REVIEW

The case against climate regulation via oceanic phytoplankton sulphur emissions

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More than twenty years ago, a biological regulation of climate was proposed whereby emissions of dimethyl sulphide from oceanic phytoplankton resulted in the formation of aerosol particles that acted as cloud condensation nuclei in the marine boundary layer. In this hypothesis—referred to as CLAW—the increase in cloud condensation nuclei led to an increase in cloud albedo with the resulting changes in temperature and radiation initiating a climate feedback altering dimethyl sulphide emissions from phytoplankton. Over the past two decades, observations in the marine boundary layer, laboratory studies and modelling efforts have been conducted seeking evidence for the CLAW hypothesis. The results indicate that a dimethyl sulphide biological control over cloud condensation nuclei probably does not exist and that sources of these nuclei to the marine boundary layer and the response of clouds to changes in aerosol are much more complex than was recognized twenty years ago. These results indicate that it is time to retire the CLAW hypothesis.

Cloud condensation nuclei (CCN) can affect the amount of solar radiation reaching Earth's surface by altering cloud droplet number concentration and size and, as a result, cloud reflectivity or albedo[1]. CCN are atmospheric particles that are sufficiently soluble and large enough in diameter to take up water vapour and serve as nuclei for cloud droplet formation. For the range of water supersaturations typical of marine boundary layer (MBL) clouds and the chemical composition of marine aerosols, the CCN population is dominated by particles between 40 and 300 nm in diameter. Although particles larger than 300 nm will activate to form cloud droplets regardless of composition, there are relatively few particles of this size. It is therefore the particles less than 300 nm in diameter that determine the CCN concentration in the remote MBL and that have the potential to change cloud properties.

Marine phytoplankton produce the osmolyte dimethylsulphonium propionate, which undergoes enzymatic cleavage to form dimethyl sulphide (DMS). Both dimethylsulphonium propionate and DMS scavenge reactive oxygen species and act as antioxidants under conditions of high ultraviolet radiation and oxidative stress[2,3]. DMS is the dominant volatile sulphur compound in ocean surface waters and is the most significant biological source of gaseous sulphur to the remote marine troposphere[4]. After emission to the atmosphere, DMS is oxidized by the hydroxyl radical to form SO_2 and methane sulphonic acid (MSA)[5]. SO_2 can be taken up by particles directly or be further oxidized to H_2SO_4. H_2SO_4 can combine with other gas-phase species to form solid particles (homogeneous nucleation), while both H_2SO_4 and MSA can condense onto existing particles contributing to the growth of those particles (heterogeneous nucleation). The end result is a particulate phase containing SO_4^{2-} and, to a lesser extent, methane sulphonate (MSA^-) derived from oceanic DMS.

In the 1980s, it was hypothesized that DMS-derived SO_4^{2-} made up the majority of the CCN in the MBL distant from continental and anthropogenic aerosol sources[6,7]. The CLAW hypothesis, named after the four authors of the Charlson et al.[7] study, was based on data available at the time that indicated that (1) non-sea-salt sulphate was ubiquitous in submicrometre marine aerosol[8,9] and (2) concentrations of sodium containing particles at cloud height were negligible (thus ruling out sea salt particles as a source of CCN)[10]. Organic species were not considered because little was known about their concentration and composition in the marine atmosphere.

The CLAW hypothesis further postulated that an increase in DMS emissions from the ocean would result in an increase in CCN, cloud droplet concentrations, and cloud albedo, and a decrease in the amount of solar radiation reaching Earth's surface. A reduction in solar radiation could result in a change in the speciation and abundance of phytoplankton producing dimethylsulphonium propionate, thus setting up a climate feedback loop between cloud albedo and surface ocean DMS concentrations (Fig. 1). The proposed climate feedback loop requires (1) that DMS is a significant source of CCN to the MBL, (2) a change in DMS-derived CCN yields a change in cloud albedo, and (3) a change in cloud albedo, surface temperature, and/or incident solar radiation leads to a change in DMS production. If any one step in the feedback loop shown in Fig. 1 has a small response, the proposed bioregulation of climate will be minimal.

The introduction of the CLAW hypothesis spawned 25 years of research in the fields of biological oceanography, atmospheric chemistry, and climate science in search of evidence for a biological regulation of climate due to marine sulphur emissions. Below we re-evaluate the individual steps in the feedback loop in the context of results from measurement and modelling studies conducted over the past two decades and conclude that a DMS bioregulation of climate is prevented by a weak sensitivity to change in each step of the feedback loop.

DMS as a source of CCN to the remote MBL

The strongest evidence for the first step in the CLAW feedback loop (the link between DMS emissions and CCN concentrations) is the coherence in the seasonal cycles of DMS, its particulate phase oxidation products (non-sea-salt SO_4^{2-} and MSA^-), and CCN. At Cape Grim, Tasmania, a remote Southern Ocean sampling site, concentrations of atmospheric DMS, non-sea-salt 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[11,12]. Similar measurements of DMS and CCN made in the boundary layer over the tropical South Atlantic[13] and the northeast Pacific Ocean[14] found that 40% to 50% of the variance in CCN concentrations could be explained by DMS. The South Atlantic observations also revealed significant correlations between non-sea-salt SO_4^{2-} or MSA^- mass concentrations and CCN[13]. Although these observations provide evidence for the atmospheric chemistry portion of the CLAW
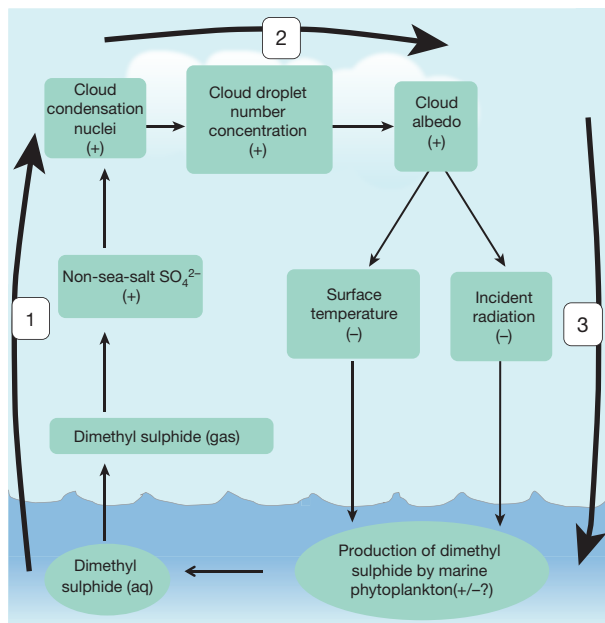
Figure 1 | Modified diagram of the climate feedback loop proposed by ref. 7. DMS, a breakdown product of phytoplankton-produced dimethylsulphonium propionate, undergoes sea-to-air transport. Once in the atmosphere, it is oxidized and these oxidation products undergo homogeneous nucleation to form new, water-soluble particles in the MBL. These particles become CCN and increase the number concentration of cloud droplets and cloud albedo. The resulting decrease in temperature at the surface of Earth and incident solar radiation then affect the rate of DMS production. The proposed climate feedback loop requires a strong response in each of the following steps: (1) a change in seawater DMS production leads to a significant change in MBL CCN concentration, (2) a change in DMS-derived CCN yields a change in cloud albedo, and (3) a change in cloud albedo, surface temperature, and/or incident solar radiation leads to a change in DMS production. The three steps are labelled in the figure.

hypothesis (that is, the conversion of SO_4^{2-} and MSA^- into CCN shown in step 1 of Fig. 1), they do not indicate the sensitivity of CCN concentration to a change in DMS emission. In addition, they do not rule out other sources of CCN. Measurements of the chemical composition of particles in the CCN size range are needed to assess all sources of CCN to the MBL.

Non-DMS sources of MBL CCN

Identification of the sources that contribute to MBL CCN requires direct chemical analysis of single particles with diameters less than 300 nm. Such measurements are sparse. Those measurements that have been reported are based on electron microscopy coupled with X-ray analysis[15–19], X-ray spectromicroscopy[20,21] and laser mass spectrometry[18]. 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[22]. Below we discuss what is known about the composition of CCN in the remote MBL on the basis of these measurement techniques and reveal the significance of sea salt and non-DMS organics.

Single-particle analysis of aerosol samples collected over the open ocean in the mid-Pacific reveal that non-sea-salt SO_4^{2-} exists in CCN-size particles[15,16] and that the number concentration in this size range can be dominated by particles containing sulphate[17]. At the same time, there is a lack of observations of pure acidic SO_4^{2-} or $(NH_4)_2SO_4$ particles in the MBL. Measurements made on the outer edge of the Great Barrier Reef and over the central Arctic Ocean reveal organic inclusions within $(NH_4)_2SO_4$ particles[19]. The organic inclusions appear to act as nuclei

for the condensation of gas-phase DMS oxidation products. Similarly, measurements of aerosol composition at Cape Grim indicate that particles formed through the condensation of sulphur-containing gases grow only by coagulating with sea salt and organics[18]. DMS will increase the CCN number concentration through coagulation and condensation only if it allows a particle to grow and/or become sufficiently soluble to activate to form a cloud droplet when entrained into a cloud. If the sea salt or organic particle was already sufficiently large to serve as a CCN, the addition of DMS-derived sulphur to the particle will not increase the number of CCN.

Sea salt as a source of MBL CCN

Unambiguous identification of sea salt as CCN requires the determination of the number concentration of sea-salt-containing particles in those particles with diameters less than 300 nm. Though few, there are measurements based on direct chemical techniques that provide evidence for sea salt as CCN. Measurements on the coast of Oahu, Hawaii, with an instrument that detects emission from thermally excited sodium atoms reveal the presence of sodium-containing particles down to the instrumental cut-off diameter of 200 nm (ref. 23). Manual transmission electron microscopy with energy dispersive X-ray analysis of aerosol samples collected over the Southern Ocean finds that up to 50% of the particles in the 50–150-nm size range contain sea salt[18]. This percentage corresponds to a number concentration of sea-salt-containing particles of up to 100 per cubic centimetre, a significant fraction of the typical MBL CCN concentration[22].

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 sulphates, and simple organics evaporate or decompose at temperatures below 300 °C (ref. 24). Refractory species, including dust, sea salt and large organic polymers, must be heated to over 600 °C for thermal decomposition to occur[24,25]. Flights across the Atlantic reveal that, at altitudes near 400 m, 20% of the measured CCN survived heating to 650 °C (ref. 25). The fraction of refractory nuclei decreased with altitude, indicating an ocean source. A similar volatility analysis onboard a research cruise in the northeast Atlantic found that for maritime, high-wind-speed air masses ($14–17\,m\,s^{-1}$), 40% of the particles with diameters between 100 and 240 nm contained a refractory component like sea salt[26].

The most compelling evidence for sea salt as CCN is provided by 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 southeast Pacific revealed that half of the particles less than 200 nm in diameter contained sulphate. 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[27]. This result is due to the lower supersaturation required for sea salt to activate and form cloud droplets compared to other species, including sulphate, for a given particle size. The experiments described above, as well as others carried out over the past several decades[22,28], show that sea-salt-containing particles in the CCN size range are present in marine air masses. Hence, contrary to what was assumed 25 years ago, observations show that sea salt makes up a large fraction of MBL CCN.

Organics as a source of MBL CCN

Ocean surface waters contain large concentrations of small particulates including phytoplankton, algae, bacteria, viruses, fragments of larger organisms and organic detritus[29,30]. Phytoplankton release or exude organic matter during growth, predation by grazing organisms and viral lysis[31]. The resulting pool of organic matter contributes to one of the largest active reservoirs of organic carbon on Earth[32] and consists of every class of carbohydrate[31]. This pool of organic matter is often referred to as dissolved organic matter but may contain colloidal material that is not truly dissolved. A growing body of evidence shows that this

seawater-dissolved organic matter is similar to organic material found in atmospheric aerosols[33–35].

Phytoplankton exudates include exopolymer gels consisting of polysaccharides that bind together smaller organic molecules such as amino acids, proteins and peptides[36]. Exopolymer gels are insoluble, thermally stable, highly surface active, highly hydrated and readily sequester dissolved organic matter[37]. Exopolymer gels bind small organic particulates into aggregates. It has been hypothesized that these aggregates are injected into the atmosphere through bubble bursting at the ocean surface, thereby contributing to the primary organic aerosol found in the remote MBL[19,35]. Once in the atmosphere, the exopolymer gels that bind the aggregates and particles together are degraded with ultraviolet light or acidification. Transmission electron microscopy analysis on particles collected during the summer at Cape Grim and other remote ocean sites have revealed the existence of individual particles with diameters between 70 and 200 nm containing organic matter in the form of exopolymer gels and airborne marine aggregates composed of exopolymer gels, aggregates of organic particles and marine microorganisms[19,35,37]. It has been suggested that the size and solubility continuum of phytoplankton exudates that exists in sea water is reflected in nascent sea spray particles[33]. This mechanism for the production of organic sea spray aerosol is depicted in Fig. 2.

Observational evidence for an organic source of CCN to the MBL is considerable. Measurements of northeast-Atlantic air masses made on the coast of Ireland reveal increased mass concentrations of organics, primarily water insoluble, in sub-500-nm particles during the summer bloom period[38]. Aerosol organic matter recently measured in samples collected in remote regions of the North Atlantic and Arctic oceans is reported to be composed of carbohydrate-like compounds containing organic hydroxyl groups from ocean emissions[20]. The abundance of carbohydrate material measured in these aerosol samples is consistent with observations made over the past decade. A review of over ten years of measurements of marine organic aerosol concluded that this ocean-derived aerosol is composed of polysaccharides, proteins and amino acids, and microorganisms and their fragments[21].

Recently, several studies have been performed involving the generation of nascent aerosols from sea water to avoid interference from constituents in the marine atmosphere that could modify newly emitted particles[39]. Despite the use of different methods in these experiments, several generalities can be made regarding the characteristics of nascent, ocean-derived particles. All experiments show a dominant submicrometre mode in the particle number size distribution with a peak diameter between 50 and 100 nm (refs 40–42). In addition, organics are significantly enriched in submicrometre particles with the degree of enrichment increasing with decreasing particle size[33,39]. These studies, along with the similarities between the composition of organic matter sampled in the ocean microlayer and in atmospheric aerosol[43], provide further evidence for an organic, wind-driven source of CCN to the MBL.

The MBL CCN budget

Under the CLAW hypothesis, an increase in the emission of DMS from the ocean results in an increase in the number of particles that act as CCN by either (1) the homogeneous nucleation of new particles in the MBL involving H_2SO_4 or (2) the growth of existing particles to CCN-size through condensation of SO_2, H_2SO_4 or MSA^-. Whether gas-phase species undergo homogeneous nucleation or condense onto existing particles depends, in part, on the surface area of the existing particles. If sufficient surface area is available, it provides a sink for condensable vapours and new particle formation is prevented[44,45]. Model calculations indicate that if precipitation removes pre-existing aerosol, thereby reducing aerosol surface area, homogeneous nucleation of new particles can occur under moderate DMS concentrations[46]. There is observational evidence for particle nucleation in the MBL under conditions of low particle surface area[44,47], but it is limited. In addition, in these and other cases[48–50], there is no evidence that the events led to particles large enough to be CCN. Hence, for conditions most typical of the marine atmosphere (large surface area of existing, primarily sea-salt particles and low SO_2 concentrations[51]), boundary layer nucleation due to DMS-derived sulphur and water vapour has little theoretical[46] or observational basis.

Unlike the remote MBL, observations of H_2SO_4-initiated particle nucleation in the free troposphere near cloud top height are numerous[47,52–55]. Gases, including DMS, and particles are entrained from the MBL into clouds. Clouds scavenge or capture the particles so that the air that is detrained from the cloud contains very low aerosol surface area concentrations[53]. The nucleation of new particles observed at cloud top height is a result of reactive gases such as DMS being pumped up to the upper troposphere through deep convective clouds. Once aloft, the reactive gases undergo gas-to-particle conversion in cloud outflow regions where the existing particle surface area is low, water vapour concentrations are high, and the actinic flux is high[47]. Simple box models[56] as well as advanced three-dimensional global models[57–60] indicate that subsidence of particles from the free troposphere can explain a significant fraction of the CCN measured in the MBL. Hence, measurements and model calculations published since the introduction of the CLAW hypothesis indicate that DMS-derived sulphate contributes to MBL CCN concentrations via particle nucleation in the free troposphere rather than in the boundary layer itself. After formation in the free troposphere, the particles may be transported thousands of kilometres before mixing down into the MBL. As a result, regions of high-DMS sea-to-air fluxes do not correlate with regions of high DMS-derived CCN concentrations[61]. The spatial decoupling between DMS production and entrainment of DMS-derived particles into the MBL prevents a local marine biota–climate feedback loop[60–62].

DMS emissions are required for models to reproduce the observed seasonal cycle in CCN at Cape Grim. 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
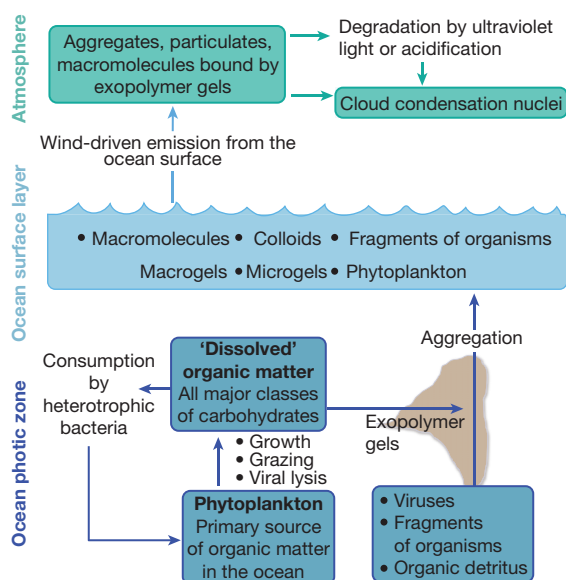
Figure 2 | Ocean-derived source of organics to the MBL CCN population.
Phytoplankton are the primary source of organic matter in the ocean. The large pool of dissolved organic matter composed of all major classes of carbohydrates resides within the ocean photic zone and is derived from phytoplankton 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 MBL CCN population either directly or after degradation by ultraviolet light or acidification.

accounting for the majority of the remainder[61]. 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 because 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 owing to high wind speeds that result in a large sea-salt source. During winter, sea-salt emissions account for over 80% of CCN. Additional modelling 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 up to 500% above a DMS-derived CCN background concentration[57]. 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. Finally, model results indicate that ocean emissions of organics provide a significant source of submicrometre aerosol mass and number to the MBL[59]. Without inclusion of organics, CCN concentrations in the MBL are underestimated[63]. The large contribution of wind-driven sea spray containing both sea salt and organics to the MBL CCN population prevents DMS from being the sole source of MBL CCN, which weakens step 1 of the CLAW feedback loop.

Sea spray aerosol production fluxes

Although recent advancements in global models have allowed for the estimation of MBL CCN budgets, large uncertainties in these estimates remain due, in large part, to uncertainties in sea-spray aerosol production fluxes. Model calculations of the diameter and number concentration of sea-spray-derived CCN are highly sensitive to emission parameterizations of sea salt and organics. Yet estimates of the size-dependent production flux of sea-salt aerosol vary by an order of magnitude, with even larger differences occurring in the size range most relevant for CCN formation[64]. Furthermore, accurate parameterizations of oceanic emissions of organics are complicated by the patchiness of biological productivity in ocean surface waters. Amounts of chlorophyll a derived from satellite observations have been used as a proxy for ocean biological activity in efforts to parameterize emissions of organics[65]. This approach is only able to account for 25% of the variance in the water insoluble organic aerosol mass concentration, indicating that chlorophyll represents only a small fraction of the parameters involved in controlling concentrations of organics in ocean surface waters.

The large pool of dissolved organic matter resulting from phytoplankton secretions has not been detected with satellite retrievals of chlorophyll, nor have non-phytoplankton particulates (bacteria, viruses, fragments of larger organisms and organic detritus). 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 sea-spray-derived organic aerosol include more complex biological processes whereby the organic component is derived from seawater diatoms[42]. 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 to constrain the production fluxes of sea spray (including sea salt and organics) and to reduce the uncertainties in model-calculated distributions of CCN over the world's oceans[64].

The DMS–cloud albedo climate feedback

Global-scale models have been used to determine the sensitivity of CCN to an increase in the emission of DMS for both present-day and globally warmed scenarios[66]. For the Southern Hemisphere, the summertime sensitivity for present-day DMS fluxes is about 0.07, indicating a 0.07% increase in total CCN (from all sources) that is attributable to a 1% increase in the flux of DMS. The sensitivity is lower for the Northern

Hemisphere (0.02%), where the aerosol abundance from all sources is higher. Global warming is predicted to lead to a shallowing of the ocean mixed-layer depth accompanied by an increase in solar radiation dose in the upper mixed layer. Under a globally warmed scenario of a 50% increase in CO_2, one model estimate indicates that the DMS flux will increase by 1%, which yields only a $\sim$0.1% increase in the global CCN concentration[66]. This low sensitivity is due to the abundance of MBL CCN derived from non-DMS sources. Other coupled ocean–atmosphere general circulation models have been used to study the impact of climate change on marine DMS emissions and CCN and have found only a weak positive global response of sulphate aerosol to increased CO_2 (ref. 67). As a result, only very large changes in the flux of DMS to the atmosphere would result in a significant impact on CCN concentration. This low sensitivity between DMS flux and CCN concentration contributes to the weak link in step 1 of the CLAW hypothesis.

The CLAW hypothesis (as proposed) assumed that, for a fixed content of liquid water in cloud, an increase in the concentration of CCN would lead to an increase in cloud albedo (see step 2 of Fig. 1). Charlson et al.[7] calculated that a 30% increase in CCN concentration would cause an increase in planetary albedo sufficient to decrease global mean surface temperature by 1.3 K. As described above, the sensitivity of CCN to the sea-to-air flux of DMS is very low, such that a 30% increase in CCN concentration would require a 300% increase in the DMS flux. Furthermore, studies performed over the past decade with high-resolution models have revealed mechanisms that occur on cloud micro- and macrophysical scales that can buffer or are counter to an increase in cloud albedo that would be attributable to an increase in CCN[68,69].

Aerosols can affect not only cloud microphysics (cloud droplet size and number concentration) but also cloud macrophysics (cloud fraction, size and morphology)[70,71]. For example, for a regime of non-precipitating clouds, dynamic feedbacks resulting from aerosol perturbations on clouds can decrease cloud fraction[70]. An increase in CCN concentration results in faster evaporation rates owing to smaller cloud droplets. The faster evaporation rate leads to enhanced entrainment of subsaturated air surrounding the cloud and a decrease in cloud fraction. In this case, the aerosol effect of an increase in cloud albedo is lessened by the reduction in cloud fraction[71]. Parameterizations that do not consider aerosol-induced changes in cloud macrophysics may misrepresent the overall impact of aerosol–cloud interactions. By assuming a high sensitivity of CCN to the flux of DMS and considering only a highly simplified relationship between aerosol and cloud albedo, Charlson et al.[7] probably significantly overestimated the response of cloud albedo to changing CCN concentrations in step 2 of the CLAW hypothesis.

Step 3 of the CLAW hypothesis assumes that changes in cloud albedo, surface temperature and/or incident solar radiation lead to changes in the production of DMS. This step is supported by time-series measurements that show a seasonal correlation between levels of downwelling solar radiation and ocean surface mixed-layer DMS concentrations[3,72]. In the low-chlorophyll waters near Bermuda, upper-ocean DMS concentrations appear to be related to the availability of incident ultraviolet radiation[72]. This correlation does not reveal information about the sensitivity of DMS production to changes in solar radiation, however. Model calculations indicate that an increase in the solar radiation dose to the ocean upper mixed layer due to a 50% increase in the atmospheric concentration of CO_2 results in only a $\sim$1% increase in global DMS ocean surface concentrations[73]. Other model simulations indicate that changes in DMS emissions due to changes in temperature and irradiance that affect ocean primary productivity are small[74]. This low sensitivity of seawater DMS concentrations to a global warming scenario indicates that the response in step 3 of the CLAW feedback loop is weak.

The post-CLAW view of MBL CCN

In 1987, Charlson et al.[7] hypothesized that oxidation products of biogenically produced DMS account for the bulk of the CCN number concentration in the remote MBL, thus providing a link between marine biota and climate. Field and laboratory experiments performed over the
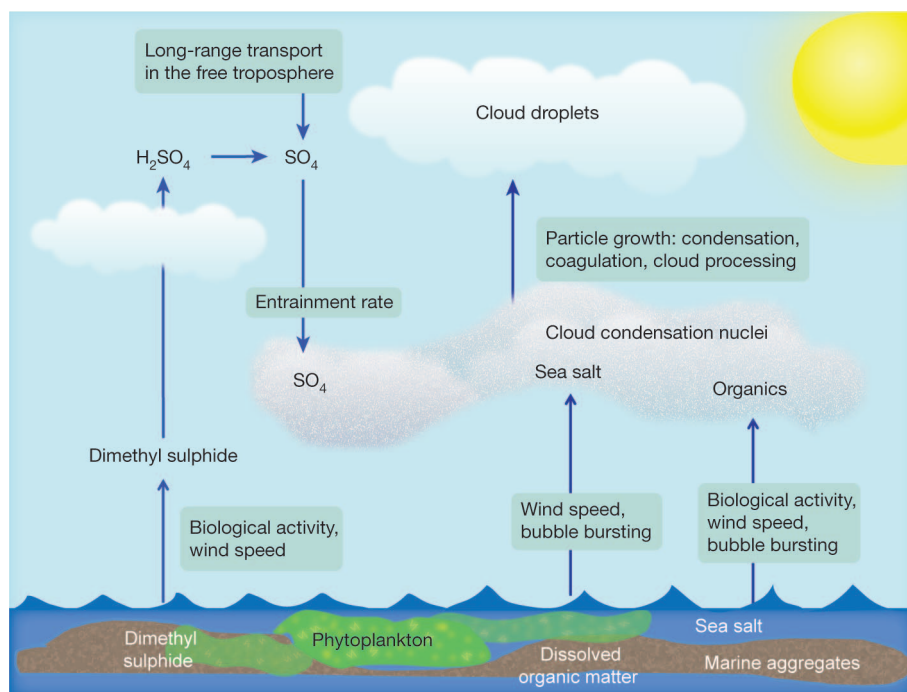
Figure 3 | Major sources and production mechanisms for CCN in the remote MBL. DMS contributes to the MBL CCN population primarily via particle nucleation in the free troposphere in cloud outflow regions with subsequent subsidence. Sea salt and organics are emitted as a result of wind-driven bubble bursting.

past decade have shown that sources of CCN to the remote MBL are more complex than was recognized by the CLAW hypothesis. Bubble bursting at the ocean surface is a major source of not just aerosol mass but also aerosol number to the MBL. This process introduces both inorganic and organic components of sea water to the atmosphere. Inorganic components are comprised of sea salt while the organic components are derived from phytoplankton and the large pool of organics in the ocean surface. Hence, the concentration of CCN in the remote MBL is a result of emissions of sea salt and organics in sea spray (dependent upon biological activity and wind speed), subsidence of DMS-derived and continentally derived particulates from the free troposphere (dependent upon oxidation and entrainment rates), and particle growth (dependent upon condensation, coagulation and cloud processing). This updated view of the multiple sources of CCN to the MBL is depicted in Fig. 3.

The evidence gained over the past 20 years of the significance of non-DMS sources of MBL CCN, the lack of observational evidence for a DMS-controlled marine biota–climate feedback, and the modelled low sensitivity between change and response in each step of the CLAW hypothesis feedback loop all indicate that it is time to retire the CLAW hypothesis. Retiring CLAW does not rule out a link between ocean-derived CCN and climate, however. Sea-salt aerosol production is expected to be affected by an increase in surface wind speed[75,76] such as has been observed in association with spring Antarctic ozone depletion[77]. In addition, because 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.

When proposed[7], the CLAW hypothesis, with its synthesis of marine biochemistry, atmospheric chemistry, cloud physics and climate dynamics into a plausible feedback loop, was visionary in scope. If the CLAW hypothesis has not stood the test of time, it is only because we now have a much better appreciation of the complexity of biogeochemistry and climate physics than when the hypothesis was first put forward. The interdisciplinary research that it motivated is now needed to address the complexity of multiple sources of CCN to the MBL and potential impacts on climate.

1. Twomey, S. The influence of pollution on the shortwave albedo of clouds. *J. Atmos. Sci.* **34,** 1149–1152 (1977).
2. Sunda, W., Kieber, D. J., Kiene, R. P. & Huntsman, S. An antioxidant function for DMSP and DMS in marine algae. *Nature* **418,** 317–320 (2002).
3. Vallina, S. M. & Simo, R. Strong relationship between DMS and the solar radiation dose over the global surface ocean. *Science* **315,** 506–508 (2007).
4. Bates, T. S., Lamb, B. K., Guenther, A. B., Dignon, J. & Stoiber, R. E. Sulfur emissions to the atmosphere from natural sources. *J. Atmos. Chem.* **14,** 315–337 (1992).
5. Andreae, M. O. *et al.* Dimethylsulfide in the marine atmosphere. *J. Geophys. Res.* **90,** 12891–12900 (1985).
6. Shaw, G. E. Bio-controlled thermostasis involving the sulphur cycle. *Clim. Change* **5,** 297–303 (1983).
7. Charlson, R. J., Lovelock, J. E., Andreae, M. O. & Warren, S. G. Oceanic phytoplankton, atmospheric sulphur, cloud albedo, and climate. *Nature* **326,** 655–661 (1987).
   This paper introduced the CLAW hypothesis proposing the link between marine biota and climate.
8. Andreae, M. O. Marine aerosol chemistry at Cape Grim, Tasmania and Townsville, Queensland. *J. Geophys. Res.* **87,** 8875–8885 (1982).
9. Savoie, D. L. & Prospero, J. M. Particle size distribution of nitrate and sulphate in the marine atmosphere. *Geophys. Res. Lett.* **9,** 1207–1210 (1982).
10. Hobbs, P. V. Simultaneous airborne measurements of cloud condensation nuclei and sodium-containing particles over the ocean. *Q. J. R. Meteorol. Soc. Soc* **97,** 263–271 (1971).
11. Ayers, G. P. & Gras, J. L. Seasonal relationship between cloud condensation nuclei and aerosol methanesulphonate in marine air. *Nature* **353,** 834–835 (1991).
    This paper presented the coherence in the seasonality of DMS-derived particulate phase sulphur species and CCN at Cape Grim, Tasmania.
12. Ayers, G. P., Cainey, J. M., Gillett, R. W. & Ivey, J. P. Atmospheric sulphur and cloud condensation nuclei in marine air in the southern hemisphere. *Phil. Trans. R. Soc. Lond. B* **352,** 203–211 (1997).
13. Andreae, M. O., Elbert, W. & de Mora, S. J. Biogenic sulphur emissions and aerosols over the tropical South Atlantic. 3. Atmospheric dimethylsulfide, aerosols, and cloud condensation nuclei. *J. Geophys. Res.* **100** (D6), 11335–11356 (1995).
14. Hegg, D. A., Ferek, R. J., Hobbs, P. V. & Radke, L. F. Dimethyl sulfide and cloud condensation nucleus correlations in the northeast Pacific Ocean. *J. Geophys. Res.* **96** (D7), 13189–13191 (1991).
15. Parungo, F. P., Nagamoto, C. T., Rosinski, J. & Haagenson, P. L. A study of marine aerosols over the Pacific Ocean. *J. Atmos. Chem.* **4,** 199–226 (1986).
16. Pósfai, M., Anderson, J. R. & Buseck, P. R. Constituents of a remote Pacific marine aerosol: A TEM study. *Atmos. Environ.* **28,** 1747–1756 (1994).
17. McInnes, L., Covert, D. & Baker, B. The number of sea-salt, sulfate, and carbonaceous particles in the marine atmosphere: EM measurements consistent with the ambient size distribution. *Tellus* **49B,** 300–313 (1997).
18. Murphy, D. M. *et al.* Influence of sea-salt on aerosol radiative properties in the Southern Ocean marine boundary layer. *Nature* **392,** 62–65 (1998).
    This paper provided direct observational evidence of significant numbers of CCN-size particles containing sea salt and organics in the remote MBL.
19. Leck, C. & Bigg, E. K. Comparison of sources and nature of the tropical aerosol with the summer high Arctic aerosol. *Tellus* **60B,** 118–126 (2008).
20. Russell, L. M., Hawkins, L. N., Frossard, A. A., Quinn, P. K. & Bates, T. S. Carbohydrate-like composition of submicron atmospheric particles and their production from ocean bubble bursting. *Proc. Natl Acad. Sci. USA* **107,** 6652–6657 (2010).

21. Hawkins, L. N. & Russell, L. M. Polysaccharides, proteins, and phytoplankton fragments: four chemically distinct types of marine primary organic aerosol classified by single particle spectromicroscopy. *Adv. Meteorol.* **2010,** 612132 (2010).

22. Clarke, A. D., Owens, S. R. & Zhou, J. An ultrafine sea-salt flux from breaking waves: implications for cloud condensation nuclei in the remote marine atmosphere. *J. Geophys. Res.* **111,** D06202 (2006).

23. Campuzano-Jost, P. *et al.* Near-real-time measurement of sea-salt aerosol during the SEAS campaign: comparison of emission-based sodium detection with an aerosol volatility technique. *J. Atmos. Ocean. Technol.* **20,** 1421–1430 (2003).

24. O'Dowd, C. D. & Smith, M. H. Physicochemical properties of aerosols over the northeast Atlantic: evidence for wind-speed-related submicron sea-salt aerosol production. *J. Geophys. Res.* **98** (D1), 1137–1149 (1993).

25. Dinger, J. E., Howell, H. B. & Wojciechowski, T. A. On the source and composition of cloud nuclei in a subsident air mass over the north Atlantic. *J. Atmos. Sci.* **27,** 791–797 (1970).

26. O'Dowd, C. D., Smith, M. H. & Jennings, S. G. Submicron particle, radon, and soot carbon characteristics over the Northeast Atlantic. *J. Geophys. Res.* **98,** 1123–1135 (1993).

27. Twohy, C. H. & Anderson, J. R. Droplet nuclei in non-precipitating clouds: composition and size matter. *Environ. Res. Lett.* **3,** 045002, 1–9 (2008).
This paper provided direct observational evidence of cloud droplets formed primarily through nucleation on sea-salt particles.

28. Peter, J. A., Blyth, A. M., Brooks, B., Lingard, J. & Smith, M. H. On the composition of Caribbean maritime aerosol particles measured during RICO. *Q. J. R. Meteorol. Soc.* **134,** 1059–1063 (2008).

29. Fuhrman, J. A. Marine viruses and their biogeochemical and ecological effects. *Nature* **399,** 541–548 (1999).

30. Wells, M. L. & Goldberg, E. D. Occurrence of small colloids in sea water. *Nature* **353,** 342–344 (1991).

31. Biersmith, A. & Benner, R. Carbohydrates in phytoplankton and freshly produced dissolved organic matter. *Mar. Chem.* **63,** 131–144 (1998).

32. Hedges, J. I. Global biogeochemical cycles: progress and problems. *Mar. Chem.* **39,** 67–93 (1992).

33. Facchini, M. C. *et al.* Primary submicron marine aerosol dominated by insoluble organic colloids and aggregates. *Geophys. Res. Lett.* **35,** L17814 (2008).

34. Leck, C. & Bigg, E. K. Evolution of the marine aerosol—a new perspective. *Geophys. Res. Lett.* **32,** L19803 (2005).

35. Bigg, E. K. Sources, nature, and influence on climate of marine airborne particulates. *Environ. Chem.* **4,** 155–161 (2007).
This paper described an organic alternative to DMS as a source of CCN to the MBL.

36. Decho, A. W. Microbial exopolymer secretions in ocean environments: their role(s) in food webs and marine processes. *Oceanogr. Mar. Biol. Ann. Rev.* **28,** 73–153 (1990).

37. Bigg, E. K. & Leck, C. The composition of fragments of bubbles bursting at the ocean surface. *J. Geophys. Res.* **113,** D11209 (2008).

38. O'Dowd, C. D. *et al.* Biogenically-driven organic contribution to marine aerosol. *Nature* **431,** 676–680 (2004).

39. Keene, W. C. *et al.* Chemical and physical characteristics of nascent aerosols produced by bursting bubbles at a model air-sea interface. *J. Geophys. Res.* **112,** D21202 (2007).

40. Tyree, C. A., Hellion, V. M., Alexandrova, O. A. & Allen, J. O. Foam droplets generated from natural and artificial seawaters. *J. Geophys. Res.* **112,** D12204 (2007).

41. Hultin, K. A. H. *et al. In situ* laboratory sea spray production during the Marine Aerosol Production 2006 cruise on the northeastern Atlantic Ocean. *J. Geophys. Res.* **115,** D06201 (2010).

42. Fuentes, E., Coe, H., Green, D., de Leeuw, G. & McFiggans, G. On the impacts of phytoplankton-derived organic matter on the properties of marine aerosol—Part 1: Source fluxes. *Atmos. Chem. Phys.* **10,** 9295–9317 (2010).

43. Bigg, E. K., Leck, C. & Tranvik, L. Particulates of the surface microlayer of open water in the central Arctic Ocean in summer. *Mar. Chem.* **91,** 131–141 (2004).

44. Covert, D. S., Kapustin, V. N., Quinn, P. K. & Bates, T. S. New particle formation in the marine boundary layer. *J. Geophys. Res.* **97,** 20581–20589 (1992).

45. Warren, D. R. & Seinfeld, J. H. Prediction of aerosol concentration resulting from a burst of nucleation. *J. Colloid Interf. Sci.* **105,** 136–142 (1985).

46. Pirjola, L., O'Dowd, C. D., Brooks, I. M. & Kulmala, M. Can new particle formation occur in the clean marine boundary layer? *J. Geophys. Res.* **105** (D21), 26,531–26,546 (2000).

47. Clarke, A. D. *et al.* Particle production in the remote marine atmosphere: cloud outflow and subsidence during ACE-1. *J. Geophys. Res.* **103** (D13), 16,397–16,409 (1998).
This paper was one of the first to provide unambiguous evidence of an upper tropospheric source of sulphur particles to the marine boundary layer.

48. Ehn, M. *et al.* in *Nucleation and Atmospheric Aerosols: 17th International Conference (Galway, Ireland, 2007)* (eds O'Dowd, C. D. & Wagner, P. E.) 1,102–1, 105 (Springer, 2007).

49. Davison, B. *et al.* Dimethyl sulfide, methyl sulfonic acid, and physicochemical aerosol properties in Atlantic air from the United Kingdom to Halley Bay. *J. Geophys. Res.* **101,** 22,855–22,867 (1996).

50. O'Dowd, C. D. *et al.* Biogenic sulphur emissions and inferred non-sea-salt sulfate cloud condensation nuclei in and around Antarctica. *J. Geophys. Res.* **102,** 12839–12854 (1997).

51. Cainey, J. & Harvey, M. Dimethylsulfide, a limited contributor to new particle formation in the clean marine boundary layer. *Geophys. Res. Lett.* **29,** 1128, doi:10.1029/2001GL014439 (2002).

52. Hegg, D. A., Radke, L. F. & Hobbs, P. V. Particle production associated with marine clouds. *J. Geophys. Res.* **95,** 13,917–13,926 (1990).

53. Perry, K. D. & Hobbs, P. V. Further evidence for particle nucleation in clear air adjacent to marine cumulus clouds. *J. Geophys. Res.* **99,** 22,803–22,818 (1994).

54. Hoppel, W. A., Frick, G. M., Fitzgerald, J. & Larson, R. E. Marine boundary layer measurements of new particle formation and the effects nonprecipitating clouds have on aerosol size distributions. *J. Geophys. Res.* **99,** 14,443–14,459 (1994).

55. Clarke, A. D., Li, Z. & Litchy, M. Aerosol dynamics in the equatorial Pacific marine boundary layer: microphysics, diurnal cycles, and entrainment. *Geophys. Res. Lett.* **23,** 733–736 (1996).

56. Raes, F. Entrainment of free-tropospheric aerosol as a regulating mechanism for cloud condensation nuclei in the remote marine boundary layer. *J. Geophys. Res.* **100,** 2893–2903 (1995).

57. Pierce, J. R. & Adams, P. J. Global evaluation of CCN formation by direct emission of sea salt and growth of ultrafine sea salt. *J. Geophys. Res.* **111,** D06203 (2006).

58. Kazil, J., Lovejoy, E. R., Barth, M. C. & O'Brien, K. Aerosol nucleation over oceans and the role of galactic cosmic rays. *Atmos. Chem. Phys.* **6,** 4905–4924 (2006).

59. Spracklen, D. V. *et al.* Evaluation of a global aerosol microphysics model against size-resolved particle statistics in the marine atmosphere. *Atmos. Chem. Phys.* **7,** 2073–2090 (2007).

60. Merikanto, J., Spracklen, D. V., Mann, G. W., Pickering, S. J. & Carslaw, K. S. Impact of nucleation on global CCN. *Atmos. Chem. Phys.* **9,** 8601–8616 (2009).

61. Korhonen, H., Carslaw, K. S., Spracklen, D. V., Mann, G. W. & Woodhouse, M. T. Influence of oceanic dimethyl sulfide emissions on cloud condensation nuclei concentrations and seasonality over the remote Southern Hemisphere oceans: a global model study. *J. Geophys. Res.* **113,** D15204 (2008).

62. Woodhouse, M. T., Mann, G. W., Carslaw, K. S. & Boucher, O. New directions: the impact of oceanic iron fertilization on cloud condensation nuclei. *Atmos. Environ.* **42,** 5728–5730 (2008).

63. Roelofs, G. J. A GCM study of organic matter in marine aerosol and its potential contribution to cloud drop activation. *Atmos. Chem. Phys.* **8,** 709–719 (2008).

64. de Leeuw, G. *et al.* Production flux of sea spray aerosol. *Rev. Geophys.* **49,** 2010RG000349 (2011).

65. O'Dowd, C. D. *et al.* A combined organic-inorganic sea-spray source function. *Geophys. Res. Lett.* **35,** L01801 (2008).

66. Woodhouse, M. T. *et al.* Low sensitivity of cloud condensation nuclei to changes in the sea-air flux of dimethyl-sulphide. *Atmos. Chem. Phys.* **10,** 7545–7559 (2010).
This study modelled the sensitivity of CCN to changes in the sea-to-air flux of DMS and found it to be low, such that the role of DMS in climate regulation is very weak.

67. Carslaw, K. S. *et al.* A review of natural aerosol interactions and feedbacks within the Earth system. *Atmos. Chem. Phys.* **10,** 1701–1737 (2010).

68. Wood, R. Cancellation of aerosol indirect effects in marine stratocumulus through cloud thinning. *J. Atmos. Sci.* **64,** 2657–2669 (2007).

69. Stevens, B. & Feingold, G. Untangling aerosol effects on clouds and precipitation in a buffered system. *Nature* **461,** 607–613 (2009).

70. Small, J. D., Chuang, P. Y., Feingold, G. & Jiang, H. Can aerosol decrease cloud lifetime? *Geophys. Res. Lett.* **36,** L16806 (2009).

71. Zuidema, P., Xue, H. & Feingold, G. Shortwave radiative impacts from aerosol effects on marine shallow cumuli. *J. Atmos. Sci.* **65,** 1979–1990 (2008).

72. Toole, D. A. & Siegel, D. A. Light-driven cycling of dimethylsulfide (DMS) in the Sargasso Sea: closing the loop. *Geophys. Res. Lett.* **31,** L09308 (2004).

73. Vallina, S. M., Simo, R. & Manizza, M. Weak response of oceanic dimethylsulfide to upper mixing shoaling induced by global warming. *Proc. Natl Acad. Sci. USA* **104,** 16004–16009 (2007).
This studied modelled the sensitivity of DMS seawater concentrations to a 50% increase in CO$_2$ and found it to be too low to be a significant offset for global warming.

74. Gunson, J. R. *et al.* Climate sensitivity to ocean dimethyl sulphide emissions. *Geophys. Res. Lett.* **33,** L07701 (2006).

75. Latham, J. & Smith, M. H. Effect on global warming of wind-dependent aerosol generation at the ocean surface. *Nature* **347,** 372–373 (1990).

76. Korhonen, H. *et al.* Aerosol climate feedback due to decadal increases in Southern Hemisphere wind speeds. *Geophys. Res. Lett.* **37,** L02805, doi:10.1029.2009GL041320 (2010).

77. Yang, X.-Y., Huang, R. X. & Wang, D. X. Decadal changes of wind stress over the Southern Ocean associated with Antarctic ozone depletion. *J. Clim.* **20,** 3395–3410 (2007).

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