

The smell of the sea: Sulphur production by marine algae

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The oceans have a distinctive smell that can transport us back to the seaside summer holidays we had as a child. But, have you ever wondered what causes that characteristic seashore smell? The air we breathe in at the coast is a cocktail of many different naturally-occurring gases, primarily originating from the oceans. One of these gases is dimethylsulphide (DMS), a sulphur gas made by oceanic plants that goes on an incredible journey from its production in the oceans to the clouds in the sky.

Production of DMSP

DMS is one of the most important components of the global sulphur cycle - a series of reactions involving biological, chemical, physical and geological processes, recycling sulphur chemicals on land, in the oceans and in the atmosphere. The majority of DMS is derived from dimethylsulphoniopropionate (DMSP), a sulphur chemical produced by most marine algae. The oceans contain two main types of algae: phytoplankton (tiny, floating single-celled algae) and macroalgae (larger multi-cellular algae commonly called seaweed). DMSP is very important to algae as it provides a number of critical cellular functions, including as an:

1. Antifreeze – DMSP allows cellular reactions to continue in the freezing conditions found in polar oceans.
2. Antioxidant – DMSP ‘mops up’ harmful chemicals produced by high light or ultraviolet radiation, acting as a natural sunscreen.
3. Osmolyte – the concentration of DMSP within cells is regulated to match the salinity of the surrounding environment, allowing survival in the salty oceans.
4. Herbivore deterrent – DMSP and DMS may be produced by algae to make them unattractive to grazers such as sea urchins, reducing grazing damage.

The production of DMSP requires a lot of energy, so algae often only regulate the amount of DMSP in their cells in response to long-term or very severe environmental stress. Additionally, once produced, DMSP cannot readily leave algal cells; it must be purposefully transported out or converted to other chemicals – actions which require yet more energy. Consequently, DMSP is often only released from algae when the cells are damaged (e.g. due to grazing activity), when the cells burst following death, or when the concentration of nitrogen, an essential nutrient for algae, in the water is low.

Conversion to DMS

When released from cells, dissolved DMSP becomes a target for many microbes. Microbial activity is an essential part of the breakdown of DMSP in the oceans. Bacteria use DMSP as food, yielding up to 15% of their carbon and energy requirements and 100% of their sulphur

requirements from this one chemical. There are two pathways for the breakdown of DMSP by bacteria in the oceans:

1. Cleavage to form DMS and either acrylate or 3-OH propionate, both of which are used as sources of energy.
2. Dimethylation to form methanethiol, another source of energy for bacteria.

Thus, only one of these pathways yields DMS. It is not currently known why there are two pathways, or what factors control which pathway is used. Some bacteria can only breakdown DMSP via one of the two pathways, others can do both. The dimethylation pathway can ultimately result in the production of methane, a potent greenhouse gas that can enhance global warming; a result that has become a concern to climate scientists. Nevertheless, during periods of high DMSP production in the surface ocean (from phytoplankton or seaweed), DMS is often also produced in large quantities.

Flux of DMS from the oceans

DMS is a 'volatile' gas – this means it is easily transferred from the oceans to the atmosphere. The concentration of DMS in the oceans is very low, around 30 – 160 ng per litre, that's little more than a billionth of a gram in one litre of seawater! However, this is a far higher concentration than in the atmosphere. These factors mean there is a constant movement of DMS from the oceans to the atmosphere to try to balance the difference in concentrations. This process is known as sea-to-air flux. It is estimated that more than 90% of the total biologically-derived sulphur emissions from the oceans are from DMS, equating to around 50% of the world's total sulphur. A flux of DMS from the oceans is also critical for many seabirds such as albatrosses, petrels and shearwaters. Where there are lots of phytoplankton (known as a 'bloom'), there are also many grazers and higher animals such as zooplankton (small crustaceans) and fish – preferred food sources for the birds. DMS released from the phytoplankton during grazing acts as a beacon to direct the seabirds to their food.

Gas flux from the oceans is primarily driven by wind speed (higher wind speeds lead to higher gas flux), and is well described by a number of physical equations. The flux of DMS from the oceans to the atmosphere is calculated by:

$$F_{DMS} = k \times \Delta C = k \times (C_W - [C_A \times H^{-1}])$$

Where F_{DMS} is the flux of DMS, k is the transfer velocity, ΔC is the difference in concentration between the water (C_W) and the air (C_A) and H is Henry's law constant, describing the solubility of DMS in water. However, due to the incredibly low DMS concentrations in air, C_A may be considered zero and the calculation of DMS flux is simplified to:

$$F_{DMS} = k \times C_W$$

Thus, the rate of sea-to-air DMS flux is dependent on the transfer velocity (k) and the concentration of DMS in the water (C_W). Whilst it is relatively easy to measure the concentration of DMS in the ocean, k is more difficult to calculate. This leads to large uncertainties associated with

predicting the sea-to-air flux of DMS. The main factors that affect k are (1) the Schmidt number and (2) wind speed.

Firstly, the Schmidt number (S_c) is the ratio between water viscosity (how thick or sticky the water is, ν) and the diffusivity of DMS (how easily DMS diffuses in liquids, D_{DMS}), and is calculated by:

$$S_c = \frac{\nu}{D_{DMS}}$$

Secondly, an increase in wind speed leads to an increase in k and thus an increase in the flux of DMS from the oceans. However, the relationship between wind speed and k is not simple. The presence of breaking waves and the formation of bubbles leads to a sharp increase in the flux of DMS from the oceans to the atmosphere. Liss and Merlivat (1986) identified three wind regimes that sequentially increase k based on the roughness of the ocean surface:

1. Smooth surface – wind speeds of up to 3.6 metres per second; low k .
2. Rough surface – wind speeds of 3.6 – 13 metres per second; intermediate k .
3. Breaking waves – wind speeds of over 13 metres per second; high k .

Other factors can also affect the flux of DMS from the oceans, including temperature (fluxes are slower from cold water), the presence of surfactants (chemicals that form a boundary between the ocean surface and overlying air) and, of course, the rate at which biological processes initially produce DMS.

The CLAW hypothesis

Flux into the atmosphere is not the end of the line for DMS, however. As was alluded in the first paragraph, DMS is also involved in a series of atmospheric processes. In the atmosphere, DMS may be readily oxidised into tiny sulphate particles and aerosols. These particles can act as cloud condensation nuclei and provide a base for water droplets to form, resulting in the formation and growth of clouds. If sufficient quantities of clouds develop, radiation from the sun may be reflected back into space (because clouds have a high albedo, or reflectivity), reducing the amount of solar energy reaching the Earth's surface. This leads to surface cooling and may help to regulate atmospheric temperature. Lower temperatures at the Earth's surface lead to a reduction in marine algal activity, reducing the amount of DMSP produced, reducing the flux of DMS into the atmosphere, subsequently leading to a reduction in cloud cover (Figure 1). This cycle was first suggested by Charlson, Lovelock, Andreae and Warren in 1987 and is termed the 'CLAW hypothesis' after the authors of the research paper.

The CLAW hypothesis has led to the suggestion that DMS may act as an 'anti-greenhouse gas', a bio-physical mechanism that may help to mitigate global warming. It has been estimated that 27% of global atmospheric sulphate is derived from DMS produced by phytoplankton in the open ocean. However, a considerable number of uncertainties still surround the CLAW hypothesis as it is extremely difficult to follow DMS molecules from their production by algae to their eventual role in cloud formation and the initiation of an atmospheric cooling effect.

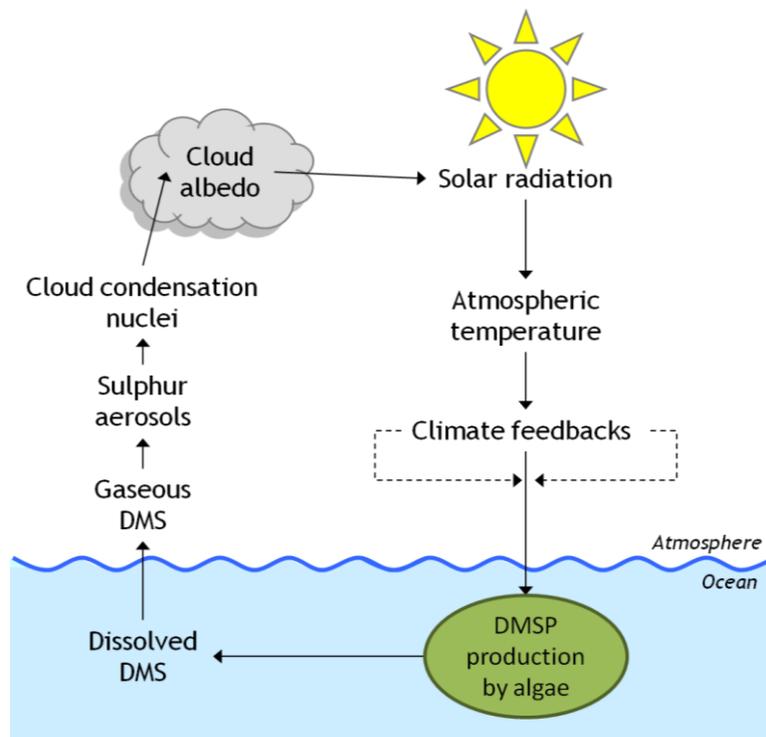


Figure 1. The proposed DMS-climate feedback cycle, termed the CLAW hypothesis by the original paper: Charlson and colleagues (1987).

Industrial interest

The CLAW hypothesis has been targeted as a ‘geo-engineering’ idea to mitigate human-induced global warming caused by increased carbon dioxide levels in the atmosphere. It has been proposed that, by adding iron to so called ‘high nutrient, low chlorophyll’ regions of the ocean, phytoplankton productivity in these areas will increase because their growth is currently restricted by the naturally limited supply of iron. It has been suggested that this will have two benefits:

1. Utilisation of carbon dioxide from the atmosphere by phytoplankton for photosynthesis.
2. Increase DMS emissions into the atmosphere, stimulating the formation of clouds and a subsequent cooling effect.

However, we do not currently understand all the biological and physical processes that may be affected by iron fertilisation. To date, only small scale experiments have been conducted, designed to lessen the uncertainties and provide evidence for larger-scale projects.

Commercial seaweed cultivation is a globally productive industry. Currently, activity is primarily located in Asia, but the European and American sectors are rapidly expanding as the pressure of a growing human population continues. Seaweed extracts are used for nutrition, bio-plastics, bio-fuels and in many cosmetic products. Concerns have been raised over the environmental impact of commercial seaweed cultivation, including the production of climatically important gases such as DMS. Understanding the production of DMS from seaweed farms has been highlighted as a specific research priority over the next decade for the UK algal bio-energy industry (Smith, 2012). This includes understanding its impact on marine systems (e.g. acting as a

microbial energy source or signalling cue for seabirds), as well as its release into the atmosphere and subsequent formation of cloud condensation nuclei.

Conclusion

DMS is a fantastically versatile chemical that is involved in a number of biological, chemical and physical processes in the oceans and atmosphere. The precursor to DMS, DMSP, is used by algae to survive the environmental stresses associated with ocean life and is a critical energy source for microbes. Amazingly, DMS may also be contributing to the clouds above your head. So, next time you are at the coast and you take a deep breath, remember the algae, bacteria and physics that went into producing the distinctive smell of fresh sea air.



References

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