Terrestrial sources and distribution of atmospheric sulphur

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SUMMARY

The general circulation model ECHAM has been coupled to a chemistry and sulphur cycle model to study the impact of terrestrial, i.e. mostly anthropogenic sulphur dioxide (SO₂), sources on global distributions of sulphur species in the atmosphere. We briefly address currently available source inventories. It appears that global estimates of natural emissions are associated with uncertainties up to a factor of 2, while anthropogenic emissions have uncertainty ranges of about $\pm 30 \%$. Further, some recent improvements in the model descriptions of multiphase chemistry and deposition processes are presented. Dry deposition is modelled consistently with meteorological processes and surface properties. The results indicate that surface removal of SO₂ is less efficient than previously assumed, and that the SO₂ lifetime is thus longer. Coupling of the photochemistry and sulphur chemistry schemes in the model improves the treatment of multiphase processes such as oxidant (hydrogen peroxide) supply in aqueous phase SO₂ oxidation. The results suggest that SO₂ oxidation by ozone (O₃) in the aqueous phase is more important than indicated in earlier work. However, it appears that we still overestimate atmospheric SO₂ concentrations near the surface in the relatively polluted Northern Hemisphere. On the other hand, we somewhat underestimate sulphate levels in these regions, which suggests that additional heterogeneous reaction mechanisms, e.g. on aerosols, enhance SO₂ oxidation.

1. INTRODUCTION

In the biosphere sulphur compounds are important as nutrients and electron carriers in metabolic pathways. A small fraction of the biogenic sulphur (ca. $0.04 \, ^{\circ}_{\circ} \, \mathrm{yr}^{-1}$) volatilizes to the atmosphere (Crutzen *et* al. 1985; Charlson et al. 1992). The sulphur occurs in different states, i.e. in its reduced, partly oxidized and fully oxidized forms, indicated by its molecular valence, S(-II), S(IV) and S(VI), respectively. In the atmosphere, the reduced sulphur species carbonyl sulphide (OCS), and to a lesser extent carbon disulphide (CS_2) , hydrogen sulphide (H_2S) and dimethyl sulphide (CH_3SCH_3) are the most abundant. Apart from OCS, these gases are efficiently oxidized by OH radicals, which limits their lifetimes to a few days (table 1). In the atmosphere CS₂ is converted into SO₂ and OCS, and H2S into SO2. Dimethyl sulphide (DMS) breaks down into SO₂ and methyl sulphonic acid (MSA). The chemical lifetime of OCS is about 20 years because of slow conversion by OH and photodissociation in the stratosphere, which is a main source of sulphate at about 20 km altitude (Crutzen 1976). However, uptake by the vegetation limits the overall OCS lifetime to a few years (Goldan et al. 1988). The partly oxidized SO2 is converted to sulphuric acid (H_2SO_4) , to a small extent in the gas phase by

hydroxyl radicals, but mostly in clouds through aqueous phase reactions with H_2O_2 and O_3 (Penkett *et al.* 1979). Both MSA and H_2SO_4 have a low vapour pressure, so they are largely present in the condensed phase, i.e. as aerosol particles or dissolved in droplets.

In the 1970s, anthropogenic SO₂ emissions from fossil fuel combustion had grown so strongly that deposition of the reaction product, sulphate, reached alarming levels, causing widespread ecosystem acidification through long-range pollution transport (Odén 1968; Rodhe *et al.* 1981). Anthropogenic emissions now dominate the atmospheric sulphur cycle, in particular in the Northern Hemisphere (Spiro *et al.* 1992). About 90% of the man-made emissions occur in northern latitudes, i.e. from the Eurasian and North American continents. On the other hand, the 10% contribution from southern latitudes accounts for roughly half the atmospheric sulphur budget in the Southern Hemisphere (Langner & Rodhe 1991).

Charlson *et al.* (1991) suggested that sulphate pollution significantly enhances the clear-sky solar radiation backscattering, which can cause a regional cooling effect downwind of the largest source areas. Therefore, the aerosols may counteract the anthropogenic greenhouse effect in some regions (Kiehl & Briegleb 1993). Nevertheless, the lifetimes of SO₂ and sulphate are relatively short, so the remote marine

Table 1. Mean lifetime and observed mixing ratios of sulphur species in the lower atmosphere in pptv (Warneck 1988; Langner et al. 1993)

species	average lifetime	marine air	clean continental	polluted continental	free troposphere	
H ₂ S	2 days	0-110	15-340	0-800	1-13	
O CS	3 years	530 ± 20	510 ± 80	520 ± 80	510 ± 60	
CS_2	1 week	30 - 45	15-45	80-300	≤ 5	
CH ₃ SCH ₃	0.5 day	5 - 400	7-100	2 - 400	≤ 2	
SO_2	2 days	10 - 200	70-200	$10^2 - 10^4$	30-260	
$\mathrm{SO}_4^{\overline{2}-}$	5 days	5-300*	10 - 120	$10^2 - 10^4$	5-70	

* Refers to non-sea salt sulphate (NSSS).

atmosphere is probably still relatively pristine. It should be realized, however, that although European and North American emissions have decreased since the 1970s, emerging economies in Africa, South America and particularly in southern Asia are associated with greatly increasing emissions.

Here, we investigate the present-day global sulphur budget and the role of anthropogenic SO_2 emissions. A source inventory is discussed in §2. Further, we have simulated the emissions, chemistry and removal processes with the coupled chemistry-general model ECHAM (Roeckner *et al.* 1995; Roelofs & Lelieveld 1995; Feichter *et al.* 1996). The model, which includes some recent improvements in the representation of multiphase chemistry and deposition processes, is described in §3. Calculated concentrations are compared with observations in §4, the results are discussed in §5, and §6 presents the conclusions.

2. SOURCE ESTIMATES

The release of sea salt sulphate into the atmosphere from sea spray may amount to several hundred Tg S yr^{-1} (Erickson & Duce 1988). However, most of it occurs in coarse particles that are removed rapidly by gravitational settling so that the sulphate does not penetrate the atmosphere deeper than a few decameters. It is generally assumed that biogenic DMS emissions, though an order of magnitude smaller than sea salt sulphate fluxes, play an important role in the marine atmospheric sulphur budget, and to a large extent control the aerosol number concentration in this environment (Andreae & Raemdonck 1983; Charlson *et al.* 1987). Terrestrial sources of reduced sulphur, on the other hand, are comparatively small (table 2). The most important example is H_2S release from swamps, marshes and estuaries, though part of the emissions occurs as DMS and other reduced sulphur compounds. The dominant source is bacterial decay of organic matter under anoxic conditions below the water table. Aerated parts of soils may contain reduced sulphur by diffusion from deeper anaerobic layers, however, this is utilized as an energy source by sulphur oxidizing bacteria in the dry top soils so that releases to the atmosphere are negligible.

Volcanoes constitute an important but highly variable and thus uncertain source of sulphur. Most of it is emitted as SO_2 from hot magma, while a small fraction is released as H_2S . Roughly half the emissions occur from non-eruptive volcanoes such as Mt Etna, and from other more or less continuous fumaroles. The other half is due to the several dozens of eruptions that occur each year over the globe. Much of these emissions occur in the free troposphere where the lifetime of sulphur is relatively long, so volcanoes play an important role in the global atmospheric sulphur budget. The unpredictable nature of these emissions and the difficulty of quantifying the strongly varying sulphur content of magma lead to large uncertainties in volcanic sulphur emission estimates.

Most of the terrestrial emissions to the present-day atmosphere are due to the combustion of coal and, to a lesser extent, of oil. Coal contains sulphur as pyrite and as organic compounds. The sulphur content of coal can be as high as 2-5%, while that of crude oil is from 1-2%. The oil refining process separates the sulphur into the heavy residues, so that the lighter products are relatively cleaner. Natural gas is usually

Table 2. Recent estimates of global sulphur sources in Tg S yr⁻¹ (modified after Möller 1995)

(A: Penner *et al.* (1994); B: Pham *et al.* (1995); C: Bates *et al.* (1992); D: Andreae & Jaeschke (1992); E: Spiro *et al.* (1992); F: Langner & Rodhe (1991); G: Warneck (1988); H: this work.)

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source	А	В	С	D	Е	F	G	Н
volcanic	3-20	9.2	9.3	7.4–9.3	9	8.5	7	7.8
terrestrial	0.1 - 5	1.2	0.3	3.8 - 4.3	1	1	7	1.1
oceanic (NSS)	12 - 40	19.7	15.4	19 - 58	12	16	36	15.5
total natural	15 - 65	30.1	25	30 - 72	22	25.5	50	24.4
biomass burning	1-4	3	2.2	2.8	2	2.5		2.3
fossil fuel use	70-85	92.4	76.8		78	70	103	67
total manmade	71-89	95.4	79		80	72.5	103	69.3
total	86 - 154	125.5	104		102	98	153	93.7

sulphur-poor, however, some gases may contain H₂S. Nevertheless, this is removed prior to its transport and distribution through pipelines because of its corrosive properties. During fuel combustion the sulphur is readily converted to SO₂ and, if it is not removed from the exhausts, it is released to the atmosphere mostly through high stacks. Several per cent of the SO_2 is converted in the hot plume, so that it is directly emitted as sulphate. Globally, about 60% of all fossil sulphur emissions occur from coal combustion, roughly 30% from the use of oil and its refined products, the remainder being due to smelters and other industries (Cullis & Hirschler 1980). Global emission estimates of this anthropogenic source are relatively well constrained at about 70 Tg S yr⁻¹ and have a relatively small uncertainty of $\pm 30\%$, whereas global estimates of natural sources have uncertainties of about a factor of 2.

3. MODEL DESCRIPTION

The general circulation model (GCM) used is the 19-layer ECHAM spectral model (version 4) that applies a hybrid coordinate system. The GCM has been derived from the ECMWF weather forecasting model. Vorticity, divergence, temperature, surface pressure, humidity and cloud water are prognostic variables. Radiation, large-scale and convective cloud formation and precipitation are calculated, as well as explicit boundary layer mixing processes. Land surface processes are described by a five-layer heat conductivity soil model and by a hydrological model to determine evaporation and runoff. The large-scale cloud scheme calculates condensation of water vapour, evaporation of cloud water, formation of precipitation by cloud droplet coalescence and sedimentation of ice crystals, and the evaporation of precipitation in unsaturated air (Roeckner et al. 1991). An elaborate description of ECHAM and the simulated climate can be found in Roeckner et al. (1992, 1995), Boer et al. (1992) and Haskins et al. (1995). The simulations have been performed at T21 resolution (ca. 5.6° latitude/ longitude). Sea surface temperatures have been prescribed.

The GCM has been coupled to a tropospheric chemistry model that considers background CH₄-CO- NO_r -HO_r chemistry, emissions of NO and CO (CH₄ is prescribed), dry deposition of $\mathrm{O}_3,\ \mathrm{NO}_2,\ \mathrm{HNO}_3$ and H₂O₂, and wet deposition of HNO₃ and H₂O₂. Vertical tracer transports have been parameterized according to Tiedtke (1989). This scheme distinguishes between penetrative, mid-level and shallow convection. Convective clouds are represented by a bulk model and include updraft and down-draft mass fluxes. The tracer transport properties of the model have been tested by Feichter et al. (1991) and Brost et al. (1991). A description and an analysis of the coupled chemistry-GCM are given in Roelofs & Lelieveld (1995). A simulation of the global sulphur cycle is presented in Feichter *et al.* (1996). For the current study the sulphur and photochemistry calculations have been performed interactively with the GCM at a 40 min time resolution.

The biogenic emissions from marine as well as terrestrial sources are assumed to occur in the form of DMS (table 2). The distribution of industrial and fossil fuel related emissions has been adopted from Benkovitz *et al.* (1997). A fraction of 95% of the fossil fuel related emissions is assumed to occur as SO₂ and the remainder as sulphate (Langner & Rodhe 1991). The volcanic and biomass burning sources have been modelled according to Spiro *et al.* (1992). The biomass burning emissions are distributed according to Hao & Liu (1994), consistent with the sources of NO_x and CO.

The sulphur chemistry scheme calculates DMS oxidation by OH and NO₃ (Feichter et al. 1996). The sole product of these reactions is SO₂. The SO₂ is oxidized in the gas phase by OH as well as in the cloud liquid phase. Dissolution of SO₂, O₃, H₂O₂ and HNO₃ is considered explicitly. In the cloud and precipitation drops, SO₂ hydrolyses and dissociates into HSO₃⁻ and H^+ , and further into SO_3^{2-} and H^+ ; HSO_3^- reacts with H_2O_2 , and SO_3^{2-} with O_3 in the aqueous phase to form sulphate. The partial differential equations describing these processes are evaluated simultaneously with a Eulerian Backward Iterative (EBI) numerical integration scheme (Roelofs & Lelieveld 1995). Mass transfer of gases between phases is calculated using the Froessling equation (Schwartz 1986). Gas phase transport limitations are considered, but not the possible gas-liquid and liquid phase diffusion limitations of aqueous phase chemistry. All accommodation coefficients are assumed to be unity. Reaction rate constants are given in Roelofs (1992).

The aqueous phase EBI module is applied to incloud and below-cloud chemistry. Input parameters for the routine are liquid water content (LWC), effective cloud droplet radius (10 μ m), pressure and temperature. Concentration changes of SO₂, O₃, HNO₃ and H₂O₂, and liquid phase H₂O₂, NO₃⁻, H⁺, HSO₃⁻, SO₃²⁻ and SO₄²⁻ are calculated interactively. Each sulphate molecule produced is assumed to be associated with one H⁺ and one NH₄⁺, so that the pH is calculated explicitly (Dentener & Crutzen 1995). The relevant cloud and rain parameters (LWC, p, T) are calculated by ECHAM. Liquid surfaces on ice and snow, which may enhance aqueous phase sulphate formation, are not considered by the model.

It is assumed that 60% of the particulate matter is taken up in droplets by nucleation-scavenging during cloud formation (Boucher & Lohmann 1995). After the calculation of aqueous phase chemistry, the precipitation formation calculation by ECHAM determines which fraction of the dissolved species is transported in rain to the grid cell below; the rest is released to the atmosphere in gaseous or particulate form. Below the cloud, the LWC and effective rain drop radius are calculated based on the empirical relationship derived by Mason (1971). Precipitation is assumed to be ice below a temperature of 0 °C, which prevents additional dissolution of gases and chemistry taking place. Below-cloud scavenging of aerosols is calculated following the parameterization of Scott (1978). Release to the atmosphere of chemical species from rain is proportional to the ECHAM-calculated precipitation/evaporation.



Figure 1. Measured (squares, see text for references), and model-calculated monthly varying SO₂ concentrations at the surface. The dotted lines indicate SO₂ concentrations in adjacent grid cells with the highest and lowest concentrations. (a) Langenburgge (53° N, 11° E); (b) Ispra (46 °N, 9° E); (c) Union County (38° N, 88° W); (d) Janiskoski (69° N, 29° E); (e) Illmitz (48° N, 17° E); (f) Franklin County (40° N, 85° W); (g) Spitzbergen (79° N, 12° E).

Dry deposition of SO_2 and sulphate is calculated using the scheme of Ganzeveld & Lelieveld (1995). In the direct vicinity of sources sub-grid scale removal of 15% of the SO_2 emissions has been assumed (Langner & Rodhe 1991). The dry deposition flux of trace gases is parameterized as the product of their concentration at a reference height and the gas-specific deposition velocity. The latter is calculated according to the 'bigleaf' and 'multi-resistance' concepts (Hicks *et al.* 1987). The turbulent transfer and the vegetation activity are computed by the ECHAM model, supplemented with reactive uptake rates for soil, water, snow and ice surfaces. Recent improvements to the deposition scheme include the use of a local surface roughness, a more realistic representation of the leaf area index (LAI), and the extension to SO₂ and sulphate aerosols (Ganzeveld *et al.* 1997). The soil resistance of SO₂ is a function of the soil pH and relative humidity (RH). During humid conditions (e.g. $\rm RH > 80\%$) SO₂ deposition is greatly enhanced by reactive uptake in water layers on soils and vegetation. The dry deposition of sulphate is largely controlled by the aerodynamic resistance and by particle size-dependent diffusion, interception, impaction and gravitational settling. Further, deposition over vegetation is a function of the canopy structure, being controlled by the turbulent transfer to the receptor surfaces, e.g. the vegetation and soils. Over land, sulphate is assumed to occur in the aerosol accumulation size range, whereas over the remote oceans 30% is assumed to be associated with large sea salt aerosols (Andreae *et al.* 1995).

4. COMPARISON OF MEASUREMENTS

Figure 1 shows the calculated and observed monthly surface SO2 concentrations at a number of locations in the relatively polluted Northern Hemisphere (measurements adopted from Husain & Dutkiewicz 1990; Galloway et al. 1993; Savoie et al. 1997). The dotted lines show the highest and lowest concentrations at the grid boundaries (i.e. the average concentration of the actual grid and the neighbouring grid with the highest and the lowest concentration), which give an indication of the horizontal concentration gradients. The results show that the SO₂ concentration variations, often characterized by a summer minimum and winter maximum, are reproduced well. Nonetheless, the surface concentrations are significantly overestimated. This is partly associated with strong horizontal concentration gradients in some locations. In such cases it is difficult to represent exactly the geographical concentration distributions with our course grid global model. Thus, it may be expected that enhancement of the model resolution improves the agreement; this remains to be tested in the future.

Further, SO₂ often has strong vertical gradients. Misrepresentation of mixing within the boundary layer, or between the boundary layer and the free troposphere, can strongly impact on the surface concentrations. It may be that these mixing processes are somewhat suppressed in the model, as previously noted in a study of NO_r (Roelofs & Lelieveld 1995). It should also be emphasized that underestimation of the SO₂ dry deposition velocities by the new scheme cannot be ruled out (Ganzeveld et al. 1996). Finally, an additional pathway for the conversion of SO₂ to sulphate may prove to be important. This is supported by our results of the monthly varying sulphate concentrations (figure 2). Especially in relatively polluted areas in Europe and the USA, the calculated sulphate concentrations are significantly lower than measured. This appears to be a common problem in global sulphur models (Feichter et al. 1996; Chin et al. 1996; Kasibhatla et al. 1997). It has been suggested that heterogeneous oxidation of SO_2 on mineral dust and other aerosols may account for part of the discrepancy (Dentener *et al.* 1996). Note that such an SO₂ oxidation pathway will increase the sulphate burden in the troposphere, however, it may not contribute to climate forcing, especially if the sulphate

becomes associated with pre-existing large dust particles. The latter is likely to be important in southeastern Asia.

5. DISCUSSION

Table 3 shows the calculated annually averaged SO₂ source and sink terms, and the burden and lifetime of SO_2 in the troposphere. We calculate that about 25 %of the SO₂ emitted per year is dry-deposited, that wet deposition is negligible and that about 75 % is transformed to sulphate. Previous sulphur modelling studies by Langner & Rodhe (1991) and Chin et al. (1996) presented SO₂ wet deposition fluxes of 14 and 20 Tg S yr⁻¹, respectively. Hence, our calculated wet deposition appears to be much lower. A likely explanation is that most SO₃ that is scavenged by precipitation is oxidized, and while in our budget calculations it is counted as sulphate, in other studies this is attributed to SO2 removal. Our calculations indicate that 21 % of the SO₂ oxidation occurs in the gas phase, 18 % by O₃ in the aqueous phase, and 61 %by H₂O₂. The calculated total SO₂ deposition is less compared to our previous study (Feichter et al. 1996) as a result of the new dry deposition formulation. This also results in a 50 % longer lifetime, and a 30 % larger tropospheric burden (table 3). Moreover, differences in the details of the aqueous phase chemistry parameterization also play a role.

Comparing our results of aqueous phase chemistry with the study of Feichter et al. (1996), it appears that the contribution by O3 to SO2 oxidation has increased from 10% to about 18%, and that of OH has decreased from about 30 % to 21 %. This is partly due to the simultaneous calculation of aqueous phase chemical processes in our model, which enhances oxidation by O_3 in the initial period after the cloud has been formed. During the initial stages the strongly pHdependent reaction between SO_3^{2-} and O_3 is not yet suppressed by sulphate and H⁺ formation. Differences in the calculated climates between the previous and current versions of the model (versions 3 and 4) have affected the results also. For example, in version 4 the boundary layer representation was improved, leading to enhanced vertical exchange with the free troposphere. Further, in version 4 the underestimation of summertime precipitation over the Northern Hemispheric continents has been reduced, resulting in a shorter sulphate lifetime in these areas.

The calculated ratio between oxidation in the gas and in the aqueous phase, about 1:5, is the same as that derived by Chin *et al.* (1996), who considered only H_2O_2 as an aqueous phase oxidant. Further, our model couples the SO₂ oxidation to H_2O_2 chemistry, thus accounting for H_2O_2 depletion. It appears that the lower sulphate production through oxidation by H_2O_2 is compensated by the quite efficient oxidation of SO₂ by O₃, although not necessarily in the same locations. The calculated total amount of SO₂ oxidized, 68.7 Tg S yr⁻¹, augmented with the 3.3 Tg S yr⁻¹ emitted as SO₄²⁻, constitutes the total sulphate source. A sulphate fraction of 25 % is dry-deposited, and 75% is removed



Figure 2. For description see opposite.

	Tg S yr^-1	fraction $(\%)$
sources		
emission	73.7	81
DMS oxidation	16.6	19
total source	90.3	100
sinks		
dry deposition	21.7	24
wet deposition	0.2	0
total deposition	21.9	24
$SO_{2} + OH (g)$	14.9	16
$SO_2 + O_3$ (aq)	12.2	13
$SO_{2} + H_{2}O_{2}$ (aq)	41.6	46
total oxidation	68.7	76
total burden (Tg S)	0.56	
mean lifetime (days)	2.3	

Table 3. Model-calculated annual average SO_2 budget in the troposphere

 Table 4. Model-calculated annual average sulphate budget in the troposphere

	Tg S yr^{-1}	fraction $(%)$
sources		
emission	3.3	5
SO ₂ oxidation	68.7	95
total source	72	100
sinks		
dry deposition	18.1	25
wet deposition	53.9	75
total deposition	72.0	100
total burden (Tg S)	1.05	
mean lifetime (days)	5.25	

by precipitation (see table 4). The global columnintegrated sulphate burden is presented in figure 3. It shows maximum sulphate levels in the Northern Hemisphere over the USA and the Eurasian continent, in particular over eastern Europe and south-eastern Asia. It should be noted that our results indicate up to several times larger sulphate burdens over the remote oceans compared to previous work, largely due to the longer SO₂ lifetime by reduced dry deposition.

6. CONCLUSIONS

We have presented a global chemistry-GCM in which the calculations for meteorology, gas phase photochemistry, aqueous phase transformations and removal by precipitation and dry deposition are directly coupled. In previous global 3-D models, the oxidant (i.e. H_2O_2) limitation of SO₂ oxidation in the aqueous phase has either been neglected or underestimated. This is particularly important during winter when photochemical activity and H_2O_2 formation are limited. Compared to an earlier version of our model, we find a substantial increase in the contribution of SO₂ oxidation by O₃ in the aqueous phase.

A second difference with previous models is the explicit and model-consistent calculation of SO_2 and sulphate dry deposition. On average, this approach yields a smaller dry removal of SO_2 and a longer SO_2 lifetime, and it results in a higher sulphate yield through SO_2 oxidation compared to models that use fixed dry deposition velocities for land, ocean, and ice surfaces.

Model-calculated surface SO_2 appears to be systematically overestimated when compared to measure-



Figure 3. Calculated annual average column sulphate burden in mg m⁻².

Figure 2. Measured (squares, see text for references), and model-calculated monthly varying sulphate concentrations at the surface. The dotted lines indicate sulphate concentrations in adjacent grid cells with the highest and lowest concentrations. (a) Spitzbergen (79° N, 12° E); (b) Mace Head (53° N, 10° W); (c) Langenburgge (53° N, 11° E); (d) Ispra (46° N, 9° E); (e) Union County (38° N, 88° W); (f) Janiskoski (69° N, 29° E); (g) Barbados (13° N, 60° W); (h) Illmitz (48° N, 17° E); (i) Albany (42° N, 74° W).

ments in Europe and North America. On the other hand, sulphate concentrations at the surface are somewhat underestimated in these areas. This is a common problem in 3-D sulphur cycle models. Unfortunately, the coupling between the photochemistry and sulphur model versions has not resolved this problem, although multiphase SO_2 oxidation processes are modelled more realistically. However, it supports the suggestion that other reaction mechanisms yet unaccounted for, e.g. on mineral dust and other aerosols, play an important role in the oxidation of SO_2 .

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Discussion

J. PLANE (University of East Anglia, UK). While there is no question that a three-dimensional global model of the atmospheric chemistry of sulphate is a highly desirable goal, I wonder if at this point it is somewhat premature? Several recent studies (Bandy *et al.*, Geophys. Res. Lett., 1996; Yvon *et al.*, J. geophys. Res., 1996) of the chemistry of DMS, SO₂, NSSS and MSA in the mid-Pacific gyre show not only discrepancies between the field observations (e.g. in the DMS/SO₂ ratio, the presence or absence of a diurnal cycle in SO₂), but also a problem with modelling the diurnal DMS

cycle. The detailed box models can only succeed in reproducing the observations if the OH concentration and the DMS evasion flux are increased beyond the upper bounds expected from models of these parameters. Until these problems are resolved, going beyond regional scale box models to a global model will remain highly uncertain.

J. LELIEVELD. Detailed box models focus on isolated system components which may be compared with results of laboratory measurements that are also performed in isolation. The large scale 3-D modelling is useful as it integrates the controlling processes and feedbacks, which enables researchers to assess the importance of system components. Further, discrepancies with field observations provide an incentive to look for a missing or misrepresentation of processes, which can be helpful in pursuing improved understanding.

D. J. FISH (University of Reading, UK). Given that the concentration of hydrogen peroxide is proportional to the square of the concentration of HO_2 , is the concentration of H_2O_2 known well enough to be able to say that differences between the modelled rate of SO_2 oxidation and the measurements must be due to missing chemistry?

J. LELIEVELD. Hydrogen peroxide is short-lived, and so its concentration is very variable. Thus, comparison of model results with local measurements is of limited value. Nevertheless, the body of measurement data is growing so that we can start using data compilations for model validation. However, more data are needed. A limited model-data comparison has been performed and obvious discrepancies are not apparent. It should be emphasized that problems cannot be ruled out as H_2O_2 calculations are quite sensitive to simulations of other gases such as ozone, carbon monoxide and NO_x .

D. J. FISH. Are the accommodation coefficients and Henry's Law constant governing the transfer of HO₂ from the gas to liquid phase well enough known?

J. LELIEVELD. Much laboratory work on accommodation coefficients has been carried out recently which has strongly improved the modelling of gas-liquid exchange processes. Uncertainties in measured Henry's Law constant are probably not very important. However, there are still a number of gases for which Henry's Law constants have not yet been measured.

G. P. AYRES (CSIRO, Australia). Average marine SO_2 concentrations shown in one of the initial tables, were put at 60–200 pptv. This is surely too high for most of the Southern Hemisphere, where values of around 10 pptv are more commonly reported away from the equator.

J. LELIEVELD. This table should be updated to include the latest measurements, e.g. in the ACE-1 campaign, that indicate that SO_2 concentrations in the marine boundary layer may indeed be lower than 60 pptv.

G. P. Ayres. An average lifetime of DMS of 0.5 days seems too short to me.

J. LELIEVELD. This DMS lifetime refers to a global mean. Since OH is highly variable, this mean value certainly does not reflect any particular case. I would agree that, for example at Cape Grim in Tasmania, the DMS lifetime is likely to be considerably larger.

G. P. Avres. Concerning comparison of model and observed SO₂ levels in polluted continental regions, high model

predictions may not only be due to a missing oxidation path. The measurements may be lower because of the night-time decrease in boundary layer height; rapid depletion of SO_2 by deposition in a shallower nocturnal surface layer would lower the average measured SO_2 levels. Does the model resolve this diurnal cycle at the surface?

J. LELIEVELD. The model does account for boundary layer variability, for example, between day and night. The highest vertical resolution is in the bottom part of the model. The lowest model layer is about 60 m deep. Nonetheless, we have indications that the boundary layer venting is not efficient enough, thus suppressing exchange with the free troposphere. This needs further analysis.

M. H. SMITH (UMIST, Manchester, UK). In your opening remarks, you dismissed the role of sea salt in the global sulphur cycle. Whilst I agree that the mass of sea salt is dominated by large particles with short atmospheric lifetimes, there are large numbers of sub-micron sea salt particles which, in our work and that of the Hadley Centre, are shown to have a significance for global climate. Secondly, I do not want to overstate my case for sea salt particles, but they can play a substantial role in aqueous phase, heterogeneous sulphur oxidation processes.

J. LELIEVELD. It was not my intention to dismiss the importance of sea salt. However, its importance is not as great as suggested by its direct emission from oceans, as these large particles are efficiently removed by gravitational settling. Nevertheless, there is still sufficient sea salt aerosol available to play a role in the radiation budget and heterogeneous chemistry. In fact, in our model, 30% of the NSS sulphate over the oceans is associated with sea salt aerosols.

R. A. Cox (University of Cambridge, UK). The advantage of using a 3-D model is the ability to see the whole picture. How important is the free troposphere relative to the boundary layer in the chemical transformation of sulphur compounds, and are there any data available with which to test the model-generated fields in the free troposphere?

J. LELIEVELD. The data available on sulphur in the free troposphere are insufficient. For example, good quality SO_2 measurements are close to being absent. However, the direct climate forcing of sulphate in the free troposphere is probably small. Nevertheless, indirect effects by transport from the free troposphere to the marine boundary layer and on cirrus clouds may be important.