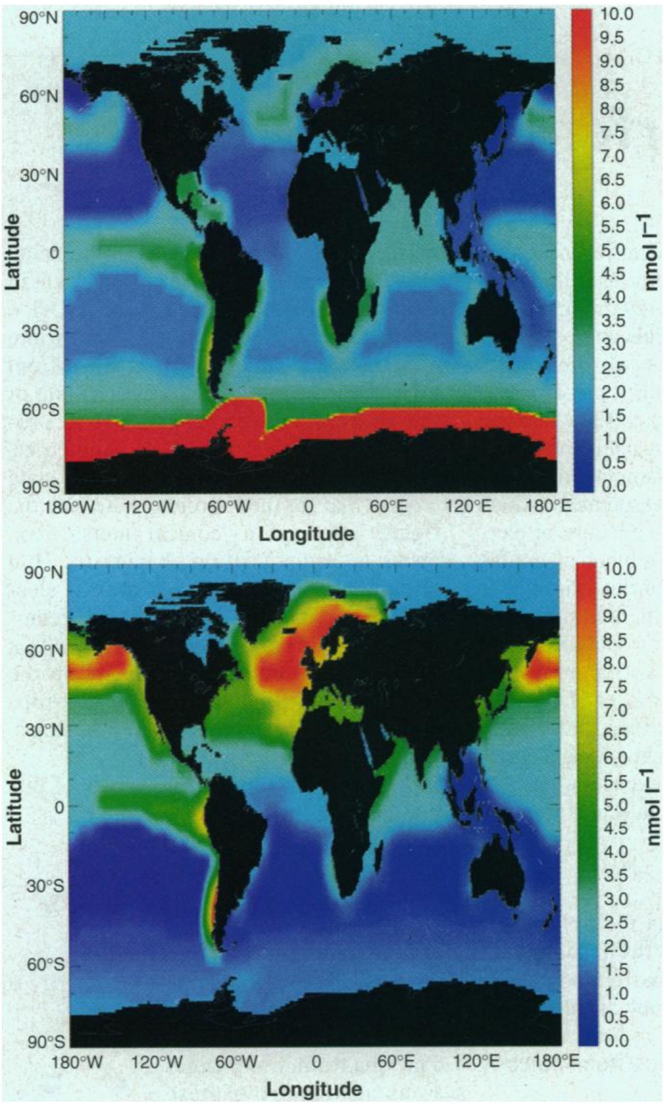
PERSPECTIVES: BIOGEOCHEMISTRY

Take the Shuttle–from Marine Algae to Atmospheric Chemistry

Peter Liss

Back in 1972, Jim Lovelock sailed on the research vessel *Shackleton* to measure dimethyl sulfide (DMS) in ocean waters as the ship traversed the Atlantic Ocean from Montevideo, Uruguay, to the United Kingdom. It was a cruise of opportunity, and the survey cost little, because the *Shackleton* was going north on its routine run after supplying British research bases in Antarctica. But the results were far from routine in their consequences. Lovelock and co-workers showed that DMS, produced by marine phytoplankton, was found in surface ocean waters throughout the Atlantic, although the concentrations were very low (*1*). It had been known for many years that the global budget of sulfur could not be balanced without a substantial flux of this element from the oceans to the atmosphere and thence to land. Before the *Shackleton* cruise, it had been assumed that hydrogen sulfide was the gas responsible for this transport, even though it had never been found in oxygenated surface ocean waters. Lovelock's cruise pointed instead to DMS as the species that could close Earth's sulfur cycle.

But why was this so important, and why is DMS still the focus of intense research? Once emitted from the sea, DMS is transformed in the atmosphere by free radicals (particularly hydroxyl and nitrate) to form a variety of products, most importantly sulfur dioxide and sulfate in the form of small particles. These products are acidic and are responsible for the natural acidity of atmospheric particles; man's activities in burning fossil fuels add further sulfur acidity to this natural process. In addition, the sulfate particles (natural and man-made) can alter the amount of radiation reaching Earth's surface both directly by scattering of solar energy and indirectly by acting as the nuclei on which cloud droplets form, thereby affecting the energy reflected back to space by clouds. This indirect effect could be a way in which the planet self-regulates its temperature (*2*), a concept on which the jury is still deliberating. Finally, removal of the DMS-derived sulfur from the air by rain and deposition of particles is an important source of this biologically important element for some terrestrial ecosystems. Thus, the environmental impact of DMS is clear. But why do marine plants produce it in the first place? One reason is that the precursor of DMS is an osmolyte that enables phytoplankton cells to survive in a saline medium like sea water. In addition, DMS from phytoplankton may act as a signaling compound to deter zooplankton from grazing them (*3*).



When the seasons change. A map of global sea surface DMS concentration (in nanomoles per liter) for January (**top panel**) and July (**bottom panel**) demonstrates the seasonal variability of DMS emissions at mid and high latitudes. In January, the highest values occur in the Southern Hemisphere, particularly in Antarctic waters and in upwelling areas off South America and Africa. In July, the pattern has flipped, with the highest concentrations in the Northern Hemisphere oceans.

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Many expeditions have collected information about DMS: They have mapped the distribution of DMS in the oceans, studied its production by marine organisms, calculated its flux to the atmosphere, and determined its effect after emission. A recently published paper attempts to bring together all the oceanic DMS data currently available (*4*). This prodigious effort by Kettle and his 31 coauthors summarizes and integrates the data from 134 expeditions, comprising in excess of 15,000 individual measurements. Concentration measurements are available for most ocean basins, with best coverage for the North Atlantic, North Pacific, and Southern oceans, whereas the Indian and southwest Pacific oceans have few data points. However, even in the best sampled areas the data are not sufficient to establish distribution changes at monthly or seasonal frequencies. Such detail is clearly necessary for a gas that is produced as a result of marine biological activity (*5*) and shows considerable seasonal variation in temperate and polar regions. Kettle *et al.* therefore have to perform complex extrapolations, interpolations, and iterations to draw up the global yearly average distribution and the seasonal and monthly patterns (see the figure).

The authors remark that there is a rough correspondence between areas of high DMS concentrations and the blooming of species of marine phyto-

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plankton that are strong DMS producers, such as coccolithophorids (*5*). However, attempts to relate the DMS concentration fields to parameters indicative of marine biological activity, such as chlorophyll concentration, plant nutrients, sea surface temperature, or clear sky irradiance, all fail to produce correlation coefficients high enough to be useful. This is a great pity because a significant relation between DMS concentration and, for example, chlorophyll (which is routinely measured by satellite) would provide a convenient route for establishing DMS concentrations at much finer time and space scales than are currently possible and would reduce the need for expensive seagoing measurements.

In the meantime, we have to focus on the processes that control formation of DMS and its release to seawater, for example, zooplankton grazing (*6*) and viral attack (*7*), coupled with modeling approaches (*8*) and additional field experiments in undersampled areas. Even if the concentration field was known with adequate spatial and seasonal coverage, however, it remains difficult to convert it into a flux distribution, because the rate of transfer of DMS from sea to air is uncertain to about a factor of two (*9*). Quantification of this sea-to-air flux is a vital prerequisite for assessing the environmental impact of DMS. Progress is most likely to come once a micrometeorological technique, such as eddy correlation or eddy accumulation, is developed that can directly measure DMS fluxes across the sea surface.

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PERSPECTIVES: CHEMICAL PHYSICS

Interfering with Water

David C. Clary

Molecular bonds can be broken by exciting them with laser light; detection of the energy of the product atoms and molecules reveals unprecedented detail about photodissociation mechanisms (*1, 2*). On page 1249 of this issue, Dixon *et al.* (*3*) use such techniques to show that two water photodissociation channels can mimic the two slits in Young's famous double-slit electronic interference measurement, which first demonstrated the wave nature of electrons. These remarkable molecular double slits show that even simple, ubiquitous molecules such as water still hold surprises.

Dissociation of water by sunlight occurs continually in Earth's atmosphere (*4*). Dixon *et al.*'s experiment takes a closer look at this process by exciting individual molecules of H_2O with light having a wavelength of 121.6 nm. The excitation leads to dissociation of the water molecules via

$$H_2O \rightarrow OH(N) + H \qquad (1)$$

producing OH radicals in their electronic ground state but with their rotational quantum states taking particular integer quantum numbers N. A sophisticated time-of-flight laser technique is used to detect the energy of the H atoms from which N can be inferred.

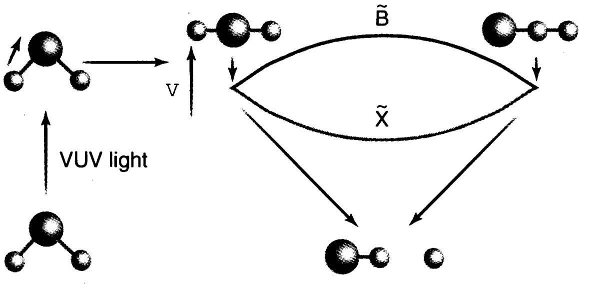
Excitation with light at 121.6 nm causes electrons in H_2O in the ground "$\tilde{X}$" electronic state to jump to antibonding orbitals, producing an electronically excited state labeled "$\tilde{B}$." In its ground electronic state, H_2O has a bent structure. If it stays bent in the $\tilde{B}$ state, dissociation to produce OH + H cannot occur because no appropriate dissociation channel can be reached from this conformation (*1*). However, if one of the H atoms moves around OH to produce linear H-O-H or O-H-H geometries, the potential energy curve for the $\tilde{B}$ state crosses that for the $\tilde{X}$ ground state (see the figure) (*5*). Such a "conical intersection" opens up a dissociation channel for H_2O to dissociate into OH and H in their electronic ground states. The change in geometry of H_2O from bent to linear leads to a considerable torque being placed on the OH molecules, which are therefore produced in highly excited rotational states, with $N = 45$ being favored (*3*).

A particularly interesting aspect of this dissociation mechanism is that two different linear geometries on the $\tilde{B}$ electronic state, H-O-H and O-H-H, can both lead to curve crossing and thus molecular dissociation, producing exactly the same OH(N) + H products (see the figure). The quantum wave functions arising from these two dissociation routes can interfere with each other to favor or disfavor the production of certain N states of OH. The experiment shows that there is a marked propensity for producing OH in odd N states for larger values of N (*3*).

To explain these results, Dixon *et al.* use a simple quantum mechanical model (*3*). The component of the molecular wave function that allows dissociation to a particular OH rotational state N is approximated as

$$\Psi_N = \psi_1 + m_N \psi_2 \qquad (2)$$

where ψ_1 and ψ_2 are wave functions associated with the linear H-O-H and O-H-H geometries, respectively, on the excited state B. The curve crossing onto the X state allows both ψ_1 and ψ_2 to describe dissociation to produce OH(N) + H. m_N represents the symmetry of the rotational wave function of OH with respect to the H-O-H or O-H-H geometries. It takes values of ±1 depending on whether the rotational state N is even or odd. From Eq. 2, two terms in the probability of producing OH in rotational state N are positive, but the third "interference" term is linear in m_N and can thus be positive or negative. m_N is determined by the parity of N, and



A molecular example of Young's double-slit interference experiment. The molecule is first excited from the ground ($\tilde{X}$) state to the excited ($\tilde{B}$) electronic state. One H atom then moves around OH, the bond length of which remains constant. The potential energy curves (*V*) for this H-atom motion are shown schematically for the $\tilde{B}$ and $\tilde{X}$ states. The two potential curves cross for linear H-O-H and O-H-H geometries, giving two gateways for dissociation into OH(*N*) + H. Red, oxygen; blue, hydrogen; VUV, vacuum ultraviolet.

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