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Anthropogenic and natural contributions to tropospheric sulfate: A global model analysis

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Abstract. A global three-dimensional model is used to examine the export of anthropogenic sulfur from northern midlatitude continents and to assess the relative importance of anthropogenic and natural sources to sulfate levels in different regions of the troposphere. Model results indicate that about 40% of the anthropogenic sulfur emitted in the United States, Europe, or eastern Asia is exported out of the continental boundary layer of these regions; the rest is removed within the regions, primarily by dry deposition of SO_2 and wet deposition of SO_4^{2-}. Export is relatively more efficient in summer than in winter. There is little nonlinearity between the magnitude of sulfur emissions in the northern midlatitude continents and the export of this sulfur to the global atmosphere. Anthropogenic influence on SO_4^{2-} decreases rapidly with altitude because of efficient scavenging of SO_2 and SO_4^{2-} in deep convective updrafts. Thus it is found that anthropogenic influence accounts on average for less than 20% of SO_4^{2-} anywhere in the upper troposphere. The main source of SO_4^{2-} in the tropical upper troposphere in the model is from biogenic dimethylsulfide (DMS) pumped in deep convective events. Volcanic emissions account for 20–40% of SO_4^{2-} in much of the middle troposphere and for up to 80% over the North Pacific; they also represent a major contributor to SO_4^{2-} in the upper troposphere at high latitudes. On a global scale, it is estimated that anthropogenic, biogenic, and volcanic emissions account for 70%, 23%, and 7%, respectively, of the global sulfur source, but that they account for 37%, 42%, and 18%, respectively, of the global column of atmospheric SO_4^{2-}. The disproportionality between source and column contribution reflects the rapid deposition of anthropogenic SO_2 and SO_4^{2-} at low altitudes. It thus appears that the anthropogenic contribution to the SO_4^{2-} aerosol optical depth is much less than would be expected simply on the basis of emissions.

1. Introduction

Sulfate aerosol cools the Earth directly by scattering solar radiation and indirectly by providing condensation nuclei for cloud formation, increasing cloud albedo. Recent estimates suggest that the global radiative forcing from anthropogenic sulfur emissions may balance the radiative forcing from anthropogenic emissions of greenhouse gases [*Intergovernmental Panel on Climate Change* (IPCC), 1995]. However, because of the short lifetime of aerosols against deposition (days – weeks), the radiative forcing associated with aerosols varies strongly with region. A critical uncertainty in assessing the climatic effect of anthropogenic sulfur emissions is the spatial and temporal extent of the anthropogenic SO_4^{2-} aerosol [*IPCC*, 1995]. We address this issue here by using a global three-dimensional model with synoptic-scale resolution based on the Goddard Institute of Space Studies general circulation model (GISS GCM). A detailed description of the model, including evaluation with observations for SO_4^{2-} and its precursors, is given by *Chin et al.* [this issue]. Here we apply the model to quantify the export (defined as the net outflow) of sulfur from northern midlatitude continents and to assess the relative contributions of anthropogenic and natural sources to SO_4^{2-} levels in different regions of the atmosphere.

The principal anthropogenic sources of sulfur to the atmosphere are coal and oil combustion, oil refining, and smelting of ores; the main natural sources are oceanic phytoplankton and volcanoes. About 70% of the global emission of sulfur to the atmosphere is anthropogenic, and 70% of this anthropogenic source is concentrated in the United States, Europe, and eastern Asia [*Spiro et al.*, 1992; *Benkovitz et al.*, 1996]. Export of pollution from these continental regions is known to make significant seasonal contributions to SO_4^{2-} levels over the North Atlantic (D. L. Savoie et at., Oceanic and anthropogenic contributions to non-sea-salt sulfate in the marine boundary layer over the North Atlantic Ocean, submitted to *Journal of Geophysical Research*, 1995), the Arctic [*Barrie et al.*, 1989], and the North Pacific [*Savoie and Prospero*, 1989]. However, it appears also that only a small fraction of the sulfur emitted from polluted continents is actually exported, the remainder being deposited over the continent of origin [*Galloway et al.*, 1984]. Understanding the processes determining the export of sulfur from polluted continents is evidently of great importance for assessing global human influence on SO_4^{2-}.

Several previous three-dimensional model studies have examined the anthropogenic contribution to SO_4^{2-} aerosol on a global scale. Comparison of the global sulfur budgets in the different

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models is presented by *Chin et al.* [this issue]. *Langner et al.* [1992], using the coarse-resolution model MOGUNTIA, found that human activity had increased the SO_4^{2-} burden by a factor of 2.8 in the northern hemisphere and a factor of 1.4 in the southern hemisphere since preindustrial time. Similar anthropogenic contributions to the SO_4^{2-} burden were found by *Penner et al.* [1994] using a higher resolution, synoptic-scale model (GRANTOUR). *Pham et al.* [1996] found in their recent study using the IMAGES model that the increase of SO_4^{2-} since preindustrial time was a factor of 4 in the northern hemisphere and a factor of 1.5 in the southern hemisphere. Our results, presented below, suggest that the global extent of human influence on SO_4^{2-} is significantly less than inferred in these previous studies.

We begin the paper with a brief description of the model (section 2); further details are given by *Chin et al.* [this issue]. We then use the model in section 3 to analyze the export of anthropogenic sulfur from the northern midlatitude continents to the global atmosphere. The relative contributions of anthropogenic and natural sources to SO_4^{2-} levels in different regions of the troposphere are examined in section 4. Conclusions are in section 5.

2. The Model

The model solves the mass conservation equations for dimethylsulfide (DMS), H_2S, SO_2, SO_4^{2-}, and methanesulfonic acid (MSA), on a global three-dimensional grid with 4° latitude x 5° longitude resolution in the horizontal, nine layers in the vertical, and a time step of 4 hours. The grid follows that of the GISS GCM II [*Hansen et al.*, 1983]. The vertical resolution (sigma coordinate) is such that the boundary layer below 2.6 km is resolved by three layers and the free troposphere above is resolved by four to five layers (the top model layer is in the stratosphere). Meteorological input to the model is provided by a 1-year archive of 4-hour average quantities from the GCM, including winds, convective mass fluxes, clouds, precipitation, and other variables.

Emission of SO_2 from fossil fuel combustion and industrial activities (65 Tg S yr^{-1}) is specified from the Global Emissions Inventory Activity (GEIA) database for 1985 [*Benkovitz et al.*, 1996]. Biomass burning represents a small additional source (2.3 Tg S yr^{-1}). Biogenic sulfur emissions include DMS from the ocean (22 Tg S yr^{-1}) and H_2S and DMS from terrestrial vegetation and soils (0.9 Tg S yr^{-1}). Volcanic emissions of SO_2 include a noneruptive, continuously emitting component derived from a data base of volcanic activity for the early 1980s (2.7 Tg S yr^{-1}), and an eruptive component based on a chronology of volcanism for 1985 with daily resolution (4.0 Tg S yr^{-1}). Noneruptive emissions are emitted at the mouth of the volcano. Eruptive emissions for each individual volcano are distributed in time over the duration of the eruption, and vertically over the depth of the eruption plume, as described by *Spiro et al.* [1992] and *Chin et al.* [this issue]. Oxidation of carbonyl sulfide (OCS) is also included as a source of SO_2 in the stratosphere (0.03 Tg S yr^{-1}) following *Chin and Davis* [1995].

The model accounts for gas-phase oxidation of DMS, H_2S, and SO_2 by OH, using global three-dimensional fields of OH concentrations with 5-day resolution from *Spivakovsky et al.* [1990] and scaling the 24-hour average OH to the cosine of solar zenith angle. The model also accounts for nighttime oxidation of DMS by NO_3, and for an additional DMS oxidant as necessary to yield a DMS lifetime consistent with observed DMS concentrations in the marine boundary layer (see *Chin et al.* [this issue] for further discussion). Aqueous-phase oxidation of SO_2 by H_2O_2 in clouds is simulated as a rapid process limited solely by the availability of H_2O_2 and the frequency of cloud processing. Concentrations of H_2O_2 are specified as a function of latitude and season using the photochemical model of *Spivakovsky et al.* [1990]. The frequency of cloud processing is estimated on the basis of GISS GCM data for cloud volume fractions in individual grid boxes [*Chin et al.*, this issue].

Scavenging of SO_2 and SO_4^{2-} by precipitation is computed with the scheme described by *Balkanski et al.* [1993] and previously tested in the GISS GCM by simulation of ^{210}Pb aerosol. The scheme accounts for efficient scavenging in the wet convective updrafts of the GCM as well as for rainout and washout from large-scale precipitation. Wet scavenging of SO_2 is contingent on rapid oxidation to SO_4^{2-} and is therefore limited in polluted regions by the availability of H_2O_2. Dry deposition fluxes of SO_2 and SO_4^{2-} are computed with a resistance-in-series model [*Wesely*, 1989] as a function of surface type and meteorological conditions; the formulation accounts for seasonal changes in the deposition velocity due to snow and ice. The monthly mean SO_2 dry deposition velocities in the model are 0.3–1.0 cm s^{-1} over ocean surfaces, 0.1–0.5 cm s^{-1} over land, and ~0.1 cm s^{-1} over desert and snow; the dry deposition velocity of SO_4^{2-} ranges from 0.01 to 0.4 cm s^{-1} depending on surface roughness.

Chin et al. [this issue] present a detailed evaluation of model results with observations for SO_4^{2-} and its precursors. The model reproduces typically to with 30% the observed SO_2 and SO_4^{2-} concentrations and SO_4^{2-} wet deposition fluxes measured over the United States and Europe. Agreement to within 50% is found between model and observations for DMS, SO_2, and SO_4^{2-} at surface sites in the southern hemisphere, with some exceptions. Model results for DMS, SO_2 and SO_4^{2-} in the free troposphere are generally consistent with the few observations available. The model underestimates the observed SO_4^{2-} concentrations over the North Pacific and the North Atlantic, partly because of precipitation anomalies in the GCM; better simulation is achieved in these regions for the MSA/SO_4^{2-} concentration ratio, which reflects the relative contributions of biogenic and anthropogenic sources to SO_4^{2-} [*Savoie and Prospero*, 1989]. The observed transport of sulfate from Eurasia to the Arctic in winter and spring is reproduced in the model for the European Arctic but is underestimated for the North American Arctic.

All results presented below are from the standard model simulation described above, and from sensitivity simulations where emissions from specific sources have been reduced or removed. All the simulations are conducted for the same period of 15 months, starting from low initial conditions. Only the last 12 months are used for analyses.

3. Export of Anthropogenic Sulfur From Polluted Continents

Figure 1 shows the horizontal and vertical fluxes of total sulfur between 10°N and 70°N in summer (June – August) and winter (December – February) in the standard model, for the lower tropospheric column extending from the surface to 2.6 km (top of model layer 3). This column is taken to represent the continental boundary layer in the model [*Jacob et al.*, 1993]. The United States, Europe, and eastern Asia (as defined in Figure 1) account together for 70% of total anthropogenic sulfur emissions in the GEIA data base for 1985 [*Benkovitz et al.*, 1996].

Sulfur budgets for the U.S. boundary layer in summer and winter are given in Figure 2. Over 95% of the SO_2 source in the region is anthropogenic. About 80% of SO_2 is lost within the region by deposition and oxidation, both in summer and winter; dry deposi-

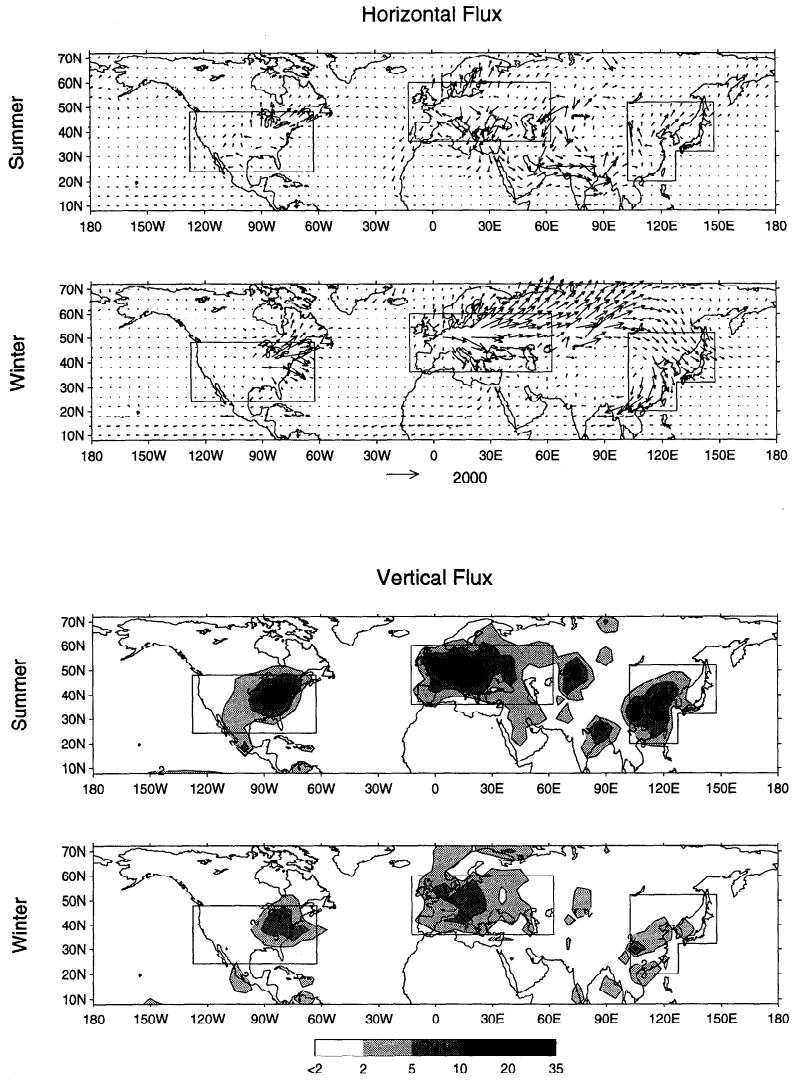

Figure 1. Seasonally averaged horizontal and upward vertical fluxes of total sulfur (mg S m^{-2} d^{-1}) between 10°N and 70°N for the 0–2.6 km column in summer (June – August) and winter (December – February). The boxed regions are referred to in the text as the United States, Europe, and eastern Asia. Surface areas for these regions are: United States, 1.43 x 10^{13} m^2; Europe, 1.79 x 10^{13} m^2; eastern Asia, 1.16 x 10^{13} m^2.

tion and aqueous-phase oxidation in clouds account together for 70% of SO_2 loss in both seasons. The dry deposition velocity of SO_2 is less in winter than in summer because of snow cover and weaker turbulence, and the supply of H_2O_2 for aqueous-phase oxidation of SO_2 is also less in winter. Thus the lifetime of SO_2 against deposition and oxidation within the region is 0.6 days in summer and 1.3 days in winter. This seasonal difference in SO_2 lifetime translates into a factor of 2 increase of SO_2 concentrations between summer and winter.

Despite the longer lifetime of SO_2 in winter, we find that the fraction of SO_2 exported out of the U.S. boundary layer (21%) is only marginally higher than in summer (17%) because of less active convection. In summer, 90% of SO_2 export in the model is by ventilation to the free troposphere, principally over the eastern United States where the emissions are concentrated. In winter, by contrast, convection is infrequent and transport to the free troposphere accounts for only 30% of export; lower troposphere advection to eastern Canada and the North Atlantic is dominant.

About 40% of the SO_2 emitted in the United States is oxidized to SO_4^{2-} within the U.S. boundary layer. This SO_4^{2-} is removed from the boundary layer by wet and dry deposition with a mean lifetime of 6 days in summer and 2 days in winter. *Rodhe and Grandell* [1972] estimated that the SO_4^{2-} lifetime against precipitation in Sweden is 4–12 days in summer and 1.5–3 days in winter; our results for the United States are comparable. The frequency of precipitation is the principal variable determining the lifetime of soluble tracers against wet deposition [*Rodhe and Grandell*, 1972; *Giorgi and Chameides*, 1986]. Because most of the sulfate is produced in cloud, we may expect the lifetime of SO_4^{2-} against precipitation to be shorter than would be defined simply from the precipitation frequency. The shorter lifetime of SO_4^{2-} in winter than in summer reflects a seasonal difference in the nature of precipitation; summertime precipitation, which is mainly convective, is more intense but less frequent than wintertime precipitation, which is primarily synoptic. We find in the model that only 30% of SO_4^{2-} produced over the United States in winter is exported, as compared to 70% in summer, because of the rapid deposition in winter.

Model results thus indicate that the fraction of anthropogenic sulfur exported out of the U.S. boundary layer ranges from 35% in

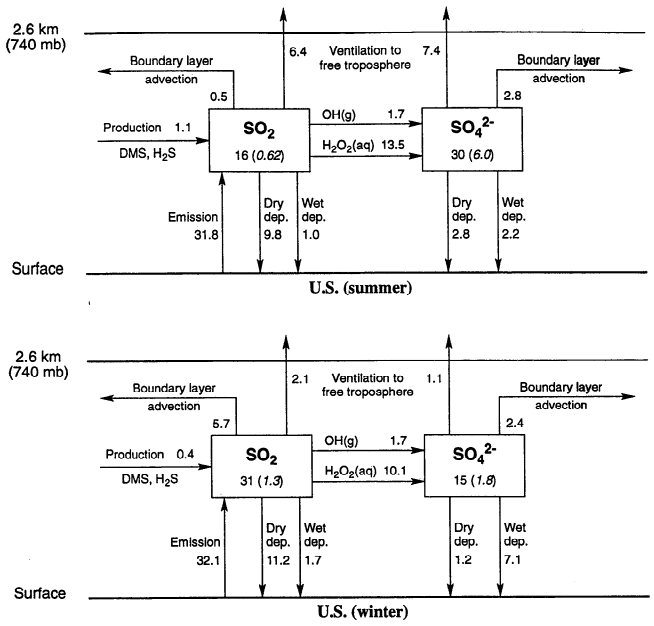

Figure 2. Regional budgets of SO_2 and SO_4^{2-} simulated by the model for the 0–2.6 km atmospheric column over the United States in summer (June – August) and winter (December – February): inventories (Gg S), fluxes (Gg S d^{-1}), and lifetimes (days, in parentheses). The horizontal extent of the U.S. region is shown in Figure 1. The lifetime of SO_2 is defined with respect to losses from oxidation and deposition. The lifetime of SO_4^{2-} is defined with respect to loss from deposition.

winter to 50% in summer. Export in winter is mostly as SO_2 (70%), while in summer it is mostly as SO_4^{2-} (60%). *Galloway et al.* [1984] previously estimated that 34% of the sulfur emitted in eastern North America is exported to the North Atlantic in the 0–5.5 km column between 25°N and 60°N on an annual basis, 40% as SO_2 and 60% as SO_4^{2-}. This estimate was made on the basis of measured atmospheric columns of SO_2 and SO_4^{2-} over the eastern United States combined with climatological mean winds for the east coast of North America. The seasonal variation of export was not discussed. Our sulfur budget for the United States is not inconsistent with that of *Galloway et al.* [1984] to the extent that the two are comparable.

Annual mean boundary layer budgets of SO_2 and SO_4^{2-} computed in the model for the United States, Europe, and eastern Asia are shown in Figure 3. All three regions are remarkably similar in the relative contributions of individual processes to the regional sulfur budgets. Net export of sulfur amounts to about 40% of the SO_2 source for each region. There is significant import of sulfur into eastern Asia in winter from industrial sources in Kazakhstan (Figure 1). The SO_2/SO_4^{2-} ratio of the exported sulfur is highest in Europe because of the relatively high latitudes and hence slow SO_2 oxidation rates.

Changes in sulfur emissions in the above regions affect the regional sulfur budgets nonlinearly because of the limitation of in-cloud SO_2 oxidation by the availability of H_2O_2. To examine the extent of this effect, we conducted a sensitivity simulation with anthropogenic SO_2 emissions decreased uniformly by 50% from the standard simulation. Table 1 shows the percentage values of the individual budget terms relative to the standard simulation for the U.S. boundary layer. The concentrations of SO_2 are 42–45% of their values in the standard simulation, i.e., a more-than-linear decrease, because of the greater relative availability of H_2O_2 for in-cloud oxidation. The concentrations of SO_4^{2-} show, by contrast, a less-than-linear decrease. The sulfur wet deposition flux (including scavenging of both SO_4^{2-} and SO_2) is 66% in winter and 59% in summer of the values in the standard simulation; this nonlinearity is similar to that previously obtained by *Misra et al.* [1989] in a regional model simulation for eastern North America. The export of sulfur from the U.S. boundary layer in winter is 44% of the value in the standard simulation, a more-than-linear decrease, because the lifetime of SO_4^{2-} against deposition in winter is less than that of SO_2. Negligible nonlinearity is found for the export of sulfur in summer because the nonlinear effects on SO_2 and SO_4^{2-} deposition nearly cancel. On an annually averaged basis, the export of sulfur from the U.S. boundary layer responds almost linearly to a decrease in anthropogenic emission, but the SO_2/SO_4^{2-} ratio of the exported sulfur decreases as the emission decreases. Similar results are found for Europe and for eastern Asia.

4. Origin of Sulfate in the Global Atmosphere

Figure 4a shows the annual mean SO_4^{2-} concentrations from the standard simulation in surface air (lowest model layer, 0–500 m above the surface), the middle troposphere (650 mbar), and the

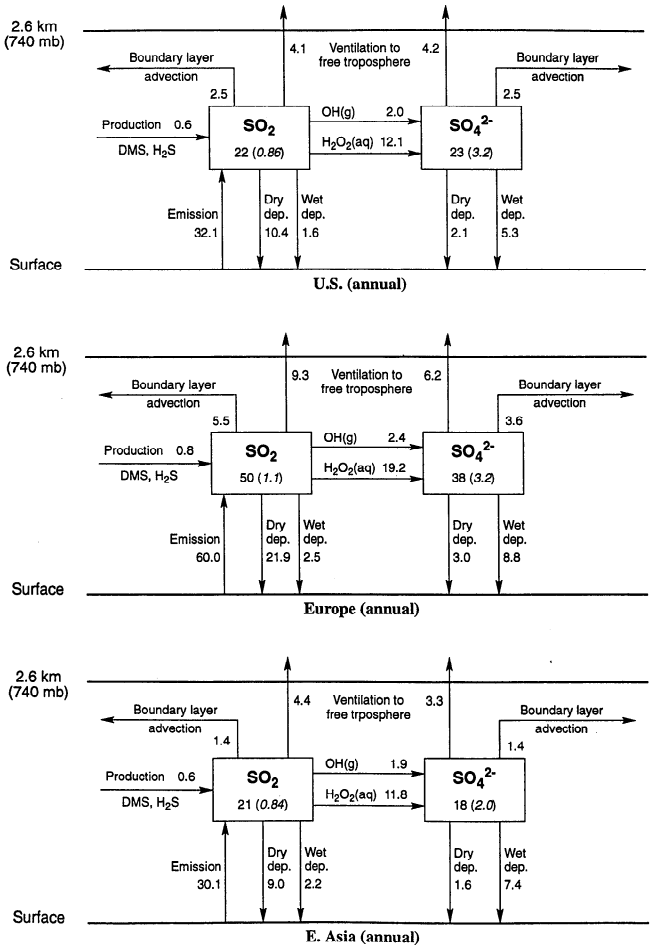

Figure 3. Annual mean regional budgets of SO_2 and SO_4^{2-} simulated by the model for the 0–2.6 km columns over the United States, Europe, and eastern Asia: inventories (Gg S), fluxes (Gg S d^{-1}), and lifetimes for SO_2 and SO_4^{2-} (days, in parentheses). The horizontal extent of each region is shown in Figure 1. See caption to Figure 2 for definition of lifetimes.

Table 1. Effect of Reducing Sulfur Emisions in the United States by 50%

	Summer, %	Winter, %	Annual, %
Anthropogenic SO_2 emission	50	50	50
SO_2 burden	45	42	44
SO_4^{2-} burden	60	66	61
SO_2 gas-phase oxidation	46	44	44
SO_2 in-cloud oxidation	60	66	62
Total sulfur dry deposition	50	47	48
Total sulfur wet deposition	59	66	63
Total sulfur deposition (dry+wet)	51	55	53
Total sulfur export	51	44	48

The table shows the percentage values of the individual sulfur budget terms for the U.S. boundary layer (see text for definition), in a simulation where anthropogenic sulfur emissions were decreased by 50% relative to the standard simulation. Values lower than 50% indicate a more-than-linear effect of emission reduction; values higher than 50% indicate a less-than-linear effect.

upper troposphere (330 mbar). The relative contributions of anthropogenic, biogenic, and volcanic sources to these SO_4^{2-} concentrations are shown in Figure 4b. The small biomass burning source is treated here as anthropogenic. We find that anthropogenic sources account for more than 90% of total SO_4^{2-} in surface air over North America and Eurasia, and also over polluted continental regions of the southern hemisphere: South America (copper smelters in Peru and Chile, coal in Brazil), southern Africa (copper smelters, biomass burning), and eastern Australia (coal). Sulfate in Arctic surface air is also dominantly anthropogenic on an annually averaged basis, reflecting the strong influx of Eurasian pollution in winter-spring [*Barrie and Hoff*, 1984]. During summer, however, SO_4^{2-} concentrations in the Arctic are low and primarily of biogenic origin, both in the observations [*Nriagu et al.*, 1991] and in the model [*Chin et al.*, this issue].

As seen in Figure 4b, anthropogenic influence on SO_4^{2-} in surface air decreases rapidly downwind of the polluted continents. The model may exaggerate this decrease, as it does not capture the seasonal anthropogenic enhancements of SO_4^{2-} observed at island sites in the North Pacific and the North Atlantic [*Chin et al.*, this issue]. It is found in the model that oxidation of biogenic DMS accounts for 20–80% of SO_4^{2-} in surface air over the northern hemisphere oceans. Volcanoes make a significant contribution to SO_4^{2-} in surface air over the North Pacific, reflecting long-range transport from continuous noneruptive emissions in Hawaii, the Pacific Rim, and central America. Anthropogenic influence on SO_4^{2-} over the southern hemisphere oceans is largely restricted to the tropical Atlantic, where polluted air masses from southern Africa and Brazil converge [*Krishnamurti et al.*, 1993]. Over most of the southern hemisphere, oxidation of biogenic DMS accounts for more than 80% of SO_4^{2-} in surface air.

Figure 4b also indicates that the anthropogenic influence on SO_4^{2-} decreases rapidly with altitude. At 650 mbar, human activity still accounts for more than 50% of SO_4^{2-} over most of the United States, Eurasia, and the high northern latitudes. At 330 mbar, however, human influence is less than 20% on average anywhere around the globe. Most of the transport of air from the surface to the upper troposphere takes place in wet convective updrafts, where SO_2 and SO_4^{2-} are efficiently scavenged by precipitation. The efficient scavenging of SO_2 and SO_4^{2-} in deep convective updrafts, as formulated in the model, appears necessary to match observed concentrations of SO_4^{2-} in the upper troposphere [*Chin et al.*, this issue]. Previous studies support the view that scavenging of soluble aerosols in deep convection is close to 100% [*Gatz*, 1977; *Balkanski et al.*, 1993]. Although wet convective pumping of SO_2 in polluted air without scavenging might be expected in winter when the scavenging efficiency of SO_2 is low (due to low levels of H_2O_2), the frequency of deep convection is also low during that time of year.

The relative importance of biogenic versus anthropogenic contributions to SO_4^{2-} increases with altitude, reflecting the injection of DMS to high altitudes in convective updrafts. In contrast to SO_2 and SO_4^{2-}, DMS is not scavenged during precipitation. Convective pumping of DMS thus represents a major source of SO_4^{2-} to the upper troposphere in the model, as previously suggested by *Chatfield and Crutzen* [1984]. This mechanism is most efficient in the tropics where convective activity is most frequent. We find in Figure 4b that the biogenic source accounts for over 80% of SO_4^{2-} in the upper troposphere throughout the tropics except in regions of large volcanic eruptions.

Volcanoes are important contributors to the SO_4^{2-} budget in the middle and upper troposphere, as shown in Figure 4b. The total volcanic source used in the model for 1985 is 6.7 Tg S yr^{-1}, slightly less than the 9-year mean value of 7.8 Tg S yr^{-1} for 1964–1972 estimated by *Spiro et al.* [1992]. Volcanic activity in 1985 was somewhat weaker than average [*Simkin and Siebert*, 1994]; there were in particular no eruptions with volcanic explosivity index (VEI) higher than 3 which would inject sulfur into the stratosphere. Six eruptions in 1985 had a VEI of 3, producing in the model eruption plumes extending to 9 km altitude: two in New Guinea, one in Indonesia, two in Kamchatka, and one in Colombia (Ruiz). The plumes from these eruptions are manifest at 330 mbar in Figure 4b. The relative contribution of eruptive volcanoes to the SO_4^{2-} budget

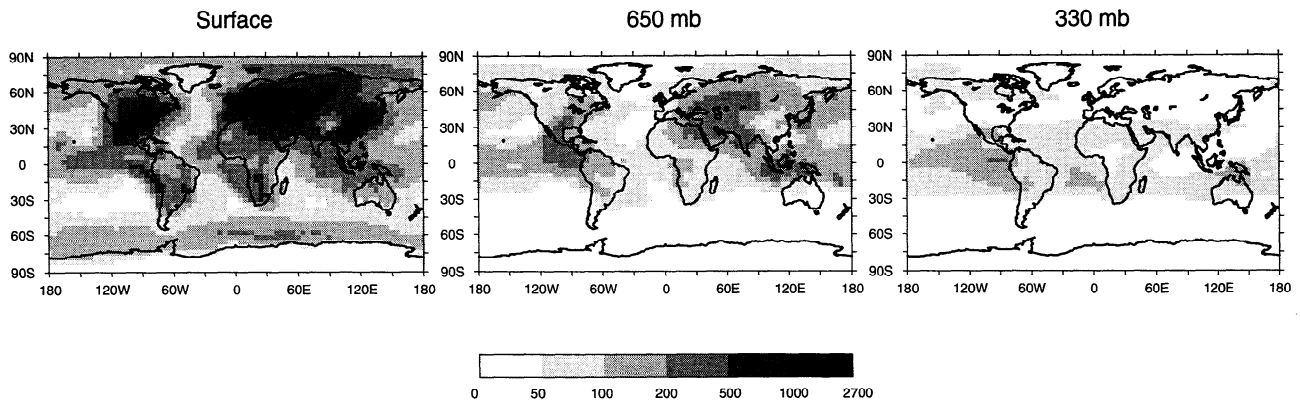

Figure 4a. Annual mean SO_4^{2-} concentrations (ppt) in surface air (0–500 m), at 650 mbar, and at 330 mbar.

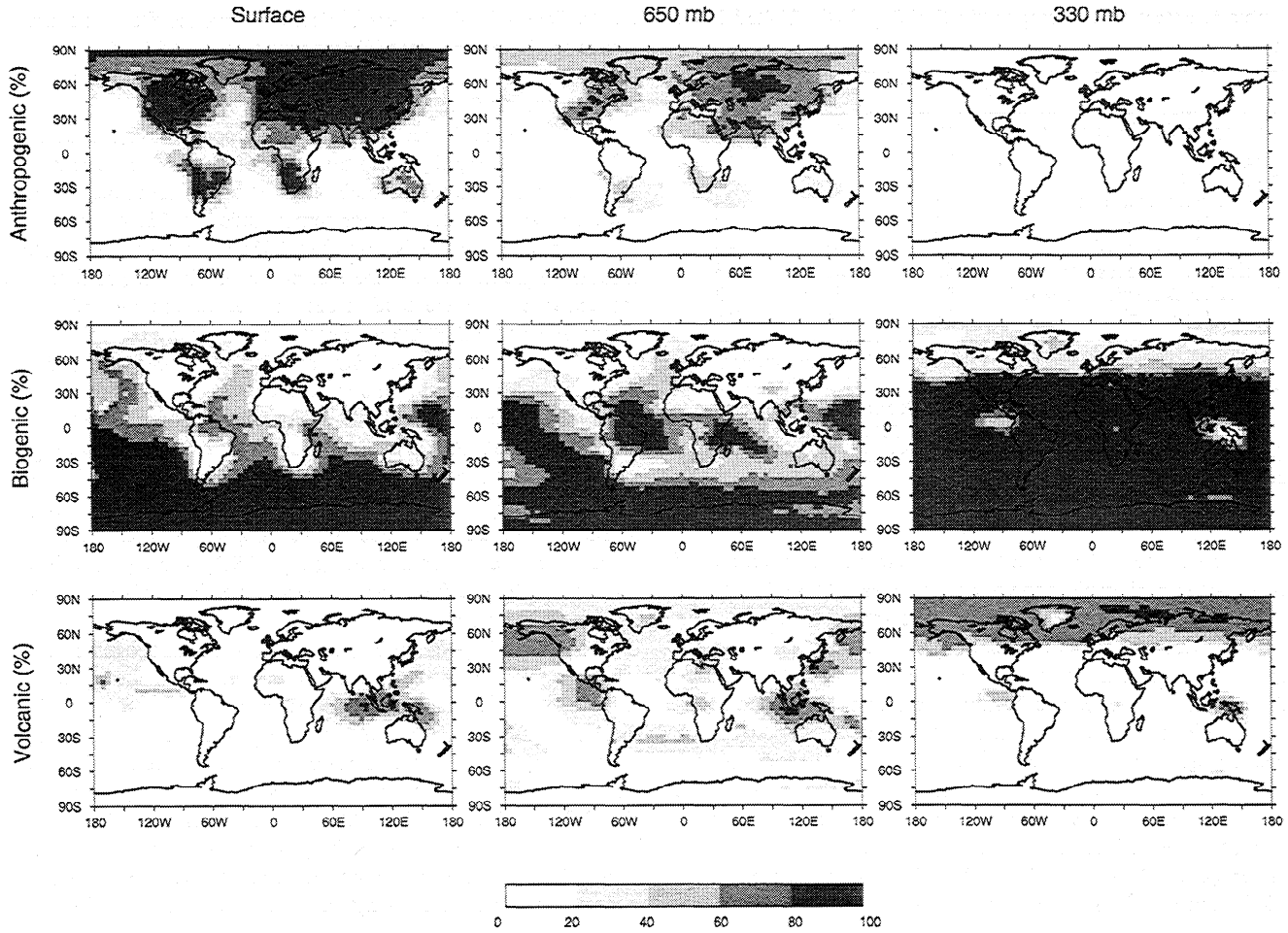

Figure 4b. Relative contributions (percents) of anthropogenic, biogenic, and volcanic sources to the annual mean SO_4^{2-} concentrations simulated by the model in surface air (0–500 m), at 650 mbar, and at 330 mbar. Anthropogenic SO_4^{2-} concentrations are obtained from the difference between the standard simulation and a simulation without anthropogenic emissions. Biogenic SO_4^{2-} concentrations are from a simulation with biogenic sources only (oceans and terrestrial). Volcanic SO_4^{2-} concentrations are obtained from the difference between the simulation without anthropogenic emissions and the simulation with biogenic sources only.

in the upper troposphere is highest at high latitudes, where the supply of DMS by deep convection is weak.

The large eruptions with VEI of 3 account together for only 1.2 Tg S yr^{-1} in our inventory for 1985, i.e., 18% of the total volcanic source. The remaining source emanates from a large number of noneruptive and weakly eruptive volcanoes, discharging SO_2 at the mouth of the crater (typically in the middle troposphere) or a few kilometers above, often continuously over the year. We find that this diffuse volcanic source accounts for 20–40% of SO_4^{2-} over much of the middle troposphere at 650 mbar; in the North Pacific this contribution rises to 60–80%, due primarily to the intense volcanic activity in Kamchatka.

The global mean vertical distribution of SO_4^{2-} production from anthropogenic, biogenic, and volcanic sources in the model is summarized in Figure 5. Most of the SO_4^{2-} in the lower troposphere is produced from anthropogenic sources, but biogenic and volcanic sources dominate at higher altitudes. The previous model simulation of *Balkanski et al.* [1993] showed that the lifetime of aerosols produced in the upper troposphere (17 days) is 4 times longer than that of aerosols produced in the boundary layer (4.4 days) because of less frequent scavenging by precipitation at high altitude. There results a strong disproportionality between the relative magnitudes of the SO_4^{2-} sources and their contributions to the global atmospheric burden of SO_4^{2-} (Table 2). Although human activity represents nearly 70% of the global sulfur source, it accounts for only 37% of the global SO_4^{2-} burden in the model. Biogenic emissions account for 42% of the global SO_4^{2-} burden although for only 23% of the source. Volcanic emissions account for only 7% of the global sulfur source but for 18% of the SO_4^{2-} burden.

Comparing results from the simulations with and without anthropogenic sulfur emissions, we find that the anthropogenic enhancement of the SO_4^{2-} burden is a factor of 1.6 globally (2.0 in the northern hemisphere and 1.2 in the southern hemisphere). *Langner et al.* [1992] previously estimated in the MOGUNTIA model that human activity had increased the global SO_4^{2-} burden by a factor of 2.8 in the northern hemisphere and 1.4 in the southern hemisphere since preindustrial time, and *Pham et al.* [1996] found an even more pronounced increase in the northern hemisphere (a factor of 4) using the IMAGES model. These discrepancies between models may reflect differences in the efficiency of transport of anthropogenic sulfur to the free troposphere, as discussed by *Chin et al.* [this issue]. Convective transport of anthropogenic sulfur is greatly restricted in our model due to efficient scavenging of SO_2 and SO_4^{2-} in wet convective updrafts. In contrast, *Pham et*

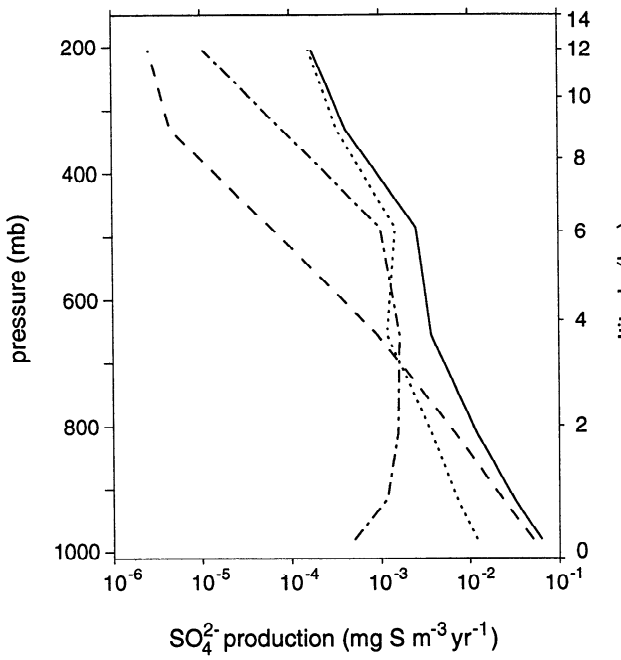

Figure 5. Annually averaged, global mean SO_4^{2-} production rates (mg S m^{-3} d^{-1}) from all sources (solid line) and from anthropogenic (dashed line), biogenic (dotted line), and volcanic (dash-dot line) sources in the model as a function of altitude. The anthropogenic and volcanic sources are for 1985.

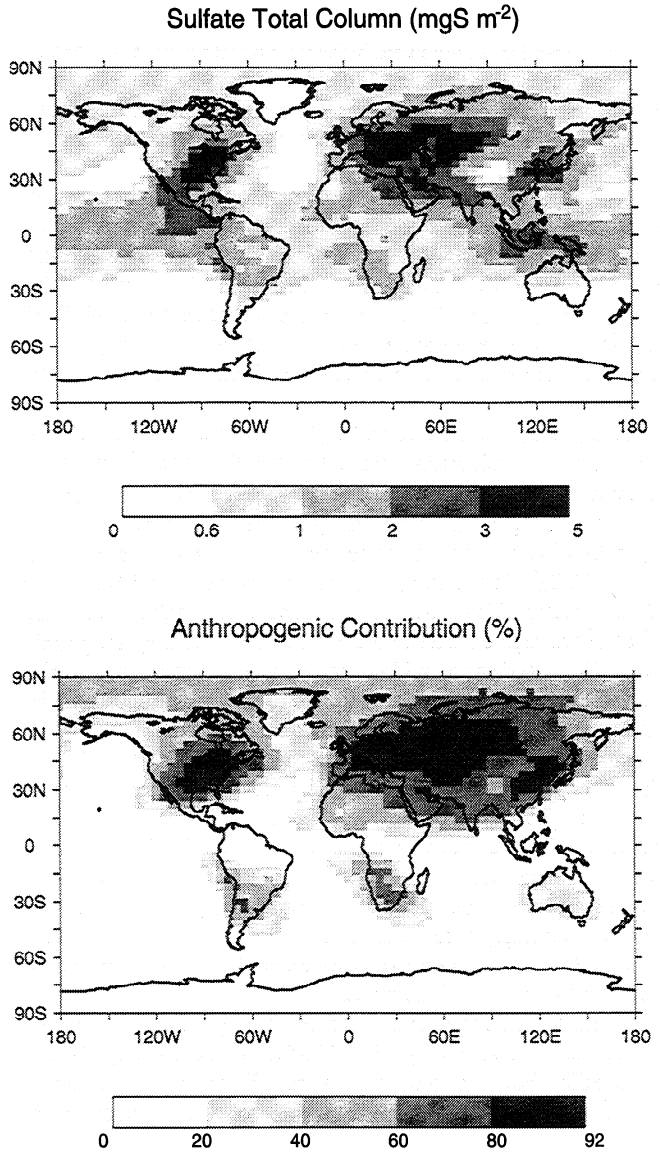

Figure 6. Global distribution of the annual mean atmospheric column of SO_4^{2-} (mg S m^{-2}) in the model, and relative anthropogenic contribution (percent) to this column.

al. [1996] allowed anthropogenic sulfur to be injected to high altitudes in deep wet convection. As pointed out by *Chin et al.* [this issue] and earlier by *Feichter et al.* [1991] and *Balkanski et al.* [1993], the decoupling of convective mass transport and precipitation scavenging operators in a model can lead to overestimates of aerosol concentrations in the free troposphere.

Figure 6 shows the global distribution of the annual mean total SO_4^{2-} column simulated by our model, along with the relative anthropogenic contribution to the column. We find that the anthropogenic contribution is 60–90% over the northern midlatitude continents, 20–40% over the extratropical oceans of the northern hemisphere, and less than 20% in the tropics and the southern hemisphere. Plots of the same quantity have been reported by *Charlson et al.* [1991], *Penner et al.* [1994], and *Pham et al.* [1996] for the MOGUNTIA, GRANTOUR, and IMAGES models, respectively. *Charlson et al.* [1991] found that the anthropogenic contribution to the atmospheric SO_4^{2-} column was 70–90% over the northern midlatitude continents, greater than 50% over the extratropical oceans of the northern hemisphere, and less than 50% in the tropics and the southern hemisphere. Similar results were found by *Penner et al.* [1994]. *Pham et al.* [1996] found an even higher anthropogenic contribution. Our total SO_4^{2-} columns in the northern hemisphere are on average about 30% less than those of *Charlson et al.* [1991] and *Penner et al.* [1994], and 50% less than those of *Pham et al.* [1996].

Table 2. Global Atmospheric Sulfur Source and SO_4^{2-} Burden in the Model

Global sulfur source, Tg S yr^{-1}	96.7	
Anthropogenic	67.4	(70%)
Biogenic	22.6	(23%)
Volcanic	6.7	(7%)
Global SO_4^{2-} burden,Tg S	0.53[a]	
Anthropogenic	0.20	(37%)
Biogenic	0.22	(42%)
Volcanic	0.10	(18%)

[a] Oxidation of carbonyl sulfide accounts for 0.016 Tg S (3%) of the global SO_4^{2-} burden, mainly in the stratosphere.

5. Conclusions

We have used a global three-dimensional model to analyze the export of anthropogenic sulfur out of polluted continents and to assess the relative contributions of anthropogenic and natural sources to SO_4^{2-} levels in different regions of the troposphere. Examination of the sulfur budget in the three principal anthropogenic source regions (United States, Europe, eastern Asia) indicates that only about 40% of the SO_2 emitted in these regions is exported from the continental boundary layer as SO_2 or SO_4^{2-},

while the rest is removed by deposition within the region. The exported fraction is somewhat higher in summer than in winter due to more intense convection. Little nonlinearity is found between the magnitude of sulfur emissions in the northern midlatitude continents and the export of sulfur out of these continents to the global atmosphere.

Anthropogenic sources represent the main contributor to SO_4^{2-} in surface air over most continental areas. Biogenic emission of DMS accounts for 20–80% of SO_4^{2-} in surface air over oceanic areas in the northern hemisphere, and for over 80% in most of the southern hemisphere. Volcanic emissions account for 20–40% of SO_4^{2-} in surface air over the North Pacific, reflecting major noneruptive sources in Kamchatka, Hawaii, Central America, and the Aleutians.

Anthropogenic influence on SO_4^{2-} in the middle and upper troposphere is considerably less than at the surface because of efficient scavenging of SO_2 and SO_4^{2-} in wet convective updrafts. In contrast, biogenic DMS can be injected to high altitudes in cloud updrafts without experiencing scavenging. Thus we find that over 80% of SO_4^{2-} in the tropical upper troposphere originates from DMS oxidation. Volcanoes are also found to be a major contributor to SO_4^{2-} at high altitudes; volcanic emissions of SO_2 are principally discharged in the middle troposphere, at the mouths of the volcanic craters, and some are injected to the upper troposphere in eruptions. We find that volcanoes account for 20–40% of SO_4^{2-} in much of the middle troposphere, and dominate the SO_4^{2-} budget in the upper troposphere at high northern latitudes. There has been much interest in the origin of SO_4^{2-} in the upper troposphere because of its role in aerosol nucleation [*Clarke*, 1992], cirrus formation [*Jensen and Toon*, 1994] and tropospheric chemistry [*Dentener and Crutzen*, 1993]. Our results suggest that this SO_4^{2-} is overwhelmingly natural; on an annual average basis, less than 20% of SO_4^{2-} in the upper troposphere in the model is anthropogenic anywhere around the globe.

Because the atmospheric lifetimes of SO_2 and SO_4^{2-} against deposition increase rapidly with altitude, we find a strong disproportionality between the relative contributions of individual sources to global sulfur emission and their relative contributions to the SO_4^{2-} atmospheric column. Thus anthropogenic sources in the model account for 70% of global sulfur emissions but for only 37% of the atmospheric SO_4^{2-} column; biogenic emissions account for only 23% of the sulfur source but 42% of the column; while volcanic emissions contribute 7% of the source but 18% of the column. From a climate perspective, it appears that the contribution of anthropogenic sources to SO_4^{2-} radiative forcing may be far less than one would estimate simply on the basis of their contribution to global sulfur emissions.

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