Atmospheric sulphur and climate—what have we learned?

R. A. COX

Centre for Atmospheric Science, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

1. BACKGROUND TO THE DISCUSSION MEETING

Global climate change is one of the foremost environmental issues as we enter the twenty-first century. Public perception of the issue centres around the global warming caused by the increases in greenhouse gases, and in particular CO_2 , released primarily as a result of the combustion of fossil fuels. The effect of changes of CO_2 on the temperature of the Earth was first described by S. Arrhenius just 100 years ago (Arrhenius 1896). Although the presence of sulphur in the atmosphere and its significance for precipitation acidity was known to nineteenth century scientists (Smith 1872), ideas on the global cycles of atmospheric sulphur only developed about 40 years ago through the work of Ericksson (1959, 1960) who described the global geochemical cycle of sulphur, and of Junge and co-workers (1961) who first described the sulphate aerosol layer in the stratosphere. Work on atmospheric sulphur greatly

expanded at this time due to concerns about pollution from the emissions of SO_2 as a byproduct from fossil fuel combustion. Terrestrial sources of H_2S were thought to be the main natural sources of atmospheric sulphur until the publication 25 years ago of James Lovelock's paper (Lovelock *et al.* 1972), where it was proposed that dimethyl sulphide (DMS) was the main natural carrier of sulphur into the atmosphere and that biota in the world's oceans were the source. Before that time most of the chemical literature on DMS related to its unwanted presence in the brewing of beer, but atmospheric chemists quickly rose to the challenge of learning how to measure it in air and sea, its abundance in the environment and its chemical reactions.

Meteorologists had also had a long interest in atmospheric sulphate particles on account of their known role as cloud condensation nuclei (CCN); their influence on visibility in the atmosphere was also a subject of interest in the context of atmospheric

Figure 1. The marine sulphur-cloud albedo-climate linkage hypothesis. Biological activity in the ocean leads to the production of volatile dimethyl sulphide (DMS) which is transferred to the atmosphere where it is oxidized to low volatility products, methanesulphonic acid (MSA) and sulphuric acid. These products create extra cloud condensation nuclei (CCN) which can increase the albedo of clouds, reflecting more sunlight to space. This acts to cool the climate.

pollution. The tie-up between complex atmospheric radiative properties and climate change was beginning to be a focus of interest in the mid 1980s when the two avenues of scientific interest—biogeochemistry of sulphur and radiative forcing of climate—were brought together in the paper of Charlson *et al.* (1987) which stimulated the scientific work that has been the subject of this Discussion Meeting.

The essential hypothesis of the Charlson *et al.* (1987) paper is illustrated in figure 1. The formation of clouds in the atmosphere requires a continued supply of cloud condensation nuclei, small particles of hygroscopic material on which liquid water can condense. A major source of such particles in the unpolluted atmosphere is oxidation of sulphur-containing gases to low volatility products such as H_2SO_4 , methane sulphonc acid (MSA) and sulphates, which can nucleate and grow into CCN.

The reflectivity of clouds for sunlight (the albedo) depends on the number density of cloud droplets. If a larger number of CCN are present when the cloud condenses, there will be more cloud particles and the cloud will reflect more energy to space, hence cooling the Earth's surface. In this way the sulphur gas emissions can influence climate and, since DMS production is controlled by biological activity in the ocean, there is a link and potential feedback between natural ecosystems and the physical climate.

The Discussion Meeting was organized in order to take stock of our knowledge of the atmospheric chemistry of sulphur, its relationship to cloud formation and properties and to climate forcing, especially with regard to the state of understanding of the various components and links involving atmospheric chemistry of sulphur and climate. The Discussion focused on four main areas: the sources, distribution and chemical transportation of sulphur compounds; the formation of aerosols and their direct and indirect (cloud) radiative properties; modelling of climate forcing by sulphate aerosols and clouds; and finally a historical perspective of atmospheric sulphur in past climates was provided through the ice core record and considered in the light of current knowledge from a geophysiological perspective. The position concerning current knowledge and future directions in each of these areas is summarized below.

2. SOURCES, DISTRIBUTION AND TRANSFORMATION OF ATMOSPHERIC SULPHUR

Studies of the sources and distribution of the sulphur compounds has demonstrated closure of the atmospheric budget of sulphur with approximately two-thirds of emissions from man-made sources, principally in the Northern Hemisphere, and the balance from natural emissions of DMS, primarily from regions of high biological productivity in the world's oceans. The fraction of SO_2 emitted from fossil fuel combustion that is oxidized to sulphate in cloud and rain droplets appears to have been underestimated in the past. The

oxidation occurs mainly in the boundary layer and leads to a mean atmospheric residence time of 2.3 days for SO_2 .

The main source of DMS is driven by the 'black box' of biochemical processes occurring in the surface layers of the ocean. The biochemistry of DMS production through its precursor, dimethyl sulphoniopropionate, which is synthesized by phytoplankton, has been investigated in detail. Although the causes of variability in its production rate have been unravelled, there are still difficulties in determining the mean global flux of DMS to the atmosphere because of the spatial and temporal variation in its production and uncertainties in the sea-air exchange velocity.

Stratospheric aerosols in the Junge layer, at 15–25 km altitude, are composed predominantly of sulphuric acid particles, which originate from two sources. First, a low background concentration of stratospheric sulphate aerosol of the order of $0.05 \text{ particles cm}^{-3}$ of radius between 0.1 and 1.0 μm , is maintained from the photochemical oxidation of carbonyl sulphide, which is present throughout the lower atmosphere at a constant concentration of approximately 0.5 ppb. Secondly, injection from large volcanic eruptions of sulphur gases, mainly SO_2 , into the stratosphere causes huge perturbations in the amount of stratospheric sulphate. These perturbations lead to well documented short-term (1–3 years) influences on global climate.

The oxidation of DMS in the troposphere constitutes a second 'black box' in atmospheric sulphur chemistry. It turns out that the mechanism of DMS oxidation is even more complex than most other volatile organic compounds investigated in atmospheric chemistry studies. Of the several possible oxidizing species (OH , HO_2 , NO_3 , Cl , BrO) it now seems that OH is the dominant oxidizing agent. The mechanism is complicated by the existence of two different initial reactions of OH with DMS, one of addition and one of H abstraction, operating in parallel at ambient temperatures.

A sequence of reactions involving the consequent sulphur-containing radicals leads to the formation of at least four sulphur-containing products including: SO_2 , SO_3 , $\text{CH}_3\text{SO}_3\text{H}$ (MSA) and CH_3SOCH_3 (DMSO). Small yields of OCS have also been reported. The dependence of the product yields on temperature and nitrogen oxides concentration arises from a competition between unimolecular and bimolecular gas phase reactions of the radicals of the type CH_3SO_x ; low temperatures and NO_x presence favouring the bimolecular reactions, leading ultimately to formation of MSA.

Field observations have provided a coherent picture of the geographical distribution as well as the diurnal and seasonal variations in the concentrations of DMS and its unique oxidation products, DMSO and MSA. However, even in the Southern Hemisphere where the signatures are clearest, because continental and man-made influences on the atmospheric chemistry are least, it has not been possible to establish quantitatively the relative yields of the different sulphur-bearing products from DMS oxidation, under field conditions.

3. FORMATION AND LIGHT SCATTERING PROPERTIES OF SULPHATE AEROSOLS

New field measurements of key reacting species (OH , SO_2 , H_2SO_4 , fine particles) have provided direct confirmation and evaluation of the rate determining step in the gas-phase oxidation of sulphur dioxide to sulphuric acid particles in continental air. The mechanisms of the important particle formation processes are emerging from this work. It appears that in the atmospheric boundary layer at least, classical theory of heteromolecular nucleation of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ particles does not describe well the rate and concentration dependence of new particle evolution. The data point to a role for ammonia (and possibly organic amines) in the nucleation of particles.

Atmospheric measurements of sulphur compounds, oxidation products, and cloud condensation nuclei have revealed strong contrasts between the Northern and Southern Hemispheres. In marine air in the Southern Hemisphere mid latitudes, a clear correlation can be seen between concentrations of DMS and the number of CCN (see paper by Ayers *et al.*, figure 15) and also between the number of CCN and cloud optical depth (see paper by Ayers *et al.*, figure 17). Studies of the Southern Hemisphere marine aerosols have provided detailed information verifying current ideas about the factors controlling the evolution and growth of the marine aerosol through microphysical/chemical interactions. The observations indicate that there is an additional wintertime source of non-sea salt sulphate which is potentially active in CCN production. It has also been shown by in-cloud studies in northern England that existing particles can be modified by chemical conversion.

Although the Southern Hemisphere data do indicate a relationship between cloud optical depth and CCN, the relationship between these properties and cloud-top albedo is more complex and other factors appear to be involved. Nevertheless there are qualitative indications of a link between cloud reflectivity (brightness) as viewed from space, and chemical composition e.g. 'ship tracks', and images of polluted air masses over the eastern north Atlantic.

4. MODELLING OF CLIMATE FORCING BY AEROSOLS AND CLOUDS

Modelling of climate processes and the evolution of climate in general circulation models (GCMs) has been an active research areas in recent years. Radiation schemes describing the forcing of climate through the emission, absorption and scattering of atmospheric radiation are now being developed to a level of increasing sophistication. Work on forcing due to sulphate aerosols, either direct forcing by the aerosol or indirect through modification of cloud properties, has only just started. Both effects seem to be potentially significant in terms of global temperature and climate.

The direct effect on global temperatures of the injection of volcanic sulphate aerosol into the stratosphere following the eruption of Mount Pinatubo in June 1991 has been clearly observed from measure-

ments and this was well predicted by a climate model (see paper by Hansen). The effect on climate due to forcing by tropospheric sulphate aerosols is less clear. A comparison of the evolution of global temperatures over the past 150 years with GCM predictions based on known changes in greenhouse gas concentrations and fossil fuel sulphur emissions indicates that the direct effect of sulphate aerosols may have had a significant effect. However, since in reality the sulphate is mixed with other components of the atmospheric aerosol, some of which absorb as well as scatter radiation, there are suggestions that the direct effect of aerosols may be smaller than has been assumed.

Studies of the indirect effect of sulphate aerosols have mostly concentrated on low altitude liquid water clouds; these studies are in their infancy. Nevertheless, GCM calculations of the climate forcing which have used various relationships between sulphate mass and cloud droplet number concentration indicating that the cooling effect may be significant (see paper by Jones & Slingo) only addressed indirect effects in liquid water clouds (near surface). As with the direct effect of aerosols, the way in which the sulphate combines with the other components of the aerosol population is a significant issue.

5. PAST AND FUTURE PERSPECTIVES

Clues as to the role of sulphate aerosols in the atmosphere have been sought in the records of past climate, especially in the ice cores, where MSA and non-sea salt sulphate ions (SO_4) have been measured along with greenhouse gases and climate indicators. In modern times there is a decreasing trend in MSA in the Antarctic but no trend is detectable in the SO_4 . There are indications that MSA levels have been influenced by the El Niño Southern Oscillation in modern times.

In the ice ages both SO_4 and MSA in Antarctica increased during the cold climate. The record of sulphate and other electrolytes in the Greenland ice show that these species are dominated by transport from the continents. Overall there is clear evidence for changes in the past which, although not inconsistent with a link between sulphate and climate, show that many complex factors influence the signatures of the physical and chemical state of the atmosphere.

Finally, the question of the role of the natural atmospheric sulphur cycle and its link to cloud radiative properties as an example of a coupled geophysiological system contributing to the regulation of the Earth's temperature was addressed. The apparent decline in biological sulphur emissions since the ice age, and even in modern times as the Earth has warmed up, would be consistent with a possible positive feedback on climate change. It is suggested that positive feedback is a manifestation of a system in failure. In the warm Earth of today, the natural sulphur cycle plays little role in homeostasis, but a simple model shows that in the glacial period, when the conditions of surface temperatures and nutrient supply are on the cold side of optimum, regulation can occur.

It was clear from the meeting that much progress has been made in the understanding of the processes

involved in this atmospheric chemistry/climate problem. Moreover, from what we have learnt it appears that the world-wide distribution of atmospheric sulphur is such that significant influences on atmospheric radiative transfer are possible, and that the basic idea of a coupling between biological systems and climate via atmospheric chemistry and clouds seems to be robust. It has been found that the processes involved are even more complex than was at first suggested by Charlson *et al.* in their 1987 paper, and this complexity is a property of all aspects of the problem.

The work discussed at this meeting represents the exciting interdisciplinary scientific activity which is needed to tackle the challenges of Earth system science today. Methodologies range from simple investigative studies such as described by J. Lovelock and G. Ayers, to large team efforts which are required, for example, in major field measurement campaigns, ice coring or satellite remote sensing missions. The modelling studies described by Lelieveld, Jones & Slingo, and Hansen demonstrate the capability to conduct detailed simulation of climate and atmospheric chemistry. Such experiments are only possible through large investment in computers and the development of sophisticated numerical models. The advancement of our knowledge of the chemistry of sulphur and its physicochemical behaviour in the atmosphere has been made possible by the ingenious development of sophisticated instru-

ments which provide exquisite sensitivity and selectivity for measurement of the chemical species and their physical properties, such as described by F. Eisele. The momentum of the developments in methodology does not seem to be abating and we can therefore look forward to even better capability for testing ideas and taking forward scientific knowledge in this area of atmospheric chemistry in the future.

REFERENCES

- Arrhenius, S. 1896 On the influence of carbonic acid in the air upon the temperature of the ground. *Phil. Mag. S.* **41**, 237–276.
- Charlson R. J., Lovelock J. E., Andreae, M. O. & Warren, S. G. 1987 Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature, Lond.* **326**, 655–661.
- Ericksson, E. 1959 The yearly circulations of chloride and sulphur in nature: meteorological, geochemical and pedalogical implications. I. *Tellus* **11**, 375–403.
- Ericksson, E. 1960 The yearly circulations of chloride and sulphur in nature: meteorological, geochemical and pedalogical implications. II. *Tellus* **12**, 63–109.
- Junge, C. E., Chagnon, C. W. & Manson, J. E. 1961 A world-wide aerosol layer. *Science*, **133**, 1478.
- Lovelock, J. E., Maggs, R. J. & Rasmussen, R. A. 1972 Atmospheric dimethyl sulphide and the natural sulphur cycle. *Nature, Lond.* **237**, 452–453.
- Smith, R. A. 1872 *Air and rain. The beginnings of a chemical climatology*. London, Longmans, Green and Co. 600 pp.