

Sources, Composition and Impacts of Ocean-Derived Aerosols

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1. Background and Significance. Wind stress on the ocean surface results in the direct injection of sea-spray aerosols into the atmosphere through breaking waves as well as indirect injection through bursting bubbles at the sea surface (Blanchard and Woodcock, 1957; see Lewis and Schwartz, 2004, for a historical review). As a result, the oceans are the largest source of aerosols by mass to the atmosphere (Warneck, 1988). The non-water mass of marine aerosols is dominated by super- μm particles composed primarily of sea salt that have relatively short lifetimes (hours to several days) against gravitational settling (Prospero, 1981). The number production flux of marine aerosols is dominated by sizes less than 200 nm, as determined from atmospheric measurements over the open ocean (e.g. O'Dowd et al., 1997) and from the surf zone in Hawaii (Clarke et al., 2006), and from aerosols produced artificially by bubbling zero air through flowing seawater (Mårtensson et al., 2003; Keene et al., 2007a). Consequently, sea salt can be a significant source of condensation nuclei and cloud condensation nuclei in marine regions. In addition to the inorganic ions associated with sea salt (e.g., Na^+ , Mg^{+2} , Ca^{+2} , K^+ , Cl^- , SO_4^{-2}), ocean-derived aerosols can contain inorganic and organic species produced through primary or secondary (gas to particle conversion) processes.

Numerous studies in coastal and productive waters (e.g., O'Dowd et al., 2004) as well as oligotrophic waters (Keene et al., 2007a) have found that marine aerosols can be highly enriched in organic matter (OM) relative to bulk seawater, with enrichments increasing with decreasing particle size. Organic matter can account for more than 50% of the non-water mass of particles ≤ 500 nm diameter (e.g., Hoffman and Duce, 1977; Keene et al., 2007a; Facchini et al., 2008). Production mechanisms, composition, and chemical properties, including solubility, of this material are not well understood. In addition, the significance of ocean-derived OM, both in terms of aerosol mass concentration and climate impacts, versus that of OM transported from continental and anthropogenic sources is not known, primarily due to the lack of data and the highly variable results from a small number of studies.

There is ample evidence to suggest that ocean-derived aerosols play an important role in controlling the Earth's radiation balance, cloud formation and properties, and chemistry of the marine atmosphere (SOLAS Implementation Plan Focus I Report, and references therein). Model estimates of top-of-atmosphere, global annual radiative forcing due to sea salt range from -1.51 to -5 W m^{-2} , depending on the emission scenario employed (IPCC, 2001). Models also indicate that sea salt aerosols can increase cloud condensation nuclei concentrations by up to 50% (Pierce and Adams, 2006). However, sea salt source functions used within different global models vary significantly, by up to a factor of five (e.g., Textor et al., 2006; Lewis and Schwartz, 2004). Emissions and chemical processing of primary ocean-derived particulate OM are now being integrated into marine aerosol source functions (O'Dowd et al., 2008; Long et al., 2009), and their incorporation into global aerosol climate models is being explored as well (E. Vignati, M. Kanakidou, personal comm.)

Several studies have been conducted since publication of the SOLAS Science Plan and accompanying SOLAS Implementation Plan Focus I report (2003) that have focused on marine aerosols including their emission and production mechanisms (e.g., Clarke et al., 2006; Keene et al., 2007a; de Leeuw et al., 2007; Nilsson et al., 2007; O'Dowd et al., 2008; Ceburnis et al., 2008; Bigg and Leck, 2008; Hultin et al., 2009), their chemical composition in coastal and high productivity regions (e.g., O'Dowd et al., 2004; Yoon et al., 2007; Facchini et al., 2008; Matrai et al., 2008), and their impact on climate (e.g., Clarke et al., 2006) and marine boundary layer chemistry (e.g., Keene et al., 2007b; Osthoff et al., 2008; Zhou et al., 2008). In spite of these efforts and related studies (e.g., McFiggins et al., 2005; Nilsson et al., 2007; O'Dowd et al., 2004; O'Dowd and de Leeuw, 2007; Sellegri et al., 2008; Witek et al., 2007), there are several fundamental questions that remain unanswered including some that were raised several years ago in the 2003 SOLAS Science Report and the Focus I Implementation Plan.

2. Questions to be addressed.

Production of ocean-derived aerosols

- What is the magnitude of size-resolved fluxes of ocean-derived aerosols, and how do they vary spatially (e.g., coastal vs. open ocean) and temporally (e.g., seasonally)?
- What are the driving forces that control fluxes of ocean-derived aerosols from the oceans (e.g., wind, wave parameters, sea surface temperature, and salinity)?
- What are the sources of organic matter present in nascent and aged marine aerosols, how do they vary seasonally in biologically productive and nonproductive regions of the ocean, and what are the implications of their chemical processing?
- How do upper-ocean biogeochemical processes affect the fluxes, and physical and chemical properties of marine aerosols?

Impacts of ocean-derived aerosols on the Earth's radiation balance and atmospheric chemistry

- What is the direct and indirect effect of ocean-derived aerosols on the Earth's radiation balance? What are size-resolved fluxes of ocean-derived CCN on global and regional scales, and how does the chemical composition of ocean-derived aerosols impact cloud drop activation?
- What is the impact of ocean-derived aerosols on the chemistry of the troposphere, and in particular on the marine boundary layer, in coastal and open oceanic regions where marine and continental air mix and over the open ocean in regions minimally influenced by continental air?
- What is the significance of ocean-derived aerosols relative to continental emissions transported out over the oceans and emissions from marine vessels?

3. What needs to be done to address these questions? Prior research efforts that examined marine aerosols have largely been small, directed studies focused on one facet of the problem (e.g., ocean biogeochemistry, aerosol production, or aerosol composition). While these studies have proved invaluable, large interdisciplinary field campaigns are required to advance our understanding of marine aerosols and their impacts on climate and the oceans. These campaigns should be conducted in representative areas of the ocean spanning the globe and covering a wide range of conditions to test and develop parameterizations for the production, composition and evolution of primary marine aerosols in relation to ambient aerosols, meteorological conditions, biogeochemical processes in the upper ocean, physical properties (e.g., water temperature, salinity) and wave characteristics. The following elements should be investigated and/or incorporated into these large campaigns:

- Sea-spray aerosol production is forced by wave breaking (rather than wind speed); therefore, quantifying wave characteristics will be an important factor in formulating accurate sea-spray aerosol production parameterizations and may be preferred over wind speed in future parameterizations.
- Controlled laboratory experiments will provide information to quantify effects of governing parameters such as seawater temperature, salinity or surfactants on aerosol production. However, such experiments require fresh seawater and should preferably be undertaken as shipboard laboratory experiments in conjunction with shipboard measurements to quantify atmospheric and oceanic driving factors (wind speed, wave breaking) (e.g., Facchini et al., 2008; Hultin et al., 2009).
- Direct measurements of size-resolved marine aerosol production rates have been made over the last decade using micrometeorological methods, and the first results of size-segregated fluxes are appearing in the literature (de Leeuw et al., 2007; Nilsson et al., 2007; Norris et al., 2008). Directly measured marine aerosol fluxes should be compared to parameterizations derived from laboratory-generated marine aerosols (Nilsson et al., 2007; Keene et al., 2007a; Mårtensson, 2007). Laboratory experiments can be designed to generate and study newly formed marine aerosols, but the relevance of such experiments to open ocean conditions is uncertain at this time. Therefore, intercomparison of laboratory-generated marine aerosols with results from independent field observations (e.g., eddy covariance measurements) is an absolute requirement to evaluate marine aerosol source function parameterizations.
- It will be equally important to characterize the composition of OM in both newly formed sea-spray aerosol particles and in the ambient aerosols since an unknown but potentially significant fraction of the submicron aerosol OM may be derived from the continents or secondary production from atmospheric, gas phase species.

Integrated field studies will further constrain the size-resolved sea-spray source functions, both with respect to the physics and the chemical composition. This research is still exploratory in nature and interdisciplinary studies involving several different communities (aerosol physicists, chemists, marine biologists, etc.) are needed to further our knowledge regarding size-resolved sea-spray source functions. Newly developed

parameterizations from field and lab studies should be fully incorporated into regional and global climate models and radiative transfer models to assess the effect of marine aerosols of known compositions on the atmospheric radiation balance, with the goal of improving the accuracy in estimates of direct and indirect forcing by ocean-derived aerosols.

Finally, field campaigns should be supported by remote sensing activities. Satellites can be valuable tools to extend the local measurements during field campaigns to larger spatial (regional to global) scales because they provide information from derived parameters such as wind speed, sea surface temperature, salinity, and ocean color as proxies for biological activity and wave characteristics, etc. Research efforts are underway to remotely sense the oceanic whitecap fraction (Anguelova and Webster, 2006), which is an important parameter in source function formulations. Direct measurements of the whitecap fraction are preferable over parameterizations in terms of wind speed and other variables because of the large uncertainties in such formulations (orders of magnitude) and observed effect of changes in wind speed on whitecap fraction (Callaghan et al., 2008). Satellite observations also provide the radiance at the top of the atmosphere and thus a direct measure for the effect of aerosols on the Earth's radiation balance. However, algorithms to deconvolve satellite-derived information are not well-developed and contain significant uncertainties when trying to separate effects of marine aerosol particles from that of other aerosol types. Therefore, their application to interdisciplinary field campaigns will be limited but also improved by such activities.

4. What is planned, possible and missing? To be determined and updated based on community input.

5. Needed co-ordination and planning tasks. The deployment of large interdisciplinary field campaigns and long-term time series studies can only be accomplished through an international effort with extensive planning and considerable lead time. To facilitate such planning and coordination, we recommend that a working group be formed and one or more workshops be held to determine how best to proceed to develop large-scale projects. Furthermore we recommend that an online discussion group be initiated to bring together interested scientists to discuss this document and get their thoughts on how best to proceed forward.

6. Prospect for answering the questions. Our understanding of the importance of marine aerosols has increased dramatically since publication of the SOLAS Implementation Plan Focus I Report in 2003. However, as outlined above, there are still huge uncertainties and gaps regarding the role of marine aerosols in affecting the Earth's radiative balance, atmospheric chemistry and oceanic feedbacks. It is expected that a concerted international effort to address the questions posed in this document will dramatically advance this field and allow for accurate assessment marine aerosol properties and processes and their impact on the coupled ocean-atmosphere system.

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