

5.12 Ocean-Derived Aerosol and Its Climate Impacts

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5.12.1	Introduction	317
5.12.2	Ocean-Derived Aerosol Production Mechanisms	317
5.12.3	Radiative Effects of Ocean-Derived Aerosol	319
5.12.3.1	Aerosol Direct Effects	319
5.12.3.2	Aerosol–Cloud Interactions	319
5.12.4	Sources and Composition of Ocean-Derived CCN	320
5.12.4.1	The Dimethylsulfide Source of Ocean-Derived CCN	320
5.12.4.1.1	Production of DMS-derived CCN	321
5.12.4.2	The Sea Spray Source of Ocean-Derived CCN	322
5.12.4.2.1	Sea salt aerosol	322
5.12.4.2.2	Organic aerosol	322
5.12.5	The MBL CCN Budget	325
5.12.5.1	Production Fluxes of Sea Spray Aerosol	325
5.12.6	The CLAW Hypothesis	327
5.12.7	Concluding Comments	328
	Acknowledgments	328
	References	328

5.12.1 Introduction

Atmospheric aerosols observed over the ocean are derived from continental and marine sources. Aerosols emitted from continental sources (fossil fuel combustion, biomass burning, dust, and biogenic emissions) can be transported across ocean basins since aerosol lifetimes and atmospheric transport times often are similar. In addition, marine vessels contribute to the aerosol burden over the oceans, particularly in coastal regions. As a result, marine aerosol number and mass concentration, chemical composition, and properties vary not only with distance from shore but also with the occurrence of transport events that can carry continental emissions over thousands of kilometers. That said, there are remote ocean regions distant from continental sources where the aerosol is derived, for the most part, from the ocean itself. Even in ocean regions impacted by continental sources, ocean-derived aerosol can make a significant contribution to the total aerosol mass concentration under high wind speed conditions. This chapter will focus on sources and properties of ocean-derived aerosol and associated climate impacts.

Aerosol particles can impact the Earth's radiation budget directly by scattering and absorbing incoming solar radiation (direct radiative forcing) or indirectly through aerosol–cloud interactions that modify cloud properties (indirect or semi-direct radiative forcing). The size and chemical composition of a particle determine if it is effective at scattering or absorbing light, as well as its ability to act as a cloud condensation nucleus (CCN). Ocean-derived aerosols are produced from direct injection into the atmosphere (primary production) and from gas-to-particle conversion in the atmosphere (secondary production). The different production mechanisms result in a broad range of particle sizes and chemical composition that have implications for the impact of ocean-derived aerosol on climate.

5.12.2 Ocean-Derived Aerosol Production Mechanisms

Bubble bursting at the ocean surface results in the production of sea spray particles composed of inorganic sea salt and organic matter. This process of wind-driven particle production is one of the largest global sources of primary atmospheric aerosol particles on a mass concentration basis (Warneck, 1988; Woodcock, 1948). When wind speeds are greater than about 5 m s^{-1} , breaking waves are formed that entrain air bubbles into ocean surface waters. These bubbles rise to the surface and burst with each bubble producing up to hundreds of film drops (so-called because they are formed by the shatter of the film surrounding the bubble) (Blanchard, 1963; Foulk, 1932). As the cavity left by the bubble fills with liquid, a jet of liquid is ejected, which breaks up into jet drops. The majority of film drops have diameters ranging from tens of nanometers up to $1 \mu\text{m}$. Jet drops are larger, ranging in size from about 1 to $25 \mu\text{m}$. Larger drops, known as spume drops, are torn directly from the crests of waves when wind speeds are greater than about 10 m s^{-1} (Monahan et al., 1983). These drops are so large (tens of micrometers to several millimeters) that they reside in the atmosphere for just seconds to minutes before falling back to the sea surface (Andreas, 1992). In contrast, sea spray particles resulting from film and jet drops can have lifetimes ranging from hours to days.

Ocean-derived aerosols can also be produced or grown by gas-to-particle conversion processes. Production occurs through nucleation of gas-phase species to form new particles (homogeneous nucleation). Growth occurs through the condensation of gas-phase species onto existing particles (heterogeneous nucleation). The composition of the resulting particles can be affected by heterogeneous chemical reactions. For example, gas-phase HNO_3 can react with NaCl in sea salt aerosol to form Na_2SO_4 and release gaseous HCl (Clegg and

Brimblecombe, 1985). In addition, as described below, gas-phase species can undergo reactions in cloud droplets. If the cloud evaporates, the residual particles that are left behind will be altered in terms of size and composition.

Examples of aerosol mass and number size distributions typically observed in the remote marine boundary layer (MBL) are shown in Figure 1. Aerosol mass concentration is dominated by particles larger than about 1 μm in diameter, while the number concentration is dominated by particles less than about 300 nm in diameter. Measurements of remote marine atmospheric aerosols reveal that sea salt dominates the marine aerosol mass size distribution, especially for diameters larger than about 600 nm (Figure 2). In contrast, non-sea-salt (nss) sulfate, which is produced from gas-to-particle conversion processes, is confined to diameters smaller than 1 μm and, hence, influences the aerosol number size distribution more than the mass size distribution.

Due to the cloud processing mentioned earlier, remote marine aerosol number size distributions have a characteristic shape. Particles that are sufficiently water soluble and large enough in diameter for a given supersaturation can take up water vapor and serve as nuclei for cloud droplets. Once formed, cloud droplets take up not only water but also other soluble gases, including sulfur dioxide, which undergoes oxidation within the droplet to form sulfate. Instead of forming rain drops that reach the surface, most cloud droplets evaporate and leave behind residual aerosol particles. Since sulfate is nonvolatile, it remains in the particulate phase when the cloud drop evaporates (Hegg and Hobbs, 1987). The residual particles are larger in diameter and contain more mass than the original particles that formed the cloud droplets. The increase in diameter and mass during cloud processing can be seen in the number size distribution as two submicrometer modes (Figure 1) (Hoppel et al., 1986). The smaller mode, less than

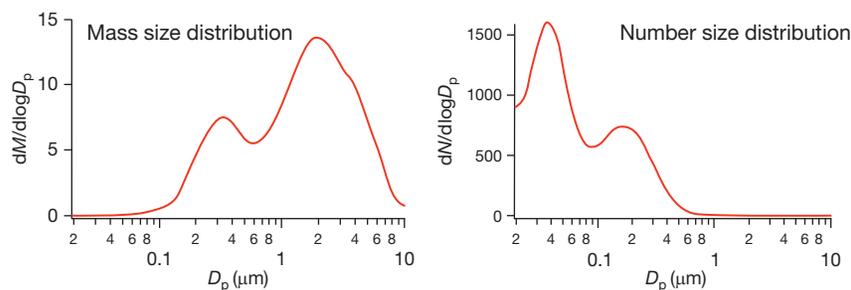


Figure 1 Marine aerosol mass and number size distributions measured over the North Atlantic. Particle diameter, D_p , is shown as the geometric diameter at 80% relative humidity (RH).

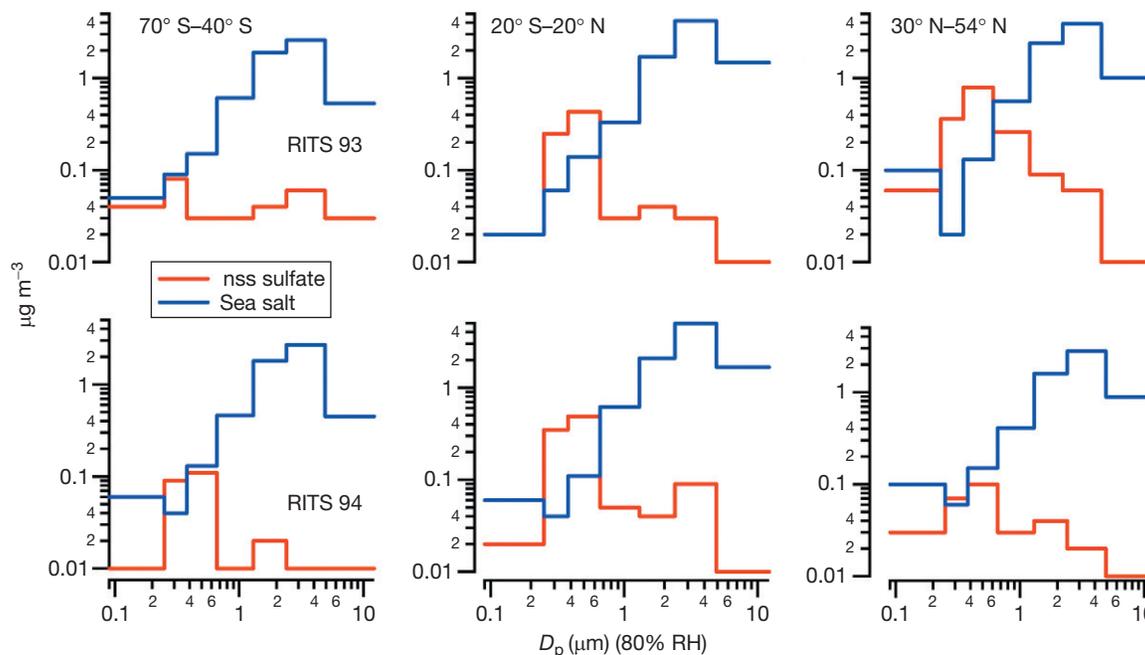


Figure 2 Average sea salt and non-sea-salt sulfate mass size distributions measured on five cruises throughout the Pacific and Southern oceans. Data are shown as a function of geometric mass diameter at 70% RH. Reproduced from Quinn PK and Coffman DJ (1999) Comment on “Contribution of different aerosol species to the global aerosol extinction optical thickness: Estimates from model results” by Tegen et al. (1997). *Journal of Geophysical Research* 104: 4241–4248, with permission from American Geophysical Union.

about 80 nm in diameter, represents the nonactivated aerosol, while the mode larger than 80 nm contains the residual aerosol that acted as the CCN.

5.12.3 Radiative Effects of Ocean-Derived Aerosol

5.12.3.1 Aerosol Direct Effects

Scattering and absorption of solar radiation by both natural and anthropogenic aerosol affect the Earth's radiation balance. In addition, both natural and anthropogenic aerosol can impact cloud microphysical (cloud droplet size and number concentration) and macrophysical (cloud fraction, size, morphology) properties. The effects due to anthropogenic aerosol are defined as climate forcings, as they are an externally imposed change on the planetary heat balance. To determine the extent of the climate forcing resulting from anthropogenic aerosol, the change in a given radiative flux due to natural aerosols (e.g., biogenic sulfur and organic species, mineral dust, and sea salt) must be understood.

For a wavelength of 0.55 μm , which corresponds to solar midvisible radiation, the most efficient particle size range for scattering light is between about 0.2 and 1 μm . As a result, nss sulfate aerosol can be an important contributor to aerosol light scattering. However, even though the majority of sea salt aerosol mass occurs in particles with diameters larger than 1 μm , it is the dominant contributor to light scattering in the MBL for both the sub- and supermicrometer size ranges (Figure 3; Bates et al., 2006; Kleefeld et al., 2002; Murphy et al., 1998; Quinn and Coffman, 1999). The mass concentration of supermicrometer sea salt is large enough to compensate for the low scattering efficiency of this size range. In addition, as can be seen in Figure 2, if the supermicrometer sea salt mass concentration is large enough, it 'tails' into the optically active size range. Consistent with this analysis, model calculations indicate that on a global scale, yearly averaged direct radiative forcing by sea salt is equal to or greater in magnitude than forcing by natural sulfate and soil dust (Jacobson, 2001;

Takemura et al., 2002). Hence, sea salt may be the most important natural aerosol chemical component in the atmosphere in terms of aerosol direct effects and scattering of solar radiation.

Measurements and model simulations have shown that sea salt dominates aerosol light scattering and, thus, directs radiative effects over remote ocean regions. At the same time, the impact of sea salt and other aerosol chemical species on cloud micro- and macrophysical properties is more complex, more uncertain, and less constrained by measurements. Hence, the rest of the chapter summarizes what is currently known about sources of ocean-derived CCN.

5.12.3.2 Aerosol–Cloud Interactions

The direct effects of ocean-derived aerosol are controlled by sea salt due to its large size and mass concentration. In contrast, the effects of ocean-derived aerosols on micro- and macrophysical properties of clouds are determined by the number concentration and composition of particles less than about 300 nm in diameter. Under certain conditions, sea salt particles larger than about 1 μm in diameter may act as giant CCN and affect precipitation rates and the magnitude of a local aerosol indirect effect (Feingold et al., 1999; Posselt and Lohmann, 2008; Rosenfeld et al., 2002). Here, however, the focus will be on ocean-derived particles with diameters less than about 300 nm.

For a given supersaturation of water, the CCN number concentration depends on the number of particles that are sufficiently large and soluble to take up water, grow, and activate to form cloud droplets. Measurements suggest that the effective supersaturation of MBL clouds ranges between ~ 0.1 and 0.4% (Hoppel et al., 1996; Hudson et al., 2000; Leitch et al., 1996; Roberts et al., 2006), although effective supersaturations up to 1% for clean stratus clouds (CCN and total particle concentrations $< 300 \text{ cm}^{-3}$) have been reported (Hudson et al., 2010). Particles larger than 300 nm will activate regardless of chemical composition, but because of their limited

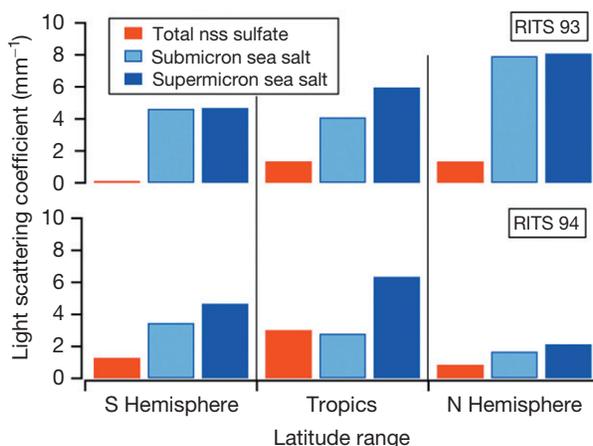


Figure 3 Calculated scattering coefficients for nss sulfate (includes nss sulfate and associated NH_4^+ and H_2O mass for both the sub- and supermicrometer size fractions), and sub- and supermicrometer sea salt (includes associated water mass). Values are based on Mie calculations and assume an externally mixed aerosol composed only of nss sulfate and sea salt. Reproduced from Quinn PK and Coffman DJ (1999) Comment on "Contribution of different aerosol species to the global aerosol extinction optical thickness: Estimates from model results" by Tegen et al. (1997). *Journal of Geophysical Research* 104: 4241–4248, with permission from American Geophysical Union.

number, they do not contribute significantly to the CCN number concentration. For particles <300 nm in diameter, chemical composition affects the critical diameter (D_c) for activation to a cloud droplet by determining the molecular weight of the solute within the droplet, density, solubility, degree of dissociation, and surface tension. For soluble compounds that do not appreciably affect droplet surface tension and the 0.1–0.4% supersaturation range of MBL clouds, Köhler theory (Köhler, 1936) predicts D_c values between about 40 and 300 nm. D_c decreases to 20–30 nm at 1% supersaturation. Hence, it is the particles <300 nm in diameter that determine the CCN concentration in the remote MBL and have the potential to alter cloud properties.

For a fixed cloud liquid water content, an increase in the concentration of CCN results in an increase in cloud droplet concentration and a decrease in the size of the cloud droplets (Twomey, 1977). Changes in the concentration and size of the cloud droplets lead to a brightening of the cloud as more solar radiation is scattered upward and less is transmitted through the cloud. CCN have also been hypothesized to affect the lifetime and extent of clouds since the occurrence of more and smaller cloud droplets reduces drizzle production and increases cloud liquid water content and fractional cloudiness (Albrecht, 1989). More recently, it has been recognized that the sensitivity of clouds and precipitation to changes in aerosol is dependent on the cloud type and geographical region (Stevens and Feingold, 2009). For example, for small, nonprecipitating cumulus clouds, aerosol perturbations can decrease rather than increase the cloud fraction as follows (Small et al., 2009). The smaller cloud droplets formed by an increase in CCN concentration can result in faster evaporation rates. The faster evaporation rates lead, in turn, to enhanced entrainment of drier air surrounding the cloud and a decrease in cloud fraction. These complexities in aerosol–cloud interactions make it inherently difficult to quantify associated radiative effects. Understanding the sources and properties of ocean-derived CCN is a starting point for assessing radiative effects due to aerosol–cloud interactions in the remote MBL.

5.12.4 Sources and Composition of Ocean-Derived CCN

Identification of all sources that contribute to MBL CCN requires direct chemical analysis of single particles with diameters <300 nm. Such measurements are sparse. Those measurements that have been reported are based on electron microscopy coupled with X-ray analysis (Leck and Bigg, 2008; McInnes et al., 1997; Murphy et al., 1998; Parungo et al., 1986; Posfai et al., 1994), X-ray spectromicroscopy (Hawkins and Russell, 2010; Russell et al., 2010), and laser mass spectrometry (Murphy et al., 1998). In addition, chemical composition has been inferred by comparing unheated and heated number size distributions with subsequent quantification of the volatile and refractory fractions of the aerosol (Clarke et al., 2006). The lack of measurement techniques that allow for the identification of chemical species that make up the MBL particle number population has led to the use of mass concentrations instead. As discussed above, different aerosol sources and production mechanisms control mass and number

concentrations. Hence, using measurements of mass to infer the sources and chemical components that contribute to the number concentration in the MBL can be misleading. The sections that follow discuss what is known about the composition of particles that dominate the concentration of CCN in the remote MBL based on all these measurement techniques.

5.12.4.1 The Dimethylsulfide Source of Ocean-Derived CCN

Marine phytoplankton produce dimethylsulfonium propionate (DMSP), an osmolyte that has been proposed to serve as an antioxidant and as a deterrent to grazing (Sunda et al., 2002). DMSP breaks down to dimethylsulfide (DMS) and several other products. DMS is the dominant volatile sulfur compound in ocean surface waters and is the most significant biological source of gaseous sulfur to the remote marine troposphere (Bates et al., 1992). After emission to the atmosphere, DMS may be oxidized by a variety of oxidants including OH and, to a lesser extent, NO_3 , halogen atoms, and halogen oxides in the gas phase, as well as O_3 in cloud droplets (Andreae et al., 1985; Barnes et al., 1991; Von Glasow and Crutzen, 2004). The first oxidation step, depending on the oxidant, results in either H abstraction or O addition (Von Glasow, 2007). The abstraction pathway results, via several intermediates, in SO_2 . SO_2 can then be taken up by particles directly to form SO_4^{2-} or can undergo aqueous-phase reactions in cloud droplets to form SO_4^{2-} . In addition, SO_2 can be oxidized to H_2SO_4 or methane sulfonic acid (MSA). The addition pathway leads to water-soluble intermediate products (dimethyl sulfoxide (DMSO), dimethyl sulfone (DMSO_2), methylsulfonic acid (MSIA), and MSA), which can condense onto existing particles and contribute to the growth of those particles through heterogeneous nucleation. In addition, MSIA can react in the gas phase to form SO_2 . The yield and fate of SO_2 controls new particle formation from DMS. Only SO_2 can be oxidized directly to gas-phase H_2SO_4 and form new particles.

In the 1980s, it was hypothesized that DMS-derived SO_4^{2-} made up the majority of the CCN in marine regions distant from continental and anthropogenic aerosol sources (Charlson et al., 1987; Shaw, 1983). The strongest evidence for a link between DMS emissions and CCN concentrations is the coherence in the seasonal cycles of DMS, mass concentrations of its particulate-phase oxidation products (nss SO_4^{2-} and methane sulfonate or MSA^-), and CCN. At Cape Grim, Tasmania, a remote Southern Ocean sampling site, concentrations of atmospheric DMS, nss SO_4^{2-} , MSA^- , and CCN all peak in the summer and are at a minimum in the winter, as is expected for parameters controlled by biological activity (Ayers and Gras, 1991; Ayers et al., 1997). This coherence in the seasonality of DMS and CCN has been interpreted as evidence for the hypothesis that DMS emissions control MBL CCN concentrations. As pointed out by the authors (Ayers and Gras, 1991; Ayers et al., 1997), however, the causal relationship is not as clear cut as suggested by the correlation. When CCN concentrations are plotted against either DMS or MSA^- concentration, a linear regression results in a positive intercept suggesting that a significant fraction of the CCN is not derived from DMS. In addition, the correlation between CCN and MSA^- concentrations increases as a function of supersaturation

so that the slope of the linear fit is larger at 1.2% supersaturation than at 0.23%. The lower supersaturation is more typical of MBL clouds suggesting a stronger influence of non-DMS-derived CCN under more realistic cloud conditions.

Similar measurements of DMS and CCN made in the boundary layer over the tropical South Atlantic (Andreae et al., 1995) and the northeast Pacific Ocean (Hegg et al., 1991) found that 40–50% of the variance in CCN concentrations could be explained by DMS. Although the remaining variance was attributed to variability in the parameters controlling the conversion of DMS to CCN (e.g., oxidation rates, cloud frequency), it could also have been the result of CCN production mechanisms unrelated to DMS oxidation products. Similar to the Cape Grim data, the correlation between DMS and CCN was stronger at both locations at 1% supersaturation than at 0.3%. The South Atlantic observations also revealed significant correlations between nss SO_4^{2-} or MSA^- mass concentrations and CCN (Andreae et al., 1995). These correlations are, however, based on mass concentrations of DMS oxidation products and not on number concentrations that control the CCN number population.

Single particle analysis of aerosol samples collected over the open ocean in the mid-Pacific reveal that nss SO_4^{2-} exists in CCN-size particles (50–500 nm in diameter) (Parungo et al., 1986; Posfai et al., 1994). In addition, the number concentration of particles with diameters between 100 nm and 1 μm can be dominated by $(\text{NH}_4)_2\text{SO}_4$ and acidic sulfate particles (McInnes et al., 1997). These data support a DMS source of sulfate aerosol. At the same time, there is a lack of observations of pure acidic SO_4^{2-} or $(\text{NH}_4)_2\text{SO}_4$ particles in the MBL. A combination of measurement techniques (automated scanning and manual transmission electron microscopy (SEM and TEM, respectively) with energy-dispersive X-ray analysis, laser ionization mass spectrometry, and aerosol volatility) was used during the first Aerosol Characterization Experiment (ACE-1) to determine the composition of individual aerosol particles over the Southern Ocean (Murphy et al., 1998). Most 50 nm particles collected at Cape Grim and Macquarie Island were found to be volatile at temperatures between 95 and 150 $^\circ\text{C}$ (suggesting a composition other than sea salt), and microdiffraction patterns of particles smaller than 100 nm suggested an ammonium sulfate crystalline structure. Larger particles (100 nm to 1 μm) were composed of a mixture of sulfate, sea salt, and carbonaceous material, with only a very few being pure sulfate. Based on the measured composition as a function of particle size, Murphy et al. (1998) concluded that particles formed through the condensation of sulfur-containing gases did not grow large enough to become CCN without coagulating with sea salt and organics such that very few pure sulfate particles were acting as cloud nuclei.

Additional evidence for the lack of CCN composed only of sulfate is provided by single-particle TEM analysis on submicrometer particles collected at Lizard Island (outer edge of the Great Barrier Reef; 14.6 $^\circ$ S, 145.5 $^\circ$ E) and over the central Arctic Ocean. These measurements revealed that three-quarters of the particles resembling $(\text{NH}_4)_2\text{SO}_4$ contained electron-dense inclusions that appeared to be airborne marine aggregates (AMAs) made up of exopolymer (EP) gels, aggregates of organic particles, and marine microorganisms (Leck and Bigg, 2008). Leck and Bigg (2008) concluded that the inclusions had

acted as nuclei for condensation of gas-phase DMS oxidation products and that, in lieu of the growth of pure sulfate particles of CCN size, this mechanism could play a major role in the development of the marine CCN population.

5.12.4.1.1 Production of DMS-derived CCN

A few cases of homogeneous nucleation involving H_2SO_4 in the MBL have been reported. Covert et al. (1992) reported observations over the eastern Pacific of a decrease in aerosol surface area concentration followed by a sharp increase in the number concentration of particles >3 nm in diameter. Similarly, Clarke et al. (1998) reported a decrease in aerosol surface area, an increase in sulfuric acid concentration, and a subsequent increase in ultrafine particle concentrations over the tropical Pacific. In both these cases, particle production occurred only after a decrease in aerosol surface area. Model results indicate that if precipitation removes preexisting aerosol and, therefore, aerosol surface area, ternary nucleation of new particles involving H_2O , H_2SO_4 , and NH_3 can occur under moderate DMS concentrations (Pirjola et al., 2000). If the surface area of existing particles is too high, then gas-phase species will condense onto existing particles rather than nucleate to form new particles. Over the oceans, the large surface area of sea spray aerosol provides a sink for condensable vapors and prevents new particle formation. Hence, homogeneous nucleation of new particles in the MBL is rare.

Unlike the remote MBL, ample evidence exists for H_2SO_4 -initiated particle nucleation in the free troposphere near cloud top height (Clarke et al., 1996; Hegg et al., 1990; Hoppel et al., 1994; Perry and Hobbs, 1994). Measurements over the Southern Ocean and the equatorial Pacific as part of ACE-1 revealed the existence of layers of newly formed particles at cloud top height (Clarke et al., 1998). Many of these layers coincided with elevated concentrations of water vapor and sulfuric acid. Both particle production and sulfuric acid concentrations were most enhanced in the early afternoon as a result of active photochemistry. The newly formed particles were observed to grow and merge with a particle mode centered near 35–60 nm over a matter of hours to a day. Aircraft flights in regions of postfrontal subsidence as well as shipboard observations of particle nuclei (Bates et al., 1998) indicated that particles formed aloft were subsequently mixed into the MBL.

The nucleation of new particles observed at cloud top height is a result of reactive gases such as DMS being pumped up to the free troposphere through deep convective clouds. Clouds scavenge most of the particles so that the air that is detrained from the cloud contains very low aerosol surface area concentrations (Perry and Hobbs, 1994). DMS and other reactive gases then undergo gas-to-particle conversion in cloud outflow regions where the existing particle surface area is low, water vapor concentrations are high, and the actinic flux is high (Clarke et al., 1998). Simple box models (Raes, 1995) and advanced three-dimensional global models (Kazil et al., 2006; Pierce and Adams, 2006; Spracklen et al., 2007) indicate that entrainment of particles from the free troposphere can explain a large percentage of the CCN concentration measured in the MBL. In addition, global model simulations have been able to reproduce the seasonal cycle in CCN observed at Cape Grim through nucleation of DMS-derived H_2SO_4 in the free troposphere followed by condensational and coagulation

growth during entrainment into the MBL (Korhonen et al., 2008). Hence, measurements and model calculations indicate that DMS-derived sulfate contributes to MBL CCN concentrations via particle nucleation in the upper troposphere rather than in the boundary layer itself.

5.12.4.2 The Sea Spray Source of Ocean-Derived CCN

5.12.4.2.1 Sea salt aerosol

As described, sea spray provides the dominant source of aerosol mass to the remote MBL in the form of sea salt. The sea spray source of sea salt aerosol number and CCN concentration is more uncertain. There are few reported direct measurements of sea salt aerosol number concentrations in any size range including the size range containing the majority of CCN ($D_p < 300$ nm). Direct chemical measurements have been made with instruments that detect emission from thermally excited sodium atoms for particle diameters from 60 to 680 nm (Hobbs, 1971) and 200 to 2000 nm (Campuzano-Jost et al., 2003) (equivalent dry NaCl diameter). Measurements conducted on flights up to 50 miles off the coast of Washington State revealed sodium-containing particles at sizes down to 60 nm with concentrations decreasing with altitude (Hobbs, 1971). Ratios of sodium-containing particles to total CCN were <10 at 0.5% supersaturation. However, the authors stated that further measurements under a wider range of sea states and atmospheric conditions were required to clarify the importance of sodium-containing particles in cloud processes (Hobbs, 1971). Measurements with a similar instrument on the coast of Oahu, as part of the Shoreline Environment Aerosol Study (SEAS), revealed the presence of sodium-containing particles down to the instrumental cutoff diameter of 200 nm (Campuzano-Jost et al., 2003).

Direct chemical evidence for the existence of submicrometer sea salt-containing particles also has been provided by manual TEM with energy-dispersive X-ray analysis. Analysis of samples of Southern Ocean air masses collected during ACE-1 found sea salt in 5–25% of the 50–150 nm (dry diameter) particles measured at Cape Grim and 5–47% of the same size particles measured at Macquarie Island (Murphy et al., 1998). These percentages correspond to a number concentration of sea salt-containing particles of about $30\text{--}100\text{ cm}^{-3}$, which represents a significant fraction of the typical MBL CCN concentration (Clarke et al., 2006).

Indirect measurements based on volatility have been used over the past several decades to infer the contribution of sea salt to the remote MBL particle population. Volatile, or non-refractory, aerosol chemical species such as H_2SO_4 , ammonium sulfates, and simple organics evaporate or decompose at temperatures below 300°C (O'Dowd and Smith, 1993). Refractory species, including dust and sea salt, must be heated to over 600°C for thermal decomposition to occur. Measurements of NaCl (O'Dowd and Smith, 1993) and sea salt aerosol (Dinger et al., 1970) indicate that decomposition begins between 650 and 700°C . Studies that infer number concentrations of sea salt-containing particles based on the lack of volatility at temperatures of 300°C or less may suffer from the interference of nss species that volatilize at temperatures $>300^\circ\text{C}$ (Bigg and Leck, 2008). Inferred sea salt concentrations based on the lack of volatility at temperatures $>600^\circ\text{C}$

are less prone to such interferences, but the sea salt concentrations will still be overestimated if there is a significant presence of equally or more refractory species. Here, the focus is on volatility experiments that involved heating to 600°C or greater.

A series of transatlantic flights revealed that at altitudes near 400 m, 20% of the cloud nuclei activated at 0.75% supersaturation survived heating to 650°C (Dinger et al., 1970). The fraction of nuclei that behaved as sea salt decreased with altitude, indicating an ocean source. The authors interpreted these refractory particles to be sea salt because their thermal response was similar to that of particles generated in the laboratory from NaCl and seawater solutions. Similarly, O'Dowd et al. (1993) performed a volatility analysis on aerosol sampled onboard a research cruise in the NE Atlantic. They identified the aerosol as sea salt if it remained on heating to between 575 and 825°C . It was found that for maritime, high-wind-speed air masses ($14\text{--}17\text{ m s}^{-1}$), 40% of the particles with diameters between 100 and 240 nm contained sea salt.

The most compelling evidence for sea salt as CCN is provided by the single-particle chemical analysis of residual particles that remain after water is evaporated from cloud droplets. Measurements of aerosol particles that were sampled below stratocumulus clouds over the SE Pacific revealed that 50% of the particles <200 nm in diameter contained sulfate. In contrast, the majority (60%) of the residual particles from evaporated cloud droplets, that is, the particles that had acted as CCN, was sea salt (Twohy and Anderson, 2008). This result is due to the lower supersaturation required for sea salt to activate and form cloud droplets compared to other species, including sulfate, for a given particle size.

Although TEM analysis on samples collected at a few locations has failed to find any evidence of sea salt in particles with diameters <200 nm (Bigg, 2007; Leck and Bigg, 2008), the experiments described above, as well as others carried out over the past several decades (Clarke et al., 2006), indicate that sea salt-containing particles can be present in marine air masses and may contribute significantly to the concentration of CCN in the remote MBL depending on the sea state and atmospheric conditions.

5.12.4.2.2 Organic aerosol

Ocean surface waters contain large concentrations of small particulates including phytoplankton, algae, bacteria, viruses, fragments of larger organisms, and organic detritus (Fuhrman, 1999; Wells and Goldberg, 1991). Phytoplankton release or exude organic matter during growth, predation by grazing organisms, and viral lysis (Biersmith and Benner, 1998). Phytoplankton exudates include EP gels consisting of polysaccharides that bind together smaller organic molecules such as amino acids, proteins, and peptides (Decho, 1990). EP gels are insoluble, thermally stable, highly surface active, highly hydrated, and readily sequester dissolved organic matter (DOM) (Bigg and Leck, 2008). EP gels also bind small organic particulates into aggregates. The resulting pool of organic matter contributes to one of the largest active reservoirs of organic carbon on Earth (Hedges, 1992) and consists of every class of carbohydrate (Biersmith and Benner, 1998). This pool of organic matter is often referred to as DOM but may contain colloidal material that is not truly dissolved. A growing body of

evidence shows that this seawater organic matter is similar to organic material found in atmospheric aerosols (Bigg, 2007; Facchini et al., 2008a; Leck and Bigg, 2005).

It has been hypothesized that the organic aggregates that accumulate in surface ocean waters are injected into the atmosphere through bubble bursting at the ocean surface, thereby contributing to the primary organic aerosol found in the remote MBL (Bigg, 2007; Leck and Bigg, 2008). Once in the atmosphere, the EP gels that bind the aggregates and particles together are degraded with ultraviolet (UV) light or acidification. TEM analysis on particles collected during the summer at Cape Grim and other remote ocean sites has revealed the existence of individual particles with diameters between 70 and 200 nm containing organic matter in the form of EP gels and AMAs composed of EP gels, aggregates of organic particles, and marine microorganisms (Bigg, 2007; Bigg and Leck, 2008; Leck and Bigg, 2008). It has been suggested that the size and solubility continuums of phytoplankton exudates that exist in seawater are reflected in nascent sea spray particles (Facchini et al., 2008b). This mechanism for the production of organic sea spray aerosol is depicted in Figure 4.

The evidence for a sea spray, organic aerosol source of CCN to the MBL is considerable. Measurements of northeast Atlantic air masses at the Mace Head, Ireland, sampling site showed elevated mass concentrations of organics, primarily water insoluble, in sub-500 nm particles during the summer time bloom period (O'Dowd et al., 2004). The mass concentration of organics was appreciably lower during the winter

corresponding to limited biological activity. Further evidence for an ocean-derived primary organic aerosol component is provided by recent measurements in the Atlantic and Arctic oceans. Russell et al. (2010) reported that the aerosol organic matter measured in remote regions of the North Atlantic and Arctic was composed of carbohydrate-like compounds containing organic hydroxyl groups from primary emissions of the ocean. This conclusion was based on the correlation of the mass concentration of organic hydroxyl groups with Na as well as wind speed and single-particle evidence of organic components surrounding NaCl. The abundance of carbohydrate material measured in the Atlantic and Arctic ocean aerosol samples is consistent with observations made over the past decade. A review of over 10 years of measurements of marine primary organic aerosol concluded that this ocean-derived aerosol is composed of polysaccharides, proteins and amino acids, and microorganisms and their fragments (Hawkins and Russell, 2010).

These observations are based on measurements of ambient aerosol and not freshly produced, nascent sea spray emissions. Recently, several studies have been performed involving the generation of nascent aerosols from seawater to avoid interferences from constituents in the marine atmosphere that can modify newly emitted particles. Remote MBL ambient aerosol is a mixture of freshly emitted particles from the ocean, particles mixed into the MBL from the free troposphere, and older particles of various ages that have been chemically modified. In addition, condensation of gas-phase species can occur

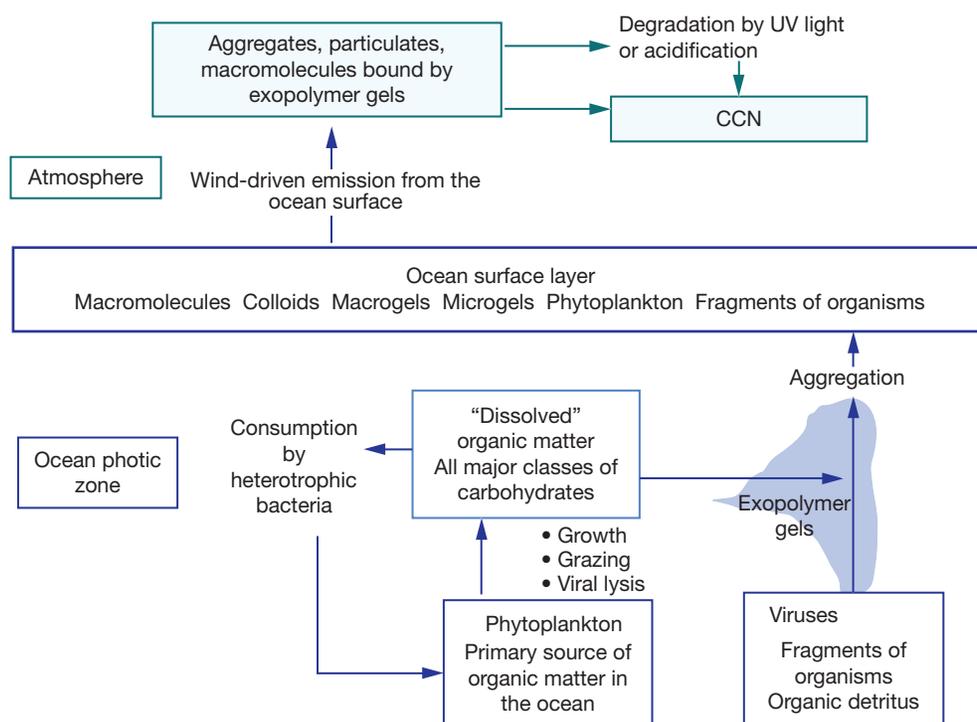


Figure 4 Production mechanism for ocean-derived, primary organic aerosol. Phytoplankton are the primary source of organic matter in the ocean. The large pool of dissolved organic matter composed of all major classes of carbohydrates resides within the ocean photic zone and is derived from phytoplankton growth, grazing by predators, and viral lysis. Also residing within the photic zone are small particulates composed of other algae, bacteria, viruses, fragments of larger organisms, and organic detritus. This organic matter becomes bound together by exopolymer gels secreted by marine organisms. The resulting aggregates are injected into the atmosphere through bubble bursting and contribute to the marine boundary layer cloud condensation nuclei population either directly or after degradation by ultraviolet light or acidification.

immediately on emission of nascent particles from the ocean surface. As a result, measurements of ambient air do not allow for an unequivocal characterization of primary, ocean-derived particles (Keene et al., 2007). Several studies have been performed over the past few years involving the generation of nascent aerosols from seawater to avoid interferences from constituents in the marine atmosphere that can modify newly emitted particles. Described below is what has been learned from these experiments about the number size distribution and chemical composition of nascent, ocean-derived aerosols. Only those experiments in which real seawater was used for aerosol generation are considered, as artificial seawater does not contain all the components that may contribute to the CCN population in the MBL.

Several approaches have been used to generate aerosols from seawater. Ideally, the method used is representative of the natural bubble bursting process that occurs at the surface ocean and accurately reproduces the properties of nascent, ocean-derived aerosol. Acknowledging that the method used can impact the properties of the aerosol particles produced (Fuentes et al., 2010a), the methods are briefly described in the following discussion. More details can be found in the references cited for each experiment.

Tyree et al. (2007) generated aerosol by passing filtered air through a stainless steel fine-pore diffuser into a glass cylinder containing real seawater. The seawater was collected from the pier at the Scripps Institute of Oceanography in La Jolla, CA. Generated foam droplets were dried, and the number size distribution of the dried particles was measured. The dried particle size distribution from unfiltered seawater was unimodal in the submicrometer size range, with the peak diameter (dry) around 100 nm. The effect of organic matter on the particle size distribution was tested by comparing results from filtered and unfiltered seawater. The unfiltered seawater produced 35–40% more total particles than the filtered seawater, but the shape of the size distribution was not affected.

Keene et al. (2007) passed particle-free air through multiple fine-pore glass frits into a high-capacity aerosol generator containing flowing seawater. The number size distribution of the generated particles was sampled along with the chemical composition. The size distribution was found to be unimodal in the submicrometer size range with a peak diameter (dry) of 80 nm. Based on measurements of mass size distributions, organic carbon was highly enriched relative to the seawater composition in all size fractions sampled. The degree of enrichment increased with decreasing particle size so that the greatest enrichment was associated with particles in the size range that dominates CCN concentrations.

As part of the Marine Aerosol Production 2006 cruise in the northeast Atlantic Ocean, Hultin et al. (2010) generated sea spray aerosol from a seawater supply system with an inlet beneath the bow of the ship. The water was continuously pumped into the top of a 1-m-high stainless steel tank and impinged on the surface as a vertical jet. Particle-free air was pumped into the bottle in excess to ensure no laboratory air entered the bottle. Generated sea spray aerosol was sampled for number size distribution and chemical composition (Facchini et al., 2008a). A number mode with a peak diameter of 100 nm dominated the submicrometer size

range. Organic carbon, mainly water insoluble, dominated this same size range with a composition similar to phytoplankton exudates (hydroxylated moieties of sugars, esters, and polyols; aliphatic groups adjacent to carbonyls, amides, and acids; and aliphatic chains with terminal methyls, typical of lipids) (Facchini et al., 2008a).

Fuentes et al. (2010b) collected seawater samples from productive and nonproductive waters on a research cruise conducted along the coast of western Africa. Primary sea spray particles were generated by the impingement of water jets on the surface of unfiltered seawater in a polyethylene tank with a capacity of 6 l. The cruise track covered both productive and nonproductive waters, with productivity being defined by the chlorophyll concentration. With higher chlorophyll concentrations (as derived from SeaWiFS), the peak diameter within the submicrometer size range was 40 nm. In nonproductive waters the peak diameter was around 52 nm. In addition, the total number concentration was higher for the productive versus nonproductive waters. Fuentes et al. (2010b) suggest that the difference in size distributions could be a result of detritus, organic macrogels, and colloidal and dissolved organic carbon in the more productive waters. Within the productive waters, however, a clear correlation between the chlorophyll concentration and the particle size distribution modal parameters (total number concentration and diameter) was not observed.

Despite differences in methods for generating nascent sea spray particles, several generalities can be made regarding the characteristics of these particles. All experiments performed with real seawater show a dominant submicrometer mode with a peak diameter between 50 and 100 nm. In addition, organic matter makes a significant contribution to the mass concentration in submicrometer size ranges, with the organics being primarily water insoluble and having a composition similar to phytoplankton exudates. These studies provide further evidence for a primary, wind-driven source of CCN to the remote MBL that is enriched in organics relative to seawater.

In addition to a sea spray source of primary organic aerosol, there is evidence for an ocean-derived source of secondary organic aerosol. Elevated concentrations of dimethyl- and diethylammonium salts (DMA^+ and DEA^+) have been observed in atmospheric aerosols in regions of phytoplankton blooms (Facchini et al., 2008b). The mass size distributions of DMA^+ and DEA^+ were found to peak in the submicrometer size range similar to that of nss SO_4^{2-} , indicating a secondary production mechanism. Similarly, measured concentrations of total organic nitrogen in submicrometer aerosols in remote marine regions have been found to be correlated with the DMS oxidation product MSA (Miyazaki et al., 2010). In addition, DMA^+ and DEA^+ have not been observed in sea spray aerosol generated in bubble bursting experiments using seawater, thus indicating the lack of a primary source. Based on these data, it has been hypothesized that DMA^+ and DEA^+ are emitted from phytoplankton and other marine sources and emitted into the atmosphere in the gas phase, where they react with H_2SO_4 or acidic sulfates to form particulate-phase salts (Facchini et al., 2008b).

Oxalic acid and other low molecular weight organic acids have been observed in atmospheric aerosols over many ocean regions remote from continental sources

(Kawamura et al., 1996; Miyazaki et al., 2010; Rinaldi et al., 2011; Turekian et al., 2003). Oxalic acid and nss SO_4^{2-} were found to be correlated in the submicrometer aerosol samples collected over the western North Pacific in summer, indicating similar secondary aerosol production mechanisms (Miyazaki et al., 2010). Carbon isotope values for oxalate associated with sub- and supermicrometer particles at Bermuda were similar to $\delta^{13}\text{C}$ reported for marine organic material, suggesting a marine source (Turekian et al., 2003). It has been hypothesized that the low molecular weight diacids found in marine aerosol result from the sea-to-air emission of ocean-derived organic matter, including unsaturated fatty acids, followed by photochemical oxidation in the aqueous aerosol phase (Kawamura et al., 1996) or during cloud processing (Crahan et al., 2004). Measurements and models indicate that the likely mechanism for production of oxalic acid in the aqueous phase involves a multistep process initiated by OH oxidation of glyoxal (Carlton et al., 2007; Crahan et al., 2004). Recently, observed concentrations of glyoxal over the remote tropical Pacific were reported to be in excess of what can be explained by the photochemistry of DOM in surface ocean waters or by oxidation of gas-phase volatile organic compounds (Sinreich et al., 2010). These large concentrations of glyoxal may be attributable, at least in part, to oxidation of organic material in sea spray after it is emitted into the atmosphere.

5.12.5 The MBL CCN Budget

The overall mix of chemical components contributing to the population of particles <300 nm in diameter will determine the impact of marine aerosol on cloud properties. For a given particle size, sea salt aerosol will activate and form a cloud droplet at a lower water supersaturation than other species, including sulfate. There is evidence that the addition of organic exudates released by phytoplankton cultures into primary marine aerosol lowers CCN activity (Fuentes et al., 2011). Measurements are required to determine regional variability in the composition and size of MBL aerosol and the ability of the aerosol to nucleate cloud droplets. Global model simulations are used to test primary and secondary mechanisms of aerosol production to explain observed CCN concentrations and derive MBL CCN source budgets.

A global chemical transport model with size-resolved aerosol microphysics has been used to explain the observed seasonal cycle in CCN at Cape Grim (Korhonen et al., 2008). It was found that both DMS and sea salt emissions were required to match measured CCN concentrations. Over the Southern Ocean (30°S to 45°S), model estimates indicate that DMS emissions increase CCN concentrations during the summer by 46%, with emissions of sea salt accounting for the majority of the remainder. The majority of the summertime DMS-derived CCN is a result of particle nucleation in the free troposphere. Only a small fraction (6%) of DMS oxidation products contribute to condensational growth of sea salt to CCN sizes since most of the sea salt is large enough to be CCN without further growth. Further south (>45°S), the contribution of DMS to the MBL CCN population decreases due to high wind speeds that result in a large sea salt source. During winter, sea salt emissions account for over 80% of CCN. Additional

modeling results confirm a significant sea salt source of CCN. In remote ocean regions, under conditions of high wind speeds, emissions of sea salt have been calculated to increase CCN concentrations by 150–500% than that of a DMS-derived CCN background concentration (Pierce and Adams, 2006). The inclusion of emissions of sea salt particles with diameters between 10 and 100 nm is required to explain observed particle number concentrations in these regions.

Global models have also been used to assess aerosol mass and number concentrations resulting from emissions of ocean-derived organics. The model results indicate that ocean emissions of organics provide a significant source of submicrometer aerosol mass and number to the MBL (Spracklen et al., 2007). Furthermore, if organics are not included, CCN concentrations in the MBL are underestimated (Roelofs, 2008). In addition, including ocean-derived organics in the model led to more cloud droplets of smaller size, which improved the agreement with measurements.

Based on the observations, laboratory studies, and model simulations described in the previous sections, the concentration of CCN in the remote MBL is a result of emissions of sea salt and organics in sea spray (dependent on biological activity and wind speed), subsidence of DMS-derived and continentally derived particulates from the free troposphere (dependent on oxidation and entrainment rates), and particle growth (dependent on condensation, coagulation, and cloud processing). A depiction of the multiple sources of CCN to the MBL is shown in Figure 5.

5.12.5.1 Production Fluxes of Sea Spray Aerosol

Although recent advancements in global models have allowed for assessments of CCN sources and formation processes as well as budgets of CCN in the MBL, large uncertainties in these estimates remain due, in large part, to uncertainties in production fluxes of sea spray aerosol. Model calculations of the diameter and number concentration of sea spray-derived CCN are highly sensitive to emission parameterizations of sea salt and organics. Figure 6 shows the range of production fluxes of sea spray aerosol as a function of particle size recently compiled by de Leeuw et al. (2011). The parameterizations vary by an order of magnitude with even larger differences occurring in the size range most relevant for CCN formation. In addition, the large sea spray aerosol production fluxes for the smallest submicrometer particles imply number concentrations in the remote MBL that are much higher than those observed. When incorporated into global model calculations, the sea spray number flux per whitecap area indicated in these parameterizations is multiplied by the area of the ocean that is covered by whitecaps to obtain the sea salt number flux from the ocean (Pierce and Adams, 2006). Estimates of whitecap coverage and, hence, sea salt number flux are calculated as a function of wind speed. The resulting sea salt emissions used in global model calculations are subject to uncertainties associated with the parameterization of the sea salt number flux per whitecap, calculated whitecap coverage, and wind speeds used in the model.

Accurate parameterizations of sea spray emissions are further complicated by the patchiness of biological productivity in ocean surface waters. Chlorophyll *a* concentration obtained

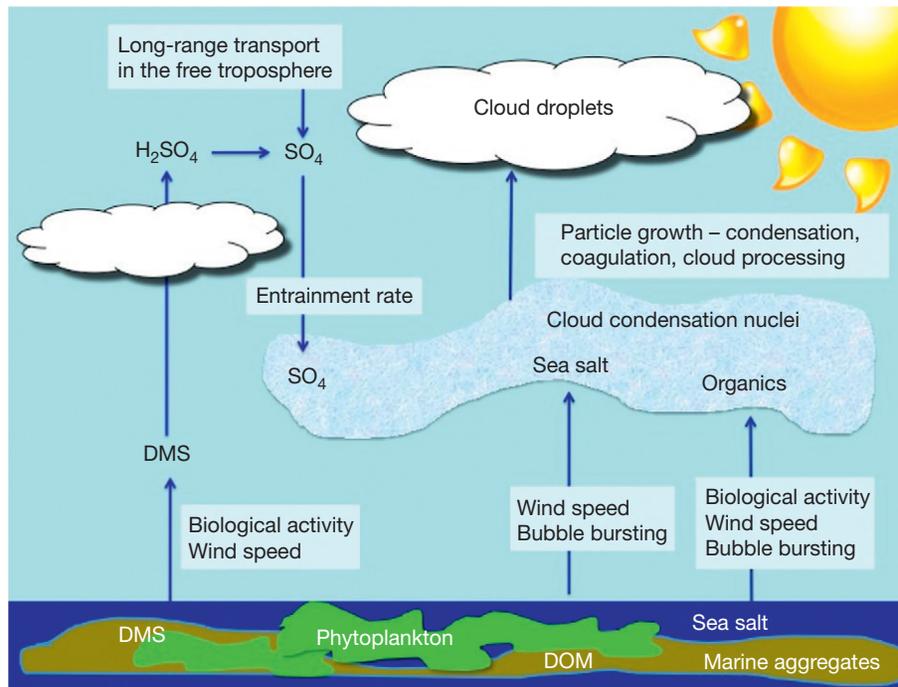


Figure 5 Major sources and production mechanisms for cloud condensation nuclei in the remote marine boundary layer. Dimethylsulfide contributes to the marine boundary layer cloud condensation nuclei population primarily via particle nucleation in the free troposphere in cloud outflow regions with subsequent subsidence. Sea salt and organics are emitted as a result of wind-driven bubble bursting. Organic matter may also be incorporated into cloud condensation nuclei through emissions of ocean-derived volatile organic compounds and secondary organic aerosol production. DOM, dissolved organic matter in ocean surface waters.

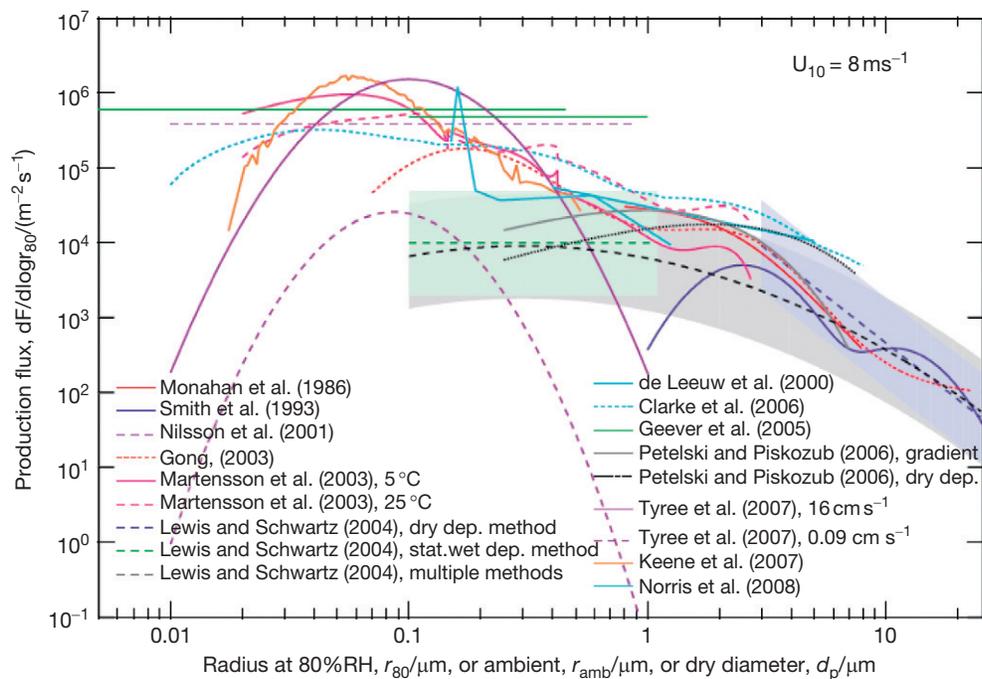


Figure 6 Parameterizations of the size-dependent sea spray aerosol production flux for a wind speed at 10 m of 8 m s^{-1} . The central values and uncertainty ranges from the review of Lewis and Schwartz (2004) based on different methods for deriving the production flux (green indicates the statistical wet deposition method, blue indicates the steady state deposition method, and gray indicates all available methods). Reproduced from de Leeuw G, Andreas EL, Anguelova MD, et al. (2011) Production flux of sea spray aerosol. *Reviews of Geophysics* 49: RG2001. <http://dx.doi.org/10.1029/2010RG000349>, with permission from American Geophysical Union.

from satellite observations has been used as a proxy for ocean biological activity in efforts to parameterize emissions of sea spray organics (Langmann et al., 2008; O'Dowd et al., 2008; Vignatti et al., 2010). Presence of chlorophyll *a*, a measure of phytoplankton abundance, is an attractive proxy for primary organic matter in sea spray aerosol because it can be determined from satellite retrievals that offer global coverage of the world's oceans. However, this approach has only been able to account for up to 30% of the variance in measured water-insoluble organic aerosol mass concentrations. The poor correlation between chlorophyll *a* and sea spray organic aerosol indicates that chlorophyll represents only a small fraction of the parameters involved in controlling concentrations of organics in ocean surface waters.

Neither the large pool of DOM resulting from phytoplankton secretions nor the nonphytoplankton particulates (bacteria, viruses, fragments of larger organisms, and organic detritus) are detected with satellite retrievals of chlorophyll. Hence, there is a need for a sea spray source function that accounts for this additional source of organic matter. Recently developed source functions of organic aerosol resulting from sea spray emissions include more complex biological processes whereby the organic component is derived from seawater diatoms (Fuentes et al., 2010b). The parameterization incorporates retrievals of chlorophyll *a* diatom biomass from satellites and first-order approximations of the amount of total organic matter resulting from diatom growth, predation by grazing organisms, and viral lysis. Although large uncertainties in the source function exist, this approach acknowledges the complexities involved in relating seawater organic matter to emissions of sea spray organic aerosols. Field observations involving multiple experimental approaches are required for constraining production fluxes of sea spray (including sea salt and organics) and for reducing the uncertainties in model calculated distributions of CCN over the world's oceans (de Leeuw et al., 2011).

5.12.6 The CLAW Hypothesis

The belief in the late 1980s that DMS was the major source of CCN over the oceans led to a proposed biological regulation of climate involving emissions of DMS from oceanic phytoplankton (Charlson et al., 1987; Shaw, 1983). The CLAW hypothesis, named after the four authors of the Charlson et al. (1987) study, proposed that DMS-produced CCN alter the albedo of clouds over the ocean since the reflectivity or albedo of clouds is controlled, in part, by the number of CCN available to nucleate cloud droplets. An increase in cloud albedo can lead to a decrease in the surface temperature of the Earth and incident solar radiation, providing a link between DMS emissions and the temperature of the Earth. Changes in Earth's temperature or the amount of solar radiation reaching the surface could then affect the speciation and abundance of phytoplankton and the production of DMS, thereby closing the feedback loop. Figure 7 shows the full climate feedback loop that forms the basis for the CLAW hypothesis.

At the time the CLAW hypothesis was proposed, there was a lack of observations to provide evidence for non-DMS sources of MBL CCN. There were little data showing significant

concentrations of sea salt particles in the CCN size range. In addition, there was a complete lack of knowledge about the number concentration and sources of organics in the marine atmosphere. Over the past 25 years, a large body of evidence has been obtained through measurements and modeling studies supporting multiple sources of ocean-derived CCN in the MBL. It is also now recognized that continental emissions can lead to particle nucleation in the free troposphere, be transported thousands of kilometers to remote ocean regions, and then get entrained into the MBL thus providing an additional source of CCN (Korhonen et al., 2008).

For the CLAW climate feedback loop to work, each step in the loop must have a strong response to a change in the relevant parameter. Global model studies have shown that the marine CCN concentration has a low sensitivity to an increase in DMS emissions due to the abundance of MBL CCN from non-DMS sources (Carslaw et al., 2010; Woodhouse et al., 2010). The low sensitivity of CCN concentration to DMS emission and the complexity of aerosol effects on cloud properties suggest that Charlson et al. (1987) overestimated the response of cloud albedo to changing CCN concentrations (Quinn and Bates, 2011). In addition, global model calculations indicate that DMS seawater concentrations have a low sensitivity to changes in temperature and the solar radiation dose to the upper ocean (Gunson et al., 2006; Vallina et al., 2007). Furthermore, a local climate feedback loop is prevented by the spatial decoupling between DMS

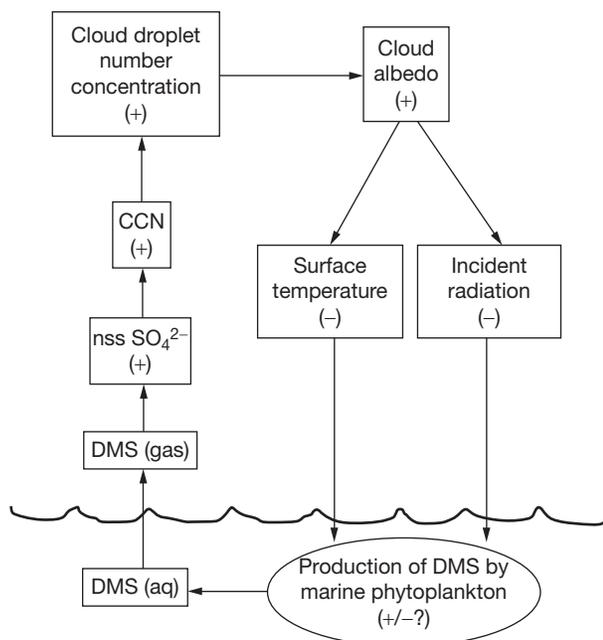


Figure 7 Modified diagram of the climate feedback loop proposed by Charlson et al. (1987). Dimethylsulfide emitted by phytoplankton in ocean surface waters undergoes sea-to-air transport. Once in the atmosphere, it is oxidized and these oxidation products undergo homogeneous nucleation to form new, water-soluble particles in the marine boundary layer. These particles become cloud condensation nuclei and increase the number concentration of cloud droplets and cloud albedo. The resulting decrease in temperature at the surface of the Earth and incident solar radiation could then impact the rate of dimethylsulfide emission.

emission in the boundary layer and CCN production in the free troposphere (Quinn and Bates, 2011).

However, the absence of a climate feedback loop based on sulfur emissions from oceanic phytoplankton does not rule out a link between ocean-derived CCN and climate. Sea salt aerosol production is expected to be impacted by an increase in surface wind speed (Korhonen et al., 2010; Latham and Smith, 1990) such as has been observed in association with spring Antarctic ozone depletion (Yang et al., 2007). In addition, since sea spray organics are emitted as particulates directly into the atmosphere, a direct link between biological production and local emission of organics, CCN production, and cloud albedo is possible.

5.12.7 Concluding Comments

Much has been learned about many aspects of ocean-derived aerosols in the past several decades, including their sources, production mechanisms, chemical composition as a function of particle size, and radiative effects. Two decades ago, marine aerosol was thought to be composed of sea salt in the supermicrometer size range and nss sulfate in the submicrometer size range. Shipboard and ground-based measurements in remote marine regions have revealed that sea salt can dominate the submicrometer aerosol mass concentration in the MBL. As a result, both sub- and supermicrometer sea salt aerosol dominate light scattering in regions not heavily impacted by continental aerosol. In addition, it is now recognized that submicrometer sea salt particles can be a source of MBL CCN.

Over two decades ago, it was thought that sulfate, derived from oceanic phytoplankton emissions, made up the majority of the MBL aerosol number concentration. Several decades of measurements and model simulations have shown that sea spray aerosol containing both inorganic sea salt and non-DMS organic matter also contribute to the MBL number and CCN concentration. A growing body of data shows that the organic matter measured in ocean-derived aerosol particles is similar to the DOM in surface seawater, indicating a potential link between ocean biology, atmospheric aerosols, and aerosol–cloud interactions. Although much information has been gained, substantial knowledge gaps remain.

Given the multiple sources of ocean-derived CCN, remaining unknowns include the production flux of sea spray aerosol (sea salt and organics) as a function of particle size and how it varies with environmental parameters, the relative contribution of the sea spray and DMS sources to the number concentration of particles in the CCN size range, how the relative contributions vary regionally, the resulting composition of individual particles, and, ultimately, the impacts on cloud properties. An additional unknown is the impact of gas-phase organic emissions from the ocean on ocean-derived aerosol properties. Also, questions remain concerning the large observed concentrations of gas-phase glyoxal in the remote MBL, including its source and impact on formation of secondary organic aerosols.

Measurements of freshly produced, nascent sea spray particles under a variety of oceanic/atmospheric conditions (e.g., high and low wind speed; high and low biological productivity) are required to improve parameterizations of

emissions of ocean-derived aerosol and to characterize their properties including chemical composition, mixing state, particle size, and cloud nucleating ability. Simultaneous characterization of the continuum of surface seawater organics ranging from ultrafiltered DOM to particulate organic carbon is required to identify the source or sources of oceanic organic matter that is incorporated into atmospheric aerosol. In addition, measurements of free tropospheric aerosol are needed to quantify the DMS source of ocean-derived aerosol and to improve the ability of models to nucleate new particles, grow them, and mix them into the boundary layer where they can impact cloud micro- and macrophysical properties.

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