A geophysiolgologist's thoughts on the natural sulphur cycle

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SUMMARY

The climate depends on the atmospheric abundance of sulphur aerosols at all levels up to the stratopause. Volcanoes, combustion and biological emissions all contribute and usually result in cooling. The history of this topic is lively and goes back at least to the eighteenth century with Benjamin Franklin's comments on the cooling effects of the sulphuric acid aerosol from the Icelandic volcano, Laki. Mitchell first drew attention to the potential cooling effects of combustion aerosols. Charlson and his colleagues proposed that emissions of dimethyl sulphide (DMS) from ocean algae might also be important. More recently, Lovelock & Kump drew attention to the decline of biological sulphur emissions with global warming and the possible consequence of a positive feedback on climate change. The geophysiological aspects, which arose from the Gaia hypothesis in the early 1970s, form an important part of the account that follows.

1. INTRODUCTION

In a way Sir Christopher Andrewes, the co-discoverer of the influenza virus, was responsible for the events that led to this meeting. He was the senior virologist at the National Institute for Medical Research (NIMR) during the 1940s and 1950s, and for some of this time was my supervisor. In addition to being an eminent virologist, he was also a keen amateur entomologist: a true member of that class of lean hyperactive naturalists who travel with a large butterfly net. He was ever alert for a new species of his favourite insect, the sawfly.

In the mid 1950s, a series of winter storms brought piles of seaweed onto the beaches of southern England. As they rotted, the heaps of weed became food for the larvae of a small fly. When summer came, the flies used up their supply of weed and came inland to seek other food. They invaded London in clouds and, remarkably, concentrated especially at dry cleaning establishments and laboratories. It seemed that they were interested in halogenated solvents. In my laboratory at the NIMR, I watched as they crawled over a bottle of chloroform, the stopper of which was not tightly closed. Being curious about these insects and their odd taste I called Sir Christopher Andrewes. He came at once and with his keen eye identified them as *Coelopa frigida*, and told me where they came from.

We wondered what was the natural compound that attracted these flies to the large algae. Could their liking for chloroform and trichlorethylene be a clue to their preference? Could it be that the fly's antennae included a biological version of the electron capture detector? We used a beach at Kimmeridge, in Dorset, as the site for our experiments. On each visit to the beach we took a set of empty jam jars, each with a small hole in the lid. The jars contained a small

quantity of candidate chemical whose attractiveness to the insects we tested. The substances chosen were those which were volatile and which had an affinity for free electrons: substances like chloroform, and other halogenated compounds, and also halogen-free electrophiles such as diethyl fumarate. A similar number of jars containing other organic compounds with no electron affinity, and empty jars, were used as controls. The jars were placed strategically along the upwind edges of the piles of rotting seaweed and left during the day. We came back in the afternoon, collected the jam jars, sealed them and counted the number of insects that had passed into each of them. We found them to be catholic in their taste for electron-attracting substances: almost any halocarbon, even DDT, and compounds like fufuraldehyde, were favoured over the neutral non-electron attaching substances.

We did not publish this research but it led me later, in the 1960s, to look at the volatile emissions from large algae that grew on the beach below a holiday cottage in south-western Ireland. The emission of dimethyl sulphide (DMS) by macro algae was discovered by Haas (1935). Challenger (1948) showed that dimethyl sulphonio propionate (DMSP) was its precursor. The Japanese scientist Ishida (1962) observed that the emission of DMS is restricted to species living in salt or brackish water, and that it was not emitted by freshwater algae. I was astonished to find that methyl iodide and a whole range of halogen compounds were also emitted by the large algae, although *Laminaria* were the richest source of these. Methyl iodide is toxic and carcinogenic, and quite unexpected outside the laboratory of an organic chemist.

This Discussion Meeting is concerned with the atmospheric chemistry of sulphur compounds emitted by algae and from urban industrial activity. In this historical account I justify the mention of halogen

emissions, whether from algae or from the urban industrial scene, because in nature and in the story itself, halogen and sulphur emissions are curiously linked.

2. TROPOSPHERIC SULPHATE AEROSOL

Summer holidays at Adrigole led serendipitously to another discovery linking atmospheric sulphur with halocarbons. On days when the air drifted from the east, from Europe it became hazy and the visibility range fell from over 50 miles to less than a mile. I wondered if we were seeing a polluted air mass that had travelled intact more than 1000 km to western Ireland.

In the summer of 1969, I took to Adrigole a gas chromatograph specifically designed to measure the presence of chlorofluorocarbons (CFCs) in the atmosphere, in particular CFC 11. My idea was that these compounds were uniquely the product of the urban industrial environment. Certainly they were not emissions from the natural environment. Indeed the CFCs are ideal tracers of the human industrial scene. When, in 1969, measurements were taken during one of these haze episodes, the abundance of the CFCs in the air rose three-fold from 50 to 150 ppt (parts per trillion), suggesting that the haze had its origin in urban industrial Europe (Lovelock 1972*b*). This suggestion was later confirmed by Cox *et al.* (1975) when members of the Atomic Energy Authority's Laboratories at Harwell joined me at Adrigole in the summer. We showed that what we saw was indeed smog, by the simultaneous monitoring in Ireland and England of the CFCs, ozone and turbidity. The turbid haze was a sulphate aerosol from combustion sources in Europe. I was also curious about the origins of the 50 ppt of CFCs in the cleaner Atlantic air. Were the CFCs travelling across from America? Or were they accumulating in the atmosphere of the world because there was no sink? One way to answer these questions would be to measure atmospheric abundance of the CFCs during a voyage between the hemispheres. I had at that time introduced the Gaia hypothesis as a short paper in *Atmospheric Environment* (Lovelock 1972*a*). The hypothesis proposed that the material conditions of the Earth were actively controlled by the biosphere, and I was seeking evidence that would confirm or deny it. The hypothesis predicted that there should be a biological mechanism for the return of elements like sulphur and iodine from the ocean to the land surfaces. These are nutritious elements, abundant in the ocean, but scarce and needed on the land. It seemed a good idea also to see if DMS and methyl iodide were emitted by the micro algae of the open ocean in sufficient quantities to satisfy the natural budget of these elements.

3. DMS AND THE NATURAL SULPHUR CYCLE

I was at that time a Visiting Professor at Reading University and with the help of Peter Fellgett, then

Professor of Cybernetics at Reading University, we applied for support from NERC (Natural Environment Research Council) and SERC (Science and Engineering Research Council). We asked for a few hundred pounds, to make measurements of DMS, methyl iodide and the CFCs aboard the *Shackleton*, which was due to make its voyage to Antarctica and back later the same year. The civil servants of both Councils thought the research worthwhile, but the academic peer reviewers condemned both proposals as pointless, and even suggested that they were bogus on the grounds that there was no way to measure CFCs at the ppt level. The conventional wisdom at the time followed the work of Conway (1942). It proposed that sulphur was transported from the sea to the land by the sea salt aerosol, and by emissions of hydrogen sulphide from the ocean surface. Proposing DMS as the sulphur carrier was regarded by the reviewers as an extravagant whim. An advantage of doing research independently is that the approval of the academic peer review is not needed. The lack of funding was inconvenient, but no deterrent. My first wife, Helen, willingly donated some of our housekeeping money to pay for the research.

The *Shackleton* was a very small ship, so small that when I went to board it in November 1971, I had great difficulty in finding it at the docks at Barry in south Wales. The mast and superstructure of the ship were below the edge of the dock, and it was necessary to look over the side of the dock to see the small vessel on which I was to travel all the way to the Southern Hemisphere. Smallness is no disadvantage for ocean research. On a small ship one is closer to the sea, and small ships are far less contaminated than some of the floating palaces of ocean research. The least source of contamination on a ship makes measurement at the ppt level difficult or impossible.

There was no method then for directly analysing DMS in the air. I was obliged to restrict measurements to the abundance of DMS in the waters of the ocean surface. The ship's Nissan bottles could not be used because the rubber gaskets used to seal them were too likely to be a source of contamination by sulphur compounds. The ship's engineer offered to modify the seals of the bottles so that no gasket was needed. While waiting for this to be done, I took advantage of an offer from the ship's galley to use a spare aluminium teapot as a water sampler, and for a time this served as the surface water collector. The DMS in the seawater samples was extracted into a hydrocarbon solvent using a separating funnel. I had found earlier that there was little or no loss of DMS from the hydrocarbon solutions kept cold and in the dark for periods as long as a year. The solvent samples were stored in the ship's refrigerator in tightly sealed vessels and analysed after the return of the vessel to the UK. Here the DMS was stripped from the solvent by a stream of nitrogen and collected in a cold trap at -180°C . The trapped sample was analysed by gas chromatography using a flame photometric detector. This was not an ideal method of analysis but at that time no other procedure would have been possible with the minuscule funding then available. Before the publication of this research (Lovelock *et al.* 1973), I received a letter from R. A.

Rasmussen who stated that he had found copious emissions of DMS from oak leaves. This was rather disconcerting for my view of sulphur transport, which saw DMS coming from the ocean to the land not vice versa. Even so I felt obliged to invite Rasmussen to be a co-author and to include his data. It was a relief to hear from him later that he had been mistaken and that the emissions from the oak leaves were of isoprene, not DMS.

The CFC measurements made daily aboard the *Shackleton* have a historical interest as the first global measurements of CFCs in the atmosphere, and they provided the base data from which Molina and Rowland (1974) developed their theory of ozone depletion and warned that the accumulation of these gases in the atmosphere represented a hazard to future generations. So polarized were the protagonists for and against the theory that there was a sort of ozone war. Truth, as always in war, was the first casualty. An example is in the first report of the US National Academy of Sciences on ozone depletion, 1976. Here it is stated that the CFC measurements of the *Shackleton* voyage were probably unreliable. This conclusion did not come from an enquiry into the method of analysis itself. It came because the observations did not fit the predictions of their theoretical models. I am glad to have this opportunity to state that, although made with simple apparatus, I now know that the *Shackleton* CFC data were accurate to about 5% (Rasmussen & Lovelock 1983); it was the early and incomplete versions of the model that were wrong.

Liss & Slater (1974) used the *Shackleton* data to estimate the flux of DMS and halocarbons from the sea to the air and vice versa. Later the German scientist Andreae (1990) made a series of careful and accurate measurements of the DMS abundance in both the air and the seawater over many parts of the world, and indeed most of our knowledge of the distribution of this gas now is thanks to this careful research. The search for the abundance of DMS on a global scale was initially inspired by geophysiological reasoning. This predicted the self-regulation of the sulphur and iodine cycles by some process involving the biota. This was not a popular line of argument, and it was strongly resisted by Neo-Darwinist biologists who saw it as anti-Darwinian. Caldiera (1988) argued that the evolution of DMS production by algae cannot be explained by the effects of this compound on the external environment of individual algae. Any beneficial effect to the individual's fitness would be far outweighed by the cost of DMS production. Much more likely, the evolution of DMS arose, as shown by Vairavamurthy *et al.* (1985), because of the need of individual organisms to regulate their internal osmotic pressure. They do so by synthesizing DMSP, the precursor of DMS. The need for osmotic regulation in the hypertonic ocean is great and the benefit outweighs the cost. As we shall see, this argument, although consistent in a Neo-Darwinian context does not contradict the emergence of larger scale self-regulation in the sulphur cycle. Algal blooms do emit DMS, and this does alter their environment, and it does so in ways that can feed back on individual algal growth rates.

4. ALGAL DMS, CCN, CLOUDS AND CLIMATE

Happily, interest in this natural sulphur compound was not stopped by doctrinal arguments of this kind. In 1986, I was invited to spend a month at the University of Washington in Seattle. While I was there I spent some time discussing with my host, Professor Charlson, the significance of cloud condensation nuclei (CCN) in the atmosphere. These are, for the most part, especially over the open oceans, tiny droplets of sulphuric acid and its ammonium salts. I asked him why was he so interested in them, and his reply astonished me. Without the CCN, he said, there could be no clouds. Of course I knew that small droplets of pure water will always have a higher equilibrium vapour pressure than larger droplets, but never had I put together in my mind the obvious fact that natural selection among cloud droplets would leave only the larger ones, which would rapidly fall out from the air as rain. In other words, without the nuclei there could be no clouds as we know them. At first I protested: surely there are always enough sea salt and other water-soluble particles floating in the atmosphere to act as nuclei? Charlson explained to me that for the greater part of the Earth's surface, that is to say over the open oceans, the numbers of sea salt particles are too small to account for the abundance of CCNs. There were a sufficient number of droplets of sulphuric acid and ammonium bisulphate, but there was no way that these could have come from either industrial or volcanic sources. Where did they come from? Such particles cannot travel far over the ocean, which means that they must be produced locally. It was one of those happy moments in science when truth suddenly dawns. The atmospheric oxidation of DMS could be the answer. We moved on to discuss these ideas with Andreae, who knew much more about the abundance of DMS in the atmosphere than we did. Our conclusions were published (Charlson *et al.* 1987).

It is worth digressing to add that Liss & Galloway (1993) have recently found that algal blooms emit ammonia and methylamines in quantities comparable with their DMS emissions, and in a manner which suggests that these emissions of sulphur and nitrogen compounds are coupled. It is tempting to think that these basic amines could, by forming salts with the sulphur acids, lessen the volatility of the nucleating particles and so increase the ease of formation of CCN.

As a geophysiological I had been seeking mechanisms for climate control. The pump down of carbon dioxide from the atmosphere by biologically accelerated rock weathering was one possible mechanism. I wondered if the association between algae in the ocean, DMS, CCN, clouds and climate could provide another. As the evidence came in it did not look promising. Far from the expected negative feedback characteristic of strong self-regulation, the cloud-algal-climate system appeared to be in positive feedback. The warmer it was, the less the algae.

Antarctic ice core measurements (Barnola *et al.* 1987; Genthon 1987; Legrand *et al.* 1992) show that the annual deposition of CO₂ falls and that of non-sea

salt sulphate (Nsss) and methane sulphonic acid (MSA) rise as we go back in time into the last glaciation. Low CO₂ suggests less greenhouse warming, and high sulphur deposition, more cooling by clouds. The rise of CO₂ and the fall of MSA and Nsss as the Earth moved out of glaciation into the present warmer period indicates a climate system in positive feedback. M. Legrand in his paper at this Discussion Meeting reports a five-fold decline in the deposition of MSA on the Greenland ice cap. Over the same 40-year period, Roemmich & McGowan (1995) observed a five-fold decline in the population of zooplankton in the north-west Pacific. If these two observations are linked, they further confirm this positive feedback. Just the opposite of what might be expected of Gaia. Regulation implies negative feedback on change, not its amplification.

I have been doing science long enough to know that a result opposite to that expected is not such bad news as a result showing no effect at all. Positive feedback could come from a system that was in failure, not from no system at all. Consider a fever; its onset is marked by positive feedback in all the systems normally used for temperature regulation. Could it be that the Earth, during the interglacial, is in a temporary state of failure, like an animal with a fever?

To look into this further we made a simple geophysiological model (Lovelock & Kump 1994). We started by assuming that marine algae affect climate primarily through their emission of DMS, which appears to be linked with cloud albedo. We also assumed that both algae and land plants affect climate through the fixation of atmospheric CO₂.

When examined under laboratory conditions, where nutrients are not limited, most plants and algae increase their growth rate exponentially up to a maximum temperature of around 30 °C. In the natural world more specific limitations set in at lower temperatures. With algae the upper layers of the sea tend to stratify at sea surface temperatures above 8 °C. This denies the algae the nutrients in the cooler, richer water below. On land, warmer temperatures are associated with higher evaporation rates and lower relative humidities, both of which limit plant growth at temperatures above about 18 °C. Model calculations, based on these constraints to growth, suggest that at the start of the springtime bloom the temperature is held almost constant as the solar flux rises. When the bloom peaks, feedback lessens, and as the bloom fades, feedback turns positive. During the early stage, the more rapid the increase of algal area cover with temperature, the better the regulation. If the growth of algae is linked directly to an albedo increase and to CO₂ removal, then there will be thermostasis, but only at relatively low temperatures.

When this model is run in a warming world, it shows that temperature is regulated well on the cold side of optimal until the sea surface temperatures rise to the level at which most of the ocean is stratified in a thermocline. There is then a sudden rise in temperature to a new stable warmer state in which regulation is by land plants only.

5. CONCLUSIONS

Satellite views of the Earth, taken to show chlorophyll density in the oceans and on the land surfaces, reveal a planet where little of the surface supports dense growth. The greater part of the 70% of the Earth's surface that is ocean supports only meagre algal growth. Dense growth is limited to the cooler polar and near polar temperate waters, and to areas of upwelling at the continental edges. On land also plant growth is denied by desert conditions in much of the tropical and warm temperate regions. Where there is growth, as in the humid tropical forests, it is often sensitive to perturbation and does not readily return if destroyed. Roemmich & McGowan (1995) reported an 80% decline in the zooplankton in the waters off southern California. This they attribute to a 1.5 °C warming of the surface waters and intensified stratification. They comment that if this is not just a local effect the global biological impacts could be devastating. Significantly, they made no comment or reference to the possible effects of their observations on global warming. Such is the stratification of science itself.

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Discussion

R. A. Cox (*Department of Chemistry, University of Cambridge, UK*). The temperature dependence of MSA in the ice cores

may reflect both changes in biological activity in the production of DMS (from which DMS is derived by atmospheric oxidation) and also temperature effects on the chemical pathways in DMS oxidation. These need to be quantified if we are to understand the significance of the signature.

J. E. LOVELOCK. I agree with Dr Cox that the abundance of MSA in the ice core samples may depend on atmospheric chemistry as well as on the biological production rate. However, as pointed out by Professor Liss (see next comment), there is a similar increase in deposition of non-sea salt sulphate during glacial periods. Taken together, the increase of MSA and NSS sulphur deposition as the climate cools support the argument that the glacial times were the more productive.

P. S. LISS (*School of Environmental Sciences, University of East Anglia, UK*). A brief comment on the exchange between Professor Lovelock and Dr Cox. The elevated levels of MSA in the glacial period are unlikely to be due to a change in the branching ratio alone, since non sea-salt sulphate shows a similar elevation in concentration in glacial times. A more likely explanation is that biological activity and production of DMS in the oceans were greater in glacial times, and this is the main determinant of the elevated MSA concentration in glacial ice cores.

P. BORRELL (*EUROTRAC, Garmisch-Partenkirchen*). Your comments on the last slide, which showed the global algal distribution, suggested that the numbers had worsened considerably due to anthropogenic influences. Is there in fact any strong evidence that things have changed considerably over the last 50 to 100 years, say, in the remote oceans or elsewhere?

J. E. LOVELOCK. Algal ecosystems do appear to have been more vigorous in glacial times than in the present interglacial. The evidence for this comes from the increased deposition of NSS sulphur and MSA on the ice caps during the glacial period. Roemmich & McGowan, in 1995, reported that plankton in the waters of the Pacific off California had declined by 80% in the past 40 years, and attributed the decline to the intensified stratification consequent upon an observed 1.5 °C increase in sea surface temperature.