

# The Atmospheric Sulphur Cycle and the role of Volcanic SO<sub>2</sub>

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## **Abstract**

A global 3-D chemistry-transport model has been applied to study the atmospheric sulphur cycle, and in particular the volcanic component. The model is in general agreement with previous studies of the global S budget. We find that volcanic emissions constitute 10% of the present-day global SO<sub>2</sub> source to the atmosphere, but form 26% of the SO<sub>2</sub> burden, and 14% of the sulphate aerosol burden. Two previous modelling studies suggested the volcanic fraction of sulphate was 18% and 35%, from sources representing 7% and 14%, respectively, of the global total SO<sub>2</sub> emission. The results are dependent upon various assumptions about volcanic emissions (magnitude, geographical location, altitude), the global distribution of oxidants, and the physical processes of dry and wet deposition. Because of this dependence upon poorly constrained parameters, it is unclear which modelling study is closest to the truth.

## **Introduction**

Sulphur occurs in Earth's atmosphere as a variety of compounds, in both gaseous and aerosol forms, and has a range of natural and anthropogenic sources. The life cycles and atmospheric burdens of these compounds are determined by a combination of physical, chemical and biological processes. Understanding the global S-cycle is important for many reasons. Most sulphur enters the atmosphere as gaseous sulphur dioxide (SO<sub>2</sub>), a

dangerous air pollutant. Sulphur dioxide has a lifetime in the atmosphere of about a day, before being deposited to the surface or oxidised to sulphate ( $\text{SO}_4$ ) aerosol. In the gas phase,  $\text{SO}_2$  oxidation occurs by reaction with hydroxyl radicals (OH), to form sulphuric acid ( $\text{H}_2\text{SO}_4$ ). Sulphuric acid is hygroscopic, and rapidly condenses, either forming new aerosols, or adding to existing ones. Sulphur dioxide gas also partitions into the aqueous phase (in cloud droplets or pre-existing aerosols), where it reacts with dissolved hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) or ozone ( $\text{O}_3$ ) to form  $\text{SO}_4$ . Sulphate is a major component of fine aerosol particles (PM<sub>10</sub> and PM<sub>2.5</sub>: particulate matter less than 10  $\mu\text{m}$  or 2.5  $\mu\text{m}$  in diameter), which can penetrate deep into the lungs, and are harmful to health. Sulphate in precipitation is an important determinant of its acidity; at high levels it causes 'acid rain', which can have devastating effects on sensitive ecosystems. Sulphate aerosols also affect Earth's radiation balance (and hence climate) through the direct scattering of sunlight (Charlson *et al.*, 1992), and also indirectly via modification of cloud albedoes (Twomey, 1977) and lifetimes (Jones *et al.*, 2001), influencing both radiation and the hydrological cycle (Penner *et al.*, 2001). These links between atmospheric sulphur, climate, and the environment assume an even greater relevance since global anthropogenic emissions (60-100  $\text{Mt}(\text{S}) \text{ yr}^{-1}$ ) currently account for about 70% of all sulphur emissions, the remainder emanating from oceanic plankton (13-36  $\text{Mt}(\text{S}) \text{ yr}^{-1}$ ), volcanoes (6-20  $\text{Mt}(\text{S}) \text{ yr}^{-1}$ ), biomass burning (1-6  $\text{Mt}(\text{S}) \text{ yr}^{-1}$ ), and land biota and soils (0.4-5.6  $\text{Mt}(\text{S}) \text{ yr}^{-1}$ ) (Penner *et al.*, 2001). On a regional scale, and in particular over N.E. America, Europe, and S.E. Asia, the anthropogenic fraction is much higher.

Spatial and temporal variations in the local lifetimes of sulphur compounds in the atmosphere mean that atmospheric concentrations do not necessarily linearly relate to

emissions. To link concentrations to emissions, complex atmospheric models are required; the first such modelling study was carried out by Langner and Rodhe (1991). These models allow simulation of the global S-cycle through the synthesis of emissions, transport, chemistry and deposition processes (see Rodhe (1999) for an historical review).

This paper briefly reviews global model estimates of the major components in the tropospheric S-cycle. New model results are then presented, with a particular focus on the volcanic fraction of the S-cycle. Results are compared with similar studies carried out by Chin and Jacob (1996) and Graf *et al.* (1997), which indicated that volcanic sulphur formed sulphate at a much higher efficiency compared to other sources, because the emissions are at a higher altitude, where lifetimes are longer. Clearly, it is important to understand the behaviour of natural sulphur compounds so that we can assess the anthropogenic impact on the atmospheric S-cycle.

### ***Recent model estimates of the atmospheric S-cycle***

There have been several recent detailed reviews of the global sulphur cycle (Rodhe, 1999; Penner *et al.*, 2001), compiling results from a series of studies over the last decade (Langner and Rodhe, 1991; Pham *et al.*, 1995; Chin *et al.*, 1996; Chin and Jacob, 1996; Feichter *et al.*, 1996; Graf *et al.*, 1997; Chuang *et al.*, 1997; Roelofs *et al.*, 1998; Restad *et al.*, 1998; Kjellström, 1998; Adams *et al.*, 1999; Koch *et al.*, 1999; Lohmann *et al.*, 1999; Rasch *et al.*, 2000; Barth *et al.*, 2000; Chin *et al.*, 2000). Figure 1 illustrates the main features of the tropospheric sulphur cycle, and indicates fluxes, burdens, and lifetimes, for both this study, and the average results of 11 models, as reported by the Intergovernmental Panel on Climate Change (IPCC) in their latest report (Penner *et al.*, 2001).

Anthropogenic sulphur is almost exclusively emitted as SO<sub>2</sub> and is associated with fossil fuel use and industry (Benkovitz *et al.*, 1996). Over the last decade or so, SO<sub>2</sub> emissions have fallen in Europe (NEG-TAP, 2001), and to a lesser extent in N. America (EPA, 2001), through efforts to reduce acid rain, but have increased in parts of the developing world (e.g. S.E. Asia). These recent changes partially explain the spread in global totals of anthropogenic emissions used in global models. Similar emissions trends are expected over the first part of this century, but by 2100, global anthropogenic S emissions are predicted to be 20-60 Mt(S) yr<sup>-1</sup>, below present day levels (Nakićenović *et al.*, 2000). Biomass burning emissions of SO<sub>2</sub> (Spiro *et al.*, 1992) are partly natural and partly anthropogenic, but are relatively small compared with the other sources of sulphur.

Lovelock *et al.* (1972) discovered that oceanic phytoplankton were a major source of dimethyl sulphide (DMS: (CH<sub>3</sub>)<sub>2</sub>S), and Charlson *et al.* (1987) suggested a possible biosphere-climate feedback, via the influence of sulphate on clouds, the Earth's radiation budget, ocean temperatures and plankton productivity. In the context of current global warming predictions for the next 100 years, oceanic DMS emission projections show relatively minor changes (Kettle *et al.*, 1999; Penner *et al.*, 2001). DMS is oxidised in the atmosphere by OH and nitrate (NO<sub>3</sub>) radicals, mainly to SO<sub>2</sub>, but with a significant fraction (~25% in the model used in this study) forming methane-sulphonic acid (MSA), and a small fraction (<2%) forming SO<sub>4</sub> directly.

The main other sources of S are volcanoes, which emit both SO<sub>2</sub> and hydrogen sulphide (H<sub>2</sub>S), which rapidly oxidises to SO<sub>2</sub> in the atmosphere. Andres and Kasgnoc (1998) estimated, based on volcanic gas measurements over the last 30 years, a global mean S flux of 9.3 Mt(S) yr<sup>-1</sup> for these two gases. This flux varies in time and space, and is made

up of contributions from continuously degassing volcanoes (e.g. Etna, Italy), sporadically erupting volcanoes (e.g. Popocatepetl, Mexico), and major individual explosive events (e.g. Pinatubo, Philippines). Large explosive events, like the Mt. Pinatubo eruption in 1991, will add most S directly to the stratosphere, where it will oxidise to sulphuric acid aerosol, and then slowly settle into the troposphere over the years following the eruption. These large individual events cannot sensibly be studied in a time-averaged sense, but require case-study investigations. This study focuses instead on the ‘background’ volcanic component, introduced by continuously and sporadically active volcanoes, which generally emit their S into the free troposphere (i.e. above the boundary layer), and sometimes explosively lofting S to levels throughout the troposphere (i.e. altitudes up to ~10-15 km). Estimates of the volcanic S source strength vary widely, and modellers have used values as low as 2.9 Mt(S) yr<sup>-1</sup> (Pham *et al.*, 1995) to as high as 14 Mt(S) yr<sup>-1</sup> (Graf *et al.*, 1997). The source strength, geographical location, and vertical spread of emissions will all influence their fate and overall contribution to the global S-cycle.

Two other sources of sulphur are carbonyl sulphide (OCS) and carbon disulphide (CS<sub>2</sub>), both with minor oceanic and biomass burning sources (Andreae and Crutzen, 1997; Kjellström, 1998), and possibly volcanic sources of similar magnitude (Andres and Kasgnoc, 1998). Carbon disulphide has a lifetime of about a week, oxidising to OCS and SO<sub>2</sub>. Carbonyl sulphide has a relatively long lifetime (9 years), and is consequently well mixed throughout the atmosphere. In the absence of large explosive volcanic eruptions, OCS is the main source of stratospheric sulphate aerosol, where its slow oxidation generates a constant small flux (~0.1 Mt(S) yr<sup>-1</sup>) of SO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>. Sea-spray is also a major source (40-320 Mt(S) yr<sup>-1</sup>) of sulphate aerosol to the marine boundary layer

(Berresheim *et al.*, 1995). This study, in common with most others, neglects the contributions of OCS and CS<sub>2</sub>, and only considers the non-sea-salt sulphate (nss-SO<sub>4</sub>) part of the S-cycle.

Figure 1 indicates that about 60% of SO<sub>2</sub> is oxidised to SO<sub>4</sub> rather than being deposited to the surface as SO<sub>2</sub>. Most oxidation occurs in the aqueous-phase, and the main oxidant is H<sub>2</sub>O<sub>2</sub>. Sulphate aerosol has a typical atmospheric lifetime of around 5 days before it is deposited to the surface, mainly through wet deposition.

### ***STOCHEM-Ed model***

STOCHEM-Ed is a global 3-D Lagrangian chemistry-transport model (CTM), developed initially at the UK Met. Office (Collins *et al.*, 1997, 1999, 2000), and latterly at the University of Edinburgh. The main difference between the model version used here and those previously described is an increased vertical resolution in both the driving GCM (General Circulation Model), and the CTM, particularly at tropopause levels. The meteorological input to this version of the model is generated on-line by HadAM3, an atmosphere-only version of the Unified Model GCM (Johns *et al.*, 1997). The GCM has a resolution of 3.75° longitude by 2.5° latitude, with 58 vertical levels, and supplies fields every 3 hours to STOCHEM-Ed (Johnson *et al.*, 2001). The CTM atmosphere is divided into 50,000 equal mass air parcels, which are advected using a 4<sup>th</sup> order Runge-Kutta scheme, with interpolated winds, and an hourly time-step. For the purposes of mixing and model output, the Lagrangian air parcels are mapped to a grid of resolution 5° by 5°, with 22 vertical levels; this grid is also used for adding emissions to the model. Boundary layer and convection parameterisations are included, and these have been tuned using <sup>222</sup>Rn observations (Stevenson *et al.*, 1998). Winds used by the CTM are interpolated

from the GCM grid to each air parcel location, using linear interpolation in the horizontal and cubic in the vertical. Other meteorological variables (e.g. cloud distributions) are kept fixed over the 3-hr chemistry model time-step. The transport scheme is fully mass conservative, and has been compared with observations of both long-lived and short-lived tracers (Collins *et al.*, 1998; Stevenson *et al.*, 1998). Within each air parcel, the chemistry of 70 compounds is simulated, including the oxidation of methane (CH<sub>4</sub>), carbon monoxide (CO), several non-methane hydrocarbons, and the fast photochemistry of the nitrogen oxides (NO<sub>x</sub>: the sum of NO and NO<sub>2</sub>), O<sub>3</sub>, and several related oxidants and free radical species. Several previous model validation studies and model intercomparisons have assessed the model's performance for species such as NO<sub>x</sub>, OH, HO<sub>2</sub>, CO and O<sub>3</sub> (Collins *et al.*, 1999; Kanikidou *et al.*, 1999a,b). The chemical mechanism also has a detailed description of several sulphur compounds, including DMS oxidation (Jenkin *et al.*, 1996), and aqueous-phase chemistry. The reactions involving sulphur compounds (excluding DMS) are given in Table 1. Further details of the secondary aerosol (including sulphate) simulated by the model are presented by Derwent *et al.* (in press).

In the boundary layer, several species, including SO<sub>2</sub> and sulphate, are dry deposited. The model discriminates between land, ocean, and ice, and uses deposition velocities for SO<sub>2</sub> of 6, 8, and 0.5 mm s<sup>-1</sup> over these surfaces, and values of 2, 1, and 0.05 mm s<sup>-1</sup> for sulphate aerosol. The model calculates deposition rates using these velocities, together with the boundary layer height, and an effective vertical eddy diffusion coefficient derived from the surface stresses, heat flux and temperature.

Soluble species (including SO<sub>2</sub>, sulphate, NH<sub>3</sub>, and H<sub>2</sub>O<sub>2</sub>) are subject to wet removal through precipitation scavenging. Species-dependent scavenging rates are taken from

Penner *et al.* (1994), and vary between large-scale and convective precipitation. Wet removal from large-scale precipitation only occurs below ~400 hPa (~6 km), whereas it initiates in convective clouds when the precipitation rate exceeds  $10^{-8} \text{ kg m}^{-2} \text{ s}^{-1}$ . A simple scavenging profile in convective clouds is used, with a constant rate from the surface to ~850 hPa (~1.5 km), and then a linear decrease to zero at the cloud top. Because most convection of large vertical extent occurs in the tropics, very little wet removal occurs above 400 hPa in the extra-tropics.

The S emissions used are similar to those listed in Penner *et al.* (2001). Anthropogenic ( $71 \text{ Mt(S) yr}^{-1}$ ) and biomass burning ( $1.4 \text{ Mt(S) yr}^{-1}$ ) emissions of  $\text{SO}_2$  are taken from the EDGAR v2.0 database (Olivier *et al.*, 1996), representative of the year 1990. Biomass burning emissions are then distributed using the monthly maps of Cooke and Wilson (1996). Monthly varying emissions of DMS from oceans ( $15 \text{ Mt(S) yr}^{-1}$ ) and soils ( $1 \text{ Mt(S) yr}^{-1}$ ) are also included (Bates *et al.*, 1992). Volcanic emissions of  $\text{SO}_2$  total  $9.0 \text{ Mt(S) yr}^{-1}$ , based upon emissions magnitudes and distribution estimated for 1980 by Spiro *et al.* (1992). These data show peaks associated with the Mt. St. Helens (USA) eruption of 1980, and the continuously high  $\text{SO}_2$  output of Mt. Etna (Sicily). More recent estimates of volcanic emissions (Andres and Kasgnoc, 1998) are of similar total magnitude, but vary somewhat in spatial distribution, due to the considerable fluctuations in gas output of specific volcanoes, depending on their state of activity. To simulate the vertical spread of volcanic emissions in the model, they are distributed evenly from the surface up to ~300 hPa (~8 km). Note that ‘the surface’ does not equate with sea level, as the GCM has orography, albeit at a resolution that will tend to flatten most volcanic peaks. This assumption of an even vertical distribution of volcanic emissions represents a

'best guess' of where volcanic emissions effectively enter the atmosphere. Most previous estimates of the global magnitude and geographic distributions of volcanic emissions (e.g. Andres and Kasgnoc, 1998; Graf *et al.*, 1997) have not suggested vertical profiles. One exception is Chin *et al.* (2000), who use a more sophisticated methodology for incorporating volcanic emissions. These authors emit volcanic SO<sub>2</sub> from continuously active volcanoes (Andres and Kasgnoc, 1998) at altitudes within 1 km above the crater altitude. For sporadically active volcanoes they use the actual eruption dates and duration of individual eruptions, and the volcanic explosivity index (VEI) to estimate the volcanic cloud height (Simkin and Siebert, 1994). They estimate the amount of SO<sub>2</sub> emitted by an individual eruption using a relationship between VEI and SO<sub>2</sub> flux (Schnetzler *et al.*, 1997), or satellite measurements of SO<sub>2</sub> amount from the Total Ozone Mapping Spectrometer (TOMS: Bluth *et al.*, 1997). Finally, the SO<sub>2</sub> is released from the top third of the volcanic cloud.

Many volcanoes passively degas SO<sub>2</sub> from their summits and flanks. Others emit most SO<sub>2</sub> during sporadic explosive eruptions of varying magnitude that will loft the gas to various heights. The inherent variability in the magnitude and location of volcanic emissions means that calculations of the 'volcanic component' of the S-cycle inevitably have a high uncertainty. Further research is required to better characterize the vertical profiles of volcanic emissions to the atmosphere, and it should be noted that this represents perhaps the largest uncertainty in modelling the fate of volcanic SO<sub>2</sub>.

## ***Results and Discussion***

Two simulations have been carried using the model: one for present day conditions including volcanic emissions, and a second with volcanic emissions switched off. Each

simulation was 16 months in length, starting in September, with the first 4 months considered as spin-up and not used in the analysis. All other factors (meteorology, non-volcanic emissions) were kept fixed between the two runs. The only differences between the two runs relate to the difference in volcanic SO<sub>2</sub>, and any effects this has on the chemistry. The simulation with no volcanic SO<sub>2</sub> will have slightly different oxidant (OH and H<sub>2</sub>O<sub>2</sub>) concentrations, however these species are mainly determined by the background photochemistry, and sulphur has a minor impact upon them. Even very large volcanic perturbations, such as the 1783 Laki eruption have been shown to have relatively small effects on oxidants (Stevenson *et al.*, submitted to JGR 2002). Monthly mean concentrations and integrated reaction and deposition fluxes were calculated on the models 3-D output grid. Annual and global average fluxes, burdens and lifetimes of the main components of the S-cycle are shown in Figure 1, and annual and zonal (longitudinal) average concentrations and lifetimes for SO<sub>2</sub> and sulphate are shown in Figures 2 and 3. Lifetimes are defined as the burden divided by the total loss rate, either globally integrated (Figure 1), or locally (Figures 2 and 3).

It is beyond the scope of this paper to present a comparison of modelled and observed SO<sub>2</sub> and sulphate concentrations. Stevenson *et al.* (submitted to JGR, 2002) presented a limited comparison for the model at a few sites and concluded that the model simulated the correct magnitudes for SO<sub>2</sub> and sulphate, and successfully captured the seasonal cycles of these species in Europe. Derwent *et al.* (in press) present a more comprehensive validation of the model's sulphate aerosol fields with global observations, and conclude that the model is performing well.

In general, the model's S-cycle is quite similar to the IPCC average values, and is within the range of all other models for each category. The flux of SO<sub>2</sub> gas-phase oxidation is a little on the low side, and this version of the model is known to have slightly low OH concentrations, so the ratio of gas-phase to aqueous-phase oxidation may be underestimated. The DMS source is also lower than the IPCC average (but well within the range of uncertainty associated with this source), and the detailed DMS oxidation scheme employed also results in less of the DMS ending up as SO<sub>2</sub> (several models assume all DMS is oxidised to SO<sub>2</sub>). The volcanic source is close to the IPCC average, although less than the study of Graf *et al.* (1997), who used a value 56% higher. The burden of SO<sub>2</sub> (0.29 Mt(S)) is 37% lower than the IPCC average, and the SO<sub>2</sub> lifetime (1.1 days) is similarly 39% lower, despite the similar magnitude of total S sources, indicating that the SO<sub>2</sub> sink processes must operate more efficiently in the STOCHEM-Ed model. The SO<sub>4</sub> burden (0.81 Mt(S)) is 5% higher than the IPCC average, and the lifetime (5.3 days) is 8% longer, indicating that SO<sub>4</sub> removal is slightly less efficient than the average of other models.

Figure 2a shows the zonal (averaged around all longitudes) annual mean distribution of SO<sub>2</sub> simulated by the model, clearly showing highest concentrations in the polluted Northern Hemisphere (NH), particularly in mid-latitudes near the surface, close to the main industrial source regions. Due to the short lifetime of SO<sub>2</sub> (Figure 2c), the remote troposphere has relatively low concentrations, except for regions with significant natural sources. Very little SO<sub>2</sub> reaches the stratosphere, but note that the model lacks sources from OCS or large explosive volcanic eruptions. Figure 3a shows the corresponding SO<sub>4</sub> distribution. Sulphate has a longer lifetime, particularly in the upper atmosphere (Figure

3c), where the lack of clouds mean the only removal mechanism is transport to the lower atmosphere.

A further simulation of the present-day atmosphere, where volcanic emissions are switched off, allows the volcanic component to be isolated. The annual global fluxes, burdens and lifetimes of the volcanic component are also shown in Figure 1. The volcanic component of the SO<sub>2</sub> distribution (Figure 2b) shows that volcanic SO<sub>2</sub> dominates large regions of the free troposphere, particularly in the tropics (Indonesia and Central America), but also in the NH (N. America, Japan, Kamchatka) and Antarctica (Erebus). Clearly, it is the NH volcanic emissions, into a region with relatively long lifetime (Figures 2b,c) that results in the long lifetime of the volcanic component. These results are highly dependent upon the geographic distribution of volcanic emissions. Because volcanic emissions are added to the atmosphere at higher altitudes than other S sources, they are less likely to be deposited to the surface as SO<sub>2</sub>, and more likely to be oxidised to SO<sub>4</sub>. Oxidant concentrations generally decrease with increasing height (and latitude) through the troposphere, largely because their main precursor is H<sub>2</sub>O, which rapidly decreases in concentration as temperatures fall. This results in longer SO<sub>2</sub> lifetimes at higher altitudes and latitudes (Figure 2c), and hence the volcanic fraction of the SO<sub>2</sub> budget has a much longer lifetime (3.0 days), and makes a contribution to the total SO<sub>2</sub> burden of 26%, despite only making up 10% of the source. These results are similar to those of Graf *et al.* (1997), who found that volcanic S accounted for 35% of the SO<sub>2</sub> burden, from 14% of the total source.

Graf *et al.* (1997) found a similar contribution (36%) of volcanic S to the global SO<sub>4</sub> burden, but we find the fraction to be only 14% (Figure 3b shows the distribution), only

slightly higher than the emission component. Chin and Jacob (1996) found a global volcanic sulphate burden fraction of 18%, from a source of only 7%. The results presented here can be understood if we examine the fluxes in some detail (Figure 1). Despite making up 26% of the SO<sub>2</sub> burden, volcanic S only makes up 12% of the total SO<sub>2</sub> to SO<sub>4</sub> flux. This is largely due to the fact that the volcanic SO<sub>2</sub> has a longer lifetime, and oxidises more slowly than SO<sub>2</sub> at lower altitudes. The other controls on the volcanic fraction of the SO<sub>4</sub> burden are the SO<sub>4</sub> loss mechanisms, the main one being wet deposition. Modelled local SO<sub>4</sub> lifetimes lengthen with increasing altitude, and are essentially infinite above cloud top heights, but also show distinct maxima at latitudes of 15-20°, in the relatively cloud-free descending limbs of the Hadley Cells (Figure 3c). Hence both the latitude and altitude of volcanic emissions are important. We find that volcanic SO<sub>4</sub> has a lifetime of 6.2 days, slightly (17%) longer than average SO<sub>4</sub> (5.3 days). Wet deposition schemes in global models are quite poorly constrained and variable (e.g. Roelofs *et al.*, 2001; Penner *et al.*, 2001), and this is a major source of uncertainty in modelling S budgets.

Graf *et al.* (1997) defined the ‘efficiency’ of a S source as the fractional contribution to the SO<sub>4</sub> burden divided by the fractional source strength, and found a value of 2.6 for volcanic S, compared to 0.74 for non-volcanic sources. Chin and Jacob (1996) found similar values of 2.6 and 0.85, respectively. In this study we find a less marked difference: 1.4 for volcanic S, and 0.96 for non-volcanic sources.

## **Conclusions**

We have simulated the tropospheric S-cycle, and isolated the volcanic component, using a 3-D global chemistry-transport model. Modelled global S budgets are broadly in

line with those reported by the IPCC (Penner *et al.*, 2001). Results indicate that despite making up only 10% of the SO<sub>2</sub> source in the model, volcanic S makes up 26% of the SO<sub>2</sub> burden, and 14% of the SO<sub>4</sub> burden. The relatively large contribution of volcanic S to the SO<sub>2</sub> burden is due to the longer SO<sub>2</sub> lifetime at higher altitudes and latitudes, through reduced losses from deposition and oxidation. The lower contribution of volcanic S to the SO<sub>4</sub> burden (compared to the SO<sub>2</sub> burden) stems from the slower oxidation rates of SO<sub>2</sub> that limit the source of SO<sub>4</sub>, and also the less variable lifetime of SO<sub>4</sub> with latitude (Figure 3c). The results for SO<sub>2</sub> are similar to those found by Graf *et al.* (1997), but these authors, together with Chin and Jacob (1996), also found that the large volcanic contribution was carried forward to SO<sub>4</sub>, in contrast to the results presented here. The volcanic contribution to the global budget is clearly influenced by several factors, including: (i) the magnitude and location of volcanic emissions; (ii) the assumed altitude profile of the emissions; (iii) the distributions of oxidants; and (iv) the deposition schemes employed by models. All of these require careful consideration if we are to further constrain the global S budget and its volcanic component.

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Gas-phase reactions	Rate constant <sup>a</sup>
$\text{SO}_2 + \text{OH} + \text{M} \rightarrow \text{H}_2\text{SO}_4 + \text{HO}_2$	Complex <sup>e</sup> : $A_6(A_3)^{(1/A_7)}$
Species	Henry's Law Coefficients <sup>b</sup>
$\text{SO}_2$	$1.23 \times 10^0 \exp(3120 \text{ T}^*)$
$\text{O}_3$	$1.1 \times 10^{-2} \exp(2300 \text{ T}^*)$
$\text{HNO}_3$	$3.3 \times 10^6 \exp(8700 \text{ T}^*)$
$\text{H}_2\text{O}_2$	$7.36 \times 10^4 \exp(6621 \text{ T}^*)$
$\text{NH}_3$	$7.5 \times 10^1 \exp(3400 \text{ T}^*)$
$\text{CO}_2$	$3.4 \times 10^{-2} \exp(2420 \text{ T}^*)$
Aqueous-phase equilibria	Equilibrium constants <sup>c</sup>
$\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HSO}_3^-$	$1.7 \times 10^{-2} \exp(2090 \text{ T}^*)$
$\text{HSO}_3^- \rightleftharpoons \text{H}^+ + \text{SO}_3^{2-}$	$6.0 \times 10^{-8} \exp(1120 \text{ T}^*)$
$\text{HNO}_3 \rightleftharpoons \text{H}^+ + \text{NO}_3^-$	$1.8 \times 10^{-5} \exp(-450 \text{ T}^*)$
$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	$1.8 \times 10^{-5} \exp(-450 \text{ T}^*)$
$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	$4.3 \times 10^{-7} \exp(-913 \text{ T}^*)$
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	$1.0 \times 10^{-14} \exp(-6716 \text{ T}^*)$
Aqueous-phase reactions	Rate constants <sup>d</sup>
$\text{HSO}_3^- + \text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{SO}_4^{2-} + \text{H}_2\text{O}$	$([\text{H}^+]/([\text{H}^+]+0.1)) 5.2 \times 10^6 \exp(-3650 \text{ T}^*)$
$\text{HSO}_3^- + \text{O}_3 \rightarrow \text{H}^+ + \text{SO}_4^{2-} + \text{O}_2$	$4.2 \times 10^5 \exp(-4131 \text{ T}^*)$
$\text{SO}_3^{2-} + \text{O}_3 \rightarrow \text{SO}_4^{2-} + \text{O}_2$	$1.5 \times 10^9 \exp(-996 \text{ T}^*)$

**Table 1.** Main sulphur chemistry included in the model (excluding DMS reactions). T is temperature (K);  $\text{T}^* = (1/\text{T}) - (1/298)$ ; [M] is the molecular density of air (molecules  $\text{cm}^{-3}$ );  $[\text{H}^+]$  is the hydrogen ion concentration ( $\text{mol l}^{-1}$ ).

<sup>a</sup>Units:  $(\text{cm}^3 \text{ molecule}^{-1})^{(\text{no. of reactants} - 1)} \text{ s}^{-1}$

<sup>b</sup>Units:  $\text{mol l}^{-1} \text{ atm}^{-1}$

<sup>c</sup>Units:  $(\text{mol l}^{-1})^{(\text{no. of products} - \text{no. of reactants})}$

<sup>d</sup>Units:  $\text{mol l}^{-1} \text{ s}^{-1}$

<sup>e</sup> $A_1=[\text{M}]3.0 \times 10^{-31}(\text{T}/300)^{-3.3}$ ;  $A_2=1.5 \times 10^{-12}$ ;  $A_3=0.6$ ;  $A_4=0.75-1.27 \log_{10} A_3$ ;  $A_5=A_1/A_2$ ;

$A_6=A_1/(1+A_5)$ ;  $A_7=1+(\log_{10} A_5/A_4)^2$

## **Figures**

**Figure 1.** The global atmospheric sulphur budget, for 1990 emissions. The numbers in bold refer to results from the STOCHEM-Ed model used in this study. Numbers in the shaded boxes refer to the volcanic component. Numbers in italics are from the IPCC Third Assessment Report (Penner *et al.*, 2001). Fluxes are in Mt(S) yr<sup>-1</sup>, burdens in Mt(S), and lifetimes in days. Sulphate in sea-salt aerosol, and fluxes from minor sulphur compounds (e.g. OCS, CS<sub>2</sub>) are not considered in this study.

**Figure 2.** Zonal annual mean (latitude against altitude) results from the model: (a) 1990 SO<sub>2</sub> (pptv); (b) volcanic fraction (%); (c) SO<sub>2</sub> lifetime (days).

**Figure 3.** Zonal annual mean (latitude against altitude) results from the model: (a) 1990 SO<sub>4</sub> (pptv); (b) volcanic fraction (%); (c) SO<sub>4</sub> lifetime (days).