uncertainty when applicable.

Minor Points: The authors could be more explicit regarding the term “organics”.

We agree with the reviewer. The updated manuscript also includes meticulous separation of organic aerosols in the marine boundary layer from marine-source primary organic aerosol.

Language errors: Too many to list. I appreciate that one of the authors is not a native English speaker. However, if the authors are unable to address these issues, they should solicit the assistance of a technical editor.

As many language errors as possible have been corrected in the updated manuscript.

Notation: SSA: Sea-salt aerosol typically refers to inorganic sea-salt constituents. Referring to the organic components of sea-salt aerosol is potentially confusing. OM, OC, POC: These seem to be used interchangeably and inconsistently.

The updated manuscript explicitly describes each of these components to remove potential confusion.

Specific comments:

1. Introduction: P21782 – L6: Is it not just as important that the community's understanding of the production mechanism and the fractionation leading to OM enrichment is still so incomplete?

We agree with the review that these are important open questions. The updated manuscript adds the following: "It has been known for quite some time that large amounts of organic matter can be incorporated in submicron SSA (Blanchard, 1964), although the mixing state of sea-salt and organics, chemical fractionation of the organic matter, and the production mechanism leading to enrichment (relative to seawater) of organics in SSA is still not well characterized."

P21782 – L 25: The authors state "some" of the open questions addressed in the review. A comprehensive review should address all major outstanding questions relevant to the topic. Examples: 1) OM aging: How does it age? Is the OC associated with freshly produced marine aerosol conservative with respect to chemical degradation or uptake of condensable organic gases over the average lifetime of the aerosol. If not, what are the implications for interpretation of OC associated with ambient marine aerosol? 2) Fractionation process. 3) Chemical speciation.

We agree with the reviewer. The updated manuscript has been expanded considerably to address these issues. New section (2.6) discusses photochemical oxidation of marine primary organic aerosol in the clean marine boundary layer. Available measurements for the chemical speciation have also been included.

P21781 – L16: What are sulfates? If the authors simply mean SO_4^{2-} , then forgive me, but also specify it as such.

The updated manuscript replaces sulfates with "sulfate."

2. Chemistry: This section lacks a discreet discussion of what we know about the specific chemical make-up of marine OM, what its potential or hypothetical sources are, what methods

are used to analyze it, and what their limitations are. For example, “lipoid” is not defined. But lipids and lipoids may have very different sources and surface-active behavior than polysaccharides or humic acids. What is the potential implication of this? What is the biogeochemistry of the various known OM components? What are their properties? What can their composition say about their sources?

The updated manuscript has additional discussion of marine organic aerosol chemistry and measurement techniques. Discussion has also been included on how complementary spectroscopic, isotopic, and microscopic analysis can be used for the source apportionment of organic aerosols in marine environment.

What do the different sorts of methods “miss” in their analysis? For example, why did Barger and Garrett (1970) see high concentrations of “lipoid” OM and Hoffman and Duce see so much less? Was it geography? Methodology? The authors state that the Hawaii observations are “far higher than most subsequent observations?” What observations? What can we learn about why?

Following text has been included in the updated manuscript, the “Barger and Garrett (1970) collected SSA from the Hawaiian coast on glass fiber filters and determined the concentration of chloroform extractable surface-active organic matter to be 0.7 to 7.9 $\mu\text{g m}^{-3}$, contributing 5 to 15% of airborne particulate matter. Although five fatty acids the range of 14-18 carbon atoms in length were specifically identified in relative proportions similar to their relative proportions in sea surface samples (Barger and Garrett, 1970), the fact that such high concentrations have never been reported for clean marine air samples suggests that air samples may have been influenced by terrestrial sources. Ship-borne measurements by Barger and Garrett (1976) in the Pacific Ocean near Galapagos Islands using the similar analytical technique were considerably lower, from 0.08 to 4.02 $\mu\text{g m}^{-3}$ with the majority of samples having concentrations much less than 1 $\mu\text{g m}^{-3}$ (the highest value of 4.02 $\mu\text{g m}^{-3}$ was measured off the Pacific coast of Panama). Hoffman and Duce (1974) used the hot persulfate-induced organic matter oxidation method of Menzel and Vaccaro (1964) to measure an organic aerosol concentration in Bermuda ranging from 0.15 to 0.47 $\mu\text{g m}^{-3}$.”

2.1 Bulk Aerosol Concentrations: Why is the Ovadnevaite et al. (2011) observation not included in Table 1? Why does Table 1 only include ‘select’ observations? Was there some process of selection that prevented the authors from listing all observations? If so, is this process indicative of something specific in marine OM observations in general?

To remove the confusion, in the updated Table 1 and Figure we have included all organic aerosol measurements from clean marine conditions.

P21784 L8-10: What is the SA-film vs. lipoid ratios? There is no discussion of the context, only a reporting of numbers. L13: What about Turekian et al. [2003] who found that most OC associated with marine aerosol in on-shore at Bermuda originated from terrestrial sources?

Additional discussion is included in the updated manuscript: “Over the Sargasso Sea with upwind fetch of thousands of kilometers of low biological activity (LBA, [Chl-*a*] < 0.2 mg m^{-3}) waters, Chesselet et al. (1981) and Turekian et al. (2003) found that ocean-derived organic aerosols made a minor contribution (up to 20% and 38%, respectively) to the total organic

aerosol mass concentration. On the other hand, ocean-derived carbon accounted for 45% of total organic carbon mass in the high-Arctic boundary layer aerosols (Narukawa et al., 2008), 46–72% for HBA (8–36% for LBA waters) of the western North Pacific Ocean (Miyazaki et al., 2010), and up to 80% of the total organic aerosol mass concentration at Mace Head, Ireland (Ceburnis et al., 2011) with a ~3000 km upwind fetch over HBA waters of the North Atlantic Ocean.”

2.2 Bulk Aerosol Composition: P21785 L8: Were the ecosystems similar? What about ocean region? What about the fact that there is significant DOC in oligotrophic water? Is this not surface active? Would the inclusion of WSOC in organic aerosol support or challenge the current view regarding OM sources in bulk aerosol. This line merits its own paragraph, if not section or even separate review.

We agree with the reviewer that these are interesting questions and perhaps warrant a review on the chemical composition of marine organic matter in the oceans. In the updated manuscript we have considerably expanded discussion of chemical composition of organics in seawater. However, we limit the descriptions to the scope of this study.

L9: This is an important point with many potential sources. Why only Russell? What are the implications of this conclusion? L13: This should go into a methods section that identifies processes for identifying OM from marine sources. What is the Pee Dee Belemnite standard?

The updated manuscript includes the following changes: 1) “Relative to sea-salt, organic concentration in the subsurface seawater, sea surface microlayer, and sea spray aerosols can be very different, with the organic/sea-salt ratio increasing from $\sim 10^{-4}$ in the subsurface water to $\sim 10^{-3}$ in the sea surface microlayer and ~ 0.1 (with isolated values up to 1) in the aerosol (see Russell et al. (2010) for summary). This suggests that processes within the water column selectively transport organic matter to the surface and from the surface to the atmosphere. The chemical structure-discriminating transfer of organics from the marine surface has been recently studied in depth (Schmitt-Kopplin et al., 2012), with adsorptive bubble separation processes.” 2) “Stable carbon isotopic analysis of marine aerosol samples can provide information that is complementary to and unique from organic biomarker analysis. The value of $\delta^{13}\text{C}$ (given by $(R_{\text{sample}}/R_{\text{standard}}-1)\times 1000$, where R is the $^{13}\text{C}/^{12}\text{C}$ ratio and the isotope standard is Belemnite from the little PeeDee formation in South Carolina (Craig, 1953)) was shown to be approximately $-20 \pm 2\text{‰}$ for dissolved organic matter in low- and mid-latitude oceans and approximately $-27 \pm 2\text{‰}$ for organic carbon derived from terrestrial plants (Fry et al., 1998; Boutton, 1991; Michener and Schell, 1994; Hansell and Carlson, 2002). Beginning with Chesselet (1981), several studies have used the $\delta^{13}\text{C}$ of marine aerosols to differentiate the influence of marine and terrestrial sources of organic aerosol in different locations and seasons (Cachier, 1989; Fang et al., 2002; Turekian et al., 2003; Wang and Kawamura, 2006; Narukawa et al., 2008; Miyazaki et al., 2010; Ceburnis et al., 2011; Kawamura et al., 2012). Limitations to $\delta^{13}\text{C}$ quantitative estimates include ambiguity of oceanic and terrestrial sources in most coastal (and some open ocean) environments and lower $\delta^{13}\text{C}$ values for polar waters (Hansell and Carlson, 2002 and references therein). Analysis of the $^{14}\text{C}/^{12}\text{C}$ ratio (Stuiver and Polach, 1977; Reimer et al., 2004) has also been used for quantification of marine ($\Delta^{14}\text{C} = -50\text{‰}$), continental ($\Delta^{14}\text{C} = 100\text{‰}$) and fossil fuel ($\Delta^{14}\text{C} = -1000\text{‰}$) sources of organic aerosols in marine atmosphere (Ceburnis et al., 2011). Due to its greater dynamic range ($\sim 1200\text{‰}$) ^{14}C may potentially be a more sensitive source tracer than ^{13}C . Using both ^{13}C and ^{14}C isotope analysis for chemical quantification of the organic matter in

seawater and marine aerosols, several studies have shown that ocean biological activity can considerably influence marine organic aerosol composition.”

P21786 L8: Ceburnis et al. (2011) report $\delta^{13}C$ for marine OC in the range of ~ -24 to -20 ‰, within the range reported by Turekian et al. (2003) for all OC (~ -25 to -22 ‰). Turekian et al. are clear that their data are NOT from clean air. This should be pointed out. If the Ceburnis et al. result is valid, can the Turekian OC/SS ratios be included in Table 1? If not, why not?

The updated manuscript includes a discussion of the Turekian et al. (2003) results and the concentrations are now listed in Table 1 and Figure 1. However, we are hesitant to include the organic/sea-salt values in Figure 2 due to the considerable continental influence.

L12: There is little mention of Savoie et al. (2002) result showing that, on average, only 10% to 15% of particulate nss-SO₄ in the “clean” sector at Mace Head is biogenic.

As the Savoie et al. (2002) study considers only nss-SO₄, we do not think that it is appropriate to mention in this review. However, the updated manuscript now includes the following discussion of Mace Head clean marine conditions: “At Mace Head, Ireland, from which many marine aerosol field studies have occurred, the criteria for clean marine conditions includes onshore wind direction, BC concentration $< 0.05 \mu\text{g m}^{-3}$, and particle number concentration $< 700 \text{ cm}^{-3}$ to prevent incursions of European pollution observed by Savoie et al. (2002).”

L14: The correlation between Chl and Mg is very weak in Gaston et al (2011). It should also be pointed out that Chl and DMS are often poorly correlated; and that it may be just as likely that the correlation between DMS and Mg is due to wind-speed mediated fluxes.

The results of Gaston et al. (2011) are refined in the updated manuscript as follows: “Using an aerosol time-of-flight mass spectrometer in the Indian Ocean, Gaston et al. (2011) detected magnesium (Mg)-type particles containing Mg²⁺, Ca²⁺, K⁺, and organic carbon that were suggested to be from exopolymer secretions, cell debris or fragments, viruses, bacteria, or organics released by lysed cells. These particles were strongly correlated to fresh sea-salt and atmospheric concentrations of DMS, and weakly correlated to surface [Chl-*a*] (Gaston et al., 2011). In the Arctic, Orellana et al. (2011) found that marine-source organic microgels stabilized by Ca²⁺ ionic bonds and identifiable by staining with chlortetracycline were a major contributor to CCN concentrations. Because they are independent of terrestrial and anthropogenic proxies such as black carbon and radon, these spectroscopic, isotopic, and microscopic analyses of organic aerosols are valuable tools in identifying a marine source and should supplement field measurements of organic mass concentrations.”

2.3 Size-resolved Aerosol Concentrations: It almost sounds like the authors are saying that it is the size of the particle that causes there to be variation in OM across the size distribution. This is, of course, not true. They are simply co-varying quantities.

In Oppo et al. (1999) model, the size of the particle does affect the relative amounts of organic matter and sea-salt. The discussion section of the updated manuscript now includes the following: “Despite the development of an adsorption model describing how the aerosol size affects the relative contributions of organic matter and sea-salt, it is still an open question whether this is the case or if they are simply co-varying quantities.”

P21786 L23: To my knowledge, inorganic composition of freshly produced marine aerosol is typically constant across full size distributions. If the authors are referring to ambient aerosol, then this demands a discussion of inorganic gas/aerosol chemistry. If they are referring to organic composition, then it should be specified.

The updated manuscript contains the following clarification: “The mass contribution of organic matter in sea spray has been repeatedly shown to vary considerably with aerosol size.”

P21787 L10: O’Dowd et al. (2004) do not describe how OM fraction is related to productivity. They simply present evidence suggesting a link in the NE. Atlantic. Further, it should be pointed out that the designation of ‘high’ biological activity is used only qualitatively in this review. The N. Atlantic is marginally productive. If Chl-a alone is used, it should be pointed out that the ~1 ug/L Chl-a seen in the N. Atlantic is an order of magnitude lower than other regions. Also, reviewing Keene et al (2007) shows how a significant amount of organic aerosol is produced in water with two orders of magnitude less Chl-a. This is not discussed anywhere except in the glancing attention given to bubble-method results.

The updated manuscript now includes a definition of high biological activity and describes in more detail the Keene et al. (2007) results with the following: “In bubble bursting experiments replicating nascent SSA emission, Keene et al. (2007) and Facchini et al. (2008b) found that the OM_{SSA} can be up to ~80% at the smallest (geometric mean diameter of 130 nm and aerodynamic diameter between 125 and 250 nm for Keene et al. (2007) and Facchini et al. (2008b), respectively) aerosol sizes. These high OM_{SSA} values for small aerosol sizes were found in both LBA and HBA waters, with Long et al. (2011) proposing a Langmuir functional relationship between bulk aerosol OM_{SSA} and [Chl-a]. High organic mass fractions in accumulation mode SSA have not been found in all bubble-bursting experiments.”

L29: The Fuentes paper is based on algal exudate from single-species microcosm experiments without any mention of the composition of the exudate, the impact it had on the bulk water properties, and generated up to concentrations far in excess of high-end DOC or TOC concentrations in the ocean. It is unlikely that the results from this experiment are representative of aerosols produced from natural seawater.

The updated manuscript includes the following description of the Fuentes et al. (2010) study: “Using laboratory grown phytoplankton monocultures to generate exudate at unnaturally high concentrations, Fuentes et al. (2011) estimated (through HTDMA measurements) a submicron aerosol organic volume fraction ranging from 8 to 37%.”

General: What are the moments of the size distribution in general, and with respect to OC? Where do these occur with respect to the moments in the enrichment distribution? There is some discussion of this, but it is sparse and not easy to distill.

The following statements are given at the end of the sections describing aerosol chemistry and size distribution: 1) “Despite some contradictory results, these GF and volatility measurements have been successfully used to infer the aerosol chemistry at sizes difficult to measure using mass-based methods and have indicated that the amount of organics in SSA relative to sea-salt increases with biological activity and decreases with wind speed in the climate-relevant 100 to

150 nm diameter size range.” 2) “Of the studies in which the aerosol size was affected by the presence of organic compounds, the largest changes typically occurred in the Aitken and accumulation modes with diameters between ~40-90 and ~250-300 nm, respectively.”

3 Physics: 3.1 Aerosol Size Distribution :P21791 L2: In contrast, Keene et al. (2007).

The updated manuscript now includes the following description of Keene et al. (2007): “The volume size distribution of organic matter (given as soluble organic carbon) in sea spray aerosol from bubble bursting of LBA waters near Bermuda was relatively constant for aerosols below ~2500 nm in diameter but reached its highest value at the smallest geometric mean diameter (130 nm) reported (Keene et al., 2007).”

4 Marine Organic Aerosol Emissions: Can the authors expand upon this?

The updated manuscript now includes additional recent studies examining the emissions of marine organic aerosols.

5 Impact on Climate: Is there not more impact on climate than thru CCN?

We agree with the reviewer. A separate paragraph has been added to the updated manuscript discussing potential climate impact of marine POA through their ability to serve as ice nuclei (IN).