Production of atmospheric sulfur by oceanic plankton: biogeochemical, ecological and evolutionary links

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Biological production of the volatile compound dimethylsulfide in the ocean is the main natural source of tropospheric sulfur on a global scale, with important consequences for the radiative balance of the Earth. In the late 1980s, a Gaian feedback link between oceanic phytoplankton and climate through the release of atmospheric sulfur was hypothesized. However, the idea of microalgae producing a substance that could regulate climate has been criticized on the basis of its evolutionary feasibility. Recent advances have shown that volatile sulfur is a result of ecological interactions and transformation processes through planktonic food webs. It is, therefore, not only phytoplankton biomass, taxonomy or activity, but also food-web structure and dynamics that drive the oceanic production of atmospheric sulfur. Accordingly, the viewpoint on the ecological and evolutionary basis of this amazing marine biota-atmosphere link is changing.

Dimethyl sulfide (DMS, see Glossary) is the most abundant form of volatile sulfur in the ocean. Since Lovelock postulated in 1972 that DMS could account for the ‘missing’ global flux of gaseous sulfur from the oceans to the atmosphere, several oceanographic cruises have compiled data on its ubiquity and supersaturation in surface seawater. Today, DMS is well recognized as the main natural source of reduced sulfur to the global troposphere. The most recent estimates of its emission flux range from $15 \times 10^{12}$ to $33 \times 10^{12}$ g S y$^{-1}$, enough to make a major contribution to the atmospheric sulfur burden (Table 1) and, therefore, to the chemistry and radiative behavior of the atmosphere.

Introduced in the late 1980s, the idea of marine microbiota being principal factors in atmospheric chemistry and climate regulation encouraged the study of the links between plankton and atmospheric sulfur, a study that has since yielded some 1000 papers in the scientific literature. Over the years, the interest in the topic has not only increased but also diversified. DMS is produced by the enzymatic breakdown of dimethyl sulfoniopropionate (DMSP), which is an abundant compound in phytoplankton.

DMSP represents a major fraction of organic sulfur in marine particles (mainly microorganisms) and is a major sulfur carrier for the transfer of this element through the marine food web (Box 1). Processes driving the synthesis, fluxes and transformations of DMSP and DMS are being unveiled because such research is not only being addressed from a global biogeochemistry perspective but also from the perspective of other disciplines, such as cell physiology, marine ecology and chemistry.

What controls the planktonic production of atmospheric sulfur?

Phytoplankton, sulfur and climate: the CLAW hypothesis

It was originally thought that phytoplankton produce DMS directly, and many authors still imply this when describing the oceanic biogeochemical sulfur cycle. Factors controlling phytoplankton activity (e.g. light, temperature and nutrients) were therefore expected to control DMS production. In 1987, this view provided the basis for the hypothesis of a feedback between oceanic phytoplankton and climate; with Gaia (or geophysical) thinking of the Earth in the background.

The CLAW hypothesis suggests that, because the radiation budget of the Earth is sensitive to the density of cloud condensation nuclei, and the major source of these nuclei over the oceans is DMS, biological (algal) regulation of the climate is possible through the effects of temperature and sunlight on phytoplankton population and DMS production (Fig. 1). The word ‘regulation’ implies not only influence but also feedback between DMS production and cloud albedo, although the actual sign (positive or negative) of the feedback loop requires further experimental test because of the existing uncertainty on the response of biological DMS production to changes in radiation.

Evolutionary concerns on climate regulation by phytoplankton

One of the main criticisms of the CLAW hypothesis (and, by extension, of Gaia) was its evolutionary feasibility. If phytoplankton were the producers of DMS, the climate feedback hypothesis was apparently based on the altruism of algal populations. The authors of the original CLAW paper recognized that climate regulation would imply an improbable altruistic behavior of phytoplankton for the biosphere; therefore they proposed as possible ‘selfish’ explanations that cloud feeding by DMS would favor phytoplankton by enhancing the return of nitrogen (N, a generally limiting resource in the surface ocean) through rainfall and by lessening harmful UV input. However, not all phytoplankton species (not even all clones within species) produce equivalent amounts of the DMS precursor; moreover, many organisms other than DMS producers also have a high N demand and are sensitive to UV. Hence, the supposed benefits of DMS production would be shared with non-DMS producers, and DMS...
Box 1. Biogeochemical roles of DMS and its biological precursor

Dimethylsulfide (DMS) and its biological precursor dimethylsulfiniopropionate (DMSP) play important roles in global sulfur biogeochemistry:

- Oceanic emission of DMS represents the main natural source of atmospheric sulfur. This emission flux is nearly enough to balance the global sulfur budget, compensating for a sulfur deficiency on the continents that is a result of runoff losses to the ocean.
- DMS emission from the global ocean equals one-third of global anthropogenic sulfur emissions. However, as the atmospheric lifetime of DMS sulfur is longer than that of anthropogenic sulfur, oceans contribute about 40% of the total sulfur burden of the atmosphere. Over oceanic regions remote from continents (such as most of the Southern Hemisphere), the vast majority of atmospheric sulfur comes from oceanic DMS. Oxidation of DMS in the marine atmosphere produces sulfur aerosols that, either directly or by acting as cloud condensation nuclei, scatter solar radiation thereby influencing the radiative balance of the Earth. This has been suggested to be part of one of the major self-regulated feedback mechanisms linking global biosphere and climate,
- Because it is an abundant component in many phytoplankton taxa, is valuable as a compatible solute, and because it contains a methylated, reduced sulfur moiety, DMSP is very prone to microbial degradation and very appetizing for bacteria and grazers. It therefore represents a major carrier for sulfur transfer through microbial food webs and organic sulfur cycling in the pelagic ocean.
- One of the products of microbial DMSP degradation, methanethiol, is very reactive with trace metals and could, therefore, affect metal availability and chemistry in seawater.

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are several possible factors that control phytoplankton production of DMSP:

Taxonomy. Some species of phytoplankton produce more DMSP than do others. As a general rule, haptophytes (including coccolithophorids and small flagellates) and small dinoflagellates produce more, or have higher intracellular concentrations of, DMSP than do diatoms.

Nitrogen availability. Andreae first suggested that the relative production of DMSP and its N analog, gly betaine (GBT), depends on contemporaneous N availability, so that the algae switch between the synthesis and accumulation of GBT (under N repletion) and DMSP (under N deficiency). This suggestion was later supported by the discovery of a transamination step in the DMSP synthesis pathway in the coccolithophorid Emiliania huxleyi. In recent experimental work with batch and chemostat cultures, however, a red proc (‘switching’) relationship with DMSP content was not evident even though GBT levels varied with a varying N supply.

It might be that evolutionary adaptation to N availability had a greater influence on DMSP synthesis by algae than did short-term acclimation to N availability. This would explain the taxonomic patterns observed: most diatoms have evolved to produce more GBT or other N osmolytes; conversely, small haptophytes (e.g. coccolithophorids) and many small dinoflagellates are typical of more N-deficient conditions, so they have evolved to produce more DMSP. This implies that the probability of finding higher levels of DMSP is greater under conditions of N depletion because of phytoplankton succession, and one should not expect strong shifts in DMSP levels in response to very short pulses of N supply. A significant exception to this hypothetical rule is the haptophyte Phaeocystis, which forms dense coastal blooms in high-nitrate, silicate-deficient conditions, but which exhibits high intracellular DMSP concentrations.

Light. It is still unclear whether DMSP biosynthesis is directly light dependent. Although dark uptake of exogenous sulfate is common in microalgae, there is little evidence for dark DMSP production. A recent study has found that the DMSP synthesis rate in oceanic phytoplankton was a diurnal process that was strictly proportional to 14C fixation (photosynthesis) (R. Simó et al., unpublished). There is also no clear answer as to whether DMSP production responds to

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DMSP turnover and DMS production

Now we understand a little more about why and how many microalgae contain DMSP. However, the path linking phytoplankton to DMS through DMSP is not straightforward. Attempts to correlate DMS to phytoplankton biomass (chlorophyll a concentration) or activity (primary production) on large spatial or temporal scales have failed. This might be not only because of the taxonomy dependence of DMSP production in algae, but also because most DMSP breakdown into DMS requires DMSP being released extracellularly. Exudation by healthy algae represents only a small fraction of DMSP release, which occurs mostly through cell lysis (autolysis and viral attack) and grazing. In grazing, a fraction of the algal DMSP is assimilated by the grazer. Some of the released DMSP is then converted into DMS by algal and/or bacterial DMSP lyases, either free in solution, attached to particles or in the guts and vacuoles of grazers. A large fraction of DMSP is, however, utilized through other pathways that do not produce DMS. Particularly, DMSP demethylation and demethiolation represents a source of reduced sulfur that can be assimilated readily into protein by microorganisms at a lower energetic cost.

A novel insight into what controls DMS production can be obtained by splitting the production flux into two terms:

$$\text{DMS production flux} = \text{DMSP flux} \times \text{DMS yield}$$

where the DMSP flux is the DMSP consumption rate and the DMS yield is the DMS production efficiency from DMSP consumption (i.e. DMS production rate $\times 100$/DMSP consumption rate).

DMS flux. DMS is very labile, with turnover times of between a few hours and one to two days. It is released and consumed at high rates and does not accumulate in large amounts in dissolved form in seawater. The DMS flux is, therefore, related to the rate of phytoplankton loss, which is influenced by herbivore grazing pressure, viruses, competition for resources and environmental (e.g. nutrients, turbulence and radiation) stress, and is also related to the growth efficiency and the sulfur demand of grazers. The DMS flux is, therefore, part of food-web dynamics.

DMS production yield. This term has been addressed recently from two different perspectives. According to Kiene et al., DMS production yield would result from the combination of seawater DMSP concentration and the bacterial sulfur demand. In my opinion, DMS concentration should be redefined as the 'DMSP flux' defined above. In any case, this relates to phytoplankton taxonomy and loss rate. Bacterial sulfur demand is assumed to depend on heterotrophic bacterial production. The higher their sulfur demand, the more DMSP the bacteria will use as a sulfur source for biomass production, and the less will be wasted as DMS. Thus, low DMSP concentration (flux) with high sulfur demand would lead to higher DMSP assimilation and lower DMS yield, whereas high DMSP with low sulfur demand...
Box 3. The bacterial switch

Marine bacteria are involved in both dimethylsulfide (DMS)- and non-DMS-producing degradation pathways of dimethylsulfiniopropionate (DMSP). Bacteria therefore exert a controlling role on DMS production efficiency by switching DMSP degradation towards more or less DMS production. Once this switching role is recognized, two questions arise that are crucial to our understanding of the quantitative contribution of bacteria to net DMS production:

1. Is DMSP a (universal) substrate for most DMS production:
   a. Is the bacterial switch crucial to our understanding of the quantitative contribution of bacteria to net DMS production?
   b. Does the switch have a controlling role on DMS production efficiency by switching DMSP degradation towards more or less DMS production?

2. Is DMSP use a characteristic of only a few bacterial metabolisms?
   a. Are marine bacteria involved in both DMSP and DMS utilization (Fig. 2)?
   b. Are bacterioplankton involved in both DMSP and DMS utilization (Fig. 2)?

Perhaps the answer is both: only a few lineages of bacteria process DMSP, but they are so abundant that they account for a large fraction of total bacterial activity. The combined techniques of radioactive 35S-DMSP tracing and FLUORESCENT IN-SITU HYBRIDIZATION, using either MICROAUTORADIOGRAPHY or FLOW-CYTOMETRY SORTING, will help answer these questions. This explains why global attempts to correlate phytoplankton taxonomy, physiology and activity with DMS production have been unsuccessful.

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directly DMS concentration with chlorophyll a levels have failed. It might also explain why, in the Equatorial Pacific over a period of 15 years, DMS concentrations during El Niño events were not significantly different from those in the background years, although important reductions in chlorophyll a levels and primary production accompanied such events. Shifts in the food web towards more microbial-dominated webs (fewer large cells, less particle sedimentation and high production–grazing coupling) would have compensated for the apparent loss of potential DMS generation through the decrease in chlorophyll a and primary production, with higher biomass-specific DMS production.

A similar food-web related explanation has been given for the 'summer DMS paradox'. In the large oligotrophic regions of the global surface ocean, maximum DMS concentrations occur in summer when sunlight is maximum but surface chlorophyll a concentrations are at their annual minimum. Again, higher efficiency in food-web DMS production together with lower DMS consumption would compensate for a lower DMS generation potential.

The 'summer DMS paradox' supports the CLAW hypothesis because stronger sunlight and higher temperatures correspond with higher DMS concentrations (Fig. 1). However, this apparent link between food-web DMS production and incident radiation flux reinforces the controversy of how DMS might have evolved to be a biogenic product for climate regulation. If it was hard to explain that a phytoplankton population (individual or species) might produce something for the good of the community, it is even harder to think that members of the whole plankton community (constituted by parts that even compete among themselves for resources) ‘agree’ to produce something for the good of them all and the biosphere. This could be regarded as a fully Gaian mechanism in that a community with a stabilizing feedback (i.e. with an environment-altering trait that benefits the community, for example, moisture retention and nutrient recycling within rainforests) would tend to persist and spread through evolution by selection at the ecosystem level.

An alternative explanation, based only on the selfish adaptation of individuals or populations can be given. In summer, phytoplankton succession favors populations more adapted to N deficiency, populations that would therefore synthesize more DMSP per individual. Coupling between primary production, algal lysis and grazing by microzooplankton is tighter in summer and involves a larger fraction of primary production (because of smaller cell size and consequent reduced sinking). This would lead to higher DMS flux per biomass in the surface layer. Shallow mixing causes bacterial activity to be reduced by UV-B damage and to be limited by the lack of nutrients. This would decrease DMS assimilation, increase DMS production and decrease DMS consumption, all leading to higher net DMS production. All these effects ‘at the individual or population level’ would result in higher net DMS production in summer, when incident radiation is higher. The negative feedback response of the oceanic DMS emission to changes in incident solar radiation (suggested in the CLAW hypothesis) is, therefore, feasible through changes in vertical mixing and water-column light regime, and without necessarily calling for altruism or natural selection at the ecosystem level.

Prospects

To improve our understanding of the role that biogenic volatile sulfur from the ocean plays in global biogeochemistry and climate, we should prioritize research on:

- Further understanding the links between DMSP, DMS and food-web structure and dynamics. A way to achieve this is by introducing temporal and/or spatial variability in the study of the processes of DMS cycling. Most studies in the open ocean have provided snapshots of the DMS cycle, which are useful for revealing potential couplings or uncouplings. However, these results should be used with caution when extrapolated to longer timescales. Only the observation of the changes in process rates through seasons, through short-term (e.g. storms) and long-term (e.g. El Niño) overturning events, through BIOGEOCHEMICAL PROVINCES or MESOSCALE HYDRO_DYNAMIC STRUCTURES will help unravel the dynamics of the sulfur cycle in relation to a dynamic environment and biota. This is relevant to research on how the ocean responds as a sulfur source to global warming. Climate warming has the potential to alter food-web structure and dynamics, thereby impacting the net air–sea exchange of gases. This seems clear for CO₂ and O₂, and should be the same for DMS.

- Opening the ‘black box’ of microbial metabolisms involved in the production and consumption of volatile sulfur, so that we are able to identify which microorganism does what and ask what controls their distribution and activity. As outlined in Box 3, a first step towards such identification will be provided by molecular techniques for bacterial ‘functional diversity’ that are currently being developed.

- Being able to define ‘DMS-producing pelagic ecosystems’ (i.e. community structures and dynamics favorable to net DMS production); what they are like, how they work, when and where they occur, and in response to what physical FORCINGS. This should make use of other concepts such as those of ‘biogeochemical provinces’

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Albedos: measurement of the ability of a surface to reflect light; in a global sense, the proportion of solar radiation reaching the Earth that is reflected back into space. It plays an important role in regulating the heat balance of the globe. White surfaces, such as clouds and ice or snow cover, have a high contribution to regional and planetary albedo.

Biogeochemical provinces: 56 regions of the global oceans defined by A. Longhurst on the basis of differentiated ocean currents, fronts, topography and recurrent features in the sea surface chlorophyll a field.

CLAW hypothesis: hypothesis released in 1987 by Charlson, Lovelock, Andreae and Warren, which states that regulation of climate by oceanic phytoplankton is possible through the production of dimethylsulfide (DMS). This DMS oxidizes in the atmosphere, changes cloud albedo and, therefore, affects temperature and sunlight. These, in turn, have feedback effects on phytoplankton population and DMS production. The link between phytoplankton and climate made by the CLAW hypothesis has been proposed as one of the testable processes in the Gaia theory.

Cloud condensation nuclei (CCN): tiny airborne particles (generally of submicronic size) that serve as nuclei for water condensation in clouds. The amount and size of CCN determines the optical depth of the cloud and, therefore, the cloud albedo. Hygroscopic sulfate aerosols formed upon atmospheric oxidation of DMS are excellent CCN.

Compatible solute: a cytoplasmatic organic solute that occurs at concentrations high enough to be active but that is compatible with metabolism and has no inhibitory effects (unlike inorganic ions). Major functions of compatible solutes are protecting proteins and stabilizing membranes under conditions of high ionic strength (osmoprotection) and freezing temperatures (cryoprotection).

DMS: dimethylsulfide (H2C-S-CH3); the most abundant and ubiquitous volatile sulfur compound in marine environments, where it occurs at concentrations of up to 300 nm (usually 1-10 nm) as a product of the enzymatic cleavage of dimethylsulfoniopropionate (DMSP). DMSP: dimethylsulfoniopropionate [(H3C)2-S-CH2-CH2-COO-], an abundant intracellular component in many phytoplankton taxa, where it acts as a compatible solute. It breaks down enzymatically into DMS and acrylic acid.

DMSP lyase: enzyme that cleaves DMSP. It occurs in some algae, protozoa, bacteria and fungi, either intracellularly or ectoplasmatically.

Forcing: change to an environmental variable induced by an environmental factor; for example, radiative forcing caused by changing concentrations of aerosols or CO2, for example wind speed forcing on ocean mixing.

Gaia Theory: first released as hypothesis by J.E. Lovelock in the 1970s as the notion of the biosphere as an adaptive control system that can maintain the Earth in homeostasis that is comfortable for life. It evolved into theory as a numerical basis was introduced. In its latest formulations, the theory proposes that life and the abiotic Earth have evolved together as the single entity Gaia with emerging regulatory feedback mechanisms that have kept surface environmental conditions in some degree of homeostasis. Lovelock named the science of Gaia geophysiology. Although the Gaia Theory is still controversial, it has been influential in the rise of Earth system science.

Mixing layer: surface layer of the water column of the oceans. It has a homogeneous density, and is ‘separated’ from the water beneath by a density gradient (pycnocline). Although it is generally known as mixed layer, some authors distinguish between the ‘mixed’ layer (i.e. the layer above a strong pycnocline dictated by the seasonality of the heat flux and by major currents; it can either be well mixed by turbulence or in transient stagnant conditions evolved from past mixing) and the ‘mixing’ layer (i.e. the layer actually in turbulent mixing; its thickness changes in the short term as a rapid response to changes in heat flux and wind speed). The depth of the mixed–mixing layer governs, among other things, the exposure of dissolved substances and planktonic organisms to solar radiation.

SOLAS: Surface Ocean–Lower Atmosphere Study: a new international program associated with the International Geosphere–Biosphere Programme (IGBP). Its goal is to achieve quantitative understanding of ocean–atmosphere interactions and feedback, and how this coupled system affects and is affected by climate and environmental change.
Opinion

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