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Human impact on the atmospheric sulfur balance

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ABSTRACT

The paper reviews the development in our understanding of the atmospheric part of the global sulfur cycle, including the role played by C.-G. Rossby and his colleagues in the 1950s, and presents a brief assessment of the current knowledge. Measurements of the concentrations of sulfur compounds in air, precipitation, ice cores and sea water during the past 25 years, together with recent development in three-dimensional tracer transport modeling, have resulted in a reasonably consistent picture of the burdens and fluxes of the main sulfur compounds in the atmosphere. It is clear that man's activities, in particular the burning of fossil fuels, are having a large impact on the atmospheric sulfur balance. Even on a global scale, the man-made emissions of gaseous sulfur compounds are likely to be two to three times as large as the natural sources. In and around the most heavily industrialized regions this ratio exceeds ten over extended areas. Nevertheless, there are several important issues that need to be resolved. Some of these are directly linked to the urgent problem of reducing the uncertainty in the estimate of direct and, in particular, indirect climate forcing due to man-made sulfate aerosols. One such issue is the magnitude of the wet scavenging of SO_2 and aerosol sulfate during upward transport into and within the free troposphere in connection with convective and frontal cloud systems which has a decisive influence on the sulfate concentrations in the upper troposphere. Another uncertain process is the rate of oxidation of SO_2 in cloud droplets and on aerosol particles. A fundamental question that remains to be answered is to what degree man-made sulfur emissions have increased the *number* of aerosol particles that can act as cloud condensation nuclei.

1. Introduction

Sulfur is one of the key elements in the chemical functioning of the earth. It is an essential plant nutrient mainly because it is a fundamental component in many proteins. Sulfur in the form of sulfate ion is the second most abundant anion in sea water and it is an important factor in the acid/base balance of natural waters, e.g., rivers, precipitation and cloud water. The connection of sulfate ion to acidity makes it important for the pH of natural rainwater (Charlson and Rodhe, 1982), as well as for the man-made "acid rain" problem (Odén, 1968; Rodhe et al., 1995). Aerosol sulfate has also been identified as an important contributor to the scattering of sunlight (Charlson et al., 1991) and as a major component of condensation nuclei in the atmosphere (Junge, 1963; Charlson et al., 1987). Both these effects make atmospheric sulfate a potentially important player in the natural global climate system and also a vehicle for man-made impact on it (Charlson et al., 1992; IPCC, 1996). Furthermore, sulfate aerosols provide surfaces for heterogeneous chemical reactions that could be of great importance both in the lower troposphere (Dentener and Crutzen, 1993) and in the upper troposphere and lower stratosphere (Solomon, 1990). In addition, gaseous sulfur dioxide is a potent air pollutant affecting both plants, animals, including humans, and material in heavily polluted areas. There are thus very good reasons to study the cycling of sulfur in the environment and, in particular its distribution in the atmosphere.

The first attempt to describe the global sulfur cycle was made by Conway (1942). Based mainly

on river run-off data and estimates of release of sulfate through weathering, he estimated that 370 Tg S/yr was deposited over the continents and he speculated that release of H_2S from the sea, mainly from the continental shelves, was the main source. During the following two decades, refined estimates were made by Junge and Werby (1958), Junge (1960) and Eriksson (1963) based essentially on extrapolations to global scale of precipitation chemistry measurements in Europe and North America. Their estimate of the emission of gaseous sulfur compounds into the atmosphere, assumed to be mainly in the form of H_2S, ranged from 130 to 280 Tg S/yr. The reason for such high values (compared to what we know today) was that these authors were not aware of the substantial bias associated with the measured concentrations of sulfate in precipitation due to long range transport of man-made sulfur pollution. This problem was realized by Granat et al. (1976) who used remote unpolluted deposition data to estimate a global flux of about 30 Tg S/yr.

Until the early 1970s, all global sulfur budgets were based on the assumption that the main natural volatile sulfur compound was H_2S. The implication of the sea as the main source of this H_2S posed a difficult problem, since H_2S is known to be oxidized on time scales of hours in sea water. It was thus difficult to imagine how this compound could escape from the bottom of the sea, where it is formed under unaerobic conditions, to the atmosphere and one had to invoke some hypothetical process whereby H_2S was formed by organisms in the surface water, or, alternatively, that the H_2S source was located on land. This dilemma was resolved in 1972 when Lovelock et al. (1972) reported measurements of substantial concentrations of another volatile sulfur compound, dimethyl sulfide (DMS), in surface sea water. DMS is now known to be an almost ubiquitous component of surface sea water, formed by biological processes (Andreae, 1986). The main part of the excess (non sea-salt) sulfur observed in marine areas unaffected by man-made pollution and volcanoes, is now believed to originate from DMS rather than H_2S.

The first realistic estimate of the global emission of DMS from the oceans, based on actual measurements of DMS in surface water and in the air above it, was made by Nguyen et al. (1978). Their estimate, followed by several others, was consistent with the indirect estimate of 30 Tg S/yr by Granat et al. (1976).

The budget estimates of atmospheric sulfur by Junge and Eriksson were made possible by the first systematic measurements of the chemical composition of precipitation which had been carried out during the preceding years. In 1948, the Swedish soil scientist Hans Egnér at the Agricultural College in Uppsala initiated a precipitation chemistry network in order to study the input of nutrients to Scandinavian soils. The network was later expanded to include much of central and western Europe (Emanuelsson et al., 1954; Rossby and Egnér, 1955). A similar network was run for some years in the USA in the mid 1950s (Junge and Werby, 1958).

When C.-G. Rossby came in contact with Egnér in the early 1950s, he soon realized the importance also for atmospheric scientists to become engaged in the study of the large scale distribution of chemical components like sulfur and nitrogen species. Not only could meteorologists contribute to the interpretation of the observed deposition patterns, but chemical deposition data could also provide useful indicators of the transport characteristics of the atmosphere (Rossby and Egnér, 1955). Historical deposition records could also be used to deduce past circulation changes. Thoughts by Rossby on these matters are clearly expressed in his fascinating and extraordinarily far-sighted review "Current problems in meteorology", which appeared in Swedish in 1957 and in a translated version in the Rossby Memorial Volume in 1959 (Rossby, 1959). In this essay, Rossby included a map showing the wet deposition of excess sulfate over Scandinavia and concluded that "a tongue of high concentration extending from southernmost Sweden northwards indicates with good probability that there is an airborne contribution to Sweden's sulphur provision from Germany's industry". To my knowledge, this is the first scientifically based statement on long-range transport of sulfur pollutants. (A poet's intuitive impression of this process appeared much earlier: In 1866, the Norwegian play writer Henrik Ibsen (1866) wrote that "Britain's suffocating coal dust, is slowly descending over the (Norwegian) countryside, soiling all that is green ...")

The finding by Rossby and his colleagues regarding long-range transport did not make any major impact until another Swedish soil scientist,

Svante Odén, more than 10 years later, connected the increasing acidity in many Swedish lakes and rivers to a corresponding acidification of precipitation and suggested that the main cause of these changes was the long-range transport of sulfur from pollution sources in the UK and on the European continent (Odén, 1968). This was the discovery of the acid rain problem. A first attempt to quantify the long-range transport of sulfur was made by Rodhe (1972; see also Sweden's Case Study, 1972). It has been followed by a large number of more detailed studies.

Since the discovery of the acidification problem by Odén in 1968, great efforts have been devoted to studies of the sulfur balance of the most polluted regions, especially in Europe and North America. The appearance of additional sulfur polluted regions, e.g., China (Zhao and Xiong, 1988), and the realization that sulfate aerosols also play an important role in the global climate system (Charlson et al., 1987, 1990, 1991 and 1992) have stimulated the interest in the distribution of sulfur compounds throughout the global atmosphere (Rodhe et al., 1995; IPCC 1996).

The present paper is an attempt to summarize the main aspects of the current understanding of the atmospheric sulfur balance and to discuss some of the major remaining uncertainties. The presentation starts with a brief review of the global fluxes to and from the atmosphere. Because of the limited residence time in the atmosphere of most of the sulfur compounds (of the order of days or weeks), the relative importance of man-made and natural emissions is very unevenly distributed geographically. The discussion is therefor divided into four types of atmospheric compartments: polluted mid-latitude boundary layer, polluted tropical/subtropical boundary layer, free troposphere and stratosphere.

2. Global fluxes

The most important fluxes of sulfur compounds to, within and from the atmosphere are shown in Fig. 1 and the nature of the largest emissions and their uncertainties are summarized in Table 1. The numbers are based essentially on the global models of Feichter et al. (1996), Chin et al. (1996) and Kjellström (1998) and references therein. Emissions of sulfate associated with sea spray and soil dust have been excluded from the figure and the table on the grounds that it occurs in chemical forms that do not contribute to acidification of

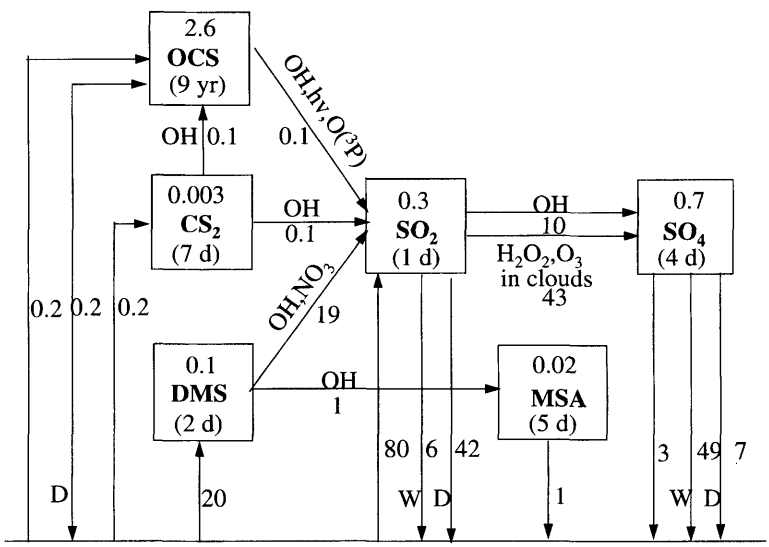

Fig. 1. The main reservoir contents (Tg S) and fluxes (Tg S/yr) in the atmospheric sulfur balance. Number in brackets refer to the residence times.The main oxidants responsible for the different oxidation processes have been indicated. D and W refer to dry and wet deposition, respectively. Data from several sources including Feichter et al. (1996), Chin et al. (1996) and Kjellström (1998).

Table 1. *Annual sulfur emissions to the atmosphere, around the year 1990 excluding sea salt and soil dust*

Oceans (DMS)	20	(10–50)
Soils and veg. (DMS)	2	(1–4)
Volcanoes (SO_2)	8	(4–16)
Total natural	30	(15–70)
Industrial (SO_2)	70	(60–80)
Biomass burning (SO_2)	3	(1–5)
Total man-made	73	(60–85)

The values given in brackets represent the approximate range of values published in recent literature. The ranges may be taken as a rough measure of the uncertainty. Unit: Tg S/yr.

precipitation (however they may take part in acidifying processes occurring in soils and fresh waters). Whereas sea-salt represents an entirely natural source of atmospheric sulfur, the emissions of sulfur in soil dust could have a man-made component (Ryaboshapko, 1983). The gaseous sulfur emissions (SO_2 and DMS) are oxidized in the atmosphere within a few days to form acidic compounds (sulfuric acid or methanesulfonic acid). These occur mainly as sub micrometer size aerosol particles, which may contribute substantially to the number of cloud condensation nuclei (CCN). The sulfuric acid is normally neutralized to a certain degree in the atmosphere and a common molecular form of the sulfate is ammonium bisulfate (NH_4HSO_4) or ammonium sulfate ($(NH_4)_2SO_4$).

All flux estimates shown in Table 1, except the industrial emissions, are associated with a large relative uncertainty. The uncertainty in the estimated flux of DMS from the oceans is particularly noteworthy. A large part of this uncertainty is due to the difficulty in translating measured concentrations of DMS in ocean surface water into a flux of DMS across the ocean-atmosphere interface (Kettle et al., 1999).

As can be seen from Fig. 1, OCS and CS_2 contribute little to the global sulfur fluxes. However, because of its low chemical reactivity, OCS has a much longer residence time in the atmosphere than the other sulfur compounds and it is the most abundant sulfur compound on a global scale. The long residence time also implies that OCS can be transported into the stratosphere more readily than the other sulfur compounds and its contribution to the formation of aerosol sulfate there becomes relatively more important (see below).

The removal of sulfur from the atmosphere is dominated by precipitation scavenging ("wet deposition"), much of it preceded by the uptake of aerosol sulfate during the nucleation of cloud droplets, and by direct uptake, mainly of SO_2, at the surface ("dry deposition"). In polluted areas, with high concentration of SO_2 in surface air, dry deposition is normally the largest removal process. In most remote regions wet deposition dominates over dry deposition.

Table 1 shows that man-made sulfur sources probably dominate over the natural ones even as global totals. In the polluted regions this dominance is even more pronounced (see below). The historical evolution of the northern hemisphere man-made emissions (Fig. 2) shows that these are likely to have surpassed the natural emissions around World War I. The trend in high northern latitude man-made emissions and the estimated magnitude of the natural fluxes are broadly consistent with the observed trend in sulfate recorded in Greenland ice cores (Legrand, 1995). Because of the larger distance to man-made sulfur sources, Antarctic cores do not show a similar trend.

3. Mid-latitude polluted boundary layers

Several studies have been made of the sulfur balance of the polluted boundary layer in Europe and North America and of the long-range transport of sulfur compounds within these regions (for reviews, see, e.g., Galloway and Rodhe (1991), WMO (1996)). Long-range transport models used for this purpose are based on sulfur emission inventories and simplified descriptions of chemical transformations in the atmosphere and of wet and dry removal processes. In those cases where the contribution from natural sources has been explicitly included, it has been estimated from measurements of atmospheric sulfur in the outskirts of the polluted regions or from measurements of DMS concentrations in surrounding seas. Most of the models contain some empirical parameters that have been determined from observations of the distribution of sulfur in air and precipitation within the regions in question.

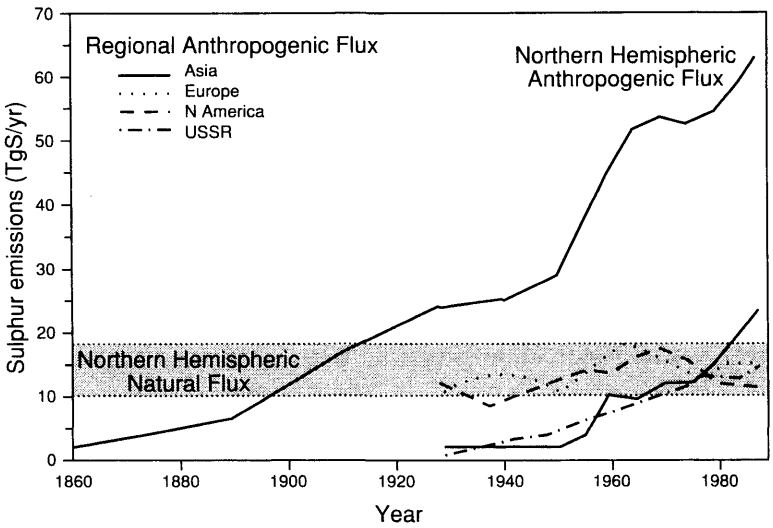

Fig. 2. The evolution of northern hemisphere and regional man-made sulfur emissions since 1860 (Dignon and Hameed, 1989; IPCC, 1996). Reproduced by permission of IPCC.

Budget calculations, showing the contribution of sulfur emissions in each individual European country to the deposition in any other European country, have been estimated each year since the mid 1970s with the aid of the EMEP model and its predecessors developed in Norway (Nordö, 1976; Eliassen and Saltbones, 1983; Sandnes and Styve, 1992). Such calculations have been instrumental in convincing policy makers (and even several originally skeptical scientists) about the reality of long-range transport and such budgets have no doubt played a very important rôle as a scientific rationale for the international agreements to reduce sulfur emissions in Europe.

Despite the success of models of long-range sulfur transport, it should be realized that there are still processes that are not well understood and quantified. This includes the oxidation of SO_2 to sulfate. Models based on the current understanding of oxidation pathways and rates do not seem to be able to simulate high enough aerosol sulfate concentrations, especially in winter at high latitudes (Shaw and Rodhe, 1983; Feichter et al., 1996; Kasibhatla et al., 1997). We may have to look for another oxidation pathway in addition to those already identified.

Despite a considerable improvement in our understanding and quantification of the dry deposition of sulfur compounds (Ganzeveld et al., 1998), potentially important uncertainties remain, e.g., regarding the magnitude of the uptake of SO_2 by the cuticle of leaves and needles (Granat and Richter, 1995).

The man-made sulfur emissions in Europe, including the Former Soviet Union (FSU) states west of the Ural Mountains, have now (1996) decreased by about 55% since 1980 (EMEP/MSC-W, 1997), i.e., to a value close to that of 1950. Fig. 3 shows model simulations of the sulfur deposition in southern Sweden since 1880 based on a historical emission inventory and the EMEP transport model (Mylona, 1997). The variations in the deposition since the 1950s are consistent with precipitation chemistry measurements. Although the recent decline is a considerable improvement as far as the acid deposition is concerned, the current deposition still exceeds the "critical load" (the level above which damage to sensitive ecosystems can be expected) in large parts of Scandinavia, the Alps and other regions characterized by ecosystems with small acid buffering capacity.

The nature of the sulfur balance over a polluted region is illustrated in Fig. 4 (Galloway and Rodhe, 1991), which summarizes the budget terms of several atmospheric sulfur budgets of eastern US. The overall conclusion is that in a climate typical for this region about 2/3 of the emitted sulfur is deposited within a distance of 2000 km

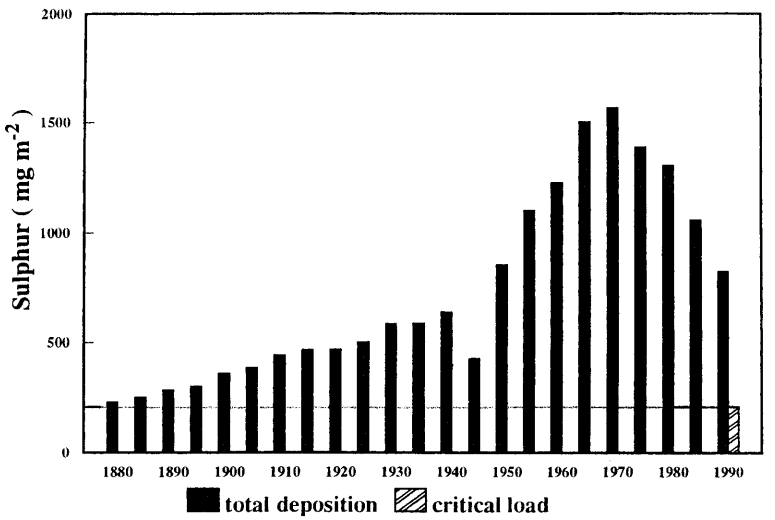

Fig. 3. Calculated historical trends of sulfur deposition in southern Sweden (Mylona, 1996).

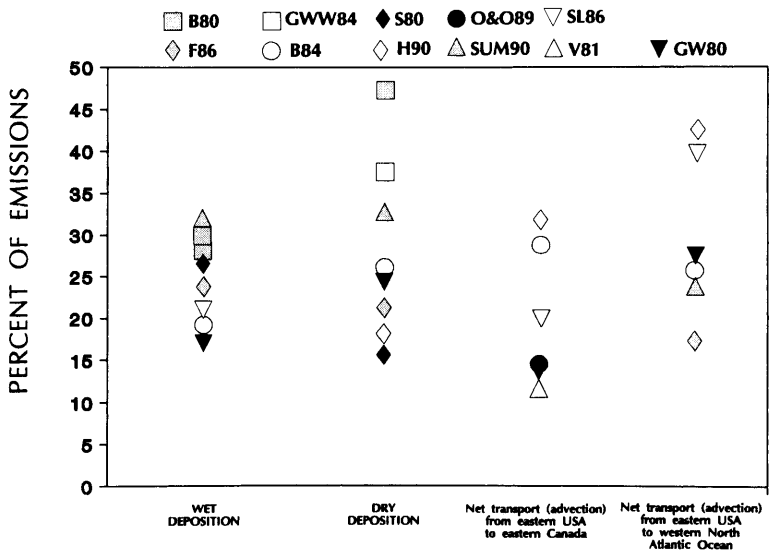

Fig. 4. Fluxes of sulfur in the atmosphere of the eastern US expressed as percent of emissions. The solid and open symbols indicate that the budgets were products of data analysis or models, respectively (Galloway and Rodhe, 1991). Reproduced by permission of the Royal Society of Edinburgh.

from the main source area, roughly equally distributed between wet and dry deposition. These numbers correspond to an average atmospheric residence time of 2–4 days (Rodhe, 1978).

The ratio between the current and the pre-industrial sulfur deposition has been estimated by Galloway and Whelpdale (1980) for North America and by Langner et al. (1992) for the globe. These estimates indicate an amplification of more than a factor of 10 as an annual mean for substantial parts of eastern US and central Europe, see Fig. 5. During the winter season, when natural emissions are small, man-made sources are even more dominating.

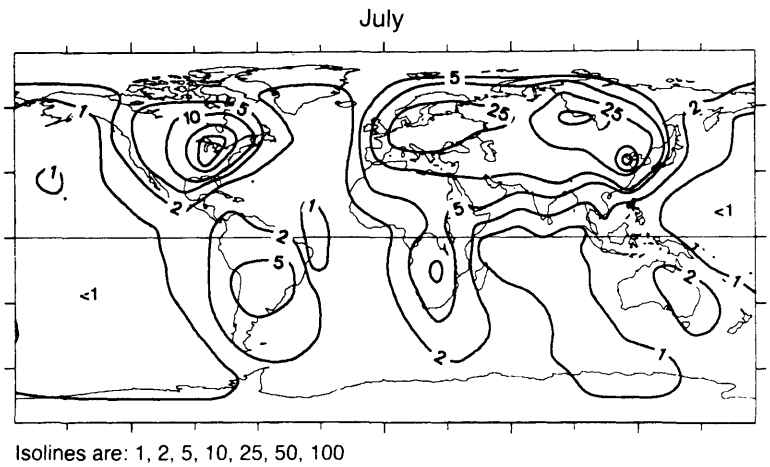

Fig. 5. The ratio between current and pre-industrial concentration of aerosol sulfate at 900 hPa in July. From model calculations by Langner et al. (1992). Reproduced with permission from *Nature*, Macmillan Magazines Limited.

4. Polluted tropical/subtropical boundary layer

Whereas man-made sulfur emissions are declining in Europe and North America, a rapid increase is taking place in many tropical and subtropical countries, e.g., India and China (Fig. 2). The annual rate of increase of SO_2 emissions form the energy sector between 1986 and 2000 has been estimated to 4% in China, 3.5% in India and 9% in Thailand (Foell and Green, 1991). If these trends continue, the atmospheric sulfur balance in these regions will soon become as affected as it is in Europe and eastern North America. A projection to the year 2020 indicates that about 10^7 km^2 in south and east Asia could by then be receiving an annual deposition of more than 1 g S/m^2, a deposition rate that is known to cause serious environmental effects in sensitive ecosystems in the polluted mid-latitudes (Rodhe et al., 1992).

Only few attempts have yet been made to model the long-range transport of sulfur pollutants in tropical regions (Arndt and Carmichael, 1995; Robertson et al., 1995). Compared to the situation in mid-latitudes, the following differences need special consideration.

- In many tropical and subtropical regions, e.g., northern Africa, Middle East, Australia and northwestern India, alkaline soil dust is a common component of air and precipitation. The dust particles interact with the sulfur cycle in at least three important ways: (1) they provide a surface on which SO_2 can be absorbed and oxidized to sulfate thereby reducing the lifetime of SO_2 and also decreasing the potential for formation of new CCN (Dentener et al., 1996); (2) they neutralize the acidity of clouds and precipitation caused by the sulfur pollutants; (3) in areas with high concentration of sulfate (as gypsum) in soils windblown soil dust could be an important term in the sulfur budget (Ryaboshapko, 1983); the Aral Sea area, for example, has been estimated to receive 0.1–1 Tg S/yr from such emissions (Brimblecombe et al., 1989). In such regions sulfur transport models have to take the occurrence of soil dust into account.
- The depth of the boundary layer is larger and the mixing of boundary layer air into the free troposphere in connection with convective motions is more frequent, especially during the wet season. A key question is how much of the sulfur compounds (SO_2 and aerosol sulfate) is scavenged in the updraft clouds and how much actually reaches the middle and upper troposphere. One important factor for the scavenging of SO_2 is the acidity of the cloud droplets; high acidity will make the uptake of SO_2 in the droplets less efficient and allow more SO_2 to penetrate through the cloud filter separating the boundary layer and the free troposphere (Rodhe, 1983). Alkaline substances such as ammonia and carbonates in soil dust will play an important role in

maintaining the efficiency of the cloud filter for SO_2 by lowering the pH of the cloud droplets.

- Higher concentrations of OH and H_2O_2 tend to make the oxidation of SO_2 more efficient than at higher latitudes. On the other hand, extended dry periods with little cloudiness act to reduce the oxidation. Consequently, sulfur budgets in these regions will have to be considered for dry and wet seasons separately.

A better understanding of the atmospheric sulfur balance in tropical and many subtropical regions is hampered by a severe lack of high quality and regionally representative observations (Whelpdale et al., 1996).

5. Free troposphere

Even though only about 25% of the sulfur emitted by man-made processes may escape into the free troposphere before it is brought back to the surface (Chin and Jacob, 1996), more than half of the total column abundance of sulfate is located in the free troposphere (see below). This is because of the longer residence time of the sulfate in this compartment, a few weeks on the average compared to 2–4 days in the PBL, due to less efficient removal processes. A good understanding of the sulfur balance of the free troposphere is therefor essential for estimates of the climate impact of aerosol sulfate. Unfortunately, very few observations of sulfur compounds have been made in this part of the atmosphere and any estimate of their global abundance has to rely on chemical transport models that can not yet be properly validated against observations.

Some of the first comprehensive estimates of the global distributions of the main sulfur compounds were carried out with three-dimensional transport models based on observed climatology of wind and cloudiness (Langner and Rodhe, 1991; Langner et al., 1992; Pham et al., 1995). Other similar studies have been made based on off-line versions of general circulation models (GCMs) (Erickson et al., 1991; Penner et al., 1994; Chin et al., 1996). Recently, sulfur schemes have been included on-line in GCM simulations (Feichter et al., 1996; 1997) and attempts are now being made to run sulfur schemes in GCM simulations nudged to observed weather for specific periods. In this way simulated concentrations of sulfur compounds can be more meaningfully compared with observations carried out during short term measurement campaigns.

The results of the different global model simulations show substantial differences. The estimated global burden of sulfate in the whole atmosphere varies between 0.53 Tg S in Chin et al. (1996) and 1.1 Tg S in Lohmann and Feichter (1997) with all of the others in the range 0.6–0.8 Tg S. The low value of Chin et al. is associated with an assumed high efficiency of wet removal in Cb clouds in their model, whereas the high value of Lohmann and Feichter is caused by a less efficient wet scavenging due to a negative feedback process between the sulfate aerosols and the precipitation formation mechanism.

Fig. 6 shows annually and zonally averaged concentrations of sulfate estimated by Chin et al. (1996) and by Feichter et al. (1996).The widespread impact of man-made emissions between 30° and 60° in the NH is clearly visible in both panels. In the upper troposphere there is a large difference in concentration between the two simulations: Feichter et al. giving a factor of four higher values at 200 hPa. Direct emissions of sulfur from aircraft have not been included in any of these estimates, but Kjellström et al. (1998) have shown that such emissions make only a small contribution (less than 1%) to the sulfate concentration even at that level. It is an urgent task to try to narrow the uncertainty in the estimate of the sulfate concentration in the upper troposphere where there is a potential for a substantial impact of sulfate from man-made sources on the microphysics and radiation balance of cirrus clouds (Ström et al., 1997).

An estimate of the contribution of natural and man-made sources to the abundance of SO_2 and sulfate in the PBL and the free troposphere (above 850 hPa) is shown in Table 2 (Erik Kjellström, personal communication). The estimate is based on simulations with the ECHAM-4 model (Kjellström et al., 1998). Both DMS and volcanoes have their largest impact on the sulfur balance of free troposphere; DMS because it is readily transported into this region without being scavenged by precipitation (DMS is not very soluble in water) and volcanic emissions because most of them occur on mountains penetrating into the free troposphere. More than half of the SO_2 from man-made emissions remains in the PBL, but 70% of

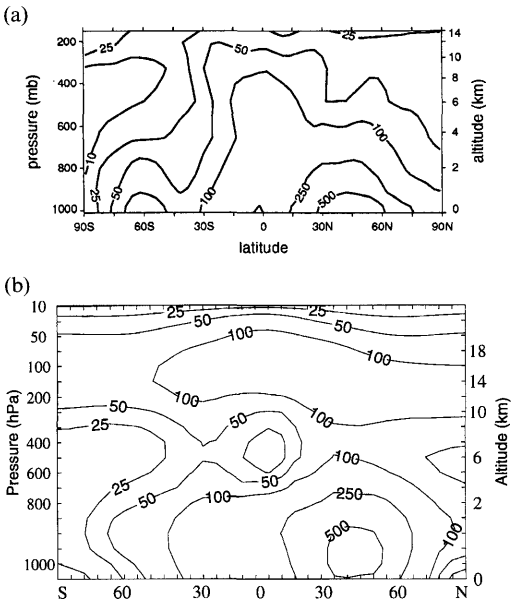

Fig. 6. Annually and zonally averaged concentrations of sulfate. Simulations by (a) Chin et al. (1996), reproduced from J. Geophys. Res. 101, (b) Feichter et al. (1996) reprinted from Atmospheric Environment with permission from Elsevier Science. Unit: pptv.

Table 2. *Contribution of natural and man-made sources to the annual mean sulfur burden in the planetary boundary layer (PBL) and in the free troposphere (FT)*

	SO_2		SO_4^{2-}	
	PBL	FT	PBL	FT
Natural sources				
DMS	2.5	5.5	4.6	12
volcanoes	0.1	7.9	2.7	11
Man-made sources	18	13	16	37
Total	21	26	23	60
Ratio: current/pre-ind.	8.1	1.9	3.2	2.6

The separation between PBL and FT is here taken to be 850 hPa. Based on the ECHAM model (Kjellström et al., 1998). Unit: 10^{10} g S.

the sulfate burden from this source is located in the free troposphere. Furthermore, the table shows that even as a global average the concentrations of SO_2 and sulfate in the PBL are likely to have increased by a factor of 8 and 3, respectively, since pre-industrial times. The amount of sulfate in the free troposphere is estimated to have increased by almost a factor of 3.

A most important question, not the least in connection with issue of the indirect climate forcing by sulfate aerosols, is how this increase in sulfate mass loading has influenced the number concentration of aerosol particles in general and of CCN in particular. Unfortunately, this question cannot yet be answered in any credible way (IPCC, 1996).

6. Stratosphere

The existence of a persistent layer of high aerosol concentration in the stratosphere around 20 km was first noted by Junge and his colleagues in the late 1950s (Junge et al., 1961). They also noted that sulfate (or sulfuric acid) was a major component of this aerosol. Many measurements since then have shown that the aerosol concentration in the "Junge" layer is increased for a few years following large volcanic eruptions but also that there is a background level which has to have a non-volcanic source. In 1976, Crutzen suggested

that oxidation of OCS, transported up from the troposphere, could be the source of the sulfate. Recent studies (Golombek and Prinn, 1993; Chin and Davis, 1995; Kjellström, 1998) have shown that contributions from other sulfur containing compounds, in particular SO_2, are likely to be as important as OCS for maintaining the Junge layer during non-volcanic periods. Kjellström's analysis, which is based on simulations with the ECHAM GCM with all the sulfur compounds shown in Fig. 1 (except MSA) explicitly treated, indicates that SO_2 might even be the dominating source, see Fig. 7.

According to Fig. 7, about 85% of the input of SO_2 to the stratosphere is through vertical transport of this gas from the troposphere, the remaining fraction being oxidation of DMS (9%) and OCS (6%). The same proportions also apply to the formation of sulfate through oxidation of SO_2 within the stratosphere. Because of the limitations of the model used by Kjellström (1998), these numbers should not be accepted uncritically, but they do indicate that OCS is unlikely to be the only important source of the background Junge layer.

It is interesting to note that the magnitude of the man-made impact on the stratospheric sulfur balance (during non-volcanic periods) is substantial regardless of whether SO_2 or OCS is the main sulfur source, because both these sulfur carrying gases have large contributions from man-made sources. The numbers given in brackets in Fig. 7 indicate that 40% of the OCS and 30% of the influx of SO_2 from the troposphere are of man-made origin. To the extent that these numbers are realistic, the background sulfate levels in the stratosphere should have become correspondingly augmented during the industrial era.

Again, a word of caution is appropriate. The simulated flux of SO_2 to the stratosphere is critically dependent, i.a., on how the vertical transport of SO_2 within the troposphere and between the troposphere and stratosphere is modeled and current models are far from perfect in this regard. The relative importance of man-made and natural sources of OCS is therefor still not well established (Kjellström, 1998). This question would be independently resolved if the pre-industrial concentration of OCS could be determined from ice cores. A reduction of the uncertainty associated with the vertical flux of SO_2 will require carefully designed measurements below and above the tropopause in those parts of the world where the upward mass flux is most important (e.g., the Indonesian region).

7. Concluding remarks

This brief review of the atmospheric sulfur balance has demonstrated that the main sulfur compounds and the approximate magnitude of their fluxes to and from the global atmosphere have now been reasonably well established. It is clear that man-made emissions today have a pro-

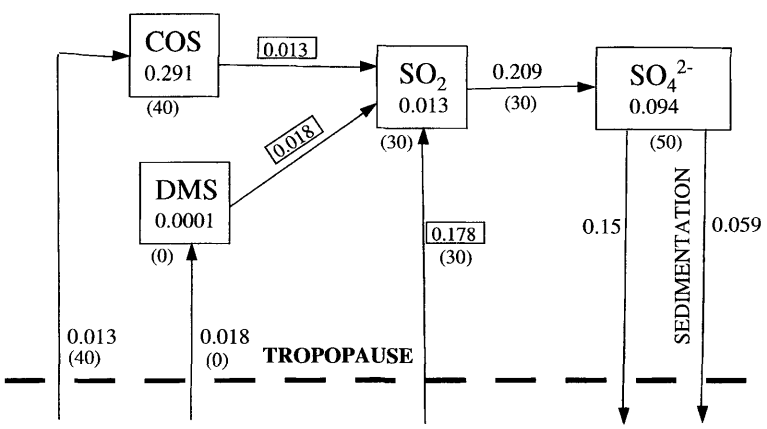

Fig. 7. Global burdens (Tg S) and fluxes (Tg S/yr) of sulfur in the stratosphere during non-volcanic periods. Numbers in brackets represent the man-made contribution in percent. Modified from Kjellström (1998).

found influence on the concentrations of SO_2 and sulfate, not only in the PBL within and around the heavily industrialized regions in the northern hemisphere — where the concentration have experienced a more than tenfold increase over extended areas — but also throughout the northern hemisphere free troposphere and probably also in the stratosphere around the whole globe.

There are certainly also important limitations in our understanding of the sulfur cycle. Some of the remaining issues are listed below.

- The efficiency of the vertical transport of SO_2 and aerosol sulfate to and within the free troposphere, as well as the scavenging by precipitation associated with this vertical transport, need to be better understood and quantified. Differences in the description of these processes is the main reason for the large discrepancies (up to a factor of five) between current global models' simulation of the sulfate concentration in the upper troposphere.
- There are indications that we should have to look for a mechanism for the oxidation of SO_2 in addition to those that are currently considered in the models, c.f. Section 3.
- The interaction of SO_2 with soil dust, sea-salt and other aerosol types need to be better understood. In dry climates the uptake of SO_2 on soil dust particles should be explicitly modeled.
- The estimated range in the magnitude of the DMS source and its spatial and seasonal variations are still embarrassingly large.
- The sources, and sinks, of OCS need to much better quantified so that the relative importance of man-made and natural sources can be established.
- Obviously, more measurements are needed to address these issues. More sophisticated models of the atmospheric sulfur balance will, no doubt, be developed during the coming years. But they are unlikely to give us a better insight until they can be validated against an expanded set of observations of sulfur compounds, particularly in the middle and upper troposphere.

Even if all the issues listed above were resolved we would still not be in the position to provide the necessary input to climate models for the estimate of the indirect climate forcing of sulfate aerosols. Such estimates have to be based on an understanding of the impact of an increased amount of sulfate in the atmosphere on the number concentration of cloud condensation nuclei (CCN). To go beyond the empirical approach that has been used so far (Boucher and Lohmann, 1995) requires an explicit modeling of the dynamics of aerosol formation and growth. A further discussion of this fundamental problem is beyond the scope of this paper.

In the future, special attention will have to be placed on the effects of the rapidly increasing man-made sulfur emissions in tropical and subtropical countries. One of the issues here is the possibility of a rapid vertical transport in convective cloud systems and a potentially important impact on the sulfate concentrations in the upper troposphere and lower stratosphere and thereby on climate as well as on the ozone chemistry.

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