The effects of sulfur emissions from HSCT aircraft: A 2-D model intercomparison

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Abstract. Four independently formulated two-dimensional chemical transport models with sulfate aerosol microphysics are used to evaluate the possible effects of sulfur emissions from high-speed civil transport (HSCT) aircraft operating in the stratosphere in 2015. Emission scenarios studied are those from Baughcum and Henderson [1995], while assumptions regarding the form of emitted sulfur are similar to those of Weisenstein et al. [1996]. All models show much larger increases in aerosol surface area when aircraft sulfur is assumed to be emitted as particles of 10 nm radius rather than as gas phase SO2. If we assume an emission index (EI) for SO2 of 0.4 gm (kg fuel burned)-1 in 2015, maximum increases in stratospheric sulfate aerosol surface area range from 0.1 μm2 cm-3 to 0.5 μm2 cm-3 with sulfur emitted as SO2 gas and from 1.0 μm2 cm-3 to 2.5 μm2 cm-3 with sulfur emitted as particles. Model differences in calculated surface area are deemed to be due mainly to differences in model transport. Calculated annual average ozone perturbations due to aircraft emissions with EI(NOx)=5, EI(H2O)=1230, and EI(SO2)=0.4 range from -0.1% to -0.6% at 45°N for sulfur emission as SO2 gas and from -0.4% to -1.5% with sulfur emission as 100% particles. The effect of zonal and temporal inhomogeneities in temperature on heterogeneous reactions rates is accounted for in the Atmospheric and Environmental Research model and the Università degli Studi L'Aquila model and significantly increases the calculated ozone depletion due to HSCT, particularly for the cases with concurrent increases in aerosol surface area. Sensitivities to polar stratospheric clouds, background chlorine amount, additional heterogeneous reactions, and background aerosol loading are also explored.

1. Introduction

High-speed civil transport aircraft, known as HSCTs, could be flying commercial routes by 2015. These aircraft would operate at cruise speeds between Mach 2.0 and Mach 2.4, which necessitate flying in the stratosphere at altitudes between 18 and 21 km. HSCT engines are expected to emit large amounts of water vapor and carbon dioxide and relatively small amounts of nitrogen oxides (NOx), sulfur dioxide, carbon monoxide, and hydrocarbons. These emissions could perturb stratospheric chemistry, aerosol concentrations, and ozone. Early studies [e.g., Johnston et al., 1989] indicated that NOx emissions have the largest effect on ozone, leading to significant decreases. Formal assessments of the effects of HSCTs have been performed under the NASA Atmospheric Effects of Aviation Program (AEAP), which has reported predicted changes in ozone from a number of two-dimensional (2-D) atmospheric models, based on forecast emission scenarios of a global fleet of 500 HSCT aircraft [Albritton et al., 1993; Stolarski et al., 1995]. These more recent assessments have included the effects of heterogeneous chemistry occurring on the background sulfate aerosol layer [World Meteorological Organization (WMO), 1993], which has been found to significantly decrease ozone sensitivity to HSCT NOx emissions [Weisenstein et al., 1991; Bekki et al., 1991]. However, they have not considered possible perturbations to the sulfate aerosol layer by emission of sulfur from HSCT engines.

Some 2-D studies of the effect of HSCT sulfur emissions have been conducted by individual modeling groups. Bekki and Pyle [1993] modeled the impact of a fleet of HSCTs, assuming an emission index (EI) for NOx of 20 (i.e., 20 g NOx per kilogram of fuel burned)
and $\text{EI}(\text{SO}_2)$ of 2 (i.e., 2 g $\text{SO}_2$ per kilogram of fuel burned). They concluded that the $\text{SO}_2$ emissions could potentially double the aerosol surface area of the northern hemisphere lower stratosphere. Bekki and Pyle [1993] found decreased sensitivity of ozone to HSCT emissions for their model scenario but pointed out that the increased aerosol levels also increased the model sensitivity to chlorine abundance in the lower stratosphere. Pitari et al. [1993] modeled an emission scenario with $\text{EI}(\text{NO}_2)=15$ and $\text{EI}(\text{SO}_2)=1.0$. They found increases in aerosol surface area in the northern hemisphere lower stratosphere of up to 60% along with enhanced ozone depletion. Tie et al. [1994] also used $\text{EI}(\text{NO}_2)=15$ and $\text{EI}(\text{SO}_2)=1.0$. They predicted a 10-20% increase in aerosol surface area and found that the associated ozone changes were small in comparison with the total impact of HSCT emissions. The above studies were performed by putting the sulfur emissions along the flight paths as gas phase $\text{SO}_2$. Weisenstein et al. [1996] modeled an HSCT scenario with $\text{EI}(\text{NO}_2)=5$ and $\text{EI}(\text{SO}_2)=0.4$, evaluating the impact with sulfur emissions assumed to be all gas phase $\text{SO}_2$, all 10 nm particles, and a 10% particles/90% $\text{SO}_2$ gas mix. Increases in sulfate aerosol surface area were found to be up to 60% for sulfur emission as $\text{SO}_2$ gas and up to 200% when emissions were assumed to be all particles. Ozone depletion due to HSCTs was enhanced by the increased sulfate surface area, from 0.1% without sulfur emissions to 1.3% with sulfur emissions as 100% particles with 3 ppbv of chlorine on an annual average basis at 47$^\circ$N.

Because the previously discussed modeling results used different emission scenarios and contained variations in chemical reaction rates and background gas concentrations, the results cannot be compared directly. This paper will present results from four independently formulated 2-D stratospheric models, each of which includes sulfate aerosol microphysics and uses identical emission scenarios and standardized chemical rates [from DeMore et al., 1994]. These models are the Atmospheric and Environmental Research (United States) 2-D model, the University of Cambridge (England) 2-D model, the Università degli Studi L’Aquila (Italy) 2-D model, and the Novosibirsk State University (Russia) 2-D model. While these models can calculate aerosol microphysics on the scale of their model grid boxes (typically 10$^\circ$ latitude by 2 km in the vertical), they cannot account for microphysics and heterogeneous chemical processing that may occur in the aircraft plume or wake. Conditions in the wake, particularly in the first few seconds after emission, are very different from ambient conditions. Sulfur dioxide may be converted to $\text{SO}_3$ or $\text{H}_2\text{SO}_4$ in the early stages of wake evolution or in the engine or nozzle [Brown et al., 1996b]. As a result of the high supersaturations possible in an aircraft wake, $\text{H}_2\text{SO}_4$ can form new sub-micron size aerosol particles through homogeneous nucleation or by condensation onto soot particles [Brown et al., 1996c; Kärcher and Fahey, 1997]. A very high density of aerosol particles would lead to substantial coagulation in the wake [Kärcher and Fahey, 1997; Danilin et al., 1997]. The detailed chemistry and physics of sulfur in aircraft plumes are not well known. Nevertheless, a recent stratospheric measurement in the plume of the Concorde aircraft [Fahey et al., 1995] indicated that a substantial fraction of the emitted sulfur was converted to aerosol particles within 16 min after exhaust. A measurement of aerosols in the exhaust trail of a military aircraft at 23 km [Hofmann and Rosen, 1978] indicated nearly complete conversion of emitted sulfur to aerosols after 18 hours.

The 2-D models employed in this study will adopt assumptions regarding the atmospheric state of the emitted sulfur at the point when the emitted material is diluted to grid box size (a time period of roughly 1 week). This approach will enable us to calculate the global impact of aircraft sulfur emissions in lieu of knowing the details of chemistry in the engine, nozzle, and wake regimes. The amount of sulfur put into each grid box is given by the product of the adopted EI for $\text{SO}_2$ and the fuel burn in that grid box. We consider three assumptions regarding the phase of the emitted sulfur: (1) all sulfur remains in the form of $\text{SO}_2$ gas, (2) 10% of the emitted sulfur is converted to aerosol particles of 10 nm radius, and (3) 100% of the emitted sulfur is converted to 10 nm aerosol particles. Greater changes in the aerosol surface area of the stratosphere are to be expected under assumption 3. The 100% conversion of aircraft-emitted sulfur to aerosol particles within 1 week cannot be ruled out on the basis of atmospheric measurements to date, so we take this case as the upper limit. Assumption 2 represents the lower limit of aerosol formation in the plume as determined by the Concorde measurements [Fahey et al., 1995] within 1 hour of emission. Assumption 1 is included for historical reasons and is similar to theoretical calculations for aerosol formation in aircraft plumes when sulfur is assumed emitted as $\text{SO}_2$ and reaction with OH is the only oxidation mechanism [Brown et al., 1996a].}

We will start with descriptions of the four models to be used in this comparison, including the similarities and differences of their microphysical, chemical, and dynamical formulations, in section 2. Section 3 will describe the HSCT scenario used and present results of changes in sulfate surface area and ozone. Section 4 will present additional sensitivity studies that have been performed by subsets of the four models. Section 5 will summarize the results and draw conclusions.

## 2. Model Descriptions and Comparisons

### 2.1. Atmospheric and Environmental Research Model

The Atmospheric and Environmental Research (AER) sulfur model is described by Weisenstein et al. [1997]. Aerosol processes modeled include homogeneous nucleation, coagulation, condensation/evaporation, and sed-
mation. There are 40 aerosol size bins ranging from 0.39 nm to 3.2 μm by volume doubling. Only binary sulfuric acid-water aerosols are considered. The sulfur model is not coupled to the ozone model in that the OH field in the sulfur model is fixed at precalculated values. The sulfate surface area density calculated by the sulfur model is treated as input to the photochemical model. The photochemical model with full O2, HO2, CHO2, NO2, ClO2, and BrO2 chemistry is described by Prather and Remsberg [1993] and Weisenstein et al. [1996]. Model temperature and circulation are prescribed according to climatology and do not respond to changes in aerosols or chemical species.

A temperature probability distribution is employed for the calculation of homogeneous nucleation rates and all temperature-dependent reaction rates following the methodology of Considine et al. [1994]. Monthly zonal mean temperature statistics in 1 K increments were derived for the time period from 1979 to 1986 on the basis of daily data from the National Centers for Environmental Prediction/National Center for Atmospheric Research reanalysis project [Kalnay et al., 1996]. The tropical pipe circulation [Plumb, 1996] is employed as described by Weisenstein et al. [1996], using small values of horizontal diffusion in the tropical lower stratosphere. Grid resolution is 9.5° latitude by 1.2 km in the vertical. Updates to the sulfur model [Weisenstein et al., 1997] since the publication of previous HSCT assessment results [Weisenstein et al., 1996] have somewhat reduced the calculated increases in aerosol surface area due to HSCT emissions; however, inclusion of the temperature probability distribution for calculation of reaction rates has increased the calculated ozone depletion for the same scenarios.

2.2. Novosibirsk State University Model

Included here is a fairly detailed description of the Novosibirsk State University (NSU) model, as this model has not previously been described in an English language journal. The NSU model is a zonally averaged 2-D interactive model for self-consistent calculation of diabatic circulation, temperature, and gaseous and aerosol composition of the troposphere and stratosphere. The photochemical and radiative parts of the model are described by Dyominov [1988, 1991, 1992], Dyominov and Zadorozhny [1989], Ginzburg and Dyominov [1989], and Dyominov et al. [unpublished material, 1992]. In this work, circulation and temperature are calculated self-consistently with 45 minor gas constituents: O3, O(3P), O(1D), H, OH, HO2, H2O2, H2O, NO, NO2, NO3, N2O5, HNO3, HNO4, N2O, CO, CH4, CH3, CH2O, CH3O2, CH3O, CH3CO, CH3CO2NO2 (peroxyacetyl nitrate), Cl, ClO, HOCl, ClONO2, HCl, ClCl, Cl2, Br, BrO, HBrO, HBr, BrO2, Cl2S(S)Cl (dimethylsulfide, or DMS), CS2, H2S, OCS, S, SO, SO2, SO4, HSO3, and H2SO4. Additional chlorine and bromine source gases are included in the model but not calculated interactively. These include the organic chlorine species CFC13 (CFC-11), CF2Cl2 (CFC-12), CF2ClFCl2 (CFC-113), CHF2Cl (HCFC-22), CH3CFC12 (HCFC-141b), and CH3CCL3 and the organic bromine species CH3Br, CF2Br (H-1301) and CF2ClBr (H-1211), which are calculated only for a background atmosphere representing the year 2015 (3.0 ppbv or 2.0 ppbv of Clp and 17 pptv of Brp).

Interaction of all these gaseous components is governed by 157 photochemical reactions, including 26 reactions that describe interactions among the sulfate components. The diurnal variation of photolysis rates is recalculated every tenth model day. Five heterogeneous reactions are used to account for interactions between gaseous components and aerosol particles (see reactions (1)-(4) in section 2.5 and reaction (5) in section 4.4 below). The rates of heterogeneous reactions (1)-(3) and (5) are calculated by using the formula \[ k = \frac{V_T S}{4}, \]
where \( k \) is the reaction probability, \( V_T \) is the thermal velocity of gas molecules, and \( S \) is the surface area density of sulfate aerosols. Values of \( \gamma \) for heterogeneous reactions (1)-(3) are taken from Table 3-2 of WMO [1993]:
\[ \gamma_1 = 0.1, \quad \log_{10}(\gamma_2) = 1.87 - 0.074 W, \]
where \( W \) is the weight percent of H2SO4 in aerosol particles (calculated according to the formula of Hanson et al. [1994]), and
\[ \gamma_3 = 0.172. \]
The rate of heterogeneous reaction (4) is calculated according to the method of Hanson et al. [1994] and is proportional to the volume of the aerosol particles. The constant value 0.4 [Hanson and Ravishankara, 1995] is adopted for the probability of heterogeneous reaction (5).

The temperature stratification of the atmosphere is determined by the heat balance equation. Calculation of atmospheric heating and cooling rates takes into account heat fluxes due to convection, turbulent heat exchange, and radiative transfer in three spectral ranges: UV and visible (0.175-0.9 μm), near infrared (0.9-4.0 μm), and infrared (>4.0 μm). The radiative fluxes in the UV and visible part of the spectrum are computed by taking into account scattering on air molecules and aerosol particles, reflection from clouds and the Earth's surface, and absorption by oxygen, ozone, and nitrogen dioxide. In the near infrared, absorption by water vapor (in the 0.94, 1.1, 1.38, 1.87, 2.7, and 3.2 μm bands) and by carbon dioxide (in the 2.0 and 2.7 μm bands) is considered. Infrared fluxes account for longwave radiative absorption by CO2, O3, H2O, CH4, N2O, CFCl3, and CF2Cl2. The fine spectral structure of these constituents is taken into account in absorption bands centered around 15 μm for CO2; 9.6 μm for O3; 6.3 μm for H2O; 7.6 μm for CH4; 4.5, 7.78, 8.57, and 17 μm for N2O; 9.22 and 11.82 μm for CFCl3; and 8.68, 9.13, and 10.93 μm for CF2Cl2. For H2O, rotational bands are also taken into account.

Dynamical processes in the atmosphere are represented in the model by the residual circulation and eddy diffusion. The method of computing the residual circulation is described by Ginzburg and Dyominov [1989] and Talrose et al. [1993]. It consists of solving the
zonally averaged equations describing conservation of momentum, mass, and energy, with the momentum flux divergence due to gravity waves approximated by means of a Rayleigh friction coefficient \([\text{Garcia and Solomon, 1983}]\). The momentum flux due to breaking planetary waves is parameterized as in the model of \textit{Hitchman and Brassier} [1988]. The eddy diffusion coefficients are computed by using the method described by \textit{Brasseur et al.} [1990]. The model grid resolution is 5° latitude and 1 km in the vertical for altitudes up to 36 km, with 2 km vertical resolution from 36 to 50 km.

The 2-D model of aerosol composition of the troposphere and stratosphere is described by \textit{Golitsyn et al.} [1994]. The results of calculations with this model are also described by \textit{Dyominov and Elansky} [1995], \textit{Dyominov et al.} [1995], and \textit{Dyominov and Zadorozhny} [1996].

The aerosol 2-D model can calculate distributions of three types of aerosol particles: ice, nitric acid trihydrate (NAT), and sulfate particles, though only sulfate particles are treated in the present study. There are 30 aerosol bins in the model, with particle radii ranging from 6.4 nm to 5.2 \(\mu\)m by volume doubling. Microphysical processes simulated are nucleation (both homogeneous and heterogeneous), condensation, evaporation, coagulation, sedimentation, and washout. The classical approach is used for the calculation of the binary homogeneous nucleation rate, as discussed by \textit{Frenkel} [1975] and \textit{Hamill et al.} [1982]. The heterogeneous nucleation rate is calculated according to the method given by \textit{Hamill et al.} [1982] and employed by \textit{Pitari et al.} [1993]. Concentrations of Aitken nuclei \((0.012 \mu m \leq r \leq 0.4 \mu m)\) and large nuclei \((0.5 \mu m \leq r \leq 2.0 \mu m)\) at a surface of the Earth were assumed equal to 1800 cm\(^{-3}\) and 40 cm\(^{-3}\), respectively. Condensation and evaporation are calculated in the model following \textit{Turco et al.} [1979] and \textit{Toon et al.} [1988]. Changes of particle size distribution resulting from Brownian coagulation are described with classical relations, as described by \textit{Asaturrov et al.} [1986]. Sedimentation of aerosols and tropospheric washout follow \textit{Pitari et al.} [1993].

### 2.3. Università degli Studi-L’Aquila (Italy) Model

The Università degli Studi-L’Aquila model (hereafter referred to as the Italy model) is described by \textit{Pitari et al.} [1993]. The sulfate aerosol module calculates particle densities in 11 size bins between 0.01 and 10.25 \(\mu\)m radius by radius doubling. Microphysical processes modeled include heterogeneous nucleation, condensation, evaporation, coagulation, and sedimentation. All aerosols are assumed to contain a solid core. Polar stratospheric cloud (PSC) particle distributions (both NAT and ice) can be calculated by the Italy model but are not included here. The grid resolution is 10° latitude by 2.8 km altitude. The circulation is taken from the group’s spectral quasi-geostrophic three-dimensional model \([\text{Pitari et al., 1992}]\) but is not interactive in these calculations. Temperatures above 20 mbar are taken from the same three-dimensional model and below 20 mbar from standard references. A temperature distribution is applied at each model grid point by assuming a statistical standard deviation \([\text{Pitari, 1993}]\). The temperature distribution is applied to the calculation of the rates of the heterogeneous reactions \(\text{ClONO}_2+\text{H}_2\text{O}, \text{ClONO}_2+\text{HCl},\) and \(\text{HOCI}+\text{HCl}\).

### 2.4. University of Cambridge Model

The University of Cambridge 2-D model is described by \textit{Bekki and Pyle} [1992, 1993]. It treats aerosol particles in 25 size bins between 0.01 and 2.5 \(\mu\)m with volume doubling bin spacing. Microphysical processes included in the Cambridge model are heterogeneous and homogeneous nucleation, condensation, evaporation, coagulation, and sedimentation. The homogeneous nucleation is parameterized by assuming arbitrarily that new sulfuric acid particles are formed at a constant rate \([\text{Bekki and Pyle, 1992}]\) in the tropical upper troposphere in order to provide a source of nuclei in this region \([\text{Brock et al., 1995}]\). \textit{Hamill et al.} [1982] tested various nucleation mechanisms and found that a simple nucleation treatment led to overall aerosol properties similar to those obtained with sophisticated schemes. The model includes only DMS and carbonyl sulfide (OCS) as sulfur source gases, excluding surface emissions of \(\text{SO}_2\). The Cambridge model is a classical Eulerian model. The grid resolution is 9.5° latitude and 3.5 km in the vertical. The temperature and circulation are calculated interactively from forcing terms, which include solar heating by \(\text{O}_2\) and \(\text{O}_3\) and longwave cooling by \(\text{CO}_2\), \(\text{H}_2\text{O}\), \(\text{O}_3\), \(\text{N}_2\text{O}\), and \(\text{CH}_4\). The chemical scheme includes what are thought to be the most important reactions of \(\text{O}_2\), \(\text{NO}_y\), \(\text{HO}_2\), \(\text{ClO}_y\), \(\text{BrO}_y\), \(\text{CHO}_y\), and \(\text{SO}_2\). A temperature distribution is employed for the calculation of heterogeneous reaction probabilities. Monthly zonal mean temperature statistics are taken from Cospar International Reference Atmosphere \([\text{Labitzke et al., 1985}]\) climatologies. The reaction probabilities are as described for the NSU model, with \(\gamma\) of \(\text{ClONO}_2+\text{HCl}\) set to a tenth of the reaction probability of \(\text{ClONO}_2+\text{H}_2\text{O}\). The reaction \(\text{HOCI}+\text{HCl}\) is not included.

### 2.5. Model Similarities and Differences

All four models employ fairly standard classical approaches to aerosol microphysics. The processes of condensation, evaporation, coagulation, and sedimentation are treated similarly in all the models. None of the model simulations presented in this paper include PSC chemistry. While some models use heterogeneous nucleation and some use homogeneous nucleation (the NSU model uses both), nucleation is a minor process in the stratosphere (compared with condensation and coagulation) and probably does not lead to large differences in the model results to be presented here. The models also differ in the resolution and range of aerosol sizes considered. The number of size bins varies from 11 to 40 in the models, with the AER and NSU models including...
aerosol radii less than 0.01 μm and the Italy and NSU models including the largest sizes. The AER, Cambridge, and NSU models have the same size resolution, using a volume doubling scheme. The Italy model has a coarser resolution, using a radius doubling scheme. A lower size resolution has been found to produce a shift in the size distribution toward larger particles [Larsen, 1991].

The most important differences between the models are not in their microphysical formulations but in their transport circulations, temperature fields, and chemical formulations. The Cambridge and NSU models calculate temperature and circulation interactively, while the Italy model takes these fields from an off-line calculation. The AER model prescribes them (using observed late temperature and circulation) using a volume doubling scheme. The Italy model has taken from JPL-94 [DeMote et al., 1994] in all four models, the model calculated OH concentrations are different, and therefore rates of conversion from SO to H2SO4 are different. The models include heterogeneous reactions on sulfate aerosols, namely,

\[
\begin{align*}
N_2O_5 + H_2O & \rightarrow 2HNO_3 & (1) \\
ClONO_2 + H_2O & \rightarrow HNO_3 + HOCl & (2) \\
ClONO_2 + HCl & \rightarrow HNO_3 + Cl_2 & (3) \\
HOCI + HCl & \rightarrow H_2O + Cl_2 & (4)
\end{align*}
\]

of which reaction (1) is the most important on a global basis. Reactions (2)-(4) are important in the cold regions at high latitudes in winter and under high aerosol conditions. The importance of reactions on cold sulfate aerosol has been demonstrated in analysis of the observed partitioning of the radicals in both satellite and aircraft data [Michelsen et al., 1997]. The use of a temperature probability distribution in the AER and Italy models leads to enhanced importance of these reactions due to their strong temperature dependence. Rates for reactions (2)-(4) in the AER and Italy models are taken from Hanson et al. [1994], while all models use a constant γ of 0.1 for reaction (1).

3. Model Intercomparison

The sulfate aerosol surface area calculated by each of the models for annual average background (non-volcanic) conditions is shown in Figure 1. That derived from Stratospheric Aerosol and Gas Experiment (SAGE) data and adopted by modelers to represent clean background conditions [WMO, 1993] is shown in Figure 1f, and the April 1991 surface area [Yue et al., 1994] derived from SAGE II is shown in Figure 1e. The first half of 1991 (before the Mount Pinatubo eruption in June) represents a recent year that is near background conditions, though it probably includes some residual effects of volcanic activity [Thomason et al., 1997]. The actual distribution of aerosol surface area during background conditions is not well known and would of course vary from year to year.

All models reproduce the magnitude and structure of the WMO surface area, with lowest values in the tropical lower stratosphere and highest values in the high latitude lower stratosphere. In comparison with WMO the aerosol surface area of the Cambridge model is 30% low in the tropical lower stratosphere, while the Italy model is 30% high in this region. The NSU model matches WMO most closely. The AER and NSU models predict greater surface area in the northern polar region, on an annual average basis, than in the southern polar region, while the Italy model and WMO show greater surface area in the southern polar region. The Cambridge model is relatively symmetrical between hemispheres. Model tropospheres vary considerably depending on the surface sources of sulfur included in the models. The Cambridge model includes only DMS and OCS surface sources, while other models also include CS2, H2S, and SO2 surface emissions. Surface emissions of SO2 are evenly distributed with latitude in the Italy and NSU models but are weighted toward the northern hemisphere in the AER model.

Each model was run with identical parameters for aircraft emissions and similar background atmospheres, with a chlorine content of 3.0 ppbv and bromine content of 17 parts per trillion by volume (pptv). The aircraft emission scenarios employed here are those described by Stolarski et al. [1995]. These represent 500 aircraft operating in the year 2015 and burning 82x10^9 kg of fuel annually, with the geographical fuel use distribution derived by Baughcum and Henderson [1995]. The HSCT aircraft cruise at Mach 2.4, with a cruise altitude of 18-21 km. Engine emissions are specified by an emission index, or EI, defined as grams of pollutant emitted per kilogram of fuel burned. We present results for two values of EI(NOx), 5 and 15. An EI(NOx) of 5 represents a significant reduction in emission index from current supersonic aircraft (values of about 20 are typical), though technological advances in the last several
years have shown that an $\text{EI(NO}_x\text{)}$ of 5 is achievable [Stolarski et al., 1995]. $\text{EI(H}_2\text{O)}$ of 1230 is used in all calculations.

The $\text{EI of SO}_2$ is taken to be 0.4, based on projections that sulfur content in jet fuel will decline from its current average value of 0.8 [Baughcum et al., 1994]. Because these 2-D models are not formulated to calculate tropospheric aerosols, we have not included sulfur emissions from subsonic aircraft or from HSCT aircraft below 13 km. The aircraft sulfur emissions amount to $2.4 \times 10^{10}$ grams $\text{SO}_2$ per year deposited between 13 and 22 km altitude. At $45^\circ\text{N}$ and 19 km, which represents the peak of HSCT traffic, sulfur emissions amount to about 30 molecules cm$^{-3}$ s$^{-1}$ of $\text{SO}_2$. If emissions are assumed to be 100% particles of 10 nm radius, this value represents about 90 particles cm$^{-3}$ day$^{-1}$, corresponding to a surface area rate of increase of about 0.1 $\mu$m$^2$ cm$^{-3}$ day$^{-1}$.

### 3.1. Surface Area Changes

Figure 2 shows the calculated change in the annual average aerosol surface area density due to emission of sulfur from HSCT aircraft, assuming that it remains $\text{SO}_2$ until mixing dilutes the plume to grid box size (assumption 1). The spatial variation of the perturbation corresponds to the geographical distribution of fuel usage, which is concentrated in the northern hemisphere. Maximum changes in surface area range from 0.1 $\mu$m$^2$ cm$^{-3}$ in the Cambridge model to 0.2 $\mu$m$^2$ cm$^{-3}$ in the Italy model, 0.3 $\mu$m$^2$ cm$^{-3}$ in the AER model, and 0.5 $\mu$m$^2$ cm$^{-3}$ in the NSU model. After the aircraft sulfur is mixed into the global grid box as $\text{SO}_2$, reaction with
OH is the only pathway to produce $\text{H}_2\text{SO}_4$. Therefore model differences may reflect variations in calculated OH concentration, as well as the distribution of available sulfate particles on which gas phase $\text{H}_2\text{SO}_4$ may condense. As a percentage of the background surface area, calculated perturbations in the northern hemisphere lower stratosphere are up to 25% in the Italy model, up to 30% in the Cambridge model, up to 40% in the AER model, and up to 50% in the NSU model. The Cambridge and AER models show their largest percent change in the tropics because the calculated background is quite low there.

Increases in aerosol surface area under assumption 2, when 10% of the emitted sulfur is assumed to be converted to aerosol particles in the plume, are shown in Figure 3 for the four models. The aerosol particles generated in the aircraft plume are assumed to be of radius 10 nm (0.01 $\mu$m). This assumption is consistent with model calculations of the wake regime by Fahey et al. [1995] and Danilin et al. [1997]. Calculated maximum changes in aerosol surface area under this assumption are 0.4 $\mu$m$^2$ cm$^{-3}$ for the AER and Cambridge models, 0.6 $\mu$m$^2$ cm$^{-3}$ for the Italy model, and 0.8 $\mu$m$^2$ cm$^{-3}$ for the NSU model. Corresponding percentage changes are 65% for the AER model and 75% for the Cambridge, Italy, and NSU models. The inclusion of aerosol particles in the emission scenario increases the surface area perturbation for each of the models, but the amount varies from 0.1 $\mu$m$^2$ cm$^{-3}$ for the AER model to 0.4 $\mu$m$^2$ cm$^{-3}$ for the Italy model.

Calculated increases in aerosol surface area under assumption 3, when all emissions are assumed to be particles, are shown in Figure 4. The maximum surface area increases are 1.0 $\mu$m$^2$ cm$^{-3}$ in the Cambridge model, 1.5 $\mu$m$^2$ cm$^{-3}$ in the AER model, 2.0 $\mu$m$^2$ cm$^{-3}$ in the NSU model, and 2.5 $\mu$m$^2$ cm$^{-3}$ in the Italy model. These perturbations are more than double those found under assumption 2 and represent increases of up to 200% over background for each model. The Italy model calculates as much as a 300% increase over the background surface area. Note that the area of maximum perturbation is more localized under assumption 3 than under the other two assumptions because aerosols are input directly along the flight tracks as small particles with high surface-to-volume ratio.

Differences in transport rates between the models appear to account for most of the intermodel differences in surface area perturbation. Relative changes in stratospheric aerosol mass among the four models mirror relative changes in surface area. The smaller calculated surface area (and aerosol mass) perturbations are related to shorter residence times and faster transport rates in the model stratosphere. The Cambridge model has the smallest increase in surface area under assumptions 1, 2, and 3 and uses an Eulerian transport scheme with faster advection and larger diffusion coefficients than
Figure 3. Calculated annual average increase in aerosol surface area ($\mu$m$^2$ cm$^{-3}$) due to HSCT emissions with $EI(SO_2)=0.4$, assumed emitted as 10% particles and 90% $SO_2$ gas. Results are from (a) AER model, (b) NSU model, (c) Italy model, and (d) Cambridge model.

Figure 4. Calculated annual average increase in aerosol surface area ($\mu$m$^2$ cm$^{-3}$) due to HSCT emissions with $EI(SO_2)=0.4$, assumed emitted as 100% particles of 10 nm radius. Results are from (a) AER model, (b) NSU model, (c) Italy model, and (d) Cambridge model.
the other models. The Italy model has a small increase in surface area under assumption 1 but the largest increase in surface area under assumption 3. It uses a relatively slow transport rate, which yields a greater increase in stratospheric aerosol mass due to HSCT emissions. Surface area increases under assumption 1, however, also depend on the background particle size distribution. With the coarser resolution of aerosol sizes in the Italy model the background distribution is shifted toward larger particles. Condensation on larger particles provides a smaller surface area increase than does condensation on smaller particles.

To illustrate how the aerosol size resolution and calculated background aerosol distribution influence the HSCT surface area perturbation, we show in Figure 5 calculated aerosol size distributions for the AER, Italy, and Cambridge models under background and HSCT conditions at 45°N and 20 km in March. Under background conditions the AER model shows a maximum in number density at 0.04 μm radius, while the Italy and Cambridge models, which do not consider particles smaller than 0.01 μm, shows peak number densities at 0.08 and 0.06 μm, respectively. The Cambridge and AER models use a finer size resolution than the Italy model and show background size distributions that include more small particles and fewer large particles. The shape of the size distributions in the AER and Cambridge models are similar, though the total particle number density is smaller in the Cambridge model.

With addition of HSCT sulfur as gas phase SO₂ the Italy model shows a decrease in number density for particles less than 0.08 μm radius and an increase for particles greater than 0.08 μm. The Cambridge model results are similar, but decreases in number density are evident only for particles less than 0.03 μm. Such changes in particle number density are typical when condensation onto existing particles is the only mechanism for converting gas phase H₂SO₄ into aerosols. The AER model shows evidence for new particle production by nucleation, as the number of particles less than 0.001 μm is increased by addition of HSCT gas phase emissions. The gas phase sulfur emissions increase nucleation in the stratosphere by 150%, though only 6% of the emitted sulfur undergoes nucleation, while 94% condenses onto existing particles. With HSCT emissions as 100% particles, coagulation is the main process for interaction between the background distribution and the new particles. The AER and Cambridge models show similar size distributions for particles between 0.01 and 0.1 μm. The Italy models show a greater redistribu-

Figure 5. Calculated aerosol number density \( dN/d(\log r) \) as a function of particle radius for the (a) AER, (b) Italy, and (c) Cambridge models. The solid line represents the background distribution, the dashed line represents a simulation including HSCT emissions of sulfur as SO₂ gas, and the dotted line represents a simulation including HSCT emissions of sulfur as 10 nm particles.
tion of injected sulfur into particle sizes between 0.01 and 1 μm. When the background distribution contains particles smaller than 0.01 μm, as in the AER model, these small particles preferentially coagulate with the injected 0.01 μm particles, somewhat reducing the surface area of the combined background/HSCT distribution in comparison with the distribution expected without this interaction. Note, however, that it is not possible to distinguish the relative importance of differences in transport and differences in aerosol size resolution on the basis of these calculations.

The sensitivity of these results to the assumed size of aerosol particles at plume breakup has been investigated with the AER and NSU models. Calculations were performed with particle sizes ranging from 0.4 nm to 80 nm. The maximum impact on aerosol surface area was found for particles in the 2.5 to 20 nm range. Smaller particles coagulate faster with background aerosols, reducing the surface area increase, and larger particles are removed more rapidly by sedimentation. Input of 80 nm particles resulted in less than half the surface area perturbation calculated for 10 nm particles under assumption 3. A calculation with 0.4 nm particles produced a peak aerosol surface area enhancement which was 25% less than that with 10 nm particles under assumption 3. A modeling study of the far-wake regime [Danilin et al., 1997] indicated that the particle size distribution at 1 week after emission is sensitive to the wake dilution rate. By employing a very fast, a very slow, and an intermediate dilution rate, several possible particle size distributions were obtained, with peak number densities occurring between 4 and 20 nm. Our choice of 10 nm particles falls within this range and produces approximately the largest expected impact.

3.2. Ozone Changes

Calculated changes in annual average column ozone as a function of latitude due to emission of NOx, H2O, and sulfur from HSCT aircraft are shown in Figure 6 for each of the four models. Four results are shown for each model: the solid line represents aircraft emissions with EI(NOx)=5 and no sulfur emissions, while the three dashed lines include sulfur emissions with EI(SO2)=0.4 under assumptions 1, 2, and 3. Each model used its own calculated background aerosol surface area (those shown in Figure 1) for the subsonic case (used as the baseline) and the HSCT case without sulfur emissions. Without sulfur emissions, ozone column changes due to this HSCT scenario range from -0.1% to +0.2% near the equator and from 0% to -0.7% for middle and high latitudes. All models show more ozone depletion at high northern latitudes than at high southern latitudes as a result of the asymmetry of the HSCT source. The Italy model shows little change in column ozone between 30°S and 50°N and depletions of up to 0.3% at higher latitudes. The Cambridge model shows small ozone depletion in the tropics and up to 0.5% depletion near the north pole. Both the AER and NSU models show no ozone column change at the equator and 0.6% to 0.7% depletion near the north pole. Ozone column changes at the south pole are about -0.2% to -0.3% for all models.

With addition of sulfur emissions from HSCT aircraft, all models show greater ozone depletion, which increases with concurrent increases in aerosol surface area. Increasing aerosol surface area has two effects on the ozone impact of HSCT. It reduces the amount of NOy in the active forms of NO and NO2, thus decreasing the importance of the NO2 cycle to ozone loss and reducing the impact of aircraft-emitted NO2. It also increases the amount of chlorine and HOx in the active

Figure 6. Calculated changes in annual average column ozone due to an HSCT emission scenario with EI(NOx)=5, EI(H2O)=1230, and different assumptions on sulfur emissions from the (a) AER model, (b) NSU model, (c) Italy model, and (d) Cambridge model. The solid line represents a case with no SO2 emissions, the long dashed line represents EI(SO2)=0.4 with assumption 1, the short dashed line represents EI(SO2)=0.4 with assumption 2, and the dot-dashed line represents EI(SO2)=0.4 with assumption 3. Background Cl, is 3 ppbv.
forms of ClO and HO$_2$, leading to ozone depletion. For
the EI(NO$_2$)$_\text{c}=5$ scenario the latter effect is more sig-
nificant, and there is additional ozone depletion. The
impact of sulfur emission on ozone column change is
smallest in the tropics and greatest at northern high lat-
titudes in all models except the Cambridge model. The
additional ozone column depletion under assumption 1
is less than or equal to 0.3%. Further depletion under
assumption 2 is only an additional 0.1-0.2% (compared
with results under assumption 1) except for the Italy
model, which calculates additional ozone depletion of
0.4% in the northern hemisphere. Under assumption 3
additional ozone depletion beyond that calculated un-
der assumption 2 is up to 0.6% for the AER model, 0.3%
for the NSU model, up to 1.4% for the Italy model, and
0.1% for the Cambridge model.
The Cambridge and Italy models show similar ozone
column depletion under assumption 1. The Italy model,
however, shows the largest depletion under assumption
3 (as much as 2.3% on an annual average basis), while
the Cambridge model shows the smallest depletion un-
der assumption 3 (only 0.5% at most). This difference
is consistent with the differences in calculated aerosol
surface area perturbation and treatment of heteroge-
neous chemistry. The AER and NSU models yield simi-
lar ozone responses to HSCT emissions with no fuel
sulfur, but the AER model yields greater ozone deple-
tion with fuel sulfur. Maximum annual average ozone
column changes under assumption 3 are 1.1% for the
NSU model and 1.8% for the AER model. The NSU
model calculates a larger aerosol surface area pertur-
bation than the AER model, but the AER model cal-
culates a larger ozone response because it includes a
temperature distribution. We can separate differences
in calculated aerosol surface area from differences in cal-
culated ozone depletion by using the calculated surface
area density from various models in a single model. Use
of the surface area density calculated by the Italy model
under assumption 3 in the AER model results in max-
imum annual average ozone depletion of 2.5%. Use of
the Cambridge model surface area calculated under as-
sumption 3 in the AER model results in a maximum of
1.7% annual average ozone depletion.
To further emphasize the difference between assump-
tion 1, with all sulfur emission as gas, and assumption
3, with all sulfur emission as particles, we examine in
Figure 7 the calculated changes in ozone column as a
function of latitude and season due to HSCT emissions
with EI(NO$_2$)$_\text{c}=5$ for the AER, Italy, and Cambridge
models. With emission of sulfur as all gas the AER
model shows ozone loss across all of the extratropics,
while the Italy model shows some ozone increase in
spring from 30° to 50°N and in the tropics. The Cam-
bridge model shows less than 0.3% ozone column de-
pletion at all latitudes and seasons except poleward of
50° in summer and fall. With emission of sulfur as all
particles, ozone reductions in the AER and Italy mod-
els are dramatic, occurring at all latitudes and seasons.
With these models, ozone depletion is greatest at high
northern latitudes in spring, with more than 2% ozone
depletion between 60°N and 90°N in March and April.
Ozone depletion in the southern hemisphere high lati-
tudes approaches 1% in spring. The midlatitudes and
tropics show little seasonal contrast. The Cambridge
model shows only modest changes in ozone depletion
due to particle rather than gas phase sulfur emissions,
with the greatest change in the tropics and at high lati-
dutes in spring.
Figure 8 shows profiles of ozone changes at 45°N in
June for the four models with no sulfur emissions and
with sulfur emissions under the three assumptions for
EI(NO$_2$)$_\text{c}=5$. For all of the models, HSCT emissions
without sulfur produce an ozone increase in the tropo-
sphere and an ozone decrease in the middle stratosphere
above 20 km, but the response in the lower stratosphere
(10-20 km) varies markedly between models. This var-
ation reflects the sensitivity of ozone in this region to
catalytic loss by the HO$_2$, NO$_2$, and ClO$_2$ cycles and
to transport. HSCT emissions add H$_2$O, and there-
fore HO$_2$, and NO$_2$, increasing ozone loss by their re-
spective catalytic cycles. But NO$_2$ emissions also tend
to reduce the HO$_2$ and ClO$_2$ cycles by forming HNO$_3$
and ClONO$_2$. The increase in the NO$_2$ cycle appears
to dominate the ozone response in this region in the
AER and NSU models, while reductions in the HO$_2$
and ClO$_2$ cycles dominate in the Cambridge and Italy
models. In this sensitive region of the stratosphere, dif-
fferences in model formulations of both chemistry and
transport substantially influence calculated changes in
ozone, leading to model differences in the sign and the
magnitude of the ozone response to HSCT between 10
and 20 km.
When emissions of sulfur are also considered, all mod-
els predict a more negative response to HSCT emissions
in the troposphere and lower stratosphere. The sensi-
tivities vary, however. At 15 km the difference in the
percent ozone change between the scenario with no sul-
fur emissions and that with sulfur emissions as 100%
particles is 1.1% in the Cambridge model, 1.2% in the
NSU model, 2.7% in the AER model, and 5.5% in the
Italy model. In the middle stratosphere, where the NO$_2$
cycle constitutes a large fraction of the total ozone loss,
all models calculate less ozone loss due to HSCT sulfur
emissions. The altitude at which increases in aerosol
surface area begin to cause ozone enhancement rather
than depletion varies from 20 km in the NSU model to
24 km in the Italy model and has some dependence on
absolute surface area. The Cambridge model shows the
greatest ozone increase in the middle stratosphere due
to aerosol emissions, which largely offsets the calculated
depletion at lower altitudes and accounts for the modest
change in column ozone due to aerosol emissions.
Figure 9 shows changes in annual average ozone col-
umn due to HSCT emissions for a scenario with
EI(NO$_2$)$_\text{c}=15$. The Cambridge model did not calculate
this scenario, so only three model results are shown.
With sulfur emissions omitted the ozone response is significantly larger than that for EI(NO)=5. The response is due primarily to increases in NO catalytic loss of ozone. The response to sulfur emissions is quite different from that seen with EI(NO)=5. While the southern hemisphere still shows increased ozone depletion with increasing surface area, the northern hemisphere shows a variety of responses among the models. The AER and Italy models show only a small response in the northern hemisphere to sulfur emissions under assumptions 1 and 2 but show a substantial negative response to sulfur emissions under assumption 3. In the NSU model the sulfur emissions reduce ozone depletion in the northern hemisphere. Sulfur emissions can “buffer” or reduce the effects of high NO emissions by aircraft, since heterogeneous reactions on the increased surface area reduce the amount of emitted NO that remains in active forms. The NSU model does, however, show greater ozone depletion under assumption 3 than under assumption 1 or 2.

Changes in June ozone profile at 45°N for the three models with EI(NO)=15 are shown in Figure 10. All models show substantial ozone increases in the troposphere due to emission of NO, but varying from 1.7% in the NSU model to 2.5% in the AER model and 4.0% in the Italy model. The tropospheric ozone increase is somewhat reduced by sulfur emissions. Note, however, that tropospheric ozone changes contribute little to the total column response. In the lower stratosphere the AER and Italy models show enhanced ozone depletion due to sulfur emissions, while the NSU model shows reduced ozone depletion. It is likely that the NSU model...
Figure 8. Calculated percent change in ozone due to HSCT emissions with $E_I(\text{NO}_x)=5$, $E_I(\text{H}_2\text{O})=1230$, and different assumptions on sulfur emissions in June at 45°N for (a) AER model, (b) NSU model, (c) Italy model, and (d) Cambridge model. The solid line represents a case with no SO$_2$ emissions, the long dashed line represents $E_I(\text{SO}_2)=0.4$ with assumption 1, the short dashed line represents $E_I(\text{SO}_2)=0.4$ with assumption 2, and the dot-dashed line represents $E_I(\text{SO}_2)=0.4$ with assumption 3. Background Cl$_2$ is 3 ppbv.

would show less of a positive response in this region if a temperature distribution were included and the effect of heterogeneous reactions were enhanced.

Table 1 lists percent changes in column ozone at 45°N and on a global average basis for the AER, NSU, Italy, and Cambridge models due to an HSCT fleet with NO$_x$ emission indices of 5 and 15. Global ozone changes are about one half to two thirds of the changes at 45°N for most scenarios. Calculated changes in global ozone are less than or equal to 0.2% depletion with $E_I(\text{NO}_x)=5$ and no sulfur emissions but as much as 0.8% with sulfur emissions as 100% particles. Global ozone changes with $E_I(\text{NO}_x)=15$ are up to 0.4% depletion without sulfur emissions and up to 0.5% depletion with sulfur emissions as 100% particles. Comparing the $E_I(\text{NO}_x)=5$ and the $E_I(\text{NO}_x)=15$ scenarios, we see much larger ozone depletion for $E_I(\text{NO}_x)=15$ without sulfur emissions from aircraft, but with sulfur emissions as 100% particles, ozone depletion is larger for $E_I(\text{NO}_x)=5$. Thus attempts to control NO$_x$ emissions from aircraft without concomitant reductions in fuel sulfur may not yield desired controls on ozone depletion.

4. Sensitivity Studies

4.1. Temperature Probability Distribution

To illustrate the importance of a temperature probability distribution in the calculation of ozone changes induced by HSCT emissions, we show in Figure 11 results from the AER and Italy models without a temperature distribution for the $E_I(\text{NO}_x)=5$ scenario. These ozone column changes as a function of latitude and season can be compared with those shown in Figure 7, which include the distribution. Except for the Italy model with gas phase sulfur emissions, ozone column changes are smaller without the distribution, particularly for the case with 100% particle emissions. The seasonality of ozone depletion is also changed, with maximum depletion found in fall without a temperature distribution and in spring with a temperature distribution. Northern midlatitude ozone depletion is strongly affected as well. By including a temperature distribution, annual average ozone depletion at 45°N changes from 0.81% to 1.14% in the AER model with particle emissions and from 0.90% to 1.45% in the Italy model with particle emissions. Ozone column depletion results for the
Figure 9. Calculated changes in annual average column ozone due to an HSCT emission scenario with \( \text{EI(NO}_x) = 15 \), \( \text{EI(H}_2\text{O}) = 1230 \), and different assumptions on sulfur emissions from the (a) AER model, (b) NSU model, and (c) Italy model. The solid line represents a case with no \( \text{SO}_2 \) emissions, the long dashed line represents \( \text{EI(SO}_2) = 0.4 \) with assumption 1, the short dashed line represents \( \text{EI(SO}_2) = 0.4 \) with assumption 2, and the dot-dashed line represents \( \text{EI(SO}_2) = 0.4 \) with assumption 3. Background \( \text{Cl}_p \) is 3 ppbv.

EI(\text{NO}_x) = 5 \) scenario for the AER and NSU models are quite similar without a temperature distribution in either model.

For scenarios with particle emissions, and thus greatly enhanced aerosol surface area distributions, the effect of including a temperature distribution for calculation of heterogeneous reaction rates is quite important, resulting in a doubling of the calculated ozone depletion in both polar regions in spring. Reactions (3) and (4), involving reactions with HCl on sulfate aerosol surfaces, are responsible for most of this sensitivity, with reaction (3) accounting for about two thirds of the effect and reaction (4) accounting for the remainder. The Cambridge model also uses a temperature distribution but does not calculate greatly enhanced ozone depletion with HSCT particle emissions, possibly as a result of the cruder parameterization of reaction (3) and omission of reaction (4). Our results imply that use of a temperature distribution in 2-D models and of accurate temperature fields and fluctuations in box and trajectory models is important for calculating ozone and ozone trends, especially under conditions of perturbed stratospheric sulfur, such as following volcanic eruptions. This sensitivity has been noted previously by Murphy and Ravishankara [1994], Borrmann et al. [1997], and Michelsen et al. [1997].

4.2. Polar Stratospheric Clouds

The effect of including polar stratospheric clouds (PSCs) in a 2-D model along with HSCT sulfur emissions has been investigated by the Italy model. The method of treating PSCs is described by Pitari et al. [1993] and involves heterogeneous nucleation of NAT particles on sulfate aerosols and nucleation of ice particles on NAT particles. The processes of condensation, evaporation, and sedimentation are also modeled. As shown in the paper by Pitari et al. [1993], the inclusion of PSC aerosols has the net effect of mitigating the ozone column decrease produced by supersonic aircraft. The net column change is the result of two opposite ozone anomalies, with the positive one below about 15-20 km altitude where \( \text{ClO}_x \) and \( \text{HO}_x \) catalytic cycles have a larger impact on ozone relative to the \( \text{NO}_x \) cycle.

The \( \text{NO}_2 \) increase resulting from direct aircraft emission lowers the \( \text{ClO}/\text{ClONO}_2 \) ratio, thus producing a ClO decrease with respect to the background atmosphere and also removing more OH via the three-body reaction forming HNO₃. The relative weight of the associated ozone increase is larger if the background stratospheric amount of \( \text{NO}_x \) is smaller, as is the case when PSC particles are present and a net redistribution of \( \text{NO}_y \) is produced by particle sedimentation. Chlorine processing by heterogeneous chemical reactions on PSC surfaces is another effect to be taken into account. If the surface area were kept constant, no additional ozone changes would be produced by the aircraft emissions. However, both \( \text{NO}_2 \) and \( \text{SO}_2 \) emissions from HSCT may increase the PSC particle surface available for heterogeneous chemistry by increasing the saturation ratios of HNO₃ and \( \text{H}_2\text{SO}_4 \) and then speeding up the processes of particle growth and nucleation.

Calculations with the Italy model including PSCs for both the baseline simulation and the HSCT simulation with \( \text{EI(NO}_2) = 5 \) show substantially less ozone depletion than calculations without PSCs. With the effect of a temperature distribution also included, calculated annual average changes in column ozone poleward of 40°N are 0.0% with sulfur emissions treated as \( \text{SO}_2 \) gas and -1.0% with sulfur emissions treated as 100% particles. Corresponding ozone changes without PSCs are -0.3% and -2.0%. The ozone response to HSCT emissions is less sensitive to a temperature distribution with PSCs included because reaction probabilities of \( \text{ClONO}_2 \) and HCl on PSC surfaces are assumed to be temperature independent. Results of HSCT sensitivity to PSCs in 2-D models is expected to be sensitive to model formulation, and indeed, among 2-D models that have per-
formed similar experiments, no clear consensus has been reached \[\text{Stolarski et al., 1995}].

4.3. Background Cl

The sensitivity of the HSCT ozone response to Cl is important because it is expected that Cl will decrease in the future as the atmosphere responds to reduced emissions of CFCs and other chlorine-bearing compounds. A Cl concentration of about 2.0 ppbv is forecast for 2050 \[\text{WMO, 1995}]. Figure 12 shows calculated annual average ozone column changes due to HSCT emissions with EI(NO\textsubscript{x})=5 and 2 ppbv of Cl.

Table 1. Calculated Change in Annual Average Ozone Column Due to Emissions From a Mach 2.4 HSCT Fleet in 2015

<table>
<thead>
<tr>
<th>Sulfur Emission*</th>
<th>AER 45\textdegree N</th>
<th>Global</th>
<th>NSU 45\textdegree N</th>
<th>Global</th>
<th>Italy 45\textdegree N</th>
<th>Global</th>
<th>Cambridge 45\textdegree N</th>
<th>Global</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>-0.35%</td>
<td>-0.21%</td>
<td>-0.32%</td>
<td>-0.16%</td>
<td>0.02%</td>
<td>-0.02%</td>
<td>-0.22%</td>
<td>-0.14%</td>
</tr>
<tr>
<td>0% particles</td>
<td>-0.57%</td>
<td>-0.33%</td>
<td>-0.50%</td>
<td>-0.27%</td>
<td>-0.11%</td>
<td>-0.09%</td>
<td>-0.26%</td>
<td>-0.17%</td>
</tr>
<tr>
<td>10% particles</td>
<td>-0.72%</td>
<td>-0.40%</td>
<td>-0.59%</td>
<td>-0.32%</td>
<td>-0.44%</td>
<td>-0.23%</td>
<td>-0.27%</td>
<td>-0.21%</td>
</tr>
<tr>
<td>100% particles</td>
<td>-1.14%</td>
<td>-0.63%</td>
<td>-0.83%</td>
<td>-0.44%</td>
<td>-1.45%</td>
<td>-0.77%</td>
<td>-0.36%</td>
<td>-0.30%</td>
</tr>
</tbody>
</table>

The background inorganic chlorine amount for 2015 was 3 ppbv.

* Sulfur emissions with EI(SO\textsubscript{2})=0.4 are treated as 100% gas, 90% gas and 10% aerosol particles of 10 nm radius, or 100% aerosol particles of 10 nm radius. A case with no sulfur emissions is also shown.
Figure 11. Calculated percent change in column ozone as a function of latitude and season due to HSCT emissions with EI(NO)−5, EI(H2O)=1230, and EI(SO2)=0.4 for the (a, b) AER and (c, d) Italy models under assumptions (left) 1 and (right) 3, omitting the effect of a temperature distribution on heterogeneous reaction rates. To be compared with Figure 7 including a temperature distribution. The background Cl2 is 3 ppbv.

Figure 12. Calculated changes in annual average column ozone due to an HSCT emission scenario with EI(NO2)=5, EI(H2O)=1230, and different assumptions on sulfur emissions from the (a) AER model and (b) NSU model. The solid line represents a case with no SO2 emissions, the long dashed line represents EI(SO2)=0.4 with assumption 1, the short dashed line represents EI(SO2)=0.4 with assumption 2, and the dot-dashed line represents EI(SO2)=0.4 with assumption 3. Background Cl2 is 2 ppbv. To be compared with Figures 6a and 6d.

Figure 13 shows calculated annual average ozone column changes with EI(NOx)=15 and 2 ppbv of background Cl2 for the same models. Again, calculated ozone depletion is larger for 2 ppbv of Cl2 than for 3 ppbv of Cl2 without sulfur emissions. This effect is due to reduced production of C1ONO2 when NOx is emitted by aircraft in a low-chlorine environment. Northern hemisphere ozone depletion was increased by sulfur emission with 3 ppbv of Cl2 in the AER model but is unaffected by sulfur emissions with 2 ppbv of Cl2. In the NSU model, ozone depletion in the northern hemisphere was reduced by sulfur emission with 3 ppbv of Cl2, and with 2 ppbv of Cl2 it is reduced even further.

Table 2 lists calculated ozone column change at 45°N and global average ozone column change with EI(NO)=5 and 15 and 2 ppbv of Cl2. With EI(NO2)=5 and emission of sulfur as 100% particles (assumption 3), the calculated ozone depletion at 45°N from the AER model is 1.14% with 3 ppbv of Cl2 and 0.85% with 2 ppbv of Cl2. From the NSU model, calculated ozone depletion at 45°N is 0.83% with 3 ppbv of Cl2 and 0.62% with 2 ppbv of Cl2. With EI(NO2)=15 and sulfur emis-
on sulfate aerosols. This reaction is included in the NSU results presented above with a reaction probability (\(\gamma\)) of 0.4 based on the measurements of Hanson and Ravishankara [1995]. More recent measurements of this reaction have provided a \(\gamma\) which is a function of temperature and water activity [Hanson et al., 1996]. Values of \(\gamma\) are as large as 0.8 for aerosols with acid weight percent of less than 70%, which occurs in the polar regions, though values of about 0.4 are still found over most of the stratosphere. This heterogeneous reaction has the effect of increasing active HOx, ClOx, and BrOx, mainly as a result of HOBBr photolysis [Randeniya et al., 1996], leading to enhanced ozone depletion.

AER model results including reaction (5) and using the parameterization of Hanson et al. [1996] are shown in Figure 14 for EI(NO\(_2\)) of 5 and 15. Compared with calculations that omit this reaction (see Figures 6a and 9a), ozone column changes are smaller without sulfur emissions, especially for EI(NO\(_2\))=15. Sulfur emissions cause a greater perturbation with reaction (5) than without it. With EI(NO\(_2\))=5 and sulfur emissions as 100% particles, calculated ozone depletion is 1.3% at 45\(^\circ\)N with a global average ozone depletion of 0.7%. This is 20% more depletion than that without reaction (5).

### 4.5. Background Aerosol Loading

Variations in background aerosol amount have been found to affect calculated ozone change due to HSCT emissions [Weisenstein et al., 1993]. There is uncertainty regarding the true “nonvolcanic” aerosol levels in the stratosphere, since periods free from volcanic influence have been seen only rarely in the past two decades [Hitchman et al., 1994], most recently in 1979 [Thompson et al., 1997]. The total stratospheric sulfur mass estimated for 1979 by Kent and McCormick [1984] was 570 kt. Models employing OCS photolysis as the major

#### Table 2. Calculated Change in Annual Average Ozone Column Due to Emissions From a Mach 2.4 HSCT Fleet in 2050

<table>
<thead>
<tr>
<th>Sulfur Emission*</th>
<th>AER</th>
<th></th>
<th>NSU</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>45(^\circ)N</td>
<td>Global</td>
<td>45(^\circ)N</td>
<td>Global</td>
</tr>
<tr>
<td><strong>EI(NO(_2))=5</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>-0.43%</td>
<td>-0.24%</td>
<td>-0.42%</td>
<td>-0.20%</td>
</tr>
<tr>
<td>0% particles</td>
<td>-0.55%</td>
<td>-0.31%</td>
<td>-0.47%</td>
<td>-0.23%</td>
</tr>
<tr>
<td>10% particles</td>
<td>-0.63%</td>
<td>-0.35%</td>
<td>-0.52%</td>
<td>-0.27%</td>
</tr>
<tr>
<td>100% particles</td>
<td>-0.85%</td>
<td>-0.46%</td>
<td>-0.62%</td>
<td>-0.33%</td>
</tr>
<tr>
<td><strong>EI(NO(_2))=15</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>-1.03%</td>
<td>-0.51%</td>
<td>-1.41%</td>
<td>-0.55%</td>
</tr>
<tr>
<td>0% particles</td>
<td>-0.98%</td>
<td>-0.51%</td>
<td>-1.01%</td>
<td>-0.44%</td>
</tr>
<tr>
<td>10% particles</td>
<td>-0.97%</td>
<td>-0.51%</td>
<td>-0.91%</td>
<td>-0.41%</td>
</tr>
<tr>
<td>100% particles</td>
<td>-0.96%</td>
<td>-0.52%</td>
<td>-0.78%</td>
<td>-0.35%</td>
</tr>
</tbody>
</table>

The background inorganic chlorine amount for 2050 was 2 ppbv. Other long-lived trace species were retained at their 2015 levels.

* Sulfur emissions with EI(SO\(_2\))=0.4 are treated as 100% gas, 90% gas and 10% aerosol particles of 10 nm radius, or 100% aerosol particles of 10 nm radius. A case with no sulfur emissions is also shown.
change due to HSCT emissions is smaller at higher aerosol levels, both with and without sulfur emissions. With $Ei(NO_x)=5$ the increased background aerosol surface area results in reductions in HSCT ozone column depletion at $45^\circ$N from $-3.3%$ to $-1.0%$ with sulfur emissions as 100% particles. With $Ei(NO_x)=15$ the changes are larger, reducing ozone column depletion at $45^\circ$N from $-0.5%$ to $-0.1%$ without sulfur emission and from $-1.0%$ to $-0.6%$ with sulfur emissions as 100% particles. Following this logic, we can argue that during times of volcanic enhancement of the aerosol layer, HSCT emission of NOx will lead to smaller ozone depletion, and the effect of sulfur emissions from aircraft will be reduced.

5. Summary and Conclusions

Four independently formulated two-dimensional models of trace species and sulfate aerosols have been applied to predict the effect of HSCT emissions on the stratospheric aerosol layer and on ozone. Model-predicted changes in aerosol surface area vary by a factor of 3 among the models for identical sulfur emissions. The main cause of model differences appears to be transport, which directly affects the residence time of the emitted sulfur and thus the magnitude of the surface area perturbation. However, the transport rate affects the background calculated surface area as well, and thus percentage perturbations are fairly consistent.

Deep tropospheric convection has been found to have a large effect on calculations of upper tropospheric SO$_2$ concentration [Chatfield and Crutzen, 1984; Langner and Rodhe, 1991] and potentially on stratospheric aerosol loading [Weisenstein et al., 1997]. This process has been accounted for in the AER model by imposing an SO$_2$ concentration of 40 pptv in the tropical middle and upper troposphere [Weisenstein et al., 1997] and leads to a factor of 5 increase in aerosol mass density and a factor of 2 increase in surface area density in the tropical lower stratosphere. Total stratospheric aerosol mass roughly doubles. We will present results for the HSCT impact using a "high background" aerosol surface area obtained from the AER model employing enhanced upper tropospheric SO$_2$.

Changes in calculated surface area due to HSCT emission of sulfur are smaller with the "high background" model. Increases in aerosol surface area density are reduced by 25-30% in relation to the results shown for the AER model in Figures 2-4. The percentage change over background is significantly less, especially in the low latitudes where most of the background surface area increase occurs. Calculated changes in ozone with high background sulfur and reaction (5) included are shown in Figure 15. The predicted ozone column

source of stratospheric sulfate are found to contain only about half this amount [Chin and Davis, 1995; Weisenstein et al., 1997].

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among the models. When sulfur emissions are assumed to be in the form of gas phase SO₂, maximum increases in aerosol surface area range from 25% to 50% above their respective calculated background amounts. When 10% of the sulfur is assumed to be in particles of 10 nm radius, surface area increases are greater, up to 65% or 75%. When all sulfur is assumed emitted as particles, surface area increases are much greater, up to 200% or 300%. The conclusion of Weisenstein et al. [1996] that emission of sulfur by aircraft, if it is converted to particles within the wake, could strongly perturb stratospheric aerosol concentrations is supported by all four models used in this study.

The models show larger variations in ozone response to HSCT. This finding is to be expected because the ozone response is sensitive to the partitioning of HOₓ, NOₓ, ClOₓ, and BrOₓ radicals, to transport rates, and to the background aerosol surface area. The balance between these competing processes, unfortunately, generally depends on model formulation. There is no consensus on the best way to formulate a numerical model of atmospheric ozone. Even with perfect knowledge of the atmosphere, modelers would be forced to make compromises in constructing models to keep the computational requirements modest. We will treat variations in ozone response between the models as sensitivities to model formulation. Where qualitative consensus exist among the models, we will draw more robust conclusions regarding ozone response to HSCT.

All models agree with the conclusion of Weisenstein et al. [1996] that for the HSCT scenario with EI(NOₓ)=5, which represents a very modest emission of NOₓ, aircraft emission of sulfur will increase ozone depletion. This increase is due to increased heterogeneous processing on the enhanced aerosol layer, increasing ozone loss due to the HOₓ and ClOₓ catalytic cycles. Ozone depletion is largest if all sulfur is assumed emitted as particles. With this assumption, annual average ozone depletion at 45°N is calculated to be 1.1% for the AER model, 0.8% for the NSU model, 1.5% for the Italy model, and 0.4% for the Cambridge model with 3 ppbv of Clₓ. When EI(NOₓ) is increased to 15, the models’ calculated responses to emission of sulfur differ. This variable sensitivity can be understood as differences in the relative importance of NOₓ catalytic loss of ozone (which is reduced by added sulfur) and HOₓ and ClOₓ catalytic loss of ozone (which is increased by added sulfur) in each model.

A number of model sensitivities are explored to see how the ozone response to HSCT emissions may vary under different conditions or with additional model parameterizations. An important result of these model calculations is that inclusion of a temperature distribution in 2-D models to account for deviations from the zonal mean temperature can significantly increase calculated ozone depletion due to HSCT emissions, especially when sulfur emissions are included. We recommend that use of a temperature probability distribution become a standard part of 2-D models, as it accounts for some important processes that are otherwise neglected and to which ozone is sensitive. Introduction of PSCs into the Italy model leads to smaller ozone depletion due to HSCT emissions, though this result is expected to be model dependent. With background Clₓ reduced from 3 ppbv to 2 ppbv, ozone depletion due to NOₓ emission alone is increased, but ozone depletion due to sulfur emissions is reduced (with EI(NOₓ)=5) or reversed (with EI(NOₓ)=15). Inclusion of the heterogeneous reaction BrONO₂+H₂O on sulfate aerosols leads to a slight reduction in ozone depletion without HSCT sulfur emissions and an increase in ozone depletion with sulfur emissions. This reaction should be included in future modeling studies. Increasing the background aerosol surface area leads to less ozone depletion due to HSCT NOₓ emissions and less ozone depletion due to HSCT sulfur emissions.

The recommendation for future modeling studies of HSCT impact on ozone is that sulfur emissions must be included in assessment calculations, and knowledge of chemical and microphysical processes within the plume and far wake are crucial for accurate modeling. The fractional conversion of emitted sulfur to aerosol particles depends on processes within the engine, nozzle, and near-field plume [Kärcher and Fahey, 1997; Brown et al., 1996b], and the resulting particle size distribution depends on dilution within the far wake [Danilin et al., 1997]. The fractional conversion is bracketed in this study by 10% and 100% conversion, based on direct measurements in the Concorde plume [Fahey et al., 1995]. Because the aerosol instrument did not measure particles smaller than 0.08 μm diameter and models predict a large number of such particles, the actual conversion is likely to be larger than 10% in the young plume (between 16% and 40% at 16 min, according to modeling studies by Kärcher and Fahey [1997], Danilin et al. [1997], and Yu and Turco [1997]). The modeling of heterogeneous processes between ambient species and particles within the plume and far wake is, we believe, unnecessary for prediction of the global impact of aircraft emissions because the amount of air processed within the wake is too small. Heterogeneous processing of aircraft-emitted species within the wake may prove to be important [Kärcher, 1997]. The impact of sulfur emissions from subsonic aircraft is not considered here (see Friedl et al., [1997] for a discussion of possible tropospheric and climatic effects of subsonic sulfur emissions). However, future subsonic aircraft are expected to fly at higher altitudes, depositing a larger fraction of their emissions (including sulfur) in the stratosphere. These higher-flying subsonic aircraft should definitely be considered in modeling the impact of aviation on the future global environment.

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