

Regional and global distributions and lifetimes of sulfate aerosols from Mexico City and southeast China

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Abstract. To learn what possible influence a megacity and an industrial region, both of which have poor air quality, have on the global scale, sulfate aerosol derived from Mexico City and from southeast China is examined. It is found that the highest values of sulfate from Mexico City mostly travel westward and northward. Sulfate from southeast China travels eastward, and its distribution encircles the Earth in summer and autumn. Mexico City, which emits $\sim 1\%$ of the global anthropogenic sulfur emissions, contributes $\sim 1\%$ to the global sulfate burden. Southeast China, which emits 11.6% of the global anthropogenic sulfur emissions, contributes 9% to the global sulfate burden, a nonlinear response between emissions and burden. When the anthropogenic sulfur emissions are doubled in the two regions, the sulfate burden derived from Mexico City approximately doubles, but the sulfate burden from southeast China more than doubles. An examination of the sulfate budget indicates that for sulfate derived from southeast China more sulfate is produced via gas-phase reaction, thus allowing the sulfate to be less susceptible to wet deposition. We qualitatively analyze black carbon aerosol from Mexico City and southeast China and determine that hydrophilic black carbon has a lifetime similar to sulfate aerosol when the emitted black carbon is assumed to be of hydrophilic form. When the emitted black carbon is hydrophobic and its transfer rate to the hydrophilic form is 1.9 days, which is the same as the global sulfur dioxide lifetime, the lifetime of hydrophilic black carbon is 3.5 days longer than sulfate. The difference between the two types of aerosol is attributed to the aqueous production pathway of sulfate and consequently its availability to rain out. If the transfer rate is 5 days, then hydrophilic black carbon is found in regions with little cloud activity thus increasing its lifetime to 10 days or more.

1. Introduction

The role of sulfate aerosols in cloud formation, acid precipitation, and in climate has been well recognized. From recent emission inventories, it is estimated that ~ 67 Tg of anthropogenic sulfur are emitted each year by industrial sources [Benkovitz *et al.*, 1996], while 15–30 Tg of biogenic sulfur are emitted per year [Benkovitz *et al.*, 1994, Chin *et al.*, 1996]. Previous simulations of the global sulfur cycle attribute 35–75% of the global sulfate burden to anthropogenic sources [Chin and Jacob, 1996, Rasch *et al.*, 1999]. Hence, megacities and industrial regions potentially can influence the burden and distribution of sulfate in the troposphere more

than the surrounding regions with more diffuse emissions. Furthermore, anthropogenically influenced regions likely affect cloud properties and climate. However, it is not clear to what spatial extent a particular industrial region has influence. To understand how two such regions can affect the tropospheric sulfate burden, we use the tagging feature employed by Barth *et al.* [1999] and Rasch *et al.* [1999] to examine the influence a megacity, Mexico City, and an industrial region, southeast China, have upon the sulfate distribution regionally and globally using the NCAR Community Climate Model (CCM3). Mexico City and southeast China are chosen because these two places currently emit substantial amounts of sulfur and odd nitrogen species and are expected to increase their emissions of sulfur and odd nitrogen over the next 20–30 years [Gutierrez *et al.*, 1996, Foell *et al.*, 1995].

Mexico City, which lies at 2200 m in the subtropics (19°N, 99°E), has had air quality problems for many

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years [e.g. *Garfias and Gonzalez, 1992, Streit and Guzman, 1996*]. Because of its subtropical location, Mexico City experiences light winds, dry and clear sky conditions during winter and clouds and precipitation during summer, its wet season. Although anthropogenic sulfur emissions from Mexico City are not large compared to other cities in the world (see 1985 emissions inventory for sulfur dioxide in the work of *Rasch et al. [1999]*), sulfate derived from Mexico City can indicate to which direction other pollutants (e.g., organic aerosols or ozone) may be transported. In this study, we also assess qualitatively how black carbon emitted from Mexico City contributes to the tropospheric black carbon burden.

Southeast China is a fairly large industrial region [*Foell et al., 1995*] that not only releases sulfur species, but many other pollutants such as NO_x , ozone, and carbonaceous aerosols. Much industrial growth is expected for this region in the next several decades which will lead to greater emissions of SO_2 and NO [*Foell et al., 1995*]. Southeast China is subject to much more precipitation than Mexico City with the occurrence of both winter and summer monsoons. Thus one would expect that sulfate would rain out near the emissions sources for the southeast China region.

2. Model Description

The model used for this study is the NCAR Community Climate Model version 3 (CCM3) with sulfur chemistry. The CCM3 [*Kiehl et al., 1998*] was configured to a T42 grid ($2.8^\circ \times 2.8^\circ$ horizontal resolution), 18 vertical levels, which are set on a hybrid-sigma coordinate, from the surface to the 5 hPa height, and a time step of 20 min. The CCM3 transports water vapor, chemical species and temperature consistently via a semi-Lagrangian advection scheme, a penetrative convection scheme, and a nonlocal planetary boundary layer transport scheme with a counter-gradient term. In the version of CCM3 used for this study, a prognostic cloud water scheme was employed [*Rasch and Kristjánsson, 1998*] that assumes the cloud drop concentration over land at low altitudes to be 400 cm^{-3} and the cloud drop concentration over the ocean and at high altitudes to be 80 cm^{-3} .

The representation of the sulfur chemistry in the model includes emissions of oceanic dimethyl sulfide (DMS) and anthropogenic sulfur. DMS undergoes gas-phase oxidation to form sulfur dioxide (SO_2). SO_2 , which is also emitted, can further oxidize in the gas-phase to form, as an end product, aerosol sulfate (SO_4^{2-}). A faster, but more episodic, pathway of SO_2 oxidation to SO_4^{2-} is in clouds where hydrogen peroxide (H_2O_2) and ozone (O_3) are the oxidants. SO_2 , SO_4^{2-} , and H_2O_2 can be rained out of the atmosphere or removed by dry deposition. Because the purpose of the simulation is to assess the influence of two industrial regions on the regional and global environment, the aerosol and chemical species do not feed back to the physical processes depicted in the CCM.

Details of the description of these processes that affect the chemical species are given by *Barth et al. [1999]*, but a summary of the methods used is given here. Of the different transport processes, the convective transport of trace gases and aerosols is performed on the interstitial fraction of these species in the cloudy volume, and the fraction of dissolved material in the cloud drops that do not undergo microphysical transformation to precipitation. The dissolved gases and aerosols in the cloud water are detrained at a higher model level. The emissions of the sulfur compounds are obtained from the Global Emission Inventory Activity (GEIA, [*Benkovitz et al., 1996*]). The total emission rate of anthropogenic sulfur is 67.0 Tg S per year, with 98% assumed to be SO_2 . The anthropogenic sulfur emission rate is provided at the surface and at the 100 m level for which 23 and 44 Tg S are emitted, respectively. The emission rate of DMS is 15.5 Tg S per year. The gas chemistry includes oxidation of DMS and SO_2 by hydroxyl radical, which is prescribed by monthly averaged values obtained from the IMAGES model [*Müller and Brasseur, 1995*], and generation and destruction of H_2O_2 , which includes prescribed monthly averaged values of the hydroperoxy radical, hydroxyl radical, and photolysis frequencies of H_2O_2 [*Müller and Brasseur, 1995*]. The aqueous chemistry describes the reaction of S(IV) with H_2O_2 and O_3 (monthly averaged O_3 mixing ratios are prescribed from IMAGES results, *Müller and Brasseur [1995]*) in the cloudy fraction of each grid cell using a 2-min time step so as to capture the pH dependence of the O_3 reaction. Wet deposition of SO_2 , SO_4^{2-} , and H_2O_2 is determined by the net flux of a species through a model level [*Barth et al., 1999*]. The dry deposition scheme follows the resistance method proposed by *Wesely [1989]* to determine deposition velocities for SO_2 and H_2O_2 . For aerosols, the deposition velocity is calculated similarly to *Benkovitz et al. [1994]*, which is based on the inverse sum of the aerodynamic and sub-layer resistances. The processes are calculated using operator splitting from the $n - 1$ to $n + 1$ time level (a 40 minute time step), except for the aqueous chemistry, which uses a 2-min time step.

For these simulations, we have assumed that there is no feedback of aerosol sulfate upon prescribed oxidant concentrations or photolysis frequencies. By radiatively scattering solar radiation, sulfate aerosols can alter photolysis frequencies and subsequently ozone concentrations [*Dickerson et al., 1997*] and other oxidant concentrations. To represent this interaction in a global climate model, would require an on-line calculation of photolysis frequencies and photochemistry, which departs from the focus of the current study.

Similar to *Rasch et al. [1999]* we have "tagged" the SO_2 and SO_4^{2-} species according to the region from which they were emitted. SO_2 and SO_4^{2-} from Mexico City were emitted from a boxed area between 18°N and 21°N , and 98°W and 101°W in the two lowest model levels. For the Mexico City region the model has a surface height of $\sim 1000 \text{ m}$ which is much lower than the

Table 1. Characteristics of the Three Regions in the Simulation

	Mexico City	Southeast China	Rest of World
Emissions, Tg S yr ⁻¹			
DMS	0.00	0.32	15.17
SO ₂	0.49	7.56	57.03
SO ₄ ²⁻	0.01	0.15	1.16
Area of region, km ²	3.66×10 ⁵	5.44×10 ⁶	5.05×10 ⁸

actual 2200-m elevation of the city. SO₂ and SO₄²⁻ from southeast China were emitted from a boxed area between 18°N and 35°N, and 101°E and 123°E. SO₂ and SO₄²⁻ from the remainder of the globe, hereafter referred to as rest of world, was emitted from outside of these two boxes. Table 1 lists the emission rate of sulfur from each of these regions and the size of each region.

Mexico City occupies 0.072% of the Earth's surface yet emits ~ 0.75% of the world's anthropogenic sulfur. Southeast China occupies ~ 1.1% of the Earth's surface and emits over 11% of the world's anthropogenic sulfur.

To understand the influence that Mexico City and southeast China have on the sulfate distribution, two simulations were performed. In the first, the SO₂ and SO₄²⁻ species were tagged as described and emission levels were set to 1985 values. The second simulation used the same tagging method, but anthropogenic sulfur emissions were twice the 1985 values in the Mexico City and southeast China regions.

3. Results

Barth et al. [1999] and *Rasch et al.* [1999] described a control simulation of the global sulfur cycle. *Rasch et al.* [1999] showed that after 2 years of integration with the model, the sulfur chemistry was in quasi-equilibrium. *Barth et al.* [1999] showed that results from year 3 of the simulation do not differ much from results of years 3–6 of the simulation. *Barth et al.* [1999] also showed that for locations near and downwind of Asia modeled sulfate was within a factor of 3 of observations with a tendency of the model to overpredict the mixing ratio in the upper troposphere and underpredict at the surface. Multiyear measurements of SO₄²⁻ near Mexico City were not compared. The integration period for the simulations described here was 3 years. Results from the third year are discussed below.

The aerosol column burden of sulfate derived from Mexico City, southeast China and the rest of world is shown as a function of season in Figure 1. Sulfate derived from Mexico City is mostly transported westward, but it can also be transported to the north from Northern Hemisphere spring to autumn. Small concentrations of sulfate from Mexico City can be found as far east as the eastern Mediterranean Sea. Sulfate derived from southeast China is transported eastward

with some sulfate transported westward. In Northern Hemisphere summer and autumn, sulfate derived from southeast China has encircled the Earth from ~ 12°N to 50°N. The magnitude of the amount of sulfate aerosol from southeast China is much greater than the sulfate aerosol from Mexico City, but in accord with the magnitude of the respective emissions. Over the north central Pacific, most of the aerosol sulfate column burden is from the rest of world. The annually averaged sulfate column burden from the rest of world, most likely from regions in Asia other than southeast China and somewhat from North America, contributes more than 70% to the sulfate column burden in the north central Pacific.

A cross section of the annually averaged sulfate aerosol from 90°E to 60°W is shown in Figure 2. Two latitude bands were averaged: (1) between 15 and 25°N, the latitude band where the sulfate column burden from Mexico City is greatest, and (2) between 20° and 40°N, the latitude band where the sulfate column burden from southeast China is greatest. Sulfate derived from Mexico City resides in a fairly small region (between 180°W and 90°W at altitudes between 1 and 5 km). In this region, the magnitude of sulfate derived from Mexico City is 10–50 pmol/mol air, while sulfate from the rest of world in this same region exceeds 100 pmol/mol air. Sulfate derived from southeast China in the latitude band of 20°–40°N shows transport of sulfur to the mid and upper troposphere. For the 20°–40°N latitude band, most of the sulfate in the Pacific region is derived from the rest of the world.

4. Discussion

For the Mexico City and southeast China regions, mixing ratios of hydroxyl radical and ozone are nearly the same and H₂O₂ mixing ratios are within 20%. Sulfur dioxide mixing ratios in the region surrounding southeast China, defined as 10–45°N and 90–150°E (SO₂ is 1.2 ppbv at the surface and 0.1 ppbv at 4 km), are a factor of four greater in the lower troposphere than SO₂ mixing ratios in the region surrounding Mexico City, defined as 15–25°N and 120–60°W (SO₂ is 0.3 ppbv at the surface, 0.025 ppbv at 4 km). The lifetime of SO₂ emitted from Mexico City is 1.1 days, while the lifetime of SO₂ from southeast China is 1.5 days. This

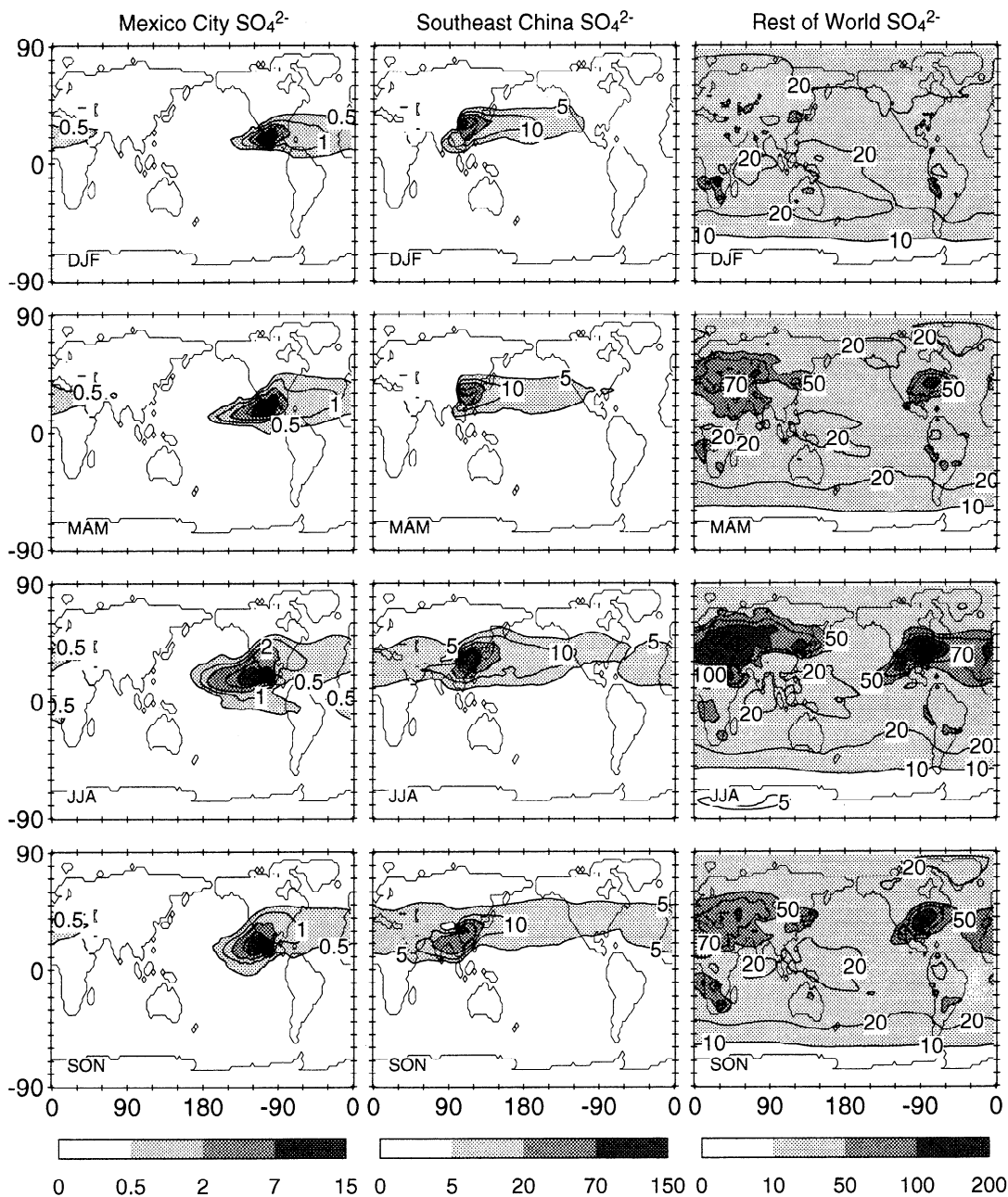


Figure 1. Sulfate column burden ($\mu\text{mol m}^{-2}$) for (left) sulfate derived from Mexico City, (middle) from southeast China, and (right) from rest of world as a function of season.

suggests that airmasses from the southeast China region are oxidant limited for production of sulfate aerosols, whereas they are SO_2 limited for the region surrounding Mexico City.

The widespread distribution of aerosol sulfate from southeast China compared to sulfate from Mexico City can partly be attributed to the oxidant limitation found in southeast China airmasses, thus enabling SO_2 to travel further downwind, but primarily can be attributed to the lighter winds found in the region surrounding Mexico City compared to the winds found in the region surrounding southeast China. The sink of aerosol sulfate via advection from the region surrounding south-

east China is 2–6 times greater than the same sink from the region surrounding Mexico City.

An examination of the SO_4^{2-} budget (Table 2) shows some differences between regions, particularly for the SO_4^{2-} production pathway. For all regions, in-cloud reaction of S(IV) and H_2O_2 is the dominant production pathway of sulfate. However, for both Mexico City and southeast China even more SO_4^{2-} is produced from the S(IV) + H_2O_2 pathway than the rest of world ($\sim 77\%$ for Mexico City and southeast China and 64% for rest of world), most likely because H_2O_2 concentrations are largest in the latitude bands of Mexico City and southeast China (see Figure 2 of Barth *et al.* [1999]). The

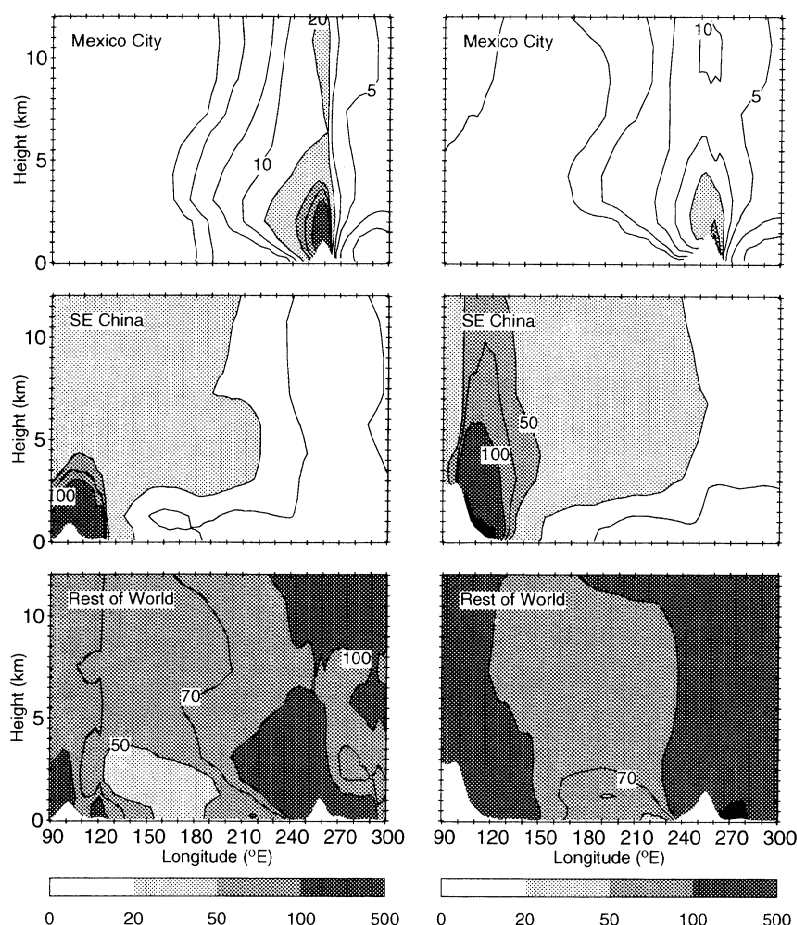


Figure 2. Annually averaged aerosol sulfate ($\text{pmol SO}_4^{2-} (\text{mol air})^{-1}$) for sulfate derived from Mexico City, from southeast China, and from the rest of world: (left) an average in the $15^\circ\text{--}25^\circ\text{N}$ latitude band; (right) an average in the $20^\circ\text{--}40^\circ\text{N}$ latitude band.

$\text{S(IV)} + \text{O}_3$ reaction contributes a much smaller fraction to the production of SO_4^{2-} for SO_4^{2-} derived from Mexico City and southeast China. Because of the slightly larger amount of in-cloud SO_4^{2-} production, there is slightly more SO_4^{2-} loss through wet deposition for Mexico City and southeast China than for the rest of world.

These small changes in SO_4^{2-} production pathway affect the SO_4^{2-} burden and lifetime. Of the total SO_4^{2-} that resides in the troposphere, SO_4^{2-} from Mexico City contributes $\sim 1.1\%$ (Table 2), similar to its percent contribution of anthropogenic sulfur emissions. Southeast China contributes $\sim 9.0\%$ to the total SO_4^{2-} burden, less than its percent contribution of anthropogenic sulfur emissions (11.6%). The lifetime of sulfate is defined as the sulfate burden divided by the sulfate destruction rate. The lifetime of sulfate derived from Mexico City is 5.5 days, while the lifetime of sulfate from southeast China is much shorter, 3.6 days. The lifetime for southeast China is similar in value to the lifetime *Rasch et al.* [1999] found for SO_4^{2-} derived from Asia (where Asia was defined as $65\text{--}170^\circ\text{E}$, $0\text{--}90^\circ\text{N}$). The lifetime for sulfate from Mexico City is similar to the lifetime *Rasch et al.* [1999] found for their rest of

world (the region that excludes Asia, North America, and Europe).

The potential of an emitted sulfur compound from a particular region to contribute to the tropospheric sulfate burden can be estimated for each tagged region. *Rasch et al.* [1999] defined this potential as

$$\text{Potential (d)} = \frac{\text{SO}_4^{2-} (\text{kg S}) \text{ derived from region}}{\text{Sulfur emitted in region (kg S/d)}}$$

The potential is an indication of how likely emitted SO_2 will actually convert to SO_4^{2-} and remain in the atmosphere as SO_4^{2-} . This is in contrast to the lifetime of SO_4^{2-} , which indicates how long the species will remain in the troposphere. The potential can also be viewed as a replacement timescale for the sulfate aerosol. Because we are interested in only the anthropogenic contribution to the tropospheric sulfate burden, we show only the potential to form sulfate from SO_2 emissions. Because anthropogenic sulfur emissions dominate in the Mexico City and southeast China regions, the sulfate burden from these two regions has not been adjusted for the

Table 2. Aerosol Sulfate Budget in the Simulation

	Mexico City	Southeast China	Rest of World
Source, Tg S yr ⁻¹	0.392	5.17	49.29
Primary emissions	0.010 (3%)	0.154 (3%)	1.16 (3%)
SO ₂ + OH	0.064 (16%)	0.747 (14%)	8.48 (17%)
S(IV) + H ₂ O ₂	0.303 (77%)	3.860 (75%)	31.62 (64%)
S(IV) + O ₃	0.015 (4%)	0.411 (8%)	8.03 (16%)
Sink, Tg S yr ⁻¹	0.411	5.24	49.20
Dry deposition	0.024 (6%)	0.25 (5%)	3.4 (7%)
Wet deposition	0.387 (94%)	4.99 (95%)	45.8 (93%)
Burden, Tg S	0.0062	0.052	0.52
Lifetime, days	5.5	3.6	3.9
Potential, days	4.6	2.5	2.4

anthropogenic fraction. However, for sulfate from the rest of world, the aerosol sulfate burden has been adjusted by the fraction of anthropogenic sulfate obtained from a previous simulation [Rasch *et al.*, 1999]. In Table 2, the potential to form sulfate is listed indicating that southeast China and rest of world have a smaller potential to contribute to the sulfate burden than does Mexico City. Compared to values estimated by Rasch *et al.* [1999] the potential to form sulfate from southeast China is much smaller than the potential of their SO₄²⁻ from Asia (region defined as 65–170°E, 0–90°N; potential of 3.2 days for SO₂ emissions), which includes the southeast China region.

The annually averaged global burden, lifetime, and potential of sulfate are listed in Table 3 for the simulation in which the anthropogenic sulfur emissions were doubled in the Mexico City and southeast China regions. The sulfate burden derived from Mexico City slightly more than doubled the burden that resulted from present day emissions. The sulfate burden from southeast China increased by a factor of 2.2 compared to the southeast China burden that resulted from present-day emissions. The lifetime of sulfate derived from Mexico City increased from 5.5 days for present day emissions to 5.8 days for doubled emissions. For sulfate derived from southeast China, the lifetime increased from 3.6 to 4.1 days. The potential of SO₂ to produce SO₄²⁻ hardly changed for sulfate from Mexico City and the rest of world, and the potential increased from 2.5 to 2.7 days for sulfate from southeast China when SO₂ emissions were doubled in this region. This change in potential occurs because the sulfate burden from southeast China increased by more than the emissions increased in the region. Thus, doubling emissions in the southeast China region produced a nonlinear response to the characteristics of sulfate derived from this region.

An examination of the sources and sinks (Table 3) of sulfate for the simulation in which anthropogenic sulfur

emissions were doubled in Mexico City and southeast China indicates that in-cloud sulfate production was H₂O₂ limited in southeast China. Thus SO₂ conversion to SO₄²⁻ by the in-cloud reaction with O₃ and by the gas-phase reaction with OH increased. Increased production of sulfate by the gas-phase reaction leads to a larger sulfate burden because the sulfate is not subject to wet deposition as readily as sulfate produced in-cloud [Barth *et al.*, 1999]. The more than doubled response in the southeast China sulfate burden can be explained by this shift in oxidation pathways.

Although this study cannot predict the fate of aerosol sulfate from doubling emissions in other industrialized regions, we can speculate as to whether other industrialized regions or megacities in the world would have a similar aerosol sulfate lifetime and potential when anthropogenic emissions are doubled. Because southeast China already has high SO₂ emissions, doubling the emissions placed the sulfur chemistry in an H₂O₂-limited regime allowing aqueous oxidation by O₃ and gas-phase oxidation by OH to oxidize more SO₂. Thus regions that have high sulfur emissions already and moderate H₂O₂ concentrations, such as Tokyo, Beijing, eastern North America, and Europe, would likely have a nonlinear response to doubled SO₂ emissions. Regions that are not oxidant limited, such as India and much of the southern hemisphere, would more likely have a linear response to doubled SO₂ emissions. Realistically, regions that increase SO₂ emissions will also increase NO and hydrocarbon emissions, which makes it unclear as to how the oxidants (H₂O₂, O₃, and OH) would change with increased emissions.

5. Other Types of Aerosols

Although this study is focused on sulfate aerosols, other types of aerosols contribute to the total aerosol burden affecting air quality, particularly visibility, and radiative feedbacks. We qualitatively examine the influ-

Table 3. Aerosol Sulfate Budget in the Doubled-Emissions Simulation

	Mexico City	Southeast China	Rest of World
Burden, Tg S	0.0127	0.113	0.52
Lifetime, days	5.8	4.1	3.9
Potential, days	4.7	2.7	2.4
Source, Tg S yr ⁻¹	0.766	10.19	49.16
Primary emissions	0.020 (3%)	.308 (3%)	1.16 (3%)
SO ₂ + OH	0.141 (18%)	1.860 (18%)	8.50 (17%)
S(IV) + H ₂ O ₂	0.579 (76%)	7.084 (70%)	31.47 (64%)
S(IV) + O ₃	0.026 (3%)	.944 (9%)	8.02 (16%)
Sink, Tg S yr ⁻¹	0.807	10.14	49.16
Dry deposition	0.045 (5.5%)	0.46 (4.5%)	3.4 (7%)
Wet deposition	0.762 (94.5%)	9.69 (95.5%)	45.8 (93%)

ence of Mexico City and southeast China on the black carbon (BC) aerosol distribution. On the basis of *Penner et al.* [1993], who found a strong correlation between BC and SO₂ concentrations in source-dominated environments where, on average, BC was 0.7 of SO₂ mass concentrations, the emissions of BC is set to 0.6 of surface SO₂ emissions resulting in an emissions of 28 Tg BC per year. Despite reducing the BC to SO₂ ratio, we believe that the magnitude of the black carbon emissions is still too large, especially compared to emission estimates by *Cooke and Wilson* [1996] of 6.6 Tg C per year and *Lioussé et al.* [1996] of 8 Tg C per year. We do feel that the spatial variability of industrial sources is representative. Furthermore, we are examining regions that are dominated by industrial emissions rather than biomass burning. In the model, black carbon is emitted as a hydrophobic aerosol. The hydrophobic BC may return to the surface through dry deposition, calculated in the same manner as sulfate dry deposition, or may transform to hydrophilic BC.

The transformation to hydrophilic BC represents the coagulation of the hydrophobic BC with sulfate or nitrate aerosols. The coagulation of aerosols depends on the concentration of each aerosol population and the size distribution of each population. For our purposes, depicting coagulation of black carbon aerosol with sulfate or nitrate aerosols would be computationally costly and therefore coagulation is described with a first-order loss rate (τ). To learn what the sensitivity of the results is to τ , simulations where the loss rate was 0, 1.9, and 5 days were performed. If $\tau = 0$ days, then all of the BC is hydrophilic. For $\tau = 1.9$ days, the hydrophobic BC has a similar lifetime as SO₂, globally estimated [*Rasch et al.*, 1999]. Once the black carbon becomes hydrophilic it is susceptible to rain out as well as dry deposition, both processes are determined in a manner similar to sulfate aerosols. To minimize the effect of the inaccurate magnitude of black carbon emissions, we discuss only the lifetime of black carbon, which is

calculated separately for the hydrophobic BC and hydrophilic BC.

Table 4 lists the lifetimes of black carbon that was emitted in the Mexico City and southeast China regions for the three simulations. The lifetime of the hydrophobic black carbon is shorter than the dictated first-order loss rate because of the dry deposition sink. The lifetime of the hydrophilic black carbon is much longer than the hydrophobic black carbon for each simulation and the lifetime of hydrophilic black carbon varies considerably depending on the first-order loss rate of hydrophobic BC. For the simulation where all the black carbon is hydrophilic ($\tau = 0$), hydrophilic BC has the shortest lifetime of 4.9 and 2.6 days for Mexico City and southeast China, respectively, compared to the other simulations. Much more of the hydrophilic black carbon is removed via dry deposition in the $\tau = 0$ simulation compared to the simulations with larger first-order loss rates. For the $\tau = 0$ simulation, the hydrophilic BC exists primarily near the surface (Figure 3) where the black carbon is emitted and is therefore more susceptible to dry and wet deposition.

For the simulation where the hydrophobic black carbon first-order loss rate is close to the SO₂ lifetime ($\tau = 1.9$ days), the hydrophilic black carbon lifetime is 9.2 and 7.2 days for Mexico City and southeast China, respectively. These lifetimes are greater than SO₄²⁻ lifetimes of 5.5 and 3.6 days (Table 2). Because most of the SO₄²⁻ is produced by in-cloud oxidation, SO₄²⁻ is highly susceptible to wet deposition which shortens its lifetime. On the other hand, the conversion of hydrophobic BC to hydrophilic BC is not accelerated by cloud encounters. Therefore there is not recently-produced hydrophilic BC available for rain out as there is in the case of sulfate.

For the simulation where $\tau = 5$ days, the hydrophilic BC lifetime is even longer, indicating that hydrophilic black carbon resides in regions with few cloud encounters. Figure 3 illustrates that for this case over 200 ng

Table 4. Lifetimes of Black Carbon for Three First-Order Loss Rates of Hydrophobic Black Carbon to Hydrophilic Black Carbon

	Mexico City	Southeast China
$\tau = 0$ days		
Hydrophobic BC	0.0	0.0
Hydrophilic BC	4.9	2.6
$\tau = 1.9$ days		
Hydrophobic BC	1.6	1.6
Hydrophilic BC	9.2	7.2
$\tau = 5$ days		
Hydrophobic BC	4.2	3.9
Hydrophilic BC	11.9	9.8

BC, black carbon

BC per kg air resides in the northern hemisphere upper troposphere and throughout the troposphere in the northern hemisphere 20°–40° latitude band.

6. Summary

To understand to what extent two industrial regions have upon their regional environment, the distribution of sulfate aerosols derived from Mexico City and from southeast China has been examined. Sulfate derived from Mexico City primarily travels westward and northward, but small concentrations can be found as far east as the Mediterranean Sea. The surface height for which anthropogenic sulfur emissions occur may be important with respect to transport direction or speed. Because the model surface height for the Mexico City region (1000 m) is much lower than the actual surface height of Mexico City (2200 m), the impact of anthropogenic emissions on the regional scale may be in error and would be better depicted with a regional chemistry transport model. Sulfate from southeast China primarily travels eastward and its distribution encircles the earth in summer and autumn. The annually averaged sulfate burden derived from Mexico City accounts for 1% of the total sulfate burden, while the sulfate burden derived from southeast China accounts for 9% of the total. The lifetime of sulfate derived from Mexico City (5.5 days) is larger than the lifetime determined for the global sulfate burden (4 days), likely because of Mexico City's subtropical location where light winds prevail. The lifetime of sulfate derived from southeast China (3.6 days) is somewhat shorter than the estimate of the global sulfate lifetime. The potential to form sulfate from each region's sulfur emissions is calculated to be 4.6, 2.5, and 2.4 days for Mexico City, southeast China, and the rest of world, respectively. Thus Mex-

ico City contributes more to the tropospheric sulfate burden per unit of SO₂ emissions than either southeast China or the rest of world.

When anthropogenic sulfur emissions were doubled in Mexico City and southeast China, the annually averaged sulfate burden doubled for Mexico City, and more than doubled for southeast China. The nonlinear response is a result of H₂O₂ limitation; thus enabling more sulfate to be produced by gas-phase reaction, which allows the sulfate to be less susceptible to wet deposition. With doubled emissions, the lifetimes of sulfate derived from Mexico City and southeast China are 5.8 and 4.1 days, respectively, indicating that with larger emissions the lifetime of sulfate increases from these regions. With doubled emissions, the potential to form sulfate from sulfur emissions in southeast China

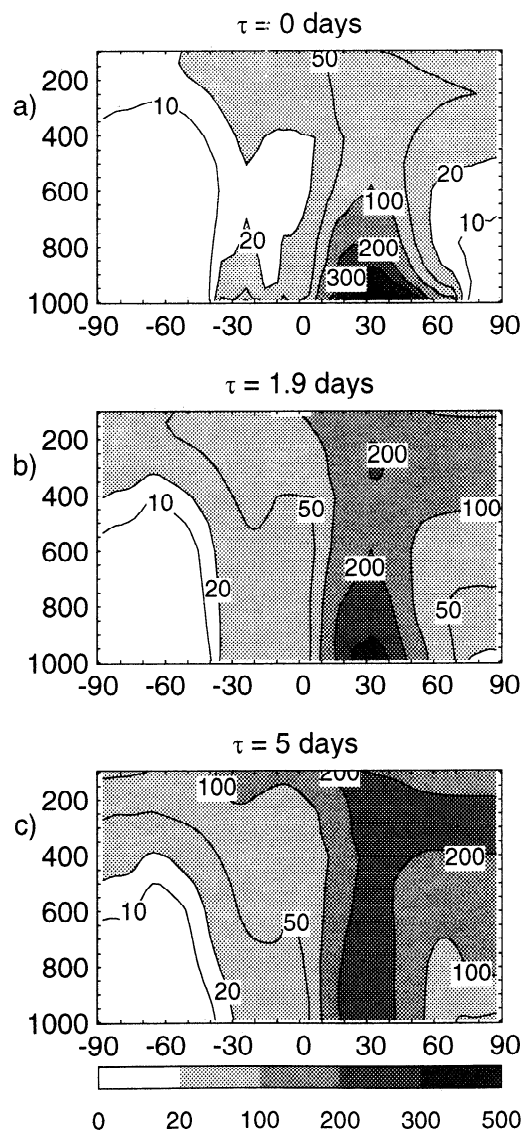


Figure 3. Annual mean of the zonally averaged hydrophilic black carbon (ng kg^{-1}): (a) First-order loss rate of hydrophobic black carbon to hydrophilic black carbon is 0 days; (b) first-order loss rate is 1.9 days; (c) first-order loss rate is 5 days.

was found to be 2.7 days, indicating that with greater emissions southeast China has a greater potential to contribute to the tropospheric sulfate burden.

Black carbon aerosol from Mexico City and southeast China was qualitatively analyzed. The lifetime of hydrophilic black carbon is highly dependent on the rate of transforming hydrophobic black carbon to the hydrophilic form. When the transfer is instantaneous, the lifetime of hydrophilic black carbon is short (2.5–5 days) because the black carbon is located mostly near the surface and is readily susceptible to dry and wet deposition. When the transfer rate is on the same order as the SO₂ lifetime, the lifetime of hydrophilic black carbon is 7–9 days, ~ 3.5 days longer than the sulfate lifetime. This difference is attributed to the aqueous production pathway of sulfate which allows sulfate to be rained out sooner than a species that is produced only in the gas-phase such as hydrophilic black carbon. When the transfer rate is extended to a 5-day lifetime, hydrophilic black carbon has a lifetime of 10–12 days, indicating that it is produced in and resides in regions with little cloud activity.

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