12.491 Biogeochemistry of sulfur

Phytoplankton, climate and the sulfur cycle: exploring the CLAW hypothesis.

Sophie Clayton

1. Introduction:

Dimethylsulfide (DMS) is a climatically important volatile sulfur compound produced by the biologically- and physically-mediated breakdown of dimethylsulphoniopropionate (DMSP), an organosulfur compound synthesized by oceanic phytoplankton. DMS is the most abundant form of volatile sulfur in the ocean, and is the main source of reduced tropospheric sulfur over the oceans (Chin *et al.*, 1996), therefore oceanic phytoplankton play an important role in the biogeochemical cycle of sulfur, providing a link between the oceanic and atmospheric sulfur cycle through the release of DMS (Lovelock, 1972). The oxidation of DMS in the troposphere leads to the formation of sulfate aerosols which act as cloud condensation nuclei (CCN), with important consequences for the radiative balance of the earth (Chin *et al.*, 1996).

The CLAW hypothesis suggests that, as a result of this, a homeostatic feedback may exist between oceanic phytoplankton and climate through the production of DMS (Charleson *et al.*, 1987). The atmospheric part of this mechanism is relatively well known (Cox, 1997), and observational studies have found correlations between cloudiness, atmospheric aerosol concentrations and phytoplankton (Cropp *et al.*, 2005; Meskhidze & Nenes, 2006). However, the physiological function of DMSP and the processes leading to the production of DMS are, as yet, less clear (Stefels *et al.*, 2007).

Attempts to identify biological and physical variables which control the production of DMS in the water column have revealed no simple relationships with phytoplankton biomass or chlorophyll concentration, suggesting a more complex regulation of DMS production by the whole planktonic sea surface ecosystem and its physical environment (Simo, 2001). Various empirical relationships with biological and geophysical data have been derived in order to try to predict sea surface DMS concentrations, but the errors associated with these make it difficult to derive meaningful, quantitative, results about the strength (and indeed the sign) of the phytoplankton-DMS-climate feedback when incorporated into coupled ocean-atmosphere climate models. Ecosystem models have also been used to explore the ecosystem production of DMS, and have proved a useful tool to better understand the dominant processes controlling sea surface DMS concentrations. However, our understanding of the

factors controlling the production of both DMSP and DMS is still fundamentally lacking, and needs to be improved before any real insight into the proposed DMS-climate feedback can be achieved.

2. Upper ocean cycling of DMS/DMSP:

It was originally thought that DMS was produced directly by phytoplankton, however, it is now clear that DMS is in fact the product of the breakdown of DMSP (produced by phytoplankton), by various upper ocean processes. The upper ocean ecosystem is very complex (as illustrated in figure 1), and the way that DMSP and DMS is cycled through it can be affected by physical and chemical processes at each step, the effect of which is difficult to quantify. As a result, there is no straightforward relationship between DMS concentration and phytoplankton biomass or chlorophyll *a*.

Several processes have been identified as important in DMS production and are briefly outlined below (see Stefels *et al.*, 2007, for a thorough review of this topic). The most fundamental control of DMS is the phytoplankton species composition. Only a limited number of species produce high concentrations of DMSP, mainly belonging to the classes *Haptophyceae* and *Dinophyceae* (dinoflagellates), some diatoms (*Bacillariophyceae*) may also produce significant amounts of DMSP. It should be noted that, although some species do not produce large concentrations of DMSP, because they occur in large blooms, the concentration of DMSP in the water column is correspondingly high, this is particularly true of *Phaeocystis* and *Emiliana huxleii*. The physiological condition of the phytoplankton cells, mediated by abiotic parameters (light, nutrients, temperature and salinity) is also important. DMSP has been found to have several physiological functions including: overflow mechanism for excess sulfur, anti-oxidant (Sunda *et al.*, 2002) and osmoregulator. In general, it has been concluded that DMS is a product of a stressed ecosystem. The production of DMSP by phytoplankton is increased under high light and high salinity conditions, additionally, a less conclusive relationship has been proposed between DMSP production and nutrient limitation. It has also been suggested that there are two regimes of DMS production, a "bloom-driven" regime in eutrophic regions where the DMS concentration are set by phytoplankton blooms, and a "stress-driven" regime in oligotrophic open ocean regions, where DMS concentrations are highly correlated to UV radiation (Toole & Siegel, 2004). If this is the case, "stress-driven" DMS production is most likely to play a climatic role as described by the CLAW hypothesis.

Studies which have quantified the size of sources and sinks of DMS and DMSP in the upper ocean sulfur cycle have proved invaluable in understanding the factors that control the concentration of DMS in surface waters. Figure 2 shows a schematic of the upper ocean seawater sulfur cycle studied over several days in the Pacific, off the Washington State coast (Bates *et al.*, 1994). It is clear from this, and other studies (e.g. Archer *et al.,* 2002), that the flux of DMS from the surface ocean to the atmosphere is in fact a very minor sink for this compound, however, global estimates show that around 1 Tmol S per year is fluxed from the ocean to the atmosphere (Anderson *et al.*, 2001).

Bacterial consumption of DMS seems to be the largest sink, and enzymatic cleavage of DMSP to DMS is an important source. Therefore the role of bacteria cannot be underestimated, and the effect of physical and chemical parameters on their metabolism will, in turn, affect sea surface DMS concentrations. Zooplankton grazing must also be taken into account as a potential sink for DMS, as it may result in the export of DMS away from the surface ocean as it is incorporated into faecal pellets. DMS is oxidized into dimethylsulphoxide (DMSO) in the upper ocean, the size of this sink is still not well known. DMSO is also produced intra-cellularly by phytoplankton in addition to DMSP (Simo, 2004). The role of DMSO needs further study, but it is clear that it should be incorporated into sulfur budgets for the upper ocean and models of DMS production.

3. Predicting sea surface DMS concentrations:
One of the biggest challenges in trying to test the CLAW hypothesis is to predict global sea surface DMS concentrations accurately enough to incorporate them into coupled ocean-atmosphere climate models. The prediction of sea surface DMS concentrations and its flux to the atmosphere primarily relies on empirically-derived relationships. Several predictive algorithms have been proposed, linking sea surface DMS concentrations to biological and geophysical data, such as ocean color (used to obtain Chl *a* concentrations), mixed layer depth (MLD) (Simo & Dachs, 2002) and the sea surface radiation dose (SRD) (Vallina & Simo, 2007), parameters which can be relatively easily obtained by remote sensing, as well as nutrient limitation parameters (Anderson *et* al., 2001) derived from ocean biogeochemical models. Although these predictive algorithms have succeeded in broadly recreating the observed sea surface DMS distributions, there are errors associated with their output, up to 100% (Belviso *et al.*, 2004) which must be taken into account. Primarily because the global database of sea surface DMS concentration observations has only limited spatial and temporal coverage, and in most cases, the predictions of these algorithms were compared against global sea surface DMS concentrations extrapolated from this data set (Kettle *et al.*, 1999).

These different algorithms may also produce contradictory results, for instance, Anderson *et al* (2001) predict rather different DMS fluxes to the atmosphere for the Southern Ocean than Simo & Dachs (2002). This is because in one case DMS concentration is taken to be a function of MLD, where shallow MLDs result in enhanced DMS concentrations (Simo & Dachs, 2002), whereas this assumption is not present in the Anderson *et al* (2001) algorithm. In the Southern Ocean, high wind speeds result in a deep MLD, according to Simo & Dachs (2001) this would predict low DMS concentrations, however, high wind stress results in enhanced sea-air gas flux, resulting in Anderson *et al* (2001) predicting higher DMS fluxes to the atmosphere in this region. This brings up an interesting question as to which physical processes control DMS concentrations. The current literature strongly suggests that the surface irradiance dose is the fundamental control on DMS concentration, so a correlation between DMS and MLD is assumed because the depth of the MLD is in part controlled by surface irradiance. However it may be possible that this relationship breaks down in

regions of high wind stress because, in those cases, the MLD is more likely to be a function of the wind stress than the surface irradiance. The calculation of the sea-air flux for DMS is not subject to such large big uncertainty, but depending on the gas transfer formulation chosen, results can vary by a factor of 2 (Anderson *et al.*, 2001). Considering the importance of the Southern Ocean in global climate system, this may an important avenue for future research.

These empirical approaches have been attractive because, as they use remotely sensed data, the hope is that they would make it easy to produce predictive DMS concentration fields for most of the global ocean, however, the parameters obtained by fitting observations in this way may not apply to conditions that were not reflected in the observations. At present it seems that they are not refined enough to be incorporated into climate models to gain accurate estimates of the magnitude of the proposed DMS-climate feedback, however, they have been very useful in pointing the way towards identifying the dominant physical forcing mechanism for DMS production. When coupled with the results of biological studies mentioned above, it seems very likely that for large parts of the ocean, sea surface irradiance is controlling, at least in part, DMS concentrations.

Considering DMS is a product of the upper ocean ecosystem, it is not unreasonable to expect that mechanistic ecosystem models may prove useful in attempting to predict DMS concentrations. This approach has been adopted in many studies and the models range widely in their degree of complexity, from zero-dimensional local simulations to global scale simulations with multiple plankton functional groups driven by ocean general circulation models (GCMs). The first marine ecosystem model incorporating sulfur dynamics was developed by Gabric *et al.* (1993), and improvements in estimating the rate parameters used in this type of model has resulted in the development of several subsequent models (Vezina, 2004). There is some debate over whether or not it is necessary to incorporate different phytoplankton functional groups into DMS ecosystem models. Using different phytoplankton groups allows for the differentiation between species which produce high and low concentrations of DMS, as well as species which do and do not produce DMSP-lyase (the enzyme used to cleave DMSP to DMS). On the other hand, Gabric *et al.* (1999) found it possible to accurately reproduce DMS dynamics at several stations around the Polar Front with only one phytoplankton compartment in the model. Clearly, these issues need to be resolved before a DMS ecosystem model can be developed to predict global scale DMS production, but this approach is likely to give more accurate results than the empirical algorithms outlined above.

4. DMS-climate feedbacks:
To date, relatively few studies have addressed this question, hardly surprising considering the large uncertainties surrounding the prediction of surface DMS concentrations. Two recent studies have incorporated different empirically derived DMS algorithms into coupled GCMs (Gunson *et al.,* 2006; Vallina *et al.,* 2007). In both cases the results suggested a negative feedback between DMS

production and climate, although regional variations were apparent, with a weak positive feedback observed at low latitudes (Gunson *et al.,* 2006). An interesting by-product of these studies is the exploration of how other feedbacks in the system interact with the DMS-climate feedback. For instance, Vallina *et al.* (2007) found that increased dust flux to the ocean and higher wind speeds in mid and low latitudes as a result of global warming would have an impact on primary production, and thus affect the production and flux of DMS to the atmosphere. However, these studies were not able to model the probable changes in species composition with global warming, and how those changes may affect DMS concentrations and the proposed feedback.

Cropp *et al.* (2007) developed a simple phytoplankton-DMS-cloud feedback model in order to test how the feedback might affect ecosystem stability. They found that when the model was run with the feedback, the ecosystem was more resilient to perturbations. This result addresses the question of why phytoplankton would evolve the ability to influence the properties of the atmosphere regulating the solar radiation dose. The stabilizing effects would, over the long term, favor ecosystems which generate them.

5. Conclusions:

There is no doubt that any changes in albedo over oceanic areas could have important climatic effects. Improved knowledge of the marine sulfur cycle would allow for more accurate quantification of sulfur fluxes to the atmosphere that drive the production of aerosols and possible subsequent changes to cloud cover. It is clear that the upper ocean ecosystem plays an important role in this process, and that our understanding of the cycling of sulfur by that ecosystem is limited. At present it is not possible to make any solid conclusions about the output of models attempting to represent climate feedbacks associated with the production of DMSP and DMS by marine ecosystems. Further questions relate to how the production of DMS might change with global warming if this warming results in shifts in ecosystem community structure. In that case, empirical relationships between DMS concentration and physical parameters may no longer hold. This highlights the importance of developing robust DMS ecosystem models which can be coupled to global ocean-atmosphere GCMs. However, this will only be made possible greater understanding of the processes which control DMSP, DMSO and DMS production. This will only be achieved by further field and laboratory experiments to constrain the production rates of these sulfur species under differing physical, chemical and biological conditions.

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Citation: Stefels, J., Steinke, M., Turner, S., Malin, G., Belviso, S. (2007). Environmental constraints on the production and removal of the climatically active gas dimethylsulphide (DMS) and implications for ecosystem modelling. Biogeochemistry, 83, pp245-275.

Figure 1. Schematic representation of the processes and pools involved in the marine biogeochemical cycling of DMSP and DMS. Dominant role of functional groups in the different processes is indicated by coloured ellipses: phytoplankton (green), zooplankton (blue), bacteria (red), abiotic factors (black). (Stefels *et al.*, 2007).

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Figure 2. Seawater sulfur cycle at the time series station during the PSI-3 experiment in the Pacific, 250 km off the Washington State coast. The concentrations represent average depth-integrated burdens in µmoles/m^2. The rates affecting these burdens are in µmoles/m^2/d. (Bates *et al.*, 1994).