BIOGENIC SULPHUR IN THE ATMOSPHERE

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ABSTRACT

The importance of biogenic sulphur gas emission to the atmosphere has been widely recognised. The most important of these gases are dimethyl sulphide (DMS), hydrogen sulphide (H_2S), carbon disulphide (CS_2) and carbonyl sulphide (COS), in order of decreasing global emission. At present, much research is aimed at determining the emission rate, distribution and chemistry of these gases, so that more accurate data for atmospheric models can be obtained. These gases have important implications for global warming and climate change, as well as for acid rain predictions. An important theory currently receiving much attention is the DMS-Cloud-Climate hypothesis, which links biogenic sulphur emission with the regulation of climate.

Some evidence has been presented in support of this theory, but conclusive proof has yet to be obtained. It seems that the number of variables influencing climate has been seriously underestimated in the past. It follows that if future climatic change is to be accurately predicted, the models employed will be extremely complex.

1. INTRODUCTION

Sulphur gas emission to the atmosphere from biological sources is currently receiving much attention. This biogenic sulphur may be critical in regulating Earth's climate, and has raised a number of issues for investigation and debate. This article constitutes a critical review of selected papers pertaining to biogenic sulphur in the atmosphere. A scan of relevant literature, dating from 1990 to the present was conducted, and two key papers were identified.

The article of Möller (1984) was an attempt to bring various estimates of biogenic sulphur fluxes into a coherent whole, and seemed to be referred to frequently. More recent reviews of this kind have been conducted but were unavailable at time of writing. Charlson, Lovelock, Andreae and Warren (1987) were the proponents of the DMS-Cloud-Climate hypothesis, which has sparked intensive research and debate and may be the key to understanding current climatic change.

This article will focus on the emission and fate of biogenic sulphur gases in the atmosphere, and will include discussion of the DMS-Cloud-Climate hypothesis in the light of more recent research efforts.

2. BIOGENIC SULPHUR GASES

Möller (1984) attempted to critically review global natural sulphur emission as reported by previous authors, and conducted his own modelling experiment based on assumptions he considered to be important (table 1). In a more recent paper, Hofmann *et al.* (1992), assessed literature dating from 1986 to 1990, and reported that natural fluxes of sulphur compounds amount to 38 to 89 Tg S y^{-1}. Thus although the estimated range of global sulphur emission has narrowed somewhat since Möller's paper of 1984, further refinement may still be necessary to improve the accuracy of atmospheric model predictions.

For the purpose of this article, however, the values presented by Möller (1984) will suffice to give an impression of the size of the fluxes involved, these being the subject of debate, although some consensus has been reached. The main gases to be considered are H_2S, COS, DMS and CS_2. Other sulphur gases are also present in the atmosphere, but at concentrations which are minor or negligible. Although methane sulphonic acid (MSA), a breakdown product of DMS, is not a direct product of biological metabolism, it will be discussed briefly, since it may have a role in determining natural rain water acidity.

Table 1: Biogenic emission of sulphur compounds in Tg S y^{-1} (After Möller, 1984)

SPECIES	LAND	SEA	GLOBAL	GLOBAL [Möller's calculations (1984)]
H_2S	0.1 - 5	0 - 48	0.1 - 66	19 - 38
DMS	0.7 - 5	2.2 -2.7	3 - 32	>15
CS_2	-	-	0.2 - 5	3.5 - 14
COS	-	-	0.1 - 2.5	1 - 1.7
TOTAL	1 - 60	2 - 75	3 - 105	24 - >70

2.1 Carbonyl Sulphide (COS)

Carbonyl sulphide (COS) makes up a small fraction of total biogenic sulphur emissions, but may nevertheless have an important role in the global sulphur cycle (Brown & Bell, 1986). Work conducted by Khalil and Rasmussen (1984) is often referred to for estimation of global COS fluxes (table 2).

Non-biogenic COS sources include volcanic emission, biomass burning, industry, photooxidation of organic sulphur compounds arising in the oceans, and the oxidation of CS_2, by OH radicals. Sources of biogenic COS include oceans, soils and marshes, where it is released as a result of microbial decomposition of organic material (Bartell *et al.*, 1993).

It has recently been proposed that the importance of COS in the marine environment is negligible, and more emphasis should be placed on emissions from soils and wetlands (Harrison *et al.*, 1992). This is interesting, because the results of Khalil and Rasmussen (1984), which imply roughly *equal* contributions of sea and land to global COS, are still widely accepted. Perhaps a revision of these fluxes is overdue.

The atmospheric residence time of COS, calculated by Khalil and Rasmussen (1984) also seems to be widely accepted. They give a value of 2 years, but Möller (1984) reported residence times of between 6 months and 7 years. Because of its extended lifetime and low reactivity in the troposphere, COS is the predominant sulphur gas in the remote troposphere, with an average concentration of 500 ppt (Rinsland *et al.*, 1992).

Table 2: Global COS estimates in Tg y^{-1} (adapted from Khalil and Rasmussen, 1984).

SOURCES	
Oceans	0.3 - 0.9
Soils	0.2 - 0.6
Volcanoes	0.01 - 0.05
Marshes	0.01 - 0.06
Biomass burning	0.1 - 0.5
Industry	0.05 - 0.45
CS_2 Oxidation	0 - 2
GLOBAL	3.8 - 5
SINKS	
Oxidation	< = 1.7
Unknown	< = 3.3

Removal of COS is effected by photolysis, reaction with O atoms and oxidation by OH radicals (Brown & Bell), 1986). These reactions remove roughly 50% of COS (Bartell *et al.*, 1993), the remainder possible being taken up by plant biomass, although conclusive proof of the latter is lacking. In the lower stratosphere, COS is dissociated mainly by solar UV radiation, to form sulphate. This contributes to the stratospheric sulphate aerosol layer, occurring between altitudes of 18 and 22 km (Rinsland *et al.*, 1992). In this way, COS could have an important influence on Earth's radiation balance and climate (Berresheim & Vulcan, 1992). Perhaps it is time to conduct more intensive research into source apportionment for COS, especially with respect to the biosphere, and determine the magnitude of its contribution to the stratospheric sulphate layer.

Brown and Bell (1986) suggested that vegetation may be the largest sink for COS on a global scale, with uptake of COS mimicking that of CO_2 during carbon fixation in photosynthesis. They estimated this to be in the order of 2 to 5 Tg Sy^{-1}, effectively naming the 'unknown' factor identified by Khalil and Rasmussen (1984) (see table 2). Much effort is currently being exerted to verify this sink, with interesting results.

In their work on sulphur gas emissions from salt marshes, Morrison and Hines (1990) were unable to decided whether these areas serve as sources or sinks of COS. It was evident, however, that emissions were affected by plant species distribution. Studies in which no evidence of a net sink of COS was observed include those of Berresheim and Vulcan (1992), and Bingemer *et al.* (1992). Bartell *et al.* (1993), however, did note a correlation between plant photosynthetic activity and COS deposition in wet meadow vegetation. Berresheim and Vulcan (1992) speculated on the possibility of plants switching between uptake and release of COS in response to environmental stresses. It seems that there is a need for more research into the metabolism of COS, CS_2 and other S-gases in plants, before this hypothesis can be validated.

2.2 Carbon Disulphide (CS_2)

Plant and soil systems are significant sources of CS_2, contributing 0.2 to 14 Tg S y^{-1} to the global sulphur cycle (Möller, 1984). Volcanoes and marshes are minor sources of CS_2, contributing roughly 0.2 and 0.1 Tg S y^{-1}, respectively, but these low values may even be overestimated (Khalil & Rasmussen, 1984). CS_2 does not appear to be emitted from the oceans, or if it is, the quantities may be so low as to be ignored by current authors.

An atmospheric lifetime for CS_2 of 12 days was reported by Khalil and Rasmussen (1984), but in his review, Möller (1984) reported a lifetime of between 7 days and 1 year. Katsoulis and Whelpdale (1990) observed that there is still a considerable degree of uncertainty with regard to the sources and extent of CS_2 emission. It is surprising that not much interest is directed at clarifying these discrepancies, especially since the oxidation of CS_2 by OH to long-lived COS is considered the primary removal mechanism of CS_2. This mechanism implies that CS_2 will influence the COS flux, and therefore, contribute to the production of sulphate in the atmosphere. As a result CS_2 could have a major role in influencing Earth's climate.

2.3 Hydrogen Sulphide (H_2S)

Before the importance of DMS was discovered, H_2S was considered to be the most abundant sulphur gas in the atmosphere (Andreae *et al.*, 1991), but numerous contradicting observations were reported. In his review, Möller (1984) reported a global flux of 0.1 through to 66 Tg S y^{-1} for H_2S, reflecting this confusion. More recently, though, some clarification has been achieved. It is recognised that only small or negligible amounts of H_2S are emitted from the ocean, possibly in the order of 0.28 Tg S y^{-1} (Andreae *et al.*, 1991). Generally, deposition of H_2S from air masses advecting from continents will dominate the H_2S flux over the oceans, but in remote open ocean areas, some H_2S may be emitted (Andreae *et al.*, 1991).

Minor amounts of H_2S are emitted from volcanoes (Katsoulis & Whelpdale, (1990) and plant biomass (Bingemer *et al.*, 1992). Most H_2S is emitted from the soil (Bartell *et al.*, 1993), where dissimilatory sulphate reduction is conducted by soil microorganisms under anaerobic conditions. In this process, sulphide serves as a final electron acceptor to form H_2S in energy-generating metabolism. This is an extremely widespread phenomenon, occurring in decaying vegetation, waterlogged soils, freshwater marshes and bogs, salt marshes and tidal flats, barrier islands, and estuaries (Katsoulis & Whelpdale, 1990), as well as in anaerobic regions of any structured soil. Brown and Bell (1986) report that inland soils may release about 17 Tg S y^{-1} with 67% of this in the form of H_2S.

The potential for H_2S production is such that without moderating effects, much more H_2S would be emitted than is currently observed. Such moderating effects include resedimentisation as metal sulphides, and re-oxidation to sulphate on encountering oxic conditions (Möller, (1984) or ubiquitous sulphur-oxidising bacteria.

H_2S has a relatively short residence time of 0.2 to 3 days, and is oxidised to sulphate via SO_2 (Spiro *et al.*, 1992). Because of its high emission over continental regions, H_2S may serve as a significant source of sulphate in the atmosphere.

2.4 Dimethyl Sulphide (DMS)

Möller (1984) proposed that 50% of atmospheric biogenic sulphur is emitted from the oceans, and that 90% of this fraction may be in the form of DMS. He estimated a flux of more than 15 Tg S y^{-1} and a DMS residence time of up to 19 hours. Based on these observations, he suggested that the role of DMS in the sulphur cycle should receive more attention. Brown and Bell (1986) confirmed these findings by estimating biogenic sulphur release from the oceans at 39 Tg S y^{-1}, 98% of which being DMS, with a residence time of less than 5 days. More recent estimates of oceanic DMS emissions are in the order of 50 Tg S y^{-1} (Spiro *et al.*, 1992) with a residence time of 8 to 48 hours (Burgermeister & Georgii, 1991).

Oceanic DMS is produced by marine phytoplankton, which manufacture an osmoregulator termed dimethylsulphoniopropionate (DMSP) to combat dehydration effects in a highly saline environment. When this is excreted, it is biodegraded to DMS, which is then emitted from the ocean surface (Kittler *et al.*, 1992). Some DMS is emitted from terrestrial environments, including soils, salt marshes and plant biomass, but the importance of this on a global scale has not been established. Harrison *et al.* (1992) found a major release of DMS from North Sea inter-tidal areas, but suggested that this was not significant compared to surrounding oceanic emissions.

It was Charlson *et al.* who finally put forward an hypothesis to describe the role of DMS in the atmosphere, based on its emission and conversion. This hypothesis has been referred to as the DMS-Cloud-Climate hypothesis (DCCH), and has sparked much interest. DCCH will be discussed in section 3 of this article.

Charlson *et al.* (1987) observed that even though DMS is excreted by phytoplankton, its concentration in surface water and emission rate to the atmosphere correlate only weakly with phytoplankton activity. The explanation given is that the concentration of DMS in surface water, and therefore its emission rate, will depend on its rate of production, as well as its rate of removal by ventilation, photolysis and microbial degradation. As a result of this interaction, Charlson *et al.* (1987) proposed that emission is highest in the warmest, most saline and most intensely illuminated ocean regions, but is independent of the rate of primary production. They suggest that a global DMS concentration gradient should be evident, with maximum values at the equator, and decreasing towards the poles, but this observation has yet to be validated.

Some evidence of latitudinal variation has been reported (eg Kreidenweis *et al.*, 1991), but other authors do not agree. Huebert *et al.* (1993) observed such a trend in only two of five latitudinal transects in the Pacific, and Li and Barrie (1993) found evidence of strong DMS emission in high-latitude oceans.

It is possible that the distribution of DMS correlates with the distribution of phytoplankton species which produce much DMSP. The classes *Dinophyceae* and *Prymnesiophyceae* are particularly important with respect to DMS emission (Kittler *et al.*, 1992), and the production rate of DMS has been shown to vary by three orders of magnitude among different phytoplankton species (Charlson *et al.*, 1987). It may be of some value to integrate the efforts of marine biologists and atmospheric chemists, to determine the extent of correlation between species distribution and sulphur gas emission for DMS, as well as for other marine sulphur gases, like COS.

Mihalopoulos *et al.* (1992) initiated a step in this direction when they examined an upwelling region near Somali. They observed higher values of COS and DMS in the surrounding, warmer region and attributed this to a difference in composition of the phytoplanktonic communities in each region. By mapping oceans in terms of regions conducive to the proliferation of particular planktonic groups, it may be possible to predict so-called "hot spots" or areas of enhanced DMS/COS emission. This may provide greater understanding of the factors controlling biogenic DMS fluxes, which Anderson and Charlson (1991) considered to be mostly undefined.

Once emitted to the atmosphere, DMS may be oxidised to gas phase dimethylsulphoxide (DMSO), dimethylsulphone ($DMSO_2$), methane sulphonic acid (MSA), SO_2 or H_2SO_4 (Quinn *et al.*, 1993). Some attempts have been made to determine the relative contribution of each breakdown mechanism.

The most extensive study was conducted by Huebert *et al.* (1993), who realised that most models of biogenic sulphur fluxes assume conversion of some DMS to MSA (5 to 50%), and the remainder to non-sea-salt sulphate (nsss) via SO_2. However, this conversion may not represent reality. Based on their observations, they decided that DMS may either be converted to DMSO and $DMSO_2$ by OH addition (in which case very little SO_2 or nsss would be formed), or DMS may be oxidised to form sulphate by H atom addition from HO_2 radicals (in which case SO_2 does not serve as an intermediate). If the first option is true, they suggest that rapid deposition of sulphur would occur as DMSO, without forming sulphate aerosol, thereby effectively removing a large proportion of sulphur which would have contributed to atmospheric sulphate. Predictions of atmospheric sulphate based on direct conversion of DMS to sulphate may therefore by overestimated. Clearly, DMS breakdown mechanisms needs to be elucidated in order to generate more accurate date for modelling purposes.

2.5 Methane Sulphonic Acid (MSA)

As yet, no direct release of MSA from the biosphere has been reported. However, MSA may serve as a good indicator of biogenic emissions, because its only known source is oxidation of DMS by OH and NO_3 radicals (Davidson & Nicholas-Hewitt, 1992). In order for this to be feasible, though, factors controlling MSA emission, conversion and deposition need to be understood. Some research is currently being aimed in this direction. The most important research area regarding MSA, is understanding its contribution to the natural acidification of rain water, so that effect of anthropogenic emissions on rain acidity can be placed in a better context.

MSA is highly soluble in dilute solutions (Huebert *et al.*, 1993) and is a strong acid, with a dissociation constant greater than that of nitric acid (Mihalopoulos *et al.*, 1993) and it is though that gaseous MSA dissolves in the liquid water associated with sea-salt aerosols, and distils out of those aerosols with very little water mass. When Huebert *et al* (1993) tested this hypothesis, they decided that the equilibration of the MSA-sea salt association was governed by aerosol surface area rather than water mass. This has important implications for rain water acidity over continental regions, where smaller, drier particles are present.

Mihalopoulos *et al.* (1992) reported that problems had been experienced with the determination of atmospheric MSA concentrations using standard procedures, and that other methods (eg infra-red absorption) should be considered. This may imply that previous estimates of MSA should be reassessed in order to reduce potential inaccuracies, and may explain discrepancies in previously measured MSA:nsss ratios noted by Huebert *et al.* (1993).

3. THE DMS-CLOUD-CLIMATE HYPOTHESIS (DCCH)

It was Twomey in 1974 and 1977 who first suggested that an increase in the number of cloud condensation nuclei (CCN) could affect global climate by increasing cloud droplet concentrations and shortwave cloud albedo (Quinn *et al.*, 1993). Charlson *et al.* (1987) recognised that the biosphere may contribute to this effect, and formulated what will be referred to as the DMS-Cloud-Climate hypothesis (DCCH). They proposed that a dynamic interaction exists between marine biota and Earth's climate, with biogenic sulphur being converted into sulphate aerosols which affect cloud albedo, and therefore Earth's climate. Climate in turn will affect oceanic DMS emissions, creating a closed feedback loop. Subsequent to the publication of this hypothesis, intensive research efforts have been directed at validating DCCH, since it may be a key to understanding climate change.

Hegg *et al.* (1991) decided that validation of Charlson *et al.'s* hypothesis (1987) involved three requirements: (a) proof of a quantitative relationship between gaseous precursors and sulphur particles; (b) demonstration of the growth of new sulphur particles to sizes sufficient to serve as CCN; and (c) demonstration of a relationship between CCN and cloud droplet distribution. Most studies have concentrated on one or more of these problems, but as yet, results tend to be inconclusive.

3.1 The conversion of gaseous precursors to sulphur particles.

Charlson *et al.* (1987) decided that sea salt particles did not serve as CCN, because their concentration at cloud height is too low. This led to the proposition that DMS emission is sufficient for it to serve as the gaseous precursor of sulphate CCN in the remote and unpolluted marine atmosphere. A number of authors based their work on this assumption, extending it by presuming sulphate to be the final breakdown product of DMS, with SO_2 as an important intermediate (Lin *et al.*, 1992; Kreidenweis *et al.*, 1991). However, their final results and the work of Huebert *et al.* (1993) have cast doubt over this assumption, especially the role of SO_2.

Huebert *et al.* (1992) presented evidence for alternative DMS breakdown mechanisms, some of which may not involve SO_2. This complex situation was hinted at by the results of Anderson and Charlson (1992), and Kreidenweis *et al.* (1991) who found the dependence of particle concentration on DMS source strength to be highly non-linear. As Hegg *et al.*, (1991) succinctly put it, "Aitken nuclei are not synonymous with CCN and DMS flux is not sulphate mass" which has often been assumed.

Despite this debate, sufficient evidence has been obtained to suggest that sulphur-containing compounds from DMS breakdown are indeed responsible for particle production in the marine boundary layer. Both Lin *et al.* (1992) and Hegg *et al.* (1991) found evidence pointing to the initial production of CCN by bimolecular nucleation of water and H_2SO_4 vapour, a process which is photochemically driven.

It seems that some confusion exists with regard to the gas-to-particle conversion of DMS breakdown products. DCCH will remain questionable until this issue can be clarified, because it is the critical link between the theories presented by Twomey (reported by Quinn *et al.*, 1993) and Charlson *et al.* (1987).

3.2 Growth of Aitken nuclei to CCN size

Assuming the gas-to-particle connection can be proved, the next step would be to demonstrate the growth of newly-formed, fine Aitken nuclei. The diameter of these particles must increase by at least 50% before they may serve as effective CCN (Lin *et al.,* 1991). In addition, this process must occur within a 12 to 14 hour time-scale, to coincide with the turnover time of CCN in the marine boundary layer (Quinn *et al.,* 1993).

A considerable amount of evidence has been gathered to demonstrate such growth. Lin *et al.* (1992) ruled out possible mechanisms like coagulation of fine nuclei, as well as scavenging of atmospheric SO_2 by fine particles, on the basis of the slow rate of these processes. They decided that condensation of gas phase H_2SO_4 and NH_3 onto fine particles was the most plausible mechanism.

Quinn *et al.* (1993) also came to this conclusion. They found that a doubling of non-sea salt sulphate, MSA and NH_4^+ mass resulted in a 50, 40 and 45% increased in the number of particles within the accumulation mode size range, respectively. Rather than changing the number of particles present in the marine boundary layer, it appears that most biogenic sulphur gases may only exert a secondary effect on climate, by improving the ability of pre-existing particles to act as CCN (Huebert *et al.,* 1993).

3.3 Relationship between CCN and cloud drop distributions

The relationship between CCN and cloud drop distribution is an entire field of study in its own right. It will therefore not be considered to any extent here. Suffice it to report that evidence has been found for a strong correlation between the concentration of CCN active at 1% supersaturation within the marine boundary layer, and the average number concentration of cloud drops in stratiform clouds that cap the marine boundary layer (Hegg *et al.,* 1991).

4. IMPLICATIONS AND MODIFICATIONS OF DCCH

When considering the variation of CCN source strength, Anderson and Charlson (1991) speculated on the possibility of a bistable system existing within DCCH, where two steady states occur. Each state may be characterised by different CCN number concentrations, removal mechanisms and cloud properties.

Lin *et al.* (1992) seem to be thinking along the same line. They concluded that CCN can be formed from small sulphate nuclei by condensation of gas phase H_2SO_4, NH_3 (and MSA), *as long as the existing CCN number concentration is below a critical value.* Such a situation could arise after heavy precipitation, or in certain free tropospheric regions. They propose that the highly non-linear influence of DMS emission on CCN observed by some authors is a result of this so-called "biogenic fail-safe mechanism". Under this hypothesis, DMS will have no impact on CCN at certain times, but at other times, its impact could be large. Such a theory seems very plausible, and could no doubt spark a new, concerted research effort in this direction.

5. OTHER CONSIDERATIONS

DCCH involves an indirect effect of sulphate aerosol on climate, where cloud properties are modified. However, it is possible that these particles may have a more direct effect on climate by backscattering of sunlight (Anderson & Charlson, 1991). In this case, sulphate derived from COS may have an important role, because the residence time of COS is long. DMS may be important because of the sheer volume of its emission.

Efforts should be made to quantify this effect, because it may be an important cooling mechanism in the atmosphere. Increasing anthropogenic sulphur emission may enhance this cooling effect, and thereby reduce the potential for global warming as predicted by Greenhouse theory (Anderson & Charlson, 1991). Such an interaction of heating and cooling effects may explain the current discrepancy between predicted and observed rates of global warming.

A further complication may be raised by work conducted at the NASA Goddard Institute for Space Studies, which suggests that the albedo of clouds is reduced at higher temperatures (Hecht, 1994). Thus, it is possible that the buffering influence of clouds on atmospheric temperatures as implied by DCCH may be overcome at some stage, if emission rates of greenhouse gases continue to increase. In this case, direct backscattering of sunlight by sulphur gases will be far more important than the influence of DCCH.

6. CONCLUSION

With the improvement of techniques and procedures, some correlation has been obtained between estimates of biogenic gas emission, but continued efforts to refine these estimates will be critical in future atmospheric modelling. This is because a very large number of variables appears to be involved, which will contribute to a large error factor in model output. It seems, however, that not much attention has been paid to the actual source of the emission, or the mechanism by which the gases are released. Knowledge of parameters which influence sulphur metabolism in the organisms involved may contribute to an improved understanding of emission rates and their seasonal and diurnal variations. Thus the efforts of biological scientists and atmospheric chemists may be integrated to improve the accuracy of biogenic sulphur emission estimates.

Much attention has been focused on biogenic sulphur emission in remote ocean regions, in order to investigate the DMS-Cloud-Climate hypothesis (DCCH). Conclusive proof has yet to be presented for this theory, since results are often conflicting, and evidence obtained seems to prompt more questions than it answers. Recent suggestions of possible modification of DCCH, however, may clarify some of this confusion.

Further fine-tuning in the future will probably establish DCCH as a powerful base from which atmospheric models can be developed.

Once the natural cycles and effects of sulphur gases are understood, future research will probably be directed at elucidating the atmospheric perturbations caused by anthropogenic sulphur gas emissions. Research directions may shift from oceanic to continental regions, where the contributions and fate of biogenic and non-biogenic COS, CS$_2$ and H$_2$S will receive more attention. Such issues as global warming, rain acidity and other facets of climatic change may then be understood in a better context, allowing the development of more accurate atmospheric models in the future.

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