

# Biological Sulfur, Clouds and Climate

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Cloud condensation nuclei (CCN) are predominantly sulfate particles, and over the oceans the major source of sulfur for these particles appears to be dimethyl sulfide, a gas produced by marine biota. The reflection of sunlight by marine stratiform clouds is a major feature of the earth's radiation budget, and these clouds will reflect more sunlight if their liquid water is distributed among more CCN, thus forming more (and smaller) droplets. These facts form the basis of a proposal that marine biogenic sulfur may be an important factor in determining the earth's climate. Key implications of this proposal are (1) the possibility of a biota-climate feedback loop if the production of biogenic sulfur is sensitive to changes in climate, (2) the possibility that anthropogenic sulfur emissions may be altering the global climate through this cloud-mediated mechanism, and (3) the possibility that anthropogenic pollution could alter climate by perturbing the sulfur-producing marine organisms.

## I. Clouds and the Earth's Radiation Budget

The earth's climate is controlled by the amount of solar energy intercepted by the planet and the fraction of that energy which is absorbed. This energy is essentially all in the form of electromagnetic radiation at wavelengths between 0.2 and 4  $\mu\text{m}$  (near-ultraviolet, visible, and near-infrared). The flux density of solar energy (summed over all wavelengths) on a surface oriented perpendicular to the solar beam at the earth's orbit is about 1370  $\text{W m}^{-2}$ . This is called the solar-constant. Most earth surfaces are not perpendicular to the solar beam, so they receive less than this. Averaged over latitude and over both day and night, the solar energy received by the earth is one-quarter of the solar constant, or 343  $\text{W m}^{-2}$ . But 30% of this energy is reflected back to space, mostly by clouds, leaving 240  $\text{W m}^{-2}$  to be absorbed. The ratio of the reflected flux to the incident flux is called the albedo, so the earth's albedo is 0.3, or 30%. If the earth had no clouds, its albedo would be about 15%. [See SOLAR RADIATION.]

Averaged over a year, the earth is close to energy balance: it emits approximately 240  $\text{W m}^{-2}$  of thermal infrared radiation (wavelengths 4–100  $\mu\text{m}$ ) to space to balance the absorbed sunlight.

Clouds affect both the incoming sunlight (shortwave) and the outgoing thermal infrared (longwave) radiation. Liquid water and ice are quite transparent for visible (wavelengths 0.4–0.7  $\mu\text{m}$ ) and near-ultraviolet (0.2–0.4  $\mu\text{m}$ ) light, somewhat absorptive for near-infrared (0.7–4  $\mu\text{m}$ ), and highly absorptive in the thermal infrared. In the longwave region clouds absorb and emit radiation, but in the shortwave they mostly just scatter it. The scattering is due to reflection and refraction at the surfaces of cloud droplets and ice crystals causing the photons of light to change their directions. A photon may undergo thousands of interactions with cloud droplets, changing direction every time, before it eventually emerges from the bottom of the cloud (and is counted as transmitted light) or the top of the cloud (and is counted as reflected light). The thicker the cloud, the more likely it is that photons coming from the sun and entering the top of the cloud will be redirected upward before reaching the bottom of the cloud, so as the thickness of a cloud increases its

albedo increases and its transmittance decreases. A thicker cloud appears brighter than a thin cloud when viewed from above and darker when viewed from below. [See CLOUDS AND THEIR EFFECT ON CLIMATE.]

The other variables controlling cloud albedo are solar elevation angle and the average size of the cloud droplets. Cloud droplet sizes are important in controlling the albedo because photons change direction only when they encounter a boundary between air and water (or air and ice). The total surface area of droplets in a cloud depends on how the liquid water is distributed among droplets of different sizes. This is the principle which is the focus of this article. It is discussed further in Section III.A.

By reflecting sunlight, clouds tend to cool the planet. But this cooling is partially compensated by their absorption of longwave radiation. Because water and ice strongly absorb longwave radiation, most clouds except cirrus are thick enough to be nearly opaque to longwave radiation. Clouds therefore block the intense longwave radiation emitted by the warm underlying surface and emit less intense radiation to space from their tops, which are generally colder than the earth's surface.

In summary, the radiative effects of clouds are controlled by quite different variables in the two wavelength regimes. Shortwave albedo of clouds is controlled by cloud thickness, droplet sizes, and (less importantly) sun angle. Longwave emission, in contrast, is essentially controlled just by the cloud-top temperature.

The relative importance of the two competing effects of clouds depends on the circumstances. The shortwave cooling effect is dominant for clouds over the ocean (and over other dark surfaces), in daytime, in summer, and for low clouds. The longwave warming effect is dominant for clouds over snow (and over other bright surfaces), at night, in winter, and for high clouds. The global energy budget is particularly sensitive to changes in average cloud cover over the eastern portion of the earth's subtropical oceans, where, typically, the only cloud in the atmosphere is a layer of low stratocumulus. Because the cloud top is not much colder than the ocean surface, the cloud's shortwave cooling effect is not significantly offset by its longwave warming effect. Such clouds cover a significant fraction of the earth's surface and, because they are at low latitudes, intercept an even larger fraction of incoming solar energy.

Because the earth's albedo (average of clear and cloudy regions) is measured from satellite to be 30%, the average clear-sky planetary albedo is about 15%, and clouds cover about half the earth, the average cloud albedo must be about 45%. Because of the great variability in cloud thickness, individual clouds can have albedos anywhere from near zero to 90%. However, satellite observations show that most clouds have albedos in the range 25–65%.

## II. Cloud Droplet Formation and Cloud Condensation Nuclei (CCN)

The potential for water vapor to condense into cloud droplets exists whenever air reaches the saturation point, i.e., a relative humidity of 100%. (This normally happens because of the cooling of an air mass as it rises and expands.) However, the equilibrium vapor pressure over the curved surface of a droplet is greater than that over a flat surface, a fact which inhibits the formation of small droplets. Indeed, both experiments and theory have shown that isolated water molecules in the vapor phase will come together in sufficient number to form an incipient droplet only if the relative humidity is greater than about 300%, unless a preexisting nucleus particle is present which can collect liquid water around it. Suitable particles are always present in the atmosphere, so supersaturation (i.e., the amount by which relative humidity exceeds 100%) rarely goes beyond a fraction of a percent before droplets begin to form on these nuclei. To be effective as a cloud condensation nucleus, the particle (or at least some fraction of it) must be soluble in water. The equilibrium vapor pressure over a solution is lower than that over a pure water surface, so a soluble particle can collect water at humidities less than 100%. As the droplet grows, the solution is diluted but the surface curvature also decreases. The competition between these two influences means that for a given mass of soluble nucleus there is a critical value of ambient supersaturation below which the particle will exist in a stable hydrated state and above which it will enter into an unstable process of spontaneous growth leading to a cloud droplet. When the latter happens, the nucleus is said to be "activated" and is counted as a cloud condensation nucleus. The number of CCN is thus a function of supersaturation.

The CCN are a subset of atmospheric aerosol particles which vary in number from fewer than  $100 \text{ cm}^{-3}$  in remote oceanic areas to several hundred in rural land areas and a few thousand in polluted urban areas. A frequent observation in remote ocean areas is that the cloud droplet number concentration is about equal to the particle number concentration, suggesting that particle number is a limiting factor for cloud droplet number. (This subject is discussed further in Section VII.C.) Thus, the droplet number concentration in remote marine clouds is expected to be sensitive to changes in particle number.

## III. Effects of CCN Number on Cloud Albedo and Lifetime

The total mass of water that condenses in a cloud is essentially independent of the number of CCN (since there are

almost always at least a few dozen per cubic centimeter) and instead depends on the temperature and humidity of the air mass and its cooling rate. However, the CCN number, by controlling how this condensed water is distributed among the droplets, does influence both the cloud albedo and the cloud lifetime. [See CLOUD DYNAMICS.]

## A. Effect on Cloud Albedo

Consider two clouds with the same liquid water content but with different numbers of CCN. The cloud with fewer CCN will consist of a few large droplets; the other cloud will consist of many small droplets. The cloud of small droplets has more total droplet surface area. (If a large drop is broken into smaller ones, additional surfaces are created.) It is at these surfaces that light rays change direction by refraction, so the reflectance is greater for the small-droplet cloud than for the large-droplet cloud of the same liquid water content. This is illustrated in Fig. 1, which shows that a dish of small glass beads is more reflective than a dish of large glass beads, although the total amount of glass is the same in both dishes. The quantitative description is as follows.

Because the volume of a droplet is proportional to the cube of the radius and the surface area is proportional to the square of the radius, the total surface area of droplets in a cloud is inversely proportional to the droplet radius (actually, a surface area-weighted mean radius, or effective radius,  $r_{\text{eff}}$ ). Because of diffraction of light around droplets, the droplets actually scatter more light than that intercepted by their geometric cross sections by about a factor of 2. This factor is called the scattering efficiency,  $Q_{\text{sca}}$ , so the scattering cross section of a cloud droplet of radius  $r$  is  $\pi r^2 Q_{\text{sca}}$ . The total scattering cross-sectional area of all the droplets in a vertical column through the cloud, per unit area of the cloud base, is the optical thickness of the cloud,  $\tau^*$  (units square meters per square meter):

$$\begin{aligned} \tau^* &= (\pi r_{\text{eff}}^2 Q_{\text{sca}} \text{LWP}) / (\frac{4}{3} \pi r_{\text{eff}}^3 \rho_w) \\ &= (3 Q_{\text{sca}} \text{LWP}) / (4 r_{\text{eff}} \rho_w) \end{aligned} \quad (1)$$

(assuming no absorption), where LWP is the liquid water path (the vertically integrated liquid water content, grams per square meter) and  $\rho_w$  is the density of pure water ( $10^6 \text{ g m}^{-3}$ ).

The cloud albedo increases as the optical thickness increases. This will occur either when the cloud thickness (actually, the LWP) is increased or when  $r_{\text{eff}}$  is decreased. Figure 2 shows cloud albedo as a function of cloud thickness, calculated by S. Twomey, for three different number concentrations of CCN. The middle curve could represent a typical marine stratiform cloud, with  $140 \text{ CCN cm}^{-3}$  and a mean droplet radius of  $8 \mu\text{m}$ . The upper and lower curves result

from multiplying or dividing the number of CCN by a factor of 8, causing the mean radius to be halved or doubled. The figure shows that the sensitivity of cloud albedo to CCN number is about the same for all albedos in the range 0.25–0.75, which includes most clouds.

fractional change

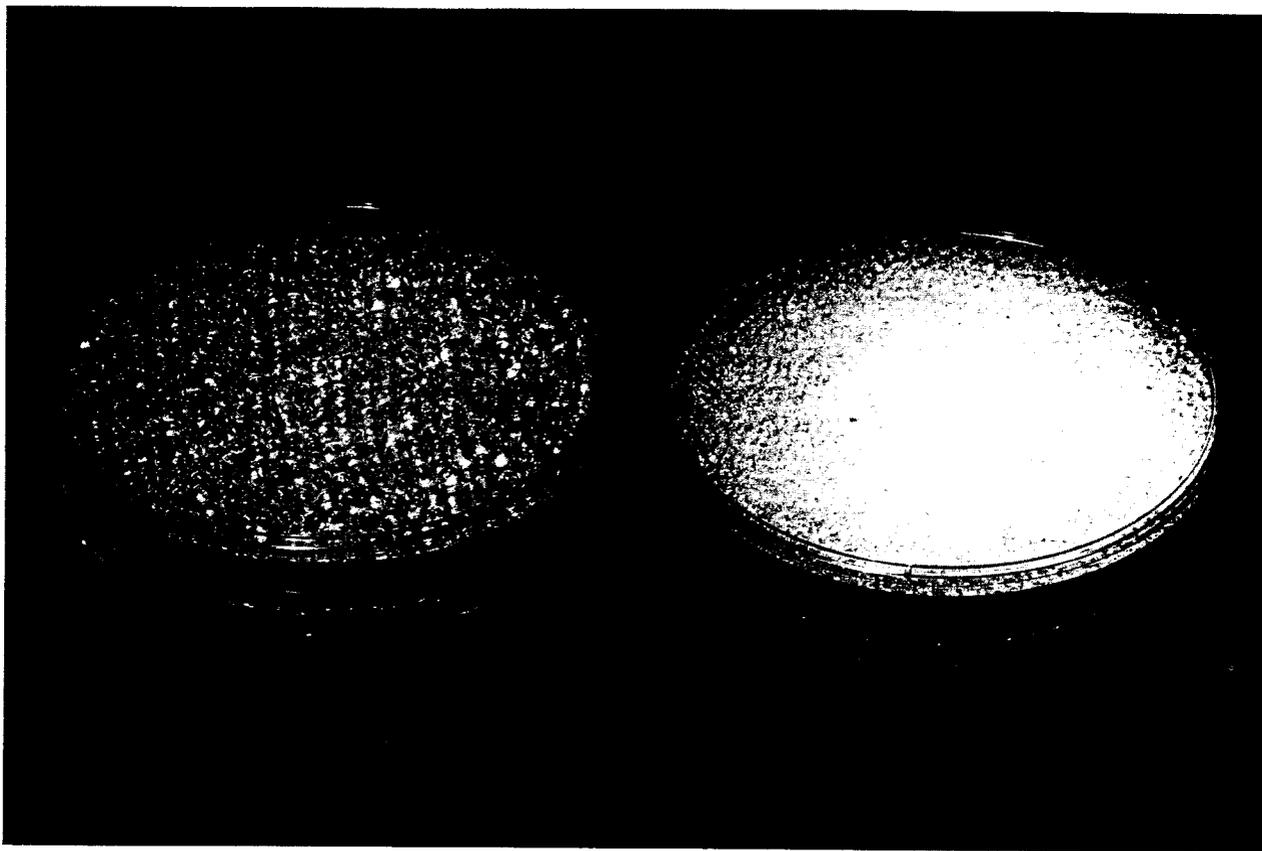
The infrared absorptance also will increase if CCN number increases, but for a different reason. Liquid water (and ice) absorbs infrared radiation so strongly that the interior of a droplet is somewhat hidden from such radiation if the droplet radius is larger than about  $10 \mu\text{m}$ . Thus, a cloud of smaller droplets, with more of its water mass exposed to radiation, is more absorptive in the infrared. However, the infrared absorptance is less sensitive than the solar albedo to changes in CCN because most clouds of liquid water are either already opaque in the thermal infrared or have tops that are not significantly colder than the underlying surface. (In the latter case, infrared absorptance by the cloud has no climatic effect.)

Evidence for the effect of CCN on cloud albedo has been seen in the relatively uniform stratocumulus clouds over the oceans. Particles in the engine exhaust of ships are active as CCN and appear to cause an increase in the number of cloud droplets (and a decrease in their mean radius). Because this results in increased cloud albedo, bright lines ("ship tracks") appear in satellite pictures of the cloud, revealing the route of the ship below the cloud. On a larger scale, part of a stratocumulus cloud deck west of California appeared brighter than the rest of the cloud system, as seen from a satellite. Its liquid water content was not different from that of the cloud system, but it had been polluted by passage over urban areas in southern California and thus contained more CCN.

## B. Effect on Cloud Lifetime

Cloud droplets are typically  $5\text{--}10 \mu\text{m}$  in radius. Their fall speeds are insignificant until they grow to  $50 \mu\text{m}$  or larger. In warm clouds (that is, in the absence of ice crystals) droplets can attain such sizes only by colliding and coalescing with other droplets. The time it takes for coalescence to result in drops large enough to fall is longer if the initial droplets are smaller. Thus an increase in CCN number could increase the lifetime of clouds, which would increase the fraction of the earth covered by cloud at any one time and thus further increase the earth's albedo. This idea is supported by the observation that the dissipation of marine stratocumulus clouds due to loss of water by drizzle is inhibited by increases in CCN number.

In addition, the system may be highly nonlinear. Because drizzle is responsible for removing CCN from the atmosphere, there may be a positive feedback which normally keeps CCN populations low ( $\sim 100 \text{ cm}^{-3}$ ) in drizzling ma-



**Fig. 1** Demonstration of the effect of droplet size on cloud albedo. Both dishes contain the same total mass of glass beads. The dish of small beads is more reflective because the total area of glass-air interfaces is greater than in the dish of large beads.

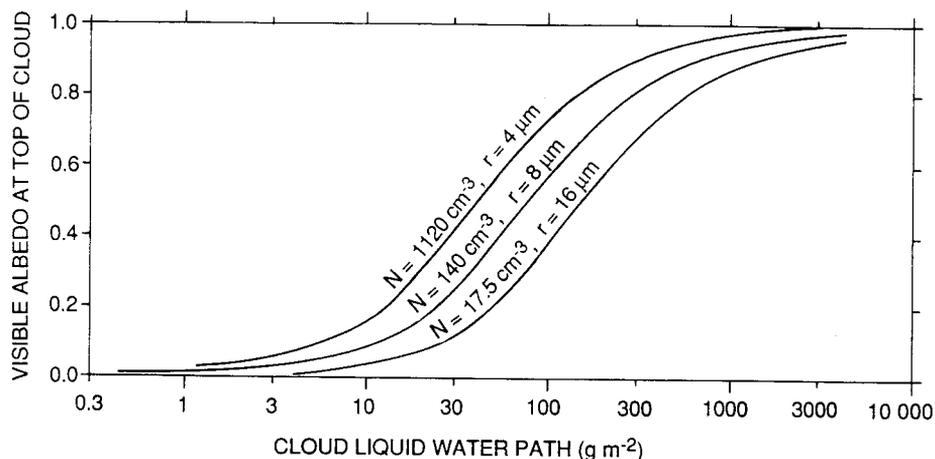
rine-cloud regimes, but the input of more CCN could potentially switch the system to a new stable state with nondrizzling clouds and high CCN populations ( $\sim 1000 \text{ cm}^{-3}$ ).

#### IV. How Sulfate Particle Number Determines CCN Number

Chemically, the marine aerosol has two dominant components: sea salt and non-sea salt (nss) sulfate. (The latter is so designated to distinguish it from the sulfate component of sea salt particles.) Sea salt particles are produced by bursting of bubbles at the ocean surface, which in turn is caused by wind blowing over the ocean, whereas nss sulfate particles are produced by chemical reactions and physical processes in the atmosphere. These different production mechanisms normally yield particles of different sizes. A typical volume distribution (that is, a plot of the amount of particulate volume

contained within each increment of particle size) for the marine aerosol (Fig. 3a) shows that the two aerosol components constitute two distinct modes of roughly equal magnitude. The larger, or coarse, mode consists primarily of sea salt, and the smaller mode consists primarily of nss sulfate. [See SEA SALT AEROSOLS.]

The number distribution (Fig. 3b) is very different from the volume distribution. Here the coarse particles make an insignificant contribution and the smaller particles, often referred to collectively as fine particles, can themselves be resolved into two modes, the accumulation and nuclei modes. The nuclei mode (not to be confused with cloud condensation nuclei) may or may not be present and is depicted in Fig. 3b with a dashed curve. This mode is an indicator of new particle formation. Given sufficient time, these new particles will grow by particle-particle coagulation and by deposition of low-volatility vapors such as sulfuric acid. Because there is a very low probability of growing beyond about  $0.5\text{-}\mu\text{m}$  diameter by these processes before being removed from the atmo-



**Fig. 2** Albedo at top of cloud as a function of liquid water path for three different number densities ( $N$ ) of CCN corresponding to three different average droplet radii ( $r$ ). The calculation is for visible wavelengths at which the cloud is nonabsorbing and for an overhead sun (elevation angle  $90^\circ$ ). For a typical maritime cloud liquid water content of  $0.3 \text{ g m}^{-3}$ , a cloud of thickness 1 km has  $\text{LWP} = 300 \text{ g m}^{-2}$ . [Modified from Fig. 12.6 of Twomey (1977).]

sphere by precipitation, the fine particles tend to accumulate over time in the size range from about  $0.05$  to  $0.5 \mu\text{m}$  (hence the term accumulation mode.)

Which of these particles act as CCN? The ability of a particle to nucleate a cloud droplet is enhanced if the particle is hydrophilic and soluble; however, both sea salt and nss sulfate possess these properties. In addition, the particle must be larger than a critical size which is determined by the level of supersaturation attained within the cloud (discussed in Section VII,C). For marine stratiform clouds, supersaturations are thought to be in the range  $0.1$ – $0.5\%$ , which corresponds to a minimum particle diameter of  $0.05$ – $0.14 \mu\text{m}$ . These thresholds are shown as vertical lines in Fig. 3b. We see in this figure that CCN in marine stratiform clouds consist of all the coarse mode particles, most of the accumulation mode particles, and essentially none of the nuclei mode particles (if present). If this depiction is accurate, it is clear that the number concentration of CCN must be controlled by the accumulation mode nss sulfates.

Two types of evidence directly support the contention that sea salt particles cannot be the numerically dominant CCN and indirectly support the idea that nss sulfates play this dominant role. First, typical sea salt number concentrations at cloud altitudes rarely exceed  $1 \text{ cm}^{-3}$ , whereas marine stratiform cloud droplet number concentrations are typically  $100 \text{ cm}^{-3}$  or more. Second, cloud chamber studies have shown that the ability of air to cause the formation of cloud droplets at modest supersaturations is all but lost if the air is first subjected to a temperature of about  $300^\circ\text{C}$  and then cooled in such a way that any volatilized material will deposit

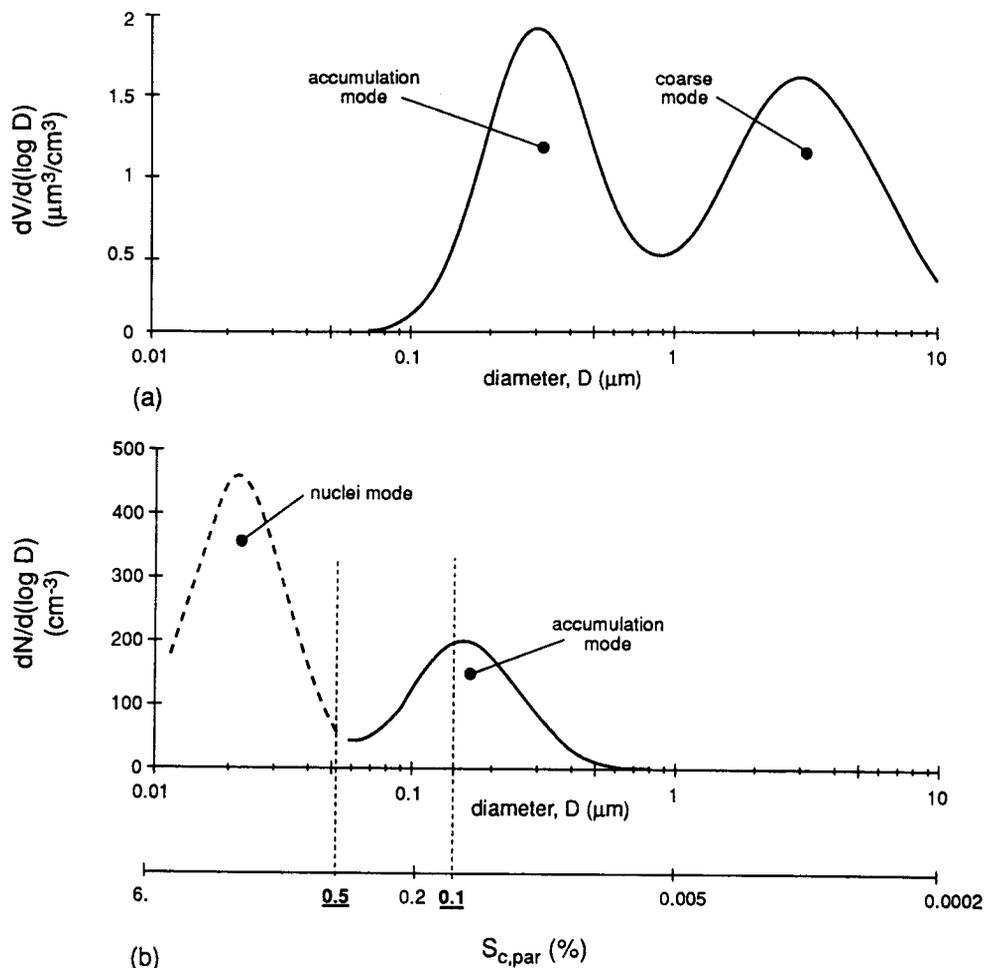
on the chamber walls. A temperature of  $300^\circ\text{C}$  is sufficient to volatilize sulfates but has no effect on sea salt particles.

## V. Dimethyl Sulfide (DMS) as a Source of Sulfate Particles over the Ocean

Where does the CCN sulfate come from? Abundant evidence suggests that in the remote marine environment it results from the oxidation of reduced-sulfur gases which are released from the ocean surface.

In 1972 J. E. Lovelock and co-workers found dimethyl sulfide gas,  $(\text{CH}_3)_2\text{S}$ , in the ocean and proposed that it, rather than hydrogen sulfide ( $\text{H}_2\text{S}$ ), constitutes the major natural flux of sulfur from the ocean to the atmosphere. In the past decade, additional reduced-sulfur gases have been found in the ocean, including methyl mercaptan ( $\text{CH}_3\text{SH}$ ), dimethyl disulfide [ $(\text{CH}_3)_2\text{S}_2$ , abbreviated DMDS], and carbon disulfide ( $\text{CS}_2$ ). In addition, an oxidized species, carbonyl sulfide (OCS), is formed photochemically in the upper ocean from reduced-sulfur compounds. However, it is thought that  $80$ – $90\%$  of the total reduced-sulfur flux from the sea is in the form of DMS.

The average sea surface concentration of DMS is about  $3 \text{ nM}$  (nanomolar or  $10^{-9} \text{ mol/liter}$ ), dropping off with depth to a nearly undetectable concentration of less than  $0.1 \text{ nM}$  below the photic zone, the sunlit upper layer (approximately  $100 \text{ m}$ ) in which photosynthesis occurs. The average concentration of DMS in the atmospheric boundary layer is a factor



**Fig. 3** Typical marine aerosol size distribution. Both (a) and (b) are based on three overlapping, log normally distributed particle populations with volume mean diameters  $D$  (micrometers) of 3.0, 0.3, and 0.03; geometric standard deviations of 2.0, 1.6, and 1.5; and total numbers (per cubic centimeter) of 0.4, 100, and 200 for the coarse, accumulation, and nuclei modes, respectively. The data are displayed so that the area under each curve is proportional to total particle volume (a) or number (b). Also shown at the bottom of (b) is the critical supersaturation corresponding to each particle size (assuming a composition of pure ammonium sulfate.) The vertical lines show the range of typical maximum supersaturations for marine stratiform clouds.

of 1000 smaller, about  $100 \text{ ng m}^{-3}$ . Studies of the Henry's law constant for DMS show that the gas is considerably supersaturated in the ocean surface; that is, its concentration in seawater is not in equilibrium with that in the air, and the net direction of the flux is from the ocean to the atmosphere. From air-sea exchange models (see Section VII,A), an average global flux of about  $2.2 \text{ mmol m}^{-2} \text{ yr}^{-1}$  has been calculated, implying a global oceanic sulfur flux of  $15\text{--}30 \text{ Tg}$  ( $10^{12} \text{ g}$ ) per year, roughly one-third of the estimated flux of sulfur from all natural sources. Despite the factor of 2 uncertainty, this is one of the best studied and quantified trace gas fluxes.

These reduced-sulfur gases all show evidence of biological origin. First, their seawater concentrations are highest at the surface or in the upper photic zone and decrease very quickly with depth. Such distributions are common for other biological compounds such as chlorophyll *a*, a photosynthetic pigment which is produced by phytoplankton, microscopic single-celled plants (algae) ubiquitous in the ocean's photic zone. Second, spatial distributions of DMS in seawater correlate roughly with distributions of algae and proxies for algae such as primary productivity ( $\text{CO}_2$  fixation) and chlorophyll concentration. Third, in laboratory studies DMS has been found in phytoplankton cultures. Finally, there are no proposed

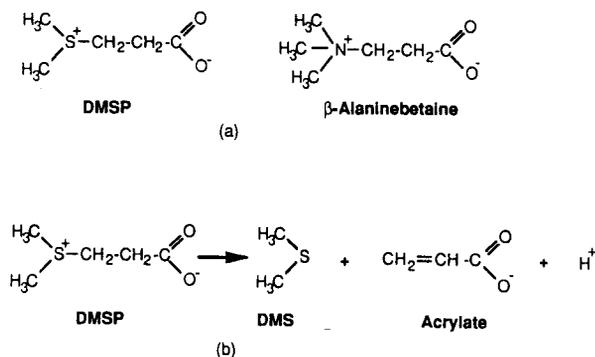
geochemical (abiotic) sources of DMS in the oceans, although there may be abiotic sinks (see below).

DMS has now been sampled in all the major oceans of the world, and in some geographic regions its seasonal variation is known (although, like most trace gas species, it has been studied much more intensively in the northern hemisphere and in the summer months). Surveys of DMS concentrations have consistently found that it is most prevalent in coastal waters, in summer, or during phytoplankton blooms (population explosions) and that its seasonality increases with latitude. These features are all consistent with biological activity, particularly photosynthesis. Furthermore, the correlations suggest that DMS is associated with particular species of phytoplankton or with particular biochemical processes. Despite this, DMS concentrations are surprisingly constant over most of the ocean, varying by perhaps a factor of 2 except for limited areas of intense seasonal production.

## VI. Biological Production of DMS and Other Sulfur Gases

Biological cycling of sulfur has, as far as we know, always been extremely active. There are two major pathways for the production of reduced-sulfur gases by organisms, both involving the reduction of sulfate ( $\text{SO}_4^{2-}$ ), the inorganic form of sulfur in the +6 oxidation state. One pathway, called dissimilatory sulfate reduction, is utilized by specialized sulfur bacteria which are found in anaerobic environments and use the sulfate ion as a terminal electron acceptor in place of oxygen (i.e., use sulfur respiration). They reduce sulfate to  $\text{H}_2\text{S}$  and use the energy from the reaction to build organic molecules. Because these organisms are killed by even trace levels of oxygen, they are found only in anoxic environments such as sediments, and most of the  $\text{H}_2\text{S}$  gas they liberate is quickly oxidized back to sulfate ion, which remains in the aqueous phase. Therefore, although the total global production of  $\text{H}_2\text{S}$  probably far exceeds the production of DMS, it contributes negligibly to the atmospheric flux of sulfur. However, it is interesting to speculate that in earlier geologic times, when the atmosphere was anaerobic, sulfur respiration might have been the major source of sulfur to the atmosphere.

The other major pathway begins with assimilatory sulfate reduction. In this process, found in all plants and most bacteria, inorganic sulfate is taken up by organisms, reduced to the -2 oxidation state, and then incorporated into biomolecules. Such molecules include the protein amino acids cysteine (important in maintaining protein structural integrity) and methionine, as well as many nonprotein amino acids. Other biomolecules utilize sulfur in intermediate oxidation states, as sulfoniums, sulfoxides, sulfones, sulfate esters, and sulfonic acids.



**Fig. 4** Dimethyl sulfoniopropionate (DMS) is similar to  $\beta$ -alaninebetaine, a common osmolyte. (b) Enzymatic cleavage of DMS results in DMS gas and acrylate.

During decay of sulfur-containing organic material, these compounds are degraded, resulting in the emission of reduced-sulfur gases. This process is sometimes referred to as desulfuration. Organic compounds containing reduced sulfur become food substrates for groups of microorganisms, particularly bacteria, which have enzymes for degrading them. In this process, the reduced-sulfur groups are split off from their parent compounds and easily volatilized. Therefore, the production of reduced-sulfur gases occurs wherever there is decay. Indeed, DMS and the other sulfur gases have been detected in nearly all biological environments: soils, sediments, marshes, and freshwater lakes and rivers, as well as marine waters.

In many of these environments, DMS is not the major reduced-sulfur gas emitted because its production depends on which organic sulfur compounds are available for degradation. Biota in the ocean produce predominantly DMS because of one sulfur compound which is present in extremely high concentrations in some macroalgae (seaweeds) and phytoplankton: dimethyl sulfoniopropionate (DMSP).

DMSP is a sulfur analog of another compound,  $\beta$ -alaninebetaine, which has a nitrogen atom in place of the sulfur (Fig. 4a). It has been convincingly demonstrated that in macroalgae these two compounds act as osmolytes, chemical species used to maintain internal cellular osmotic pressure as the environment's salinity changes. Such a feature is necessary in seaweeds, which inhabit the tidal zone and are exposed to large daily fluctuations in salinity. It appears that in the ocean, where sulfur is abundant but nitrogen is often very rare, some algae preferentially make DMSP instead of betaines. Since phytoplankton drift with the currents and are generally exposed to more constant salinity, it is questionable whether they utilize these compounds for the same purpose. Nevertheless, some groups of phytoplankton—most notably the coccolithophorids and dinoflagellates—contain extraordinary

amounts of DMSP; most of the total sulfur in these cells may be contained in this one compound.

DMSP is cleaved to form DMS and acrylic acid (Fig. 4b). At very high pH values DMSP is chemically unstable and breaks down abiotically; this is the basis for its analytical detection. However, at an ocean pH of 8.2 it is chemically stable (lifetime  $\sim 10$  years) and requires an enzyme to convert it to DMS. Many macroalgae produce this enzyme, but it has been detected in only one species of phytoplankton so far, and studies of cultures show that the production of DMS is sometimes associated with death of cells rather than with their growth. DMSP has also been found in both particulate and dissolved forms (DMSP-P and DMSP-D); the particulate form is associated with DMSP inside phytoplankton cells, and the dissolved form is thought to originate from phytoplankton cells which are broken open when the cells die or are consumed by predators. Once in the water, DMSP may be broken down by bacteria. Because bacteria from other DMS-producing environments can break down DMSP to form DMS, it is likely that oceanic bacteria also exist that can utilize this compound and liberate DMS. Furthermore, when zooplankton graze DMSP-containing phytoplankton, an increase of DMS is observed. Therefore, the production of DMS is likely to depend on the populations of phytoplankton, bacteria, and zooplankton and their complex interactions.

The flux of DMS to the atmosphere depends on its oceanic concentration, which in turn depends on both its sources and its sinks. There have been several proposed abiotic sinks for DMS in the water column: photooxidation to dimethyl sulfide (DMSO), adsorption onto clays, and reactions with metals. Of these, only photooxidation is thought to be important. However, some bacteria can utilize DMS as a carbon source, and it is possible that bacteria are the most important sink in the water column, although study of this possibility has only just begun. Figure 5 summarizes the known and hypothesized sources and sinks of DMS in the photic zone of the ocean.

## VII. Sensitivity of Climate to DMS Emissions

How sensitive is the earth's climate to a change in the flux of marine biogenic sulfur? To address this, we consider the paradigm of Fig. 6, a slightly modified version of the biota-climate feedback loop formulated by R. J. Charlson and co-workers in 1987. This figure shows a sequence of processes which connect the flux of sulfur gases from the ocean surface to climate via the modification of planetary albedo. We will consider in turn each process and its relative importance in the overall loop: the transport of gases from the sea to air; the conversion of these gases to particles, which can nucleate cloud droplets; the change in cloud droplet number,

which can affect cloud albedo and cloud lifetime; and the resulting changes in solar radiation, surface temperature, and other climate variables. The loop is closed by the assumption that the biological production of DMS is affected by climate-driven changes in the physical and chemical ocean environment. This final link is discussed in Section VIII.

### A. Transport of Gases from Sea to Air

In standard air-sea exchange models the sea-to-air flux of a dissolved gas is described by

$$F = k(C_w - C_a) \quad (2)$$

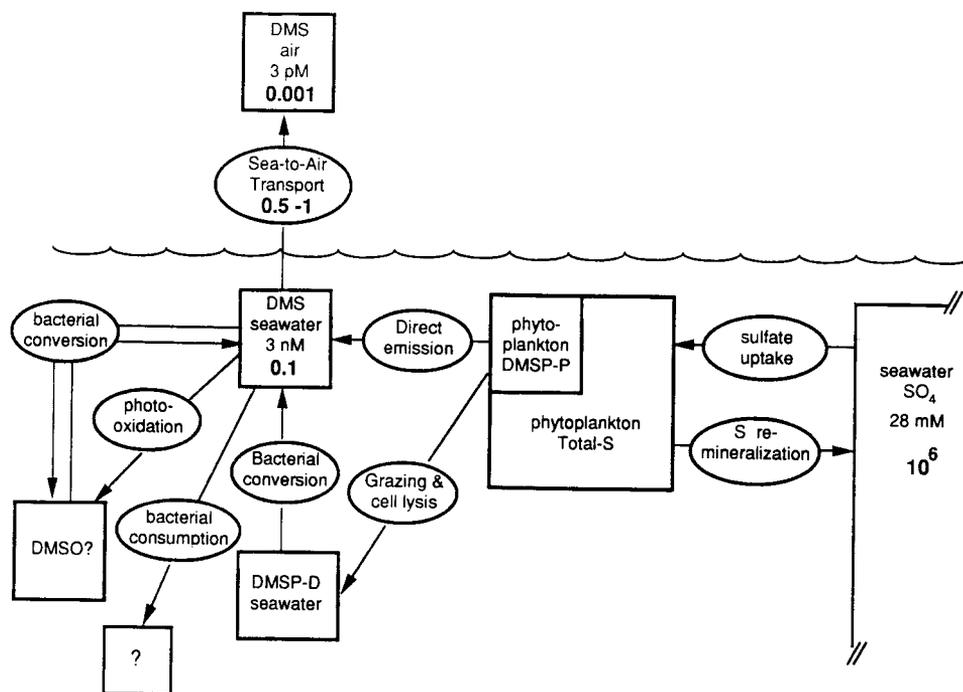
where  $F$  is the flux in units of (mass)(area) $^{-1}$ (time) $^{-1}$  (e.g., mg m $^{-2}$  s $^{-1}$ ) and  $(C_w - C_a)$  is the difference between the gas concentrations in bulk seawater and the atmosphere in units of (mass)(volume) $^{-1}$  (e.g., mg m $^{-3}$ ). For highly supersaturated gases such as DMS, where  $C_w \gg C_a$ , we ignore  $C_a$ . The proportionality constant  $k$  has units of (distance)(time) $^{-1}$  and may be interpreted as a transfer velocity;  $k$  depends on several physical parameters, including the diffusivity of the gas species in question as well as temperature and wind speed. The dependence of  $k$  on these factors has been studied empirically in wind tunnels and also by observations of radioactive tracers. [See AIR-SEA INTERACTION.]

These studies indicate that the flux of a dissolved gas depends principally on its concentration in seawater and on wind speed. The seawater concentration of DMS depends on the sources and sinks in the water column, as discussed in Section VI. However, there remains a large uncertainty as to whether the flux is controlled mostly by the variation in seawater or by the variation of wind speed.

Although they are the basis for calculating sea-to-air fluxes of trace gases such as DMS, the air-sea exchange models have one potentially major problem. In the ocean, the limiting resistance to outgassing is diffusion through the sea surface microlayer, a thin "skin," typically 10–400  $\mu$ m thick. The chemical properties of this layer, which often contains large amounts of organic lipids and oils, may differ greatly from those of bulk seawater but are extremely difficult to measure. It is also probable that the microlayer concentration of the gas species itself differs considerably from that of the bulk "surface" seawater, although flux calculations are of necessity based on the latter quantity.

### B. Gas-to-Particle Conversion

Because the dominant pathway for DMS through the atmosphere involves oxidation to sulfate [minor oxidation products include methane sulfonic acid (MSA) and DMSO], any increase in the flux of DMS from the ocean surface can be expected to cause a proportional increase in the mass of atmospheric nss sulfate. Because nss sulfate, as pointed out in Section IV, is the main constituent of the accumulation mode



**Fig. 5** Box model of DMS production in marine photic zone. DMSP is dimethyl sulfoniopropionate; DMSP-D refers to the dissolved and DMSP-P to the particulate reservoir, respectively. DMSO is dimethyl sulfoxide. Bold numbers are global estimates of sulfur burdens and fluxes assuming a global oceanic area of  $3.6 \times 10^{14} \text{m}^2$  and average photic zone depth of 100 m. Units are teramoles ( $10^{12}$  moles) or teramoles per year.

particles, which control the number population of CCN, it is plausible, but by no means certain, that an increase in the mass of nss sulfate would cause a more or less proportional increase in the number of CCN. This could come about in either of two ways.

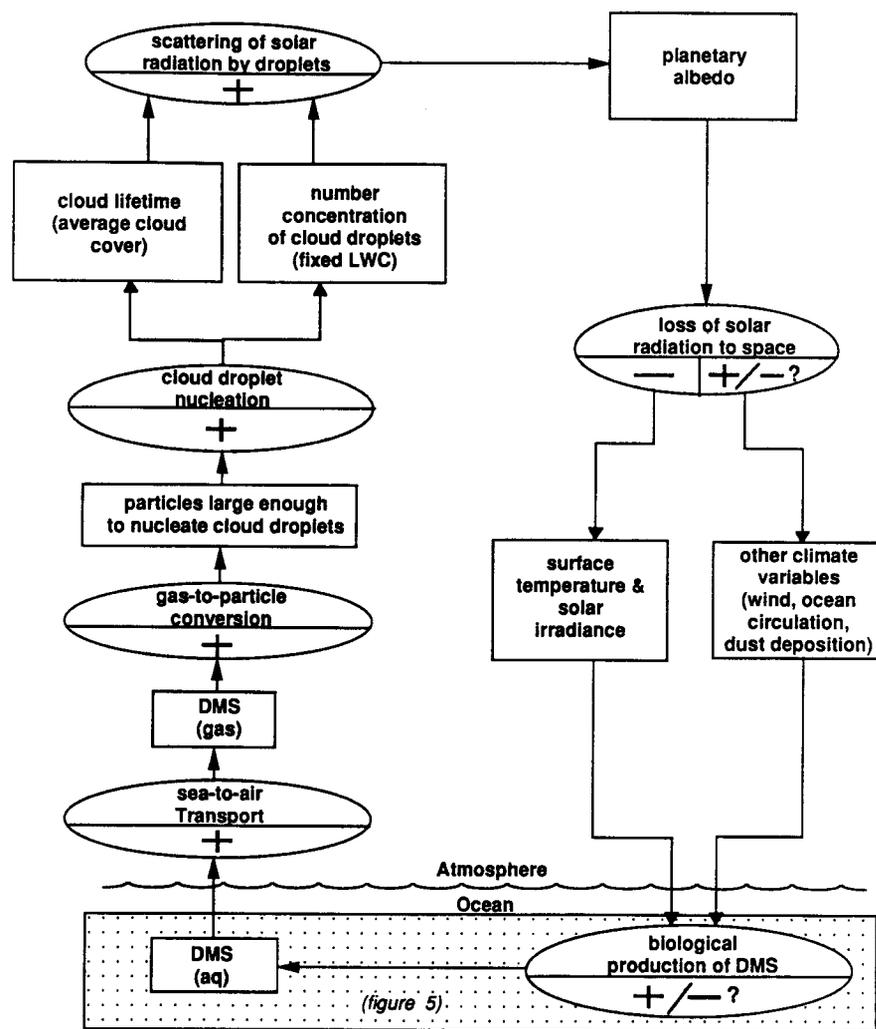
First, assume that the particle formation and growth processes are independent of the mass flux of DMS. Then an increased DMS flux would cause no change in the distribution of particle sizes (Fig. 3) but would simply increase, by an amount proportional to the mass increase, the number of particles in all size categories, including those large enough to nucleate cloud droplets. Unfortunately, the new particle formation rate (i.e., the rate at which nuclei mode particles are created) is very poorly understood and may be less dependent on the concentration of condensable sulfate than on the concentration of other required species such as water vapor and/or gas-phase ions.

A second scenario assumes no change in the new particle formation rate but notes the presence, in many cases, of a significant number of particles too small to act as CCN—the “nuclei” mode of Fig. 3b and possibly part of the accumulation mode. Even if all the additional nss sulfate were to condense onto existing particles, the effect would be to produce an increase in the number of CCN because many of

the smaller particles would grow past the threshold size required for cloud droplet nucleation. Whether the CCN number increase would be more or less than proportional to the particle mass increase would be a sensitive function of both the shape of the particle size distribution and the exact size requirement.

These two scenarios implicitly assume that the oxidation of reduced-sulfur gases to sulfate takes place in the gas phase. Only in this way is the increased mass of nss sulfate available as a gas to condense onto new or existing particles. Another possibility is that most of the oxidation to sulfate takes place in the aqueous phase, within cloud drops. Because most stratus cloud droplets reevaporate (i.e., do not precipitate), thereby returning their solute to the particulate phase, the net result of this scenario would still be an increase in particulate mass. However, the additional mass would have gone mostly to existing CCN, leaving the number of CCN largely unchanged.

It is hard to choose among these scenarios. Both the sulfur oxidation and new particle formation processes are poorly understood in the marine environment. Shipboard studies that have looked for increases in particle number corresponding to increases in DMS levels have been unable to observe such a correspondence consistently. (However, this



**Fig. 6** Conceptual diagram of the DMS-climate feedback loop. The rectangles show measurable quantities, and the ovals show processes linking the rectangles. The sign (+ or -) in an oval indicates the effect of a positive change of the quantity in the preceding rectangle on that in the succeeding rectangle. The shaded ocean box is detailed in Fig. 5. [Adapted from Charlson *et al.* (1987).]

measurement is difficult and it is questionable whether it has yet been done properly.) In short, the current range of uncertainty spans the extreme possibilities that a given increase in the *mass* of nss sulfate will cause a proportional or a trivial increase in the *number* of CCN. Further tests of the relationship between nss sulfate mass and CCN number are therefore critical for assessing the sensitivity of the link between biogenic sulfur and climate.

### C. Droplet Nucleation

When a parcel of air rises in the atmosphere it expands and cools and thereby increases in relative humidity (RH). For a

sufficient rise, the parcel will become supersaturated and a cloud will form. A supersaturated parcel of air is in an unstable state, yet because of the limited number of condensation sites, this state can be maintained over a finite period of time. Eventually, the growth of cloud droplets will draw down the excess water vapor, limiting the supersaturation to some maximum level,  $S_{m,cloud}$ , characteristic of that particular cloud. For marine stratiform clouds, typical values are thought to range from 0.1 to 0.5% (shown as vertical lines in Fig. 3b.)

Each particle within an air parcel is a potential cloud droplet nucleation site and can be classified according to the critical value of supersaturation,  $S_{c,par}$ , required to activate

it—that is, to launch it onto the path of unstable growth leading to a cloud droplet. (These values are shown as the lower coordinate in Fig. 3b.) For a given particle composition,  $S_{c,par}$  is strictly a function of particle size; larger particles have a smaller  $S_{c,par}$  and therefore grow into cloud droplets even if  $S_{m,cloud}$  is relatively small. Following this logic, within a given cloud all particles above some critical size (such that  $S_{c,par}$  is less than  $S_{m,cloud}$ ) will be activated and all particles below that size will not.

Since supersaturations in stratiform clouds are not thought to exceed 0.5%, we see from Fig. 3b that only the accumulation mode particles are important for determining the number of potential CCN. Assuming, for simplicity, that the particle size distribution and the cloud dynamics do not change, let us consider the effect of changing the number of accumulation mode particles. At low number concentrations, we would expect particle number to limit, and therefore control, cloud droplet number. As particle number increases, the larger number of condensation sites will allow the excess water vapor to be drawn down more quickly, thereby decreasing  $S_{m,cloud}$ . When particle number is large enough (or, equivalently,  $S_{m,cloud}$  is small enough) that some of the accumulation mode particles are not activated, further increases in particle number will cause a further reduction in the fraction of activated particles and thus a less than proportional increase in cloud droplet number.

In the remote marine environment, a common observation is that the number of stratiform cloud droplets essentially equals the number of accumulation mode particles. This is strong evidence that particle number limits and controls cloud droplet number. At least for modest changes in particle number, the corresponding change in cloud droplet number should be proportional.

The effect of more drastic changes in particle number can be investigated by comparing the remote marine environment, where the number of accumulation mode particles per cubic centimeter is roughly 100, to both the nonpolluted continental environment, with roughly 500, and the polluted continental environment, with roughly 2000. In the latter two environments, stratiform clouds are observed to have much higher droplet number concentrations, as well as decreased droplet sizes; however, the fraction of accumulation mode particles which are activated is considerably less than one, although still significant (i.e., usually greater than one-tenth). This implies that although particle number does not limit cloud droplet number in continental environments, as it does over the remote oceans, it is still a significant factor. Twomey has argued on theoretical grounds (combined with a knowledge of the aerosol size distribution) that cloud droplet number varies as the 0.8 power of accumulation mode particle number. If all particles are activated at a particle number of  $10\text{ cm}^{-3}$ , Twomey's theory predicts that about one-half of the accumulation mode would be activated at a particle number of 500 and about one-third at a particle

number of 2000. These figures are in reasonable agreement with observations. Thus, it appears that the number concentration of droplets in marine stratiform clouds is a sensitive function of the number concentration of accumulation mode particles for either modest or drastic perturbations of particle number.

#### D. Change in Cloud Albedo and Cloud Cover

The increase in cloud albedo due to an increase in the number of cloud droplets is readily quantified. As an example, let us arbitrarily increase the number of cloud droplets over the ocean by 30% without changing the cloud liquid water content, implying a 10% decrease in average cloud droplet radius. Clouds whose albedos are in the range 0.25–0.75 will experience an increase of 0.02 in albedo at visible wavelengths. This effect is muted by going from the top of the cloud to the top of the atmosphere (a factor of 0.9) and by including all wavelengths of the solar spectrum (another factor of 0.9), so the change in shortwave albedo at the top of the atmosphere (over these clouds) is +0.016.

Oceanic stratiform water clouds with albedos between 0.25 and 0.75 cover about 45% of the ocean or 31% of the earth. (This is a conservative estimate because we have excluded nimbostratus, cumulus, and cumulonimbus on the ground that their albedos may sometimes be greater than 0.75.) The change in shortwave albedo averaged over the earth's surface area is thus 31% of +0.016, or +0.005.

We have not considered the increase of cloud lifetime which is also likely to occur as a result of increasing CCN number because that has not yet been quantified, so this is a minimum estimate of the effect on the earth's radiation budget.

#### E. Effects on Surface Temperature and Solar Radiation

The climatic consequences of this hypothetical increase in planetary albedo can be estimated by analogy with the consequences of changing the solar constant in a global climate model. An increase of planetary albedo by 0.005 is equivalent to a decrease of the solar constant by 0.7%, if the cloud albedo is assumed to be immune to climatic feedbacks. Climate models indicate that such a decrease in solar constant would result in a decrease of  $1.3^\circ\text{C}$  in global mean surface air temperature,  $T_s$ . This is about one-third as large as the increase of  $T_s$  predicted for doubling of atmospheric  $\text{CO}_2$ . The analogy also holds for changes in the opposite direction: the effect on  $T_s$  of halving CCN number is similar to the effect of doubling  $\text{CO}_2$ , and the effect of reducing CCN number by a factor of 8 is similar to the effect of multiplying  $\text{CO}_2$  by a

factor of 8. Whether this relationship is valid for even larger changes has not been investigated.

Clouds are only weakly absorptive for solar radiation, so if cloud albedo increases then cloud transmittance decreases by about the same amount. Thus in the example we pursued above, increasing CCN number by 30% over the oceans, the solar radiation at the earth's surface would decrease by about 0.7%.

### VIII. Sensitivity of DMS Emissions to Climate

We have described how the flux of DMS from the oceans might influence climate. But because DMS production is a biological process it is necessarily affected by climate, since organisms do not live independently of their environment. This linkage forms a feedback loop whose overall sign might be negative (a thermostat) or positive (an amplifier), depending on the effect of a change in planetary albedo on the DMS flux from the ocean surface.

How might planetary albedo influence DMS production? The most obvious effects are changes in sunlight and temperature. However, climatic shifts, resulting from a change in planetary albedo, could also affect the chemical composition of the phytoplankton's environment via such mechanisms as changes in ocean circulation and upwelling or increased deposits of windblown dust from continents. We will consider three classes of compounds which might affect DMS production: salts, major nutrients (phosphate and nitrate), and trace nutrients such as iron.

Because most marine DMS appears to be derived from DMSP, a known osmolyte in macroalgae and a putative osmolyte in phytoplankton, it is likely that changes in salinity would change the amount of DMSP available for conversion to DMS. Global changes of salinity are unlikely because of the enormous pool of sea salt, but the salinity of brine pockets in sea ice is highly variable, ranging from 4 to 23%, and is determined solely by the ice temperature. The phytoplankton species associated with most DMS production in polar oceans, *Phaeocystis pouchetii*, probably spends the winter in these brine pockets, a fact which would be consistent with a large production of DMSP. A climatic shift to lower temperatures could increase brine pocket salinity as well as the areal extent of sea ice and might therefore lead to more DMS production in the polar oceans.

Widespread changes in phytoplankton nutrients, particularly nitrate and phosphate, might result from climatic changes because these compounds are minor and variable constituents of seawater. Increased upwelling of nutrients would probably increase oceanic productivity, at least regionally. Changes in micronutrients such as iron are also

possible, and the necessary amounts are even smaller. During the most recent ice age, deposition of windblown dust on the polar ice caps increased greatly (based on ice core analysis), suggesting strong global winds and implying more trace metal deposition to the oceans. The ice core records also show increased deposition of MSA and nss sulfate on the antarctic ice sheet at that time, suggesting a greater DMS flux from the oceans. (Although nss sulfate can also come from volcanoes, MSA can result only from oxidation of DMS.) This larger flux could be due to greater production of DMS, increased sea-air exchange driven by amplified surface windiness, or both.

Finally, because DMS production seems to be linked with much of the oceanic food web—the intricate and poorly understood group of microorganisms which distribute photosynthetically fixed carbon throughout the marine ecosystem—changes in the composition of this food web might have major effects on the sea-to-air flux of DMS. For example, a climate-driven change in the relative populations of high- and low-DMSP-containing phytoplankton could alter significantly the amount of DMS produced in the water column. In addition, if zooplankton grazing and bacterial consumption are important in the production and destruction of DMS, as is currently believed, the sea-to-air flux of DMS could also be sensitive to changes in the populations of these organisms.

Regardless of the complexities of the interaction between climate and oceanic biota, if the overall feedback is negative and strong it would be a mechanism of the type proposed by the Gaia hypothesis—the idea that biota modify their environment to maintain a favorable climate. However, it is quite possible that the feedback might have a different sign in different regions or even change sign over time. The ice core evidence cited earlier appears to indicate positive feedback (more DMS flux during colder epochs), at least in polar regions, but we cannot yet say whether this was true globally.

### IX. Climatic Effect of Anthropogenic Sulfur Emissions

The total mass of sulfur cycling through the global atmosphere has been drastically perturbed by industrial activity. Anthropogenic emissions of sulfur (mostly as SO<sub>2</sub> gas from coal-burning power plants and smelting operations) currently amount to some 80 Tg sulfur per year, which is similar to the best estimates of total natural emissions (mostly as reduced-sulfur gases from biological activity.) Because sulfur's atmospheric residence time (the average length of time spent by a sulfur atom during one trip through the atmosphere) is only a few days, anthropogenic sulfur is a highly localized phenomenon, mostly confined to a few days' travel distance (a few thousand kilometers) downwind of industrial regions. Within these localities (covering perhaps 20% of the northern hemisphere) levels of anthropogenic sulfur are undoubtedly many

times higher than levels of natural sulfur. On the other hand, over most of the world's oceans, especially in the southern hemisphere, the atmospheric sulfur cycle is relatively undisturbed by human activity. [See ATMOSPHERIC TRACE GASES, ANTHROPOGENIC INFLUENCES AND GLOBAL CHANGE.]

The dominant pathway of sulfur (natural or anthropogenic) through the atmosphere involves the formation of sulfate particles and removal via rain. The climatic effect of atmospheric sulfur, in turn, can be divided into the direct and the cloud-mediated effects of the sulfate particles. (The direct effect is simply reflection of sunlight back to space by the sulfate particles themselves during clear sky conditions.) Discussion of the direct effect goes beyond the scope of this article, but it should be noted that the direct effect of anthropogenic sulfur emissions may be significant.

To estimate the cloud-mediated effect of anthropogenic sulfur emissions would require consideration of all the sensitivities (except sea-to-air transfer) discussed in relation to marine biogenic sulfur emissions, but in the expanded context of both marine and continental environments. We will limit our comments to a few general observations. (1) The earth's climate is most sensitive to the albedos and lifetimes of the extensive stratocumulus decks over the eastern portion of the earth's subtropical oceans. Because they are generally remote from industrial regions, these clouds probably have not been perturbed significantly by anthropogenic sulfur, although a careful study of this has yet to be conducted. (2) In spite of the far higher particle number concentrations in continental environments, the droplet number concentration of continental stratiform clouds is likely to be quite sensitive to changes in particle number. This was discussed in Section VII,C. (3) The albedos of continental stratiform clouds are well below the 0.75 threshold discussed in Section III,A and are thus susceptible to modification by a change in cloud droplet number. (4) Surface albedo is higher over the continents than the oceans but still low enough (excluding ice sheets) that top-of-atmosphere albedo is strongly affected by a change in cloud albedo.

Based on the foregoing, a logical corollary of the theory that biogenic sulfur emissions influence cloud properties over the remote oceans is that anthropogenic sulfur emissions, locally of much greater magnitude, have caused significant changes in cloud properties in and near industrial regions. To date, attempts to detect these changes have yielded inconclusive results; however, the historical record of cloud cover and the brief satellite record of cloud albedo have not been examined carefully with this in mind.

Other evidence may come from comparisons of the northern and southern hemispheres. Because over 90% of human sulfur emissions occur in the northern hemisphere and the atmospheric mixing time between the two hemispheres is 1–2 years (far longer than sulfur's atmospheric residence time), the effects of anthropogenic sulfur should be confined

almost entirely to the northern hemisphere. In this regard, one tantalizing piece of evidence has already emerged from the geographic distribution of global warming, i.e., the 0.5°C increase in globally averaged surface air temperature observed over the last century. The temperature increase seems to have been smaller in the northern than in the southern hemisphere by about 0.1°C, suggesting that the expected CO<sub>2</sub> warming of the northern hemisphere has been partially offset by anthropogenic sulfur emissions. However, this is impossible to prove because many other factors besides CO<sub>2</sub> and sulfur affect surface air temperature. Careful comparisons of cloud albedo (from satellites) for similar regions of the northern and southern hemispheres may prove more conclusive.

## X. Possible Anthropogenic Effects on Sulfur-Producing Microorganisms

As work to understand the natural marine sulfur cycle progresses, human activity is also affecting that cycle. What are some of the anthropogenic effects on the biology of the oceans which might affect DMS production?

River transport of fertilizers has already significantly changed the biology of major bodies of water such as the North Sea. There is evidence that the populations of some of the species of phytoplankton most responsible for DMS production, such as *P. pouchetii*, are increasing in response to this fertilization. There has even been speculation that the sulfate which results from these organisms' DMS may contribute to Europe's acid rain, although the evidence so far indicates that the contribution from anthropogenic sulfur far exceeds it.

Quite the opposite kind of pollution occurs when toxic chemicals are dumped into the ocean. Although we know of no documented instance of toxic compounds affecting DMS emissions, it is easy to imagine such a scenario.

More insidious and more likely is human modification of the atmosphere, which in turn will affect DMS production. Already, synthetic chlorofluorocarbon compounds have seriously depleted the ozone layer above the Antarctic ocean during the period of the spring phytoplankton blooms, and there is concern that the food chain, which may be sensitive to ultraviolet radiation, will suffer. Changes in the greenhouse effect would, of course, have the same potential for DMS flux changes as natural climate modification. [See ATMOSPHERIC OZONE.]

## XI. Summary

The formulation by Charlson and co-workers of a testable mechanism which could link the earth's biota and its climate into a tightly coupled system (see Fig. 6) has stimulated new

directions in climate research. To date, however, there is no direct evidence that changes in biogenic sulfur emissions affect either cloud albedo or cloud lifetime. Nor has evidence been found that changes in solar energy reaching the surface or in surface temperature (other than the changes associated with the seasonal cycle) affect the emission of sulfur gases by marine biota. These connections are plausible but have yet to be demonstrated. Even if they are real—that is, if the feedback loop shown in Fig. 6 actually exists in nature—there remains the major question of whether the loop as a whole acts as a climate thermostat or an amplifier of climate change. The thermostat possibility would be attractive as a Gaian mechanism, while the positive feedback suggested by ice core evidence is attractive as an additional mechanism to explain the large shifts in global climate (i.e., ice ages) which appear to be triggered by changes in the earth's orbit. It is also possible that the feedback loop operates as a thermostat in some regions and/or eras and as an amplifier in others. Since the response time of the proposed feedback is another unknown, it would be naive to expect the marine biota to counteract human-induced global warming over the next several decades.

Some of the best, albeit indirect, evidence for a link between biogenic sulfur and cloud properties comes from studies of the effects of atmospheric pollution. These include the ship track studies discussed in Section III,A as well as the interhemisphere comparisons mentioned in Section IX.

Recent work with global climate models confirms that the earth's climate is highly sensitive to the number concentration of marine stratiform cloud droplets. Indeed, the parameterization of cloud properties in a changing climate is currently the largest source of uncertainty for these models. Understanding how the marine sulfur cycle affects CCN number is thus of great importance for global change investigations, whether or not the complete feedback loop portrayed in Fig. 6 is significant. [See ATMOSPHERIC MODELING.]

The proposal that marine biogenic sulfur influences global climate by controlling the number concentration of marine stratiform cloud droplets is thus enticingly plausible but far from established. The proposed mechanism involves a chain of connected processes with many links. The links connecting cloud droplet number to global climate are relatively well understood and indicate a high climate sensitivity. For instance, the current climate forcing due to anthropogenic greenhouse gases (about  $2 \text{ W m}^{-2}$ ) could be offset by only a 30% increase in marine cloud droplet number. However, the links connecting changes in DMS emissions to changes in cloud droplet number contain such large uncertainties that the possibility of very low climate sensitivity cannot currently be excluded. In addition, the effect that a change in "climate"—that is, surface temperature, solar radiation, or

less obvious variables—would have on the production of DMS by marine biota is completely unknown, even as to sign. Narrowing these uncertainties will require improved, global-scale monitoring of parameters such as DMS concentration and CCN number as well as intensive, process-oriented studies of the marine ecosystem and the cloudy marine atmosphere.

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## Glossary

- Absorptance** Ratio of absorbed radiation flux to incident radiation flux.
- Atmospheric aerosol particles** Solid or liquid particles in the atmosphere, other than cloud droplets, of diameter smaller than about  $10 \mu\text{m}$ .
- Cloud condensation nuclei (CCN)** Atmospheric aerosol particles which serve as the nucleation sites for cloud droplets.
- Dimethyl sulfide (DMS)** Reduced-sulfur gas produced by microbiota.  $(\text{CH}_3)_2\text{S}$ .
- Non-sea salt (nss) sulfate** Sulfate measured in the bulk aerosol mass which is in excess of its seawater ratio with sodium or chloride.
- Phytoplankton** Single-celled photosynthetic algae.
- Reflectance (or albedo)** Ratio of reflected radiation flux to incident radiation flux.
- Relative humidity** Partial pressure of water vapor in an air mass divided by its equilibrium value (for that temperature) over a flat surface of pure liquid water.
- Transmittance** Ratio of transmitted radiation flux to incident radiation flux.