Evidence for the climatic role of marine biogenic sulphur

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Oceanic dimethylsulphide (DMS) emissions and atmospheric aerosol particle populations (condensation nuclei, CN), resolved by latitude and season, appear to be directly correlated, in that CN, as measured with a condensation nucleus counter, are high (or low) in regions where DMS fluxes and incident solar radiation are high (or low). Although it has been previously hypothesized that CN are produced from DMS[1,2], we report the first attempt to correlate DMS flux and CN. As the population of cloud condensation nuclei (CCN) in marine air is a subset of the CN population[3,4], and CCN in turn control the albedo of marine clouds[5,6], DMS could be involved in climate control through a cloud albedo feedback mechanism.

The transfer of solar radiative energy to the Earth drives both atmospheric and oceanic circulation. Any process that alters this radiative transfer directly affects the climate of the planet. The surface of the unfrozen oceans, covering 70% of the planet, is relatively dark and has the potential to absorb over 90% of the incident solar energy. The presence of clouds over the oceans decreases the amount of solar radiation reaching the sea surface; thus maritime clouds, through their albedo, directly influence the radiative climate of the Earth. A knowledge of the processes determining the optical properties of clouds over the oceans is critical for refining our understanding of climate and climate change.

For a given liquid water content, the optical properties of clouds are largely determined by the number of particles within the cloud[5]. Remote marine aerosol particles consist primarily of sulphates and sea-salt[7,8]. It is generally assumed that the sub-micrometre fraction of these particles is formed by gas-to-particle conversion, and that the primary source of this sulphate is the oxidation of reduced sulphur gases emitted from the oceans[1,2,9]. The importance of these sub-micrometre sulphate aerosol particles to the backscatter of solar radiation, as well as their role as CCN influencing the albedo of marine clouds, has led to the theory that the flux of reduced sulphur from the oceans to the atmosphere may control the climate of the Earth[6,10]. Recent spatial and temporal estimates of the flux of biogenic sulphur from the ocean to the atmosphere[11,12] allow an important aspect of this hypothesis to be observationally confirmed, namely the relationship of DMS flux to aerosol particle population and solar irradiance.

Marine sub-micrometre aerosol particles are composed mainly of sulphuric acid, which is only partly neutralized by ammonia[9,13]. There are no data on the number population of non-sea-salt sulphate particles *per se*, but the total CN population over the open ocean is usually between 100 and 400 cm^{-3} and is thought to be mostly sulphate[2]. The mass concentration of these particles appears to increase over the biologically productive regions of the ocean[14] and the number population is highest during the summer months[2]. This seasonal trend is opposite to that of the sea-salt particles, which have typical number populations at cloud height of $<1.0\ cm^{-3}$ (refs 15, 16). The origin of the sub-micrometre aerosol sulphate particles is thought to be the oxidation of reduced sulphur gases emitted from the oceans[1,2]. DMS is the most abundant reduced sulphur compound in open-ocean surface waters[11,17] and is the only

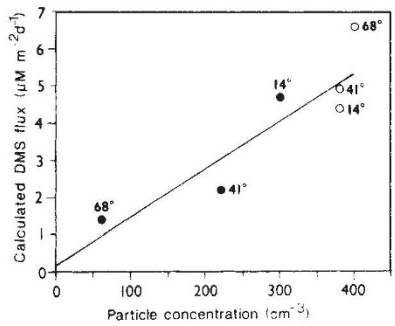

Fig. 1 Plot of calculated DMS flux[11] in $\mu M\ m^{-2}\ d^{-1}$ against particle (CN) concentration[2] in cm^{-2}. The six points represent two seasons (summer, open circles; winter, filled circles) and three latitudes (14°, 41° and 68–69°, corresponding to DMS tropical, temperate and subpolar regions). The equation of this line is flux = 0.013 (particle concentration) + 0.22, with a correlation coefficient, *r*, of 0.90. The particle data are from the Southern Hemisphere while the DMS data are from the Northern Hemisphere.

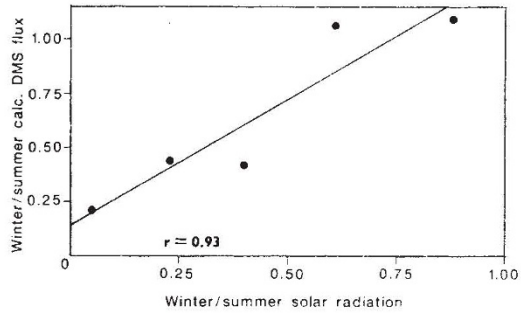

Fig. 2 Plot of the ratio of winter to summer calculated DMS fluxes in each latitudinal region (0–5°, 5–20°, 20–35°, 35–50° and 50–65° N; ref. 11) against the ratio of winter (December) to summer (June) direct solar radiation reaching the Earth. The equation of this line is flux ratio = 1.16 (radiation ratio) + 0.16, with a correlation coefficient, *r*, of 0.93. A similar relation was obtained for particle concentration and solar radiation[2].

significant source of reduced sulphur to the marine atmosphere[18]. DMS is produced by phytoplankton in the ocean's photic zone. The measured mean concentration of DMS in the atmosphere is quite low (3–12 $nM\ m^{-3}$, ref. 19) resulting in a net flux of DMS from the ocean to the atmosphere. The magnitude of this flux varies with both latitude and season, and for the non-coastal ocean ranges from 1.0 to 6.0 $\mu M\ m^{-2}\ d^{-1}$ (ref. 11). The concentrations of the atmospheric oxidation products of DMS, methane sulphonic acid (MSA) and sulphate, have been shown to vary seasonally[20–22], although the data are conflicting.

Non-nucleated sub-micrometre sulphate aerosols contribute directly to the backscatter of solar radiation and hence act to cool the surface of the Earth[10]. The net cooling effect at present, though, is smaller than the heating caused by the greenhouse effect of carbon dioxide[23]. Sub-micrometre sulphate particles, however, also serve as cloud condensation nuclei (CCN)[24] and in this capacity have a much greater effect on planetary albedo than the direct radiative effect of non-nucleated aerosols[6]. It is commonly believed that the concentration of CN is much greater than the concentration of CCN[25], but in the remote marine troposphere, where the CN population is small (100–300 cm^{-3}), the CN and CCN populations at 0.8% supersaturation converge[3,4, 26]. The number of sub-micrometre sulphate particles acting as CCN, therefore, is limited by the total particle population, and a change in CN population should have a direct effect on the optical properties of marine clouds. An increase in the population of CCN in marine stratus and altostratus clouds of

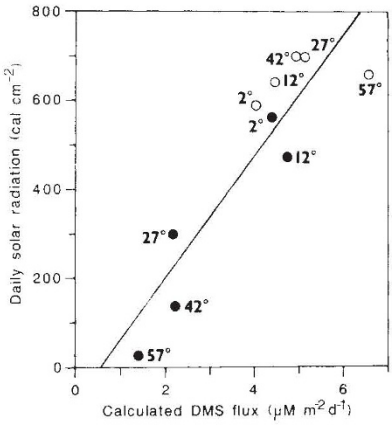

Fig. 3 Plot of calculated DMS flux[11] in $\mu M\ m^{-2}\ d^{-1}$ against daily direct solar radiation reaching the surface of the Earth in cal cm^{-2}. The ten points represent five latitudinal regions in two seasons (summer, open circles; winter, filled circles). The equation of this line is radiation = 137 (flux) − 68 with a correlation coefficient, r, of 0.90.

only 30% is calculated to increase cloud albedo by 0.02 and decrease the Earth's surface temperature by 1.3 °C (ref. 6). Variations in the optical properties of maritime clouds could therefore dramatically alter the amount of heat absorbed by the ocean, and hence could have an important function in regulating the climate of the Earth.

The hypothesis, therefore, is that biogenic DMS is emitted from the ocean and transformed in the atmosphere by gas-to-particle conversion to sub-micrometre aerosol particles. These particles act as CCN and subsequently control the albedo of clouds. This hypothesis implies a direct relation between DMS flux, CN population and CCN population. Elliott & Egami[3] and Hoppel[4] have demonstrated the high correlation between CN and CCN over the remote ocean.

There have been as yet no simultaneous observations of DMS concentrations and particle number concentrations, but DMS fluxes calculated from seawater DMS measurements in the North Pacific Ocean[11] can be related by latitude and season to total particle concentrations at four remote Southern Hemisphere sites[2]. Although the DMS data are from individual cruises throughout the Pacific Ocean, as opposed to year-long time-series at any one location, both the DMS flux and the particle number concentration vary seasonally and are highest in the summer. The amplitude of this seasonal variation increases with increasing latitude. A plot of DMS flux against particle number concentration for three latitudes (14°, 41° and 68–69° corresponding to the tropical, temperate and subpolar region DMS data) and two seasons (winter and summer) shows a close linear relationship ($r = 0.90$, Fig. 1). Despite a paucity of points, this correlation is surprising, considering that the comparison is based on regional average DMS data in the Northern Hemisphere compared with continuous particle data from the Southern Hemisphere. There is another way to regress these data because the relative changes in particle concentration correlate well with the relative changes in net solar radiation at each station[2]. Regressing the ratio of winter to summer DMS fluxes to the ratio of winter to summer direct solar radiation reaching the surface of the Earth (Smithsonian Meteorological Tables) yields $r = 0.93$ (Fig. 2). This adds support to the linear relation of DMS flux to particle number concentration. Bigg *et al.*[2] attribute the seasonal cycle of particle number concentration to the amount of radiation available for photochemical gas-to-particle transformations. The DMS flux/particle number relation shown in Fig. 1 suggests that the seasonality of particle number concentration could be attributable both to the seasonality of the marine sulphur source and to the amount of solar radiation available for photochemical gas-to-particle conversion.

To extend this apparent DMS flux/particle-number correlation to a convincing argument for a bio-controlled thermostasis of the planet requires the identification of a flux/climate relation or feedback. One obvious choice would be a temperature/flux correlation. The flux of reduced sulphur compounds from soils and plants to the continental atmosphere appears to vary directly with temperature[27]. The average seasonal variation of temperature of the near-surface ocean is, however, much less than that of the continental surface[11]. The correlation coefficient for this regression is therefore low ($r = 0.44$), indicating that variations in ocean surface temperature have little effect on the observed seasonal flux of sulphur from the ocean to the atmosphere.

Another climatic variable that could affect the flux of DMS is incident solar radiation. The relative seasonal change in solar radiation correlates well with the relative seasonal change in both DMS flux (Fig. 2) and particle number[2]. A plot of DMS flux in the North Pacific Ocean against daily direct solar radiation reaching the sea surface (Smithsonian Meteorological Tables, with a transmission coefficient of 0.8) for five latitudinal regions (0–5°, 5–20°, 20–35°, 35–50° and 50–65° N; ref. 11) and two seasons (winter DMS with December radiation, and summer DMS with June radiation) shows a linear relation with $r = 0.90$ (Fig. 3). This suggests that the flux of sulphur from the ocean to the atmosphere is linearly dependent upon the amount of solar radiation reaching the sea surface.

Is it possible that marine plankton regulate the production of DMS as part of a global biological system to control the amount of sunlight reaching the Earth? During the winter at high latitudes, when the incident solar radiation is low, very little DMS is produced. The lower concentrations of sulphur in the atmosphere should result in low concentrations of sub-aerosol particles. As there are fewer particles to act as CCN and increase the albedo of clouds, the oceans should absorb more solar energy. During the summer months, when the daily solar radiation is great, plankton produce more DMS, which should subsequently produce more aerosol particles, which in turn, through CCN, should increase the albedo of the Earth. In low latitudes, where the incident radiation remains fairly constant throughout the year, the flux of DMS also remains rather constant. Even during the 1983 El Niño/southern oscillation when marine productivity along the Equator decreased by a factor of 5–10 (ref. 28), the measured concentration of DMS[11] remained surprisingly constant. The co-varying spatial and temporal variations in DMS flux, sub-micrometre aerosol particle concentration and solar radiation are necessary but not sufficient conditions to prove the theory of climate regulation by biospheric trace gases and cloud-albedo feedback[6]. To assess this intriguing hypothesis fully, simultaneous DMS, CN, CCN and radiation measurements in different seasons and latitudes are needed, as well as a complete understanding of the microbiological and cloud microphysical processes involved.

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Boreal forests and atmosphere–biosphere exchange of carbon dioxide

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The response of vegetation growth to fluctuations in climate or anthropogenic influences is an important consideration in the evaluation of the contribution of land biota to atmospheric CO_2 variations. Here we present two approaches to investigate the role of boreal forests in the global carbon cycle. First, a tracer transport model wihich incorporates the normalized-difference vegetation index (NDVI) obtained from advanced very high resolution radiometer (AVHRR) radiances was used to simulate the annual cycle of CO_2 in the atmosphere. Results indicate that the seasonal growth of the combined boreal forests of North America and Eurasia accounts for about 50% of the mean seasonal CO_2 amplitude recorded at Pt Barrow, Alaska (71° N, 157° W) and about 30% of the more globally representative CO_2 signal at Mauna Loa, Hawaii (20° N, 156° W). Second, tree-ring width data from four boreal treeline sites in northern Canada were positively correlated with Pt Barrow CO_2 drawdown (that is, maximum–minimum CO_2 concentration) for the period 1971–1982. These results suggest that large-scale changes in the growth of boreal forests may be contributing to the observed increasing trend in CO_2 amplitude. They further suggest that tree-ring data may be applicable as indices for CO_2 uptake and remote sensing estimates of photosynthetic activity.

Seasonal oscillations of atmospheric CO_2 recorded at Northern Hemisphere stations are caused primarily by the seasonal dynamics (photosynthesis, respiration and decomposition) of the terrestrial biosphere[1,2]. These oscillations, or amplitudes, demonstrate both interannual variations and a trend towards increasing seasonal amplitude with time[3–9], and both variations may be related to fluctuations in the growth of land plants[3–9]. It has been suggested that anomalous seasonal amplitudes might have been caused by the adverse effects of drought on plant growth in Eurasia in 1975[10] and in North America in 1980[11]. Increased metabolic activity of land plants, resulting from climatic change and/or the direct effects of CO_2 or other nutrient fertilization, may be contributing to the positive trend in amplitude, which is most pronounced at northern latitudes (that is ~1% yr^{-1} at Pt Barrow[7,8]). Other possible contributing factors include changes in the seasonality and transport of fossil fuel combustion, changes in atmospheric circulation, increased ocean productivity and land-use changes related to forest regrowth[4,7,8,12,13].

The northern boreal forests are important to the study of CO_2–vegetation interaction due to their large biomass and net primary productivity. Unlike tropical forests, the seasons of net photosynthesis (net CO_2 uptake) and net respiration (net CO_2 release) are out of phase at high northern latitudes, and this asynchrony is reflected in the oscillations of atmospheric CO_2. The northern forests (latitude band 50°–70° N) also dominate the seasonal CO_2 drawdown for the globe[10,14]. It therefore seems reasonable that any changes in the seasonality of CO_2 (particularly at northern latitude stations) might reflect changes in the seasonally-variable growth of the boreal forests.

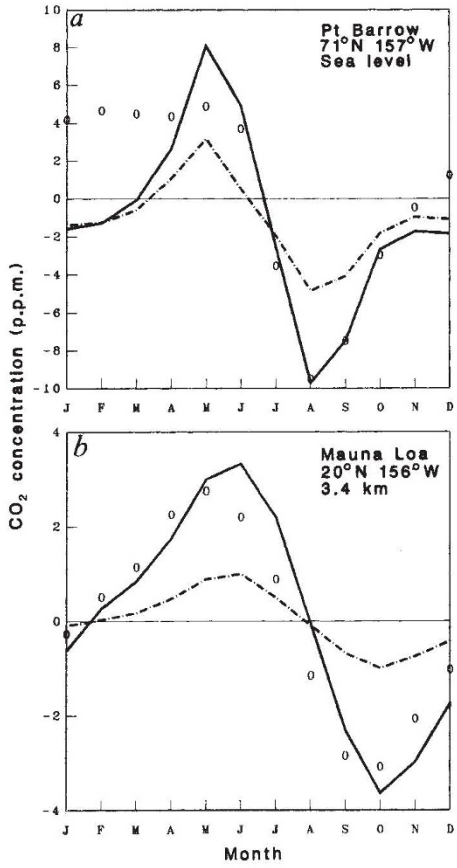

Fig. 1 Comparison of boreal (dashed line) and total (solid line) modelled annual cycles of atmospheric CO_2 at: *a*, Pt Barrow, Alaska, where it can be seen that the boreal portion is about 50% of the total amplitude; and *b*, Mauna Loa, Hawaii, where the boreal portion is about 30% of the total amplitude. Circles are observed values.

Much of the uncertainty in our understanding of atmospheric CO_2 changes has resulted from a lack of appropriate indices with which to characterize the boreal forests and other components of the biosphere[9]. The recently developed NDVI, which can monitor global-scale variations in photosynthetic activity[15–17], is a major step towards demonstrating the influence of the terrestrial biosphere on atmospheric CO_2. The inverse relationship found by Tucker *et al.*[17] between this index and atmospheric CO_2 concentration during the growing season indicates that the NDVI can be used as a measure of CO_2 uptake by the biosphere. These results suggest that a long record of NDVIs may provide information about interannual and longer term changes in photosynthetic activity, and the relationship between these changes and observed variations in atmospheric CO_2 oscillations. However, as the NDVI data have only been available since 1982, other ground-based field observations must be found.

We investigated the contribution of boreal vegetation to the total seasonal CO_2 amplitudes at Pt Barrow and Mauna Loa using a 3D atmospheric tracer transport model[13,18]. This model uses winds generated by a global general circulation model