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Key Points:

- OCS establishes about 56% of the background stratospheric aerosol burden
- Deep convection may amplify the impact of anthropogenic SO₂ emissions in Asia
- Small to moderate volcanic eruptions dominate background stratospheric aerosols

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Global atmospheric sulfur budget under volcanically quiescent conditions: Aerosol-chemistry-climate model predictions and validation

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Abstract The global atmospheric sulfur budget and its emission dependence have been investigated using the coupled aerosol-chemistry-climate model SOCOL-AER. The aerosol module comprises gaseous and aqueous sulfur chemistry and comprehensive microphysics. The particle distribution is resolved by 40 size bins spanning radii from 0.39 nm to 3.2 μm, including size-dependent particle composition. Aerosol radiative properties required by the climate model are calculated online from the aerosol module. The model successfully reproduces main features of stratospheric aerosols under nonvolcanic conditions, including aerosol extinctions compared to Stratospheric Aerosol and Gas Experiment II (SAGE II) and Halogen Occultation Experiment, and size distributions compared to in situ measurements. The calculated stratospheric aerosol burden is 109 Gg of sulfur, matching the SAGE II-based estimate (112 Gg). In terms of fluxes through the tropopause, the stratospheric aerosol layer is due to about 43% primary tropospheric aerosol, 28% SO₂, 23% carbonyl sulfide (OCS), 4% H₂S, and 2% dimethyl sulfide (DMS). Turning off emissions of the short-lived species SO₂, H₂S, and DMS shows that OCS alone still establishes about 56% of the original stratospheric aerosol burden. Further sensitivity simulations reveal that anticipated increases in anthropogenic SO₂ emissions in China and India have a larger influence on stratospheric aerosols than the same increase in Western Europe or the U.S., due to deep convection in the western Pacific region. However, even a doubling of Chinese and Indian emissions is predicted to increase the stratospheric background aerosol burden only by 9%. In contrast, small to moderate volcanic eruptions, such as that of Nabro in 2011, may easily double the stratospheric aerosol loading.

1. Introduction

The presence of an aerosol layer in the lower stratosphere was first discovered by Junge *et al.* [1961]. This aerosol layer, mainly composed of binary H₂SO₄/H₂O solution droplets, is important to the Earth's radiative balance and atmospheric chemistry. Stratospheric aerosol particles can scatter solar radiation, absorb the outwelling infrared radiation [Ramanathan *et al.*, 2001], and thus affect atmospheric dynamics [McCormick *et al.*, 1995] and the global climate [Solomon *et al.*, 2011]. They also host heterogeneous chemistry in the stratosphere, which leads to nitrogen deactivation and chlorine activation with implications for subsequent ozone depletion [Solomon *et al.*, 1986; Solomon, 1999]. This, in turn, affects the level of UV irradiance at the surface.

The stratospheric aerosol forms via a chain of chemical reactions and microphysical processes when sulfur-containing gases or preexisting particles enter the stratosphere through the tropical tropopause [e.g., Hamill *et al.*, 1997; *Stratosphere-troposphere Processes and their Role in Climate (SPARC)*, 2006]. The stratospheric aerosol burden is sustained by natural and anthropogenic emissions of sulfur-containing gases at the Earth's surface and sporadic volcanic eruptions, which can release a large amount of sulfur dioxide directly into the stratosphere. Under volcanically quiescent conditions, Junge [1974] explained the presence of the stratospheric aerosol layer by penetration of tropospheric sulfur dioxide (SO₂) into the stratosphere, which was later revised by Crutzen [1976] and Turco *et al.* [1980] proposing long-lived carbonyl sulfide (OCS) as the dominant source of stratospheric aerosols. Chin and Davis [1995] reevaluated the production of stratospheric aerosols from OCS oxidation to be 2 to 5 times smaller than estimated by Crutzen [1976],

Turco *et al.* [1980], and Sze and Ko [1979, 1980], revealing a possible overestimation of the OCS contribution to the stratospheric background aerosol in earlier studies. In a recent assessment of stratospheric aerosol properties [SPARC, 2006], the model intercomparison study of various 2-D and 3-D aerosol models suggested that the transport of SO₂ and preexisting sulfur-containing aerosol particles across the tropopause may play a large role in the lower stratosphere, while OCS is more important above 25 km.

Modeling studies have advanced our quantitative understanding of stratospheric aerosols, albeit constrained by remaining model uncertainties. Simulating stratospheric aerosols challenges our modeling ability to resolve the transport, chemistry, and microphysics of the aerosol size distribution, including the complex interactions between them. One- or two-dimensional size bin-resolving aerosol models (also called sectional models or spectral models) [e.g., Turco *et al.*, 1979; Mills *et al.*, 1999; Weisenstein *et al.*, 1997] were generally successful in simulating aerosol microphysics but are not designed to simulate tropospheric chemistry or dynamics in detail, since topography, tropical convection, surface properties, and localized emissions cannot be included [SPARC, 2006]. Further progress toward a coupling of an aerosol module into a three-dimensional general circulation model (GCM) or chemistry-climate model (CCM) has been achieved by various studies [Takigawa *et al.*, 2002; Stier *et al.*, 2005; Rasch *et al.*, 2008; Robock *et al.*, 2008; Timmreck *et al.*, 2010; Aquila *et al.*, 2012; Brühl *et al.*, 2012]. The common feature of these models is that they use either a lognormal unimodal distribution ("bulk model") or a composite of few lognormal modes ("modal model") to prescribe the particles size distribution (i.e., no detailed size bins). Such simplifications have been found to be often insufficient to accurately reproduce stratospheric aerosols when compared to a sectional aerosol model [Weisenstein *et al.*, 2007]. Recent studies [Hommel *et al.*, 2011; English *et al.*, 2011] have implemented sectional aerosol modules into a GCM or CCM. However, in these models the aerosol radiative feedbacks, which affect the model dynamics, remained decoupled. An explicit treatment of interactive aerosol feedbacks has been identified as essential to properly simulate stratospheric aerosols after large volcanic eruptions [Aquila *et al.*, 2012]. Radiative effects under aerosol background conditions or after small volcanic eruptions, albeit weaker, have also been argued to be important for climate on longer timescales [Solomon *et al.*, 2011].

Significant progress can in principle be achieved when coupling a particle size resolving aerosol module into a chemistry-climate model, which interactively includes all relevant aerosol microphysics, transport, sedimentation, and explicit treatment of the aerosol in the radiation code. However, initially the coupling of complex system modules often increases the model uncertainties so that a comprehensive validation is required. In this study, we introduce an aerosol-chemistry-climate model, possessing the above features. Applying this model, we analyze the global sulfur budget and investigate the sensitivity of the stratospheric aerosol burden to SO₂ emissions. We show detailed comparisons of aerosol optical properties and particle size distribution with satellite observations and in situ measurements. While the main purpose of this paper is to provide a more accurate and comprehensive understanding of stratospheric aerosols under background conditions, the application to strong volcanic eruptions also shows reasonable agreement, which will be shown elsewhere (Sheng *et al.*, Size-resolved stratospheric aerosol distributions after Pinatubo derived from a coupled aerosol-chemistry-climate model, manuscript in preparation for the *Journal of Geophysical Research*, 2014).

2. Model Description

2.1. CCM SOCOL

In this work, we employ an updated version of the chemistry-climate model SOCOL [Stenke *et al.*, 2013], coupled to a particle size-resolved sulfate aerosol model. SOCOL is a combination of the global circulation model (GCM) European Centre/Hamburg 5 (ECHAM5) (the middle atmosphere version) and the chemistry transport model for investigating ozone trends (MEZON). ECHAM5 [Roeckner *et al.*, 2003] is a spectral model with adjustable horizontal truncations and with a hybrid sigma-pressure coordinate system spanning from the surface to 0.01 hPa. In this study, for computational efficiency the version with the horizontal truncation T31 (i.e., $\sim 3.75^\circ \times 3.75^\circ$ latitude/longitude resolution) and with 39 hybrid vertical levels is employed. The deep ocean module in SOCOL remains decoupled, instead we used global sea surface temperatures (SSTs) and sea ice coverage prescribed by the Hadley Centre Sea Ice and SST data set [Rayner *et al.*, 2003]. The quasi-biennial oscillation is nudged in terms of a linear relaxation of the simulated zonal winds in the equatorial stratosphere to observed wind profiles. The chemistry transport part MEZON [Rozanov *et al.*, 1999; Egorova *et al.*, 2003] has the same vertical and horizontal resolutions as ECHAM5 and treats

56 chemical species of the oxygen, hydrogen, nitrogen, carbon, chlorine, and bromine groups, which interact via more than 160 gas phase reactions, 58 photolysis reactions, and 16 heterogeneous reactions in/on sulfuric acid aerosols, water ice, and nitric acid trihydrate particles. The chemical reaction rate coefficients are taken from *Sander et al.* [2011]. Photolysis rates (J) are calculated at every chemical time step (2 h) using a lookup table approach [Rozanov et al., 1999]. The chemical solver is based on the implicit iterative Newton-Raphson scheme [Ozolin, 1992; Stott and Harwood, 1993]. The chemistry module comprises the full stratospheric chemistry and a reduced set of tropospheric chemical reactions. For carbon-containing species this includes the full methane photochemistry (CH_4 , HCHO , CO , and intermediates), but no nonmethane hydrocarbons. Dry depositions of O_3 , CO , NO , NO_2 , HNO_3 , and H_2O_2 are taken into account with deposition velocities over land and sea based on *Hauglustaine et al.* [1994]. Furthermore, the tropospheric washout of HNO_3 is described in a simplified manner by a constant removal rate of $4 \times 10^{-6} \text{ s}^{-1}$; i.e., every 2 h 2.8% of the HNO_3 is removed in each tropospheric grid box. For a more detailed description we refer to *Stenke et al.* [2013] and the references therein.

2.2. Aerosol Module: Precursor Gases and Microphysics

The aerosol module is based on the AER two-dimensional model of sulfate aerosols [Weisenstein et al., 1997]. The module includes the sulfate precursor gases dimethyl sulfide (DMS), carbon disulfide (CS_2), hydrogen sulfide (H_2S), methyl sulfonic acid (MSA), carbonyl sulfide (OCS), sulfur dioxide (SO_2), sulfur trioxide (SO_3), and sulfuric acid (H_2SO_4). For the chemical reactions, we follow *Weisenstein et al.* [1997] but update the rate coefficients according to *Sander et al.* [2011], see Table 1. In comparison to the original AER code, the photolysis rate of H_2SO_4 has been updated to include photodissociation not only in the ultraviolet but also in the visible via the excitation of vibrational overtones based on *Vaida et al.* [2003] with the corrected J value suggested by *Miller et al.* [2007], and in Lyman- α region [Lane and Kjaergaard, 2008]. Additionally, the aqueous phase reactions of S(IV) with ozone (O_3) and hydrogen peroxide (H_2O_2) in cloud water [Jacob, 1986] have been taken into account. In a simplified approach, we prescribe the vertical distribution of the pH value according to *Walcek and Taylor* [1986]. The oxidants involved in the sulfur chemistry (OH , $\text{O}(^1\text{D})$, $\text{O}(^3\text{P})$, O_3 , and H_2O_2) are calculated interactively by MEZON together with all other 56 chemical species.

Detailed descriptions of the coded microphysics are provided by *Weisenstein et al.* [1997, 2007, and references therein]. Here we describe major features of the original model, and improvements implemented in our coupled model. Aerosol particles are resolved in 40 size bins from 0.39 nm to 3.2 μm . Neighboring size bins differ by volume doubling, meaning that the radius of bin i equals to $2^{1/3}$ times the radius of bin $i - 1$. The smallest bin size corresponds roughly to the size of critical embryos formed by homogeneous nucleation [Weisenstein et al., 1997]. Aerosol composition (expressed as sulfuric acid weight percent) is calculated from ambient water vapor and temperature [Tabazadeh et al., 1997].

Beyond the original AER code the composition of individual aerosol particles is allowed to be size-dependent such that, for each size bin, the water vapor pressure is corrected by the Kelvin effect [Thomson, 1871]. This implementation of the Kelvin effect on composition has become important because, unlike in the zonally averaged (and therefore smoothed) 2-D model, particles are exposed to a larger range of stratospheric dryness, and subsequently a more efficient suppression of tiny particles (close to the critical embryo size) under particularly dry conditions, such as at the upper edge of the Junge layer. All relevant microphysical processes are implemented in the module. Sulfate particles are created by binary homogeneous nucleation [Vehkamäki et al., 2002]. Particles can grow by condensation of H_2SO_4 and H_2O vapors and shrink by evaporation. Particles evaporate completely above $\sim 35 \text{ km}$ depending on sulfuric acid equilibrium vapor pressure over binary solution calculated by *Ayers et al.* [1980] including temperature correction provided by *Kulmala and Laaksonen* [1990]. The calculation of activity coefficients of water and sulfuric acid follows *Giauque et al.* [1960]. Coagulation reduces number densities of particles and is solved by a semiimplicit method [Jacobson and Seinfeld, 2004], which is another improvement beyond the original AER model code. The coagulation kernel is calculated by the empirical formula of *Fuchs* [1964]. Gravitational settling, which reduces the lifetime primarily of larger stratospheric particles, is treated following *Kasten* [1968].

Instead of the simple upwind method used in the original AER code, sedimentation adopts the numerical scheme of *Walcek* [2000] in order to minimize the numerical diffusion [Benduhn and Lawrence, 2013]. A dry deposition velocity of 1 cm s^{-1} at the ground is applied to H_2SO_4 , MSA, and SO_2 according to *Weisenstein*

Table 1. Sulfur Chemical Reactions and Rate Coefficients Included in SOCOL/AER (in Units $\text{cm}^3 \text{s}^{-1}$, Except for Photolysis Rates in s^{-1})^a

Reaction	Rate
$\text{CS}_2 + h\nu \rightarrow \text{OCS} + \text{SO}_2$	lookup table
$\text{OCS} + h\nu \rightarrow \text{SO}_2 + \text{CO}$	lookup table
$\text{H}_2\text{SO}_4 + h\nu \rightarrow \text{SO}_3 + \text{H}_2\text{O}$	Vaida et al. [2003], Miller et al. [2007], and Lane and Kjaergaard [2008]
$\text{SO}_3 + h\nu \rightarrow \text{SO}_2 + \text{O}$	lookup table
$\text{CS}_2 + \text{OH} \rightarrow \text{OCS} + \text{SO}_2$	$\frac{A}{T+B} \left(\frac{p}{p_{\text{surf}}} \right)$ $A = 1.25 \times 10^{-16} \exp(4550/T)$ $B = 1.81 \times 10^{-3} \exp(3400/T)$
$\text{CS}_2 + \text{O} \rightarrow \text{OCS} + \text{SO}_2$	$3.2 \times 10^{-11} \exp(-650/T)$
$\text{OCS} + \text{OH} \rightarrow \text{SO}_2 + \text{CO} + \text{H}$	$1.1 \times 10^{-13} \exp(-1200/T)$
$\text{OCS} + \text{O} \rightarrow \text{SO}_2 + \text{CO}$	$2.1 \times 10^{-11} \exp(-2200/T)$
$\text{H}_2\text{S} + \text{OH} \rightarrow \text{SO}_2 + \text{H}_2\text{O}$	$6.1 \times 10^{-12} \exp(-75/T)$
$\text{H}_2\text{S} + \text{O} \rightarrow \text{SO}_2 + \text{OH}$	$9.2 \times 10^{-12} \exp(-1800/T)$
$\text{H}_2\text{S} + \text{Cl} \rightarrow \text{HCl} + \text{SO}_2$	$3.7 \times 10^{-11} \exp(210/T)$
$\text{H}_2\text{S} + \text{Br} \rightarrow \text{HBr} + \text{SO}_2$	$1.4 \times 10^{-11} \exp(-2750/T)$
$\text{DMS} + \text{OH} \rightarrow \text{SO}_2 + \text{CH}_2\text{O} + \text{CH}_3\text{O}_2\text{H}$	$1.1 \times 10^{-11} \exp(-240/T)$
$\text{DMS} + \text{OH} \rightarrow \text{SO}_2 + \text{CH}_2\text{O} + \text{CH}_3\text{O}_2\text{H}$	$AB/(1+B)$ $A = 2.8 \times 10^{-12} \exp(350/T)$ $B = 5.53 \times 10^{-31} \exp(7460/T)[\text{O}_2]$
$\text{DMS} + \text{OH} \rightarrow \text{MSA} + \text{CH}_2\text{O}$	$AB/(1+B)$ $A = 7.6 \times 10^{-13} \exp(350/T)$ $B = 5.53 \times 10^{-31} \exp(7460/T)[\text{O}_2]$
$\text{DMS} + \text{NO}_3 \rightarrow \text{SO}_2 + \text{NO}_2 + \text{CH}_3\text{O}_2 + \text{CH}_2\text{O}$	$1.9 \times 10^{-13} \exp(500/T)$
$\text{DMS} + \text{ClO} \rightarrow \text{SO}_2 + \text{HOCl}$	$2.1 \times 10^{-15} \exp(340/T)$
$\text{DMS} + \text{Br} \rightarrow \text{SO}_2 + \text{HBr}$	$9.0 \times 10^{-11} \exp(-2390/T)$
$\text{DMS} + \text{BrO} \rightarrow \text{SO}_2 + \text{HOBr}$	$1.4 \times 10^{-14} \exp(950/T)$
$\text{SO}_2 + \text{OH} \rightarrow \text{SO}_3 + \text{HO}_2$	$\frac{A}{1+B} \times 0.6^{1+(\log B)^2}^{-1}$ $A = 3.3 \times 10^{-31} (300/T)^{4.3} [M]$ $B = A/1.6 \times 10^{-12}$
$\text{SO}_2 + \text{O} \rightarrow \text{SO}_3$	$\frac{A}{1+B} \times 0.6^{1+(\log B)^2}^{-1}$ $A = 1.8 \times 10^{-33} (300/T)^{-2} [M]$ $B = A/4.2 \times 10^{-14} (300/T)^{-1.8}$
$\text{SO}_2 + \text{O}_3 \rightarrow \text{SO}_3 + \text{O}_2$	$3.0 \times 10^{-12} \exp(-7000/T)$
$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$	$8.5 \times 10^{-41} \exp(6540/T)[\text{H}_2\text{O}]$
$\text{S(IV)} + \text{O}_3(\text{aq}) \rightarrow \text{S(VI)} + \text{O}_2(\text{aq}) + \text{H}^+$	Jacob [1986]
$\text{S(IV)} + \text{H}_2\text{O}_2(\text{aq}) + \text{H}^+ \rightarrow \text{S(VI)} + 2\text{H}^+ + \text{H}_2\text{O}(\text{aq})$	Jacob [1986]

^aAll gas reaction rates are taken from Sander et al. [2011] and the references therein except for the photolysis of H_2SO_4 via excitation of vibrational overtones following Vaida et al. [2003] and Miller et al. [2007], and Lyman- α induced photolysis of H_2SO_4 at high altitudes (>60 km) following Lane and Kjaergaard [2008]. Short-lived intermediate radicals such as S, SO, and HSO_3 are omitted and immediately converted to the next more stable intermediate. Balancing oxygen molecules are omitted from the reaction equations. Temperature (T) in Kelvin, pressure (p), and surface pressure (p_{surf}) in hPa. $[M]$, $[\text{H}_2\text{O}]$, and $[\text{O}_2]$ are molecule number densities with units cm^{-3} . Symbols A are in units $\text{cm}^3 \text{s}^{-1}$; symbols B are unitless).

et al. [1997]. Tropospheric wet removal rates are 5 days mean lifetime for H_2SO_4 and MSA, and 2.5 days mean lifetime for SO_2 , following Weisenstein et al. [1997].

2.3. Coupled SOCOL-AER

The aerosol module is adapted to the 3-D fields using the same vertical and horizontal resolutions as SOCOL. Sulfur chemical reactions (Table 1) are integrated into MEZON's chemical solver. The transport of each sulfur gas species and aerosol size bin is implemented in the advection scheme of Lin and Rood [1996] in ECHAM5. The SOCOL 6 band shortwave [Cagnazzo et al., 2007] and 16 band longwave [Mlawer et al., 1997] radiation schemes in the stratosphere are driven directly by the aerosol module, instead of the off-line aerosol treatment that we used in Heckendorn et al. [2009], or the data derived from SAGE II that we used in Arfeuille et al. [2013], or from climatological data. The required extinction coefficients, single scattering albedos, and

Table 2. Standard Model Setup of Boundary Conditions for Sulfur Source Gases

Species	Source	Boundary Value
SO ₂	Anthropogenic (including ship)	51.3 Tg S/yr ^a
	Biomass burning	1.9 Tg S/yr ^a
	Continuous volcanic degassing	12.6 Tg S/yr ^b
OCS	Prescribed surface mixing ratio	500 pptv ^c
DMS	Ocean	Online calculated ^d
CS ₂	Prescribed surface flux	1 Tg S/yr, 52°S–52°N ^e
H ₂ S	Prescribed surface mixing ratio	30 pptv ^e

^aDecadal historic data for the year 2000 [Lamarque et al., 2010; Smith et al., 2011]; mapped to horizontal resolution T31.

^bBased on Andres and Kasgnoc [1998] and scaled according to Dentener et al. [2006]; horizontally distributed according to volcano locations.

^cBased on Chin and Davis [1995], Kettle et al. [2002], Montzka et al. [2007], and Commane et al. [2013].

^dBased on sea surface DMS concentration fields [Kettle et al., 1999; Kettle and Andreae, 2000] using the parametrization of Nightingale et al. [2000].

^eFollowing Weisenstein et al. [1997].

asymmetry factors for each of the 22 wavelength bands are calculated from the particle size distribution in the aerosol module according to Mie theory with the refraction indices following Biermann et al. [2000].

Operator splitting approaches are used in the model: transport is calculated every 15 min, whereas chemistry, microphysics, and radiation are calculated every 2 h with 40 substeps (3 min) for the microphysical processes. SOCOL with the T31 horizontal resolution and 39 vertical levels needs about 4 h (wall-clock time) per model year using parallel computing on 32 CPUs [Stenke et al., 2013], while SOCOL-AER with the coupled aerosol module requires about 10 h for one model year.

3. Experimental Setup

The standard model setup for sulfur emissions is given in Table 2. Anthropogenic (including shipping) and biomass burning SO₂ emissions account for 53.2 teragram of sulfur per year (Tg S/yr) based on the monthly decadal emission data [Lamarque et al., 2010; Smith et al., 2011] for year 2000 conditions. The SO₂ emission due to continuous volcanic degassing is horizontally distributed according to volcano locations and set to 12.6 Tg S/yr based on the data set of Andres and Kasgnoc [1998] with suggested corrections [Graf et al., 1998; Halmer et al., 2002; Textor et al., 2004; Dentener et al., 2006]. The degassing is assumed to occur on the surface; i.e., potential hot plume ascent and exact volcano elevations are neglected (the latter are not fully resolved due to the relatively low horizontal resolution T31). OCS is almost passive in the troposphere with a lifetime of 10–100 years (depending on altitude, compare Figure 2.2 in SPARC [2006]). Its concentration is close to 500 parts per trillion by volume (pptv) in the troposphere [Chin and Davis, 1995; Kettle et al., 2002; Montzka et al., 2007; Commane et al., 2013]. Here we neglect interhemispheric OCS differences (about 15 pptv), and the annual cycle (which is less than about 16% peak to peak) and interannual variability (less than 3%) [Montzka et al., 2007]. Unlike all other sulfur species, which are described by fluxes, we prescribe the OCS mixing ratio with constant 500 pptv on the ground (which avoids having to deal with the uncertainties in plant uptake). The flux of DMS is obtained from the monthly climatological sea surface DMS concentration fields [Kettle et al., 1999; Kettle and Andreae, 2000] using the parametrization of Nightingale et al. [2000]. The surface flux of CS₂ is assumed to be 1 Tg S/yr between 52°S and 52°N, and H₂S is specified with a fixed mixing ratio of 30 pptv at the surface following Weisenstein et al. [1997].

The sensitivity of the atmospheric sulfur budget with respect to sulfur emissions is estimated in both volcanically quiescent and weak to moderate active conditions. We perform calculations for 12 background and 2 volcanically perturbed scenarios, as summarized in section 4.4 (Table 4). Each of these 12 background model simulations has been integrated over 10 years, initializing from precalculated aerosol mixing ratios [Weisenstein et al., 1997]. The first 5 years are discarded as a spin-up period, and results are analyzed based on the last 5 years. Volcanic simulations are conducted with the spin-up files of the reference scenario (REF in Table 4) for initialization. For volcanically perturbed conditions, we perform Nabro-like eruptions on 13 June of the first simulation year after the spin-up period in the region (13°N, 42°E): VoIT injects 0.7 Tg S into the free troposphere (9–14 km) in a single pulse; VoIS injects 0.7 Tg S directly into the stratosphere (16–19 km), again single pulse. In contrast to the long-term background cases, the volcanic simulations (VoIT and VoIS) are averaged over the first 6 months after the eruption and compared with the long-term averages of the background cases.

Figure 1. Vertical profiles of OCS mixing ratio calculated by SOCOL-AER (red curve) and 2-D AER (blue curve) at 5°N in (left) November compared to ATMOS version 3 observations (with a measurement uncertainty of 9% for OCS retrieval) [Gunson *et al.*, 1996; Rinsland *et al.*, 1996; Irion *et al.*, 2002] and at 65°N in (right) July compared to MkIV balloon observations (with a measurement uncertainty of 5–10%) [Leung *et al.*, 2002; Toon, 1991]. Horizontal bars: observed natural variability (± 1 standard deviation). Gray ranges: measurement uncertainties.

4. Results and Discussions

4.1. Precursor Gases

Carbonyl sulfide (OCS) and sulfur dioxide (SO_2) as well as sulfate in tropospheric aerosol particles undergoing troposphere-to-stratosphere transport are the main sources of stratospheric background aerosols. We examine the precursor gases to validate the modeling of OCS/ SO_2 oxidation and aerosol formation in the stratosphere. Here the simulated OCS is compared to measurements from the Atmospheric Trace Molecule Spectroscopy (ATMOS) satellite [Gunson *et al.*, 1996; Rinsland *et al.*, 1996] and from the Jet Propulsion Laboratory MkIV Balloon Interferometer [Leung *et al.*, 2002]. The simulated SO_2 is compared against various model results presented in SPARC [2006], MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) measurements operated quasi-continuously from July 2002 until April 2012 [Höpfner *et al.*, 2013] and ATMOS measurements in April 1985 [Rinsland *et al.*, 1995].

Carbonyl sulfide (OCS). Figure 1 shows the comparison between the calculated profiles of OCS and measurements by ATMOS (version 3) at 5–10°N in November (Figure 1, left) and by MkIV at 65°N (Figure 1, right). The calculated OCS of SOCOL-AER (red curve) is very similar to that of the 2-D AER presented in SPARC [2006] (blue curve). The model calculations are within the uncertainty (gray range) at most altitudes. For SOCOL-AER, there is only slight overestimation (near 28 km compared to the ATMOS measurements, and near 19 km compared to MkIV measurements). The modeled OCS is almost constant in the troposphere, where only the slow reaction with OH leads to OCS loss. In the stratosphere, OCS decreases rapidly due to photodissociation and chemical reactions with O and OH. The SOCOL-AER calculation shows that photodissociation accounts for about 80% of loss of OCS in the stratosphere, while O and OH account for 17% and 3%, respectively. A part of the remaining discrepancy may also be caused by the tropospheric variability of OCS, which is absent in the SOCOL-AER due to the prescribed 500 pptv surface mixing ratio.

Sulfur Dioxide (SO_2). Figure 2 (left) shows the comparison of seasonal SO_2 mixing ratio calculated by SOCOL-AER at 0–20°N with MIPAS measurements [Höpfner *et al.*, 2013]. In the upper troposphere/lower stratosphere (UTLS) region, the SOCOL-AER-calculated SO_2 match MIPAS near the tropopause (~17 km), while the agreement is less satisfactory near 22 km likely due to somewhat too high-OH concentration in the model. Even though the simulated SO_2 values are within the natural variability indicated by the measurements, they are clearly outside of the measurement uncertainty. Between 25 and 32 km, the modeled SO_2 is within 20% of MIPAS measurements, reflecting the importance of photodissociation and oxidation of OCS, which are the main sources of SO_2 in this region. Between 32 and 40 km, SOCOL-AER underestimates SO_2 compared to MIPAS measurements by factors 2–3. For example, around 35 km, the modeled seasonal SO_2 mixing ratios lie between 12 and 30 pptv, while the measured mean values range

Figure 2. (left) Seasonal SO₂ mixing ratio calculated by Socol-AER (solid lines) at 0–20°N compared to MIPAS measurements (dashed lines) extracted from Figure 8 of Höpfner *et al.* [2013]. (middle) Comparison of standard deviations of seasonal SO₂ mixing ratio between MIPAS and Socol-AER. (right) SO₂ mixing ratio calculated by Socol-AER (orange line) at 26–32°N compared to ATMOS observations (squares) taken in April–May 1985 [Rinsland *et al.*, 1995] and MIPAS observations (violet line) extracted from Figure 9 of Höpfner *et al.* [2013]. Horizontal bars: observed natural variability (± 1 standard deviation). The estimated instrumental uncertainty of MIPAS is 5–10 pptv [Höpfner *et al.*, 2013].

from 30 to 60 pptv. One reason could be that the photolysis rate of H₂SO₄ is underestimated. The photolysis of H₂SO₄ via photodissociation of vibrationally excited states of sulfuric acid under atmospheric conditions [Vaida *et al.*, 2003] has been implemented in Socol-AER as additional photolysis pathway based on the parametrization by Miller *et al.* [2007]. We use the corrected *J* values with quantum yield for collisional overtone deexcitation, which were described as a lower limit in their paper (since every collision is assumed to cause deactivation), i.e., the yellow curve in their Figure 3. The implemented Lyman-alpha photolysis of H₂SO₄ [Lane and Kjaergaard, 2008] in the model does not affect the comparison here, as it becomes significant only above 60 km. Overall, this implementation improved the agreement of Socol-AER with the ATMOS measurements (Figure 2, right), which is indeed better than that for all of the models participating in the Assessment of Stratospheric Aerosol Properties (ASAP) comparison (see Figure 6.11b in SPARC [2006]). However, the resulting enhancement appears too weak to obtain good agreement with MIPAS. Near 32 km, the MIPAS mean SO₂ mixing ratios are around 20 pptv larger than those measured by ATMOS, while Socol-AER-calculated SO₂ mixing ratios are between these two observations. It is unclear whether this disparity between the measurements is due to measurement errors or natural variability. Between 35 and 45 km, Socol-AER shows good agreement with ATMOS (within 10%). Above 50 km, SO₂-simulated Socol-AER is larger by a factor of 2 compared to ATMOS possibly owing to the lack of meteoritic material, which is suggested as a permanent sink for gaseous H₂SO₄ [SPARC, 2006]. Unfortunately, MIPAS measurements are available only up to 45 km. Another deficit might be the lack of SO₂ photolysis [Farquhar *et al.*, 2001] in the model; however, this is expected to be significant only above 70 km (as it needs to compete with SO₂ formation via SO + O₂). The modeled variability (standard deviation) of SO₂ is less by 5–10 pptv than that measured by MIPAS (Figure 2, middle). This might be explained by the fact that the variability of SO₂ measured by MIPAS is correlated with volcanic events [Höpfner *et al.*, 2013], while the free-running model simulation is performed under nonvolcanic conditions. Neglecting the variability of OCS in the model might also account for the difference between the modeled and observed variability of SO₂.

4.2. Sulfur Budget

Figure 3 shows a schematic diagram of the global atmospheric sulfur budget. The solid arrows represent net fluxes (surface emissions, wet or dry deposition, cross-tropopause transport, and chemical transformations), all in units of gigagram of sulfur per year (Gg S/yr). The dashed arrows represent one-way fluxes (either across the tropopause or for various processes). The boxes denote the burden of gas and aerosol in units of gigagram of sulfur (Gg S). Red numbers are simulated by Socol-AER. Black numbers are retrieved from the AER 2-D model or (in brackets) from the observations, both as presented in SPARC [2006]. Green numbers in the troposphere are based on the GOCART model [Chin *et al.*, 2000]. Orange numbers are taken from Chin and Davis [1995].

Figure 3. Global atmospheric sulfur budget. Solid arrows: net fluxes of surface emissions, cross-tropopause transport (horizontal dotted line), wet/dry deposition, or chemical and microphysical transformations in Gg S/yr. Arrows point to net direction. Dashed arrows: one-way fluxes, either upward/downward across the tropopause, or forward/backward for various processes. One-way fluxes across the tropopause of SO₂, CS₂, DMS, H₂S (downward), and H₂SO₄ (upward) are negligible; therefore, only the net fluxes of these short-lived species are shown here. Boxes: burdens of gases and H₂SO₄ aerosols in Gg S. Red numbers: SOCOL-AER results. Black numbers: AER 2-D results, sensitivity studies (in parentheses), and measured data (in brackets), all from SPARC [2006]. Green numbers: tropospheric GOCART model results *Chin et al.* [2000]. Orange numbers: *Chin and Davis* [1995]. Blue number: SAGE II-derived aerosol mass using the SAGE 4λ method [Arfeuille et al., 2013]. Note that SO₃ and MSA are not shown in this diagram.

In the troposphere, OCS accounts for 74% of the tropospheric total sulfur mass in our model, while short-lived SO₂ and sulfate aerosol account for 10% and 14%, respectively. The total SO₂ emission noticeably deviates among the models due to the application of different emission data. In SOCOL-AER, the decadal SO₂ emission data of *Lamarque et al.* [2010] for the year 2000 is employed. This lists about 51 Tg S/yr of anthropogenic SO₂ emissions (including ship emissions), leading to a total of ~65 Tg S/yr for SO₂ emissions when combined with the emissions from biomass burning and volcanic degassing. Conversely, when the year 1990 chosen as basis [SPARC, 2006; *Chin et al.*, 2000], the total SO₂ emissions are about 75–78 Tg S/yr, mainly because the sulfur emissions by western developed countries were decreasing in this time window. The other primary sulfur species DMS, H₂S, and CS₂ account for less than 2% of the tropospheric total sulfur burden, but they are an important source for SO₂ in the middle and upper troposphere and contribute about 26 Tg S/yr for SO₂, which is almost one third of the modeled tropospheric SO₂ total source strength of 92 Tg S/yr.

In the troposphere, there are additional major discrepancies between models, e.g., that SO₂ wet and dry deposition amounts to only 53 Tg S/yr in SOCOL-AER (similar to 52 Tg S/yr found by *Chin et al.* [2000]), whereas 2-D AER [SPARC, 2006] found 100 Tg S/yr. Furthermore, fluxes from SO₂ to the aerosol phase and aerosol deposition fluxes are comparable between this work and *Chin et al.* [2000] but have been about 5 times lower in 2-D AER. The main reason is that SPARC [2006] aimed at optimizing the performance of 2-D AER in the stratosphere, while tropospheric processes were highly simplified. In SOCOL-AER tropospheric performance has been largely improved (e.g., additional aqueous phase reactions of S(IV) with ozone (O₃) and hydrogen peroxide (H₂O₂) in cloud water content with prescribed vertical distribution of the pH value), although simplifications remain (e.g., the crude tropospheric washout scheme). These remaining

approximations may be a reason for the discrepancies of detailed wet and dry deposition fluxes between SOCOL-AER and the tropospheric GOCART model results by *Chin et al.* [2000].

The calculated net fluxes across the tropopause (dotted horizontal line in Figure 3) are calculated based on mass balance considerations. Our model suggests a total net flux of 103.1 Gg S/yr of sulfur-containing gases into the stratosphere. This flux results in a burden of 109 Gg S, supporting the stratospheric aerosols under nonvolcanic conditions. About 43% of the total sulfur flux into the stratosphere is in the form of primary tropospheric aerosol, 28% in the form of SO₂, 23% as net OCS flux, 4% as H₂S, and 2% as DMS.

It is important to note that the one-way OCS flux into the stratosphere is more than 10 times higher than the net OCS flux, i.e., about 90% of the OCS return unprocessed to the troposphere. The one-way OCS flux into the stratosphere calculated by SOCOL-AER is about 20% higher than calculated by 2-D AER, while the SOCOL-AER calculated net OCS flux is larger by ~30% compared to the 2-D AER result, obviously due to differences in transport and loss processes. For SO₂, the net flux provided by SOCOL-AER of 50.9 Gg S/yr differs even by more than 70% compared to 28.8 Gg S/yr calculated by 2-D AER in SPARC [2006], indicating differences in transport and mixing ratios at the tropopause. In addition, large amounts of sulfur-containing tropospheric aerosols enter the stratosphere (dashed arrow in Figure 3).

In the stratosphere, the calculated oxidation of SO₂ to H₂SO₄ is nearly 70% higher than calculated by the 2-D AER in SPARC [2006], revealing a stronger gaseous source through the tropopause in SOCOL-AER. The transport in the 3-D CCM, though it cannot fully resolve deep convection, depicts troposphere-stratosphere exchange processes obviously better than the 2-D model, which has to rely on 2-D parameterizations of eddy diffusion coefficients. About 85% of gaseous H₂SO₄ in the stratosphere transforms into aerosols through condensation. The calculated nucleation rate is roughly 2 orders of magnitude larger than in 2-D AER, even though the same nucleation parameterization [*Vehkamäki et al.*, 2002] is applied in both models. This difference is to be expected, as the longitudinal temperature inhomogeneity in the 3-D model triggers more effective nucleation in comparison to the zonally averaged temperature in the 2-D model. These differences in nucleation rates are partly compensated by coagulation processes, which readily reduce particle number densities after nucleation bursts. In the upper stratosphere, aerosols evaporate and release gaseous H₂SO₄ which then photolyzes back to SO₂. The higher conversion rate here is due to the enhanced photolysis rate [*Vaida et al.*, 2003; *Miller et al.*, 2007; *Lane and Kjaergaard*, 2008]. The source strength for stratospheric aerosols is 186.5 Gg S/yr (108.6 Gg S/yr in form of gas and 77.9 Gg S/yr in form of aerosols) in SOCOL-AER. The resulting stratospheric aerosol burden in SOCOL-AER is 109.0 Gg S, which is 40% less than 187.2 Gg S simulated by 2-D AER (which has a total source strength 134 Gg S/yr including 68.5 Gg S/yr in the form of gas and an upward flux 65.5 from prescribed primary aerosols). This noticeable difference between the two models is likely due to the rate of exchange of air between the troposphere and stratosphere (as an important aerosol removal process), which is generally not well represented by two-dimensional models [*Weissenstein et al.*, 1997] and remains a major uncertainty in the 2-D AER results. These fluxes in Figure 3 are hard to validate with measurements [e.g., SPARC, 2006], whereas the stratospheric aerosol burden can be verified through satellite and in situ measurements. Detailed model-observation comparisons of this sort are presented in the next subsection.

4.3. Comparisons to Stratospheric Aerosol Measurements

In this subsection, the SOCOL-AER-based calculations of aerosol extinctions from visible to IR wavelengths are examined against the SAGE II and Halogen Occultation Experiment (HALOE) satellite instruments. Specifically, the stratospheric aerosol burden is compared with data obtained by the SAGE 4λ described by *Arfeuille et al.* [2013]. Particle size distributions are compared to in situ measurements above Laramie, Wyoming, and Lauder, New Zealand [*Deshler et al.*, 2003; *Deshler*, 2008], as well as to Focused Cavity Aerosol Spectrometers (FCAS) measurements in the Northern Hemisphere lower stratosphere [*Wilson et al.*, 2008].

Comparisons with SAGE extinctions and aerosol optical depths. The Stratospheric Aerosol and Gas Experiments (SAGEs) provide the best space-time coverage of aerosol extinctions in the stratosphere [*Thomason et al.*, 1997, 2008]. Here we use the two most reliable wavelengths 525 and 1020 nm from SAGE II version 7.0, which is an update of SPARC [2006] (version 6.2). Figure 4 compares SOCOL-AER's extinctions with 2-D AER in SPARC [2006] and with SAGE II v7.0 at the equator for different seasons. The observations are averaged for 5 years (2000 to 2004). Model extinctions are calculated according to Mie theory using refractive indices provided by *Yue et al.* [1994]. In the tropical UTLS region and midstratosphere, the SOCOL-AER results are within the measured variability range; horizontal bars in Figure 4 indicate measured

Figure 4. Comparison of SAGE II version 7.0 and SOCOL-AER-calculated zonal mean extinctions at 525 and 1020 nm at the equator. SAGE II data: averaged over 5 years (2000 to 2004). Horizontal bars: observed or modeled variability (± 1 standard deviation). Estimated errors of SAGE: $\sim 20\%$ for 525 nm and $\sim 10\%$ for 1020 nm. Estimated errors of the model: 0.5–5% (reflecting uncertainties in laboratory measurements in absorption coefficients).

or modeled variability. In addition, there is an uncertainty in the precision of SAGE II extinctions of about 10% for the 1020 nm channel and 10–40% for the 525 nm channel, see Figure 4.1 in SPARC [2006]. This uncertainty corresponds to roughly twice the symbol size (circles and triangles) in Figure 4. Overall the green and red model curves agree very well with the observed extinctions. The model successfully reproduces the observed vertical gradients in the extinctions from June to November, but slightly less satisfactorily from December to May. At low altitudes deviations are unlikely to be caused by clouds, which are already filtered in SAGE II [SPARC, 2006], and more likely caused by the seasonal variability in the tropospheric sources and transport. The AER 2-D model fails to capture the vertical gradients in the extinctions near the tropopause (16–17 km). It largely overestimates the observed extinctions above the tropopause and underestimates below, likely due to the inadequacy of the tropical convection and/or the prescribed primary aerosol distribution, which was imposed in the 2-D model at the tropical tropopause, based on aircraft observations (see Figure 6.9 in SPARC [2006]). Above 35 km, neither of the two models is able to reproduce the observations, possibly because of the absence of meteoritic dust, which is a dominant source of aerosol extinctions in the upper stratosphere [Neely *et al.*, 2011]. The comparison of aerosol extinctions at midlatitudes (40–45°N) is shown in Figure 5. In the lower and middle stratosphere, SOCOL-AER successfully reproduces the observed extinctions in all seasons. However, the modeled extinctions decline rapidly above 30 km, again likely due to the lack of meteoritic dust in the model.

Table 3 summarizes the stratospheric aerosol optical depths (AODs) calculated from the model results and from SAGE II observations averaged over the volcanically quiescent years 2000–2004. The SOCOL-AER calculations show very good agreement (within 4%) with SAGE II for the globally averaged AOD and the averaged AOD over the tropics, but slightly less satisfactory in the Northern and Southern extratropics with

Figure 5. Comparison of SAGE II version 7.0 and SOCOL-AER-calculated zonal mean extinctions for 525 and 1020 nm at 45°N. SAGE II data: averaged over 5 years (2000 to 2004). Horizontal bars: observed or modeled variability (± 1 standard deviation). Estimated errors of SAGE: $\sim 20\%$ for 525 nm and $\sim 10\%$ for 1020 nm. Estimated errors of the model: 0.5–5% (reflecting uncertainties in laboratory measurements in absorption coefficients).

$\sim 10\%$ overestimation and $\sim 15\%$ underestimation, respectively (due to unknown reasons). The 2-D AER overestimates SAGE II observations by about 40% in the tropics and 20% in the extratropics.

Comparisons with HALOE extinctions. The Halogen Occultation Experiment (HALOE) provides aerosol extinction coefficients at IR wavelengths (3.46 and 5.26 μm). In contrast to the SAGE wavelengths, for which extinctions are dominated by scattering and roughly proportional to particle surface area density, aerosol extinctions at the HALOE wavelengths are mostly caused by absorption and therefore are representative of the particle volume density. Figure 6 shows comparisons of modeled and HALOE extinctions at 3.46 and 5.26 μm (the latter averaged over the period 1999–2004 at the equator). Model extinctions are calculated from Mie theory using refractive indices based on Tisdale *et al.* [1998]. The 2-D AER overestimates the HALOE-observed extinctions at the both wavelength channels in the UTLS region and decays too fast

Table 3. Comparison of Stratospheric Aerosol Optical Depth (AOD)

	AOD (10^{-4}) 20°S–20°N		AOD (10^{-4}) 20°N–60°N		AOD (10^{-4}) 20°S–60°S		AOD (10^{-4}) Global	
	525 nm	1020 nm	525 nm	1020 nm	525 nm	1020 nm	525 nm	1020 nm
SAGE II (00–04)	33.2	8.6	39.7	10.0	44.1	11.1	39.7	10.0
SOCOL-AER	32.6	8.6	40.8	10.9	37.6	9.3	38.2	9.9
AER (SPARC ^a)	47.4	12.4	51.0	12.5	54.9	13.8	52.2	13.2

^aSPARC: Stratosphere-troposphere Processes and their Role in Climate.

Figure 6. Comparison of HALOE and model-calculated extinctions at 3.46 and 5.26 μm at the equator for April and October. HALOE observations: averaged over 5 years (2000 to 2004). Horizontal bars: observed or modeled variability (± 1 standard deviation). Dashed curves: corrected HALOE 5.26 μm extinction (15–30 km) according to Figure 7 (relative mean departure) in Thomason [2012]. Estimated errors of the model: 20% (reflecting uncertainties in laboratory measurements in absorption coefficients).

with altitude. Between 17 and 35 km, SOCOL-AER calculated extinctions at 3.46 μm are in excellent agreement with HALOE, and much improved in comparison with 2-D AER results. However, SOCOL-AER has difficulties reproducing the observed aerosol extinctions at 5.26 μm . The calculations underestimate observations by a factor 1.5–3 in the stratosphere (see Figure 6, bottom row). This discrepancy is unlikely due to the lack of particles at large sizes in the model as the comparison with the optical particle counter measurements will show below, see Figure 7. This disagreement may be partly due to uncertainties in the laboratory measurements underlying the refractive indices of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solutions, which are up to 20% [Tisdale *et al.*, 1998; Biermann *et al.*, 2000]. Furthermore, Thomason [2012] found that the HALOE 5.26 μm shows large differences on the order of 0.5 to $1.0 \times 10^{-5} \text{ km}^{-1}$ (20 to 50% anomaly) relative to the HALOE 3.46 μm and SAGE II-based predictions. He attributed the anomaly to a potentially ineffective removal of N_2O , which has significant absorption at 5.26 μm . The agreement between SOCOL-AER model predictions and HALOE measurements at 5.26 μm improves significantly after a correction based on the relative mean departure presented in Figure 7 of Thomason [2012] is applied to the HALOE 5.26 μm channel, which reduces the HALOE observations (dashed curves in Figure 6 (bottom row)).

Comparisons with OPC size channels. The optical particle counter (OPC) operated at Laramie, Wyoming [Deshler *et al.*, 2003; Deshler, 2008], provides a long-term in situ stratospheric aerosol record that started regular ($\sim$ monthly) measurements in 1971. Here we use the volcanically quiescent part of the record from 1999 to 2008 to compare with our model results. We also compare the model results with the OPC at Lauder, New Zealand, under volcanically quiescent conditions (operated during January to April period from 1998 to 2001).

Figure 7. Cumulative number densities (for radii larger than stated radius in μm) calculated by SOCOL-AER compared to in situ stratospheric aerosol measurements over the period 1999–2008 at (left) Laramie and January to April during 1998–2001 at (right) Lauder [Deshler *et al.*, 2003; Deshler, 2008]. Measurements: represented as standard box plots (minimum excluding outliers, 25th percentile, median value, 75th percentile, maximum excluding outliers; for clarity outliers of the box plot are omitted). Colors: different wet particle radii (H₂SO₄/H₂O, in μm). Solid curves: model results with the annual average at Laramie (Figure 7, left) and the average over January to April at Lauder (Figure 7, right).

Figure 7 shows simulated and observed vertical profiles of cumulative particle number densities for different size channels (particles larger than specified radius). The observed natural variability of the measurements is depicted by standard box plots. For clarification in the figure, outliers of the box plots are not shown. At Laramie (Figure 7, left) below 25 km, the calculated annual mean values are generally within the range of the measurements (i.e., within the boxes or whiskers). Above 25 km, the modeled number densities start to deviate from the measurements with concentrations generally too high for particles larger than 0.15 μm and lower for condensation nuclei (particle size 10 nm). The overestimation might be partially due to the numerical diffusion of the applied sedimentation scheme in the model [Benduhn and Lawrence, 2013] since our previous simulations using a simple upwind method for sedimentation gave even higher number densities above 20 km. Too fast meridional transport from the tropics to higher latitudes might be another reason for the enhanced number densities in the larger radius channels, which would not provide the aerosol particles enough time to leave the stratosphere via gravitational settling. An underestimation of the stratospheric age of air is a common artifact of many CCMs, in particular also the ECHAM-based SOCOL family [Stenke *et al.*, 2013]. The observed increase in number densities of the condensation nuclei ($r > 10$ nm) above 25 km could be the result of freshly nucleated particles imported from Arctic regions in air that descended into the Arctic vortex region during winter and spring, termed the “stratospheric condensation nucleus layer” [Campbell and Deshler, 2014]. The modeled CN underestimates the observations due to either the lack of meteoritic materials (as shown in the previous comparisons with aerosol extinctions), or inability to accurately produce the stratospheric condensation nucleus layer. The model–observation comparisons at Lauder, New Zealand (Figure 7, right), are very similar to those at Laramie.

Comparisons with OPC volume density. A model–observation comparison of particle volume density is shown in Figure 8. At Laramie (Figure 8, left), the simulated volume density is in good agreement with the OPC measurements below 25 km and declines faster above, which could be due to the underestimation of condensation nuclei concentration (black curve in Figure 7) or due to the lack of meteoritic material in the model. At Lauder (Figure 8, right), the modeled volume density also agrees well with OPC measurement except near 16–18 km, where the model overestimates the mean values of the observations by about 20–50% (for unknown reasons).

Comparisons with FCAS particle volume distributions. Focused Cavity Aerosol Spectrometers (FCAS) were used to measure aerosol size distribution in the Northern Hemisphere lower stratosphere from 1992 to 2004 [Jonsson *et al.*, 1995; Wilson *et al.*, 2008]. We compare the modeled particle volume distributions sorted by N₂O mixing ratio (X_{N_2O}) intervals with the volcanically quiescent parts of the measurements as shown in Figure 9. The location of the FCAS measurements is shown in Figure 1 of Wilson *et al.* [2008]. For 100 ppbv $< X_{N_2O} < 150$ ppbv (which corresponds to high latitudes $> 60^\circ$ N), the calculated particle volume distribution is shifted to larger diameters by 10–15% compared to the observations. This could be due

Figure 8. Particle volume density calculated by SOCOL-AER compared to in situ stratospheric aerosol measurements averaged over the period 1999–2008 at (left) Laramie and January to April during 1998–2001 at (right) Lauder [Deshler *et al.*, 2003; Deshler, 2008]. Horizontal bars: measured variability (± 1 standard deviation). Red curves: model results with the annual average at Laramie (Figure 8, left) and the average over January to April at Lauder (Figure 8, right).

to the too fast Brewer-Dobson circulation in the model, which would allow larger particles to reach the poles, or the difference in the polar vortex between the period of 1999–2000 and the period of the free-running model calculation. The model-observation agreements improve for the intervals of 150 ppbv $< X_{N_2O} < 200$ ppbv and 200 ppbv $< X_{N_2O} < 250$ ppbv. For 250 ppbv $< X_{N_2O} < 300$ ppbv (which corresponds to the region just above the tropopause), the modeled particle volume distribution fails to capture the first mode in the observation. This disagreement is due to the fact that the model includes only sulfuric acid aerosols, while organic aerosols contribute significantly to the observed first mode (see the composition-resolved size distributions, Figure 3d in Murphy *et al.* [2014]).

Stratospheric aerosol burden. The aerosol burden can be derived by fitting the SAGE II extinctions to retrieve the particle size distribution and surface area density (SAD). To this end we employ the SAGE 4 λ method, which retrieves the aerosol size properties based on the extinctions at all SAGE II wavelengths. The extinctions at 3.46 μ m from the particle size distribution fitted by SAGE 4 λ [Arfeuille *et al.*, 2013] is within 25% of extinctions observed by HALOE right after the Pinatubo eruption and differ marginally under the

Figure 9. Normalized particle volume distributions calculated by SOCOL-AER (solid curves) compared to FCAS measurements (symbols) [Wilson *et al.*, 2008] separated by different N_2O concentration X_{N_2O} intervals: (a) 100 ppbv $< X_{N_2O} < 150$ ppbv; (b) 150 ppbv $< X_{N_2O} < 200$ ppbv; (c) 200 ppbv $< X_{N_2O} < 250$ ppbv; (d) 250 ppbv $< X_{N_2O} < 300$ ppbv. Vertical bars: ± 1 standard deviation of the measurements.

Table 4. Impact of Various Emission Scenarios (Column 1) on Total Net Tropopause-Crossing Gaseous Sulfur Fluxes Into the Global Stratosphere (Column 3), Stratospheric Aerosol Burden (Sulfur Burden Above Tropopause, Column 4), and Percentage in Burden Relative to REF (Column 5)^a

Scenario	Characteristic	Flux (Gg S/yr)	Burden (Gg S)	Fraction (%)
REF	Reference (standard model setup)	103	109	100
noSED	No gravitational sedimentation	103	210	193
noSO ₂ /TP	No SO ₂ across tropopause	52	81	74
noOCS/TP	No OCS across tropopause	62	51	47
noShLived/TP	No DMS, H ₂ S and CS ₂ across tropopause	92	106	97
noSO ₂ _DMS_H ₂ S	No SO ₂ , DMS and H ₂ S emissions	42	61	56
noASO ₂	No anthropogenic SO ₂ emissions	77	91	84
noDMS_H ₂ S	No DMS and H ₂ S emissions	79	95	87
onlySO ₂	Only SO ₂ emissions	40	35	32
noVolc	No volcanic SO ₂ degassing	87	99	91
2Volc	Double volcanic SO ₂ degassing	117	120	110
CH/IN	Double anthropogenic SO ₂ emissions in China and India (+13.4 Tg S/yr)	112	118	109
US/EU	USA and Europe + 13.4 Tg S/yr	106	112	103
VolT	REF + 0.7 Tg S, single pulse at 9–14 km	113	116	106
VolS	REF + 0.7 Tg S, single pulse at 16–19 km	335	225	206

^aValues in volcanic simulations (VolT and VolS) are averaged over the first 6 months after the eruption.

nonvolcanic conditions. The stratospheric aerosol burden derived by SAGE 4λ under volcanically quiescent conditions (based on the period 2000–2004) is 112.5 Gg S (see Figure 3). The 187.2 Gg S modeled by the 2-D AER model overestimates the SAGE-4λ data about 60%. In contrast, 109.0 Gg S calculated by SOCOL-AER differs by ~3% from 112.5 Gg S derived from the SAGE 4λ data and thus can be qualified as an excellent representation of the observational data. The aerosol extinctions comparisons with SAGE II and HALOE support our conclusion. The 2-D AER model produces too high aerosol extinctions at visible to IR wavelengths compared to SAGE II and HALOE in the UTLS region, and thus higher aerosol optical depths, because aerosols in the lower stratosphere contribute most to volume densities. This overestimation is possibly due to the imposed boundary conditions at the tropopause or the deficit of isentropic mass exchange in the 2-D model. In contrast, SOCOL-AER agrees closely with the SAGE II and HALOE measurements and properly simulates the extinction profiles in the tropical UTLS region. Furthermore, the comparisons with the in situ stratospheric aerosol measurements support our confidence in the simulated particle size distribution and volume density.

4.4. Sensitivity of Sulfur Emissions

Relative contributions of OCS versus shorter-lived gases. The impact of various emissions scenarios on the stratospheric aerosol burden is summarized in Table 4. The scenario without SO₂ transport across the tropopause (noSO₂/TP) predicts 74% of the stratospheric background aerosol burden, while the scenario with no OCS across the tropopause (noOCS/TP) predicts only 47%, even though its net tropopause-crossing gaseous sulfur flux is higher by 20% than that in noSO₂/TP. This may be explained by the fact that OCS is degrading, converting sulfur to SO₂ and later aerosol, mainly above 22 km, see fluxes above 22 km specified at upper margin of Figure 3. There the mean age of air and the residence time of sedimenting aerosol are greater than in the lower stratosphere. Conversely, the transport of SO₂ and aerosols across the tropopause remains relatively shallow due to the short chemical lifetime of SO₂ and impact of sedimentation. Sedimentation redistributes sulfur mass from the middle stratosphere to the lower stratosphere, where subsequent transport of aerosols into the troposphere leads to removal [SPARC, 2006]. Figure 6.5 of SPARC [2006] shows a reduction of roughly 12% in the stratospheric aerosol burden in the equatorial region due to sedimentation. In extratropical regions an even stronger reduction may be expected. Indeed, the calculated stratospheric aerosol burden without sedimentation (noSED in Table 4) is about 210 Gg S, which is 93% higher than the 109 Gg S calculated for the reference run. The scenario noShLived/TP predicts 97% of the stratospheric background aerosol burden, revealing that the transport of short-lived species DMS, H₂S and CS₂ across the tropopause are relatively insignificant in the stratosphere.

Figure 10. Stratospheric aerosol burdens integrated between 60°S and 60°N, and in (top) 20–30 km and (bottom) 16–30 km. Black: SAGE-II-derived burden using SAGE 4λ method [Arfeuille *et al.*, 2013]. Blue: free-running SOCOL-AER model results from the reference scenario (REF). Red: free-running SOCOL-AER model results from the scenario noSO₂_DMS_H₂S. Green: EMAC model results without organic aerosols taken from the supplement of Brühl *et al.* [2012].

In terms of surface emissions, the scenario onlySO₂ shows that SO₂ establishes about 32% of the stratospheric aerosol burden relative to REF, albeit its abundant surface emissions (~65 Tg S/yr). Turning off the short-lived species SO₂, H₂S, and DMS and keeping only OCS and its precursor CS₂ unchanged (noSO₂_DMS_H₂S) shows that OCS establishes approximately 56% of the original stratospheric aerosol burden. Interestingly, this is consistent with the EMAC-calculated nonorganic result of Brühl *et al.* [2012] as shown in Figure 10. However, Brühl *et al.* [2012] suggested that OCS contributes about 70% of the stratospheric sulfate aerosol burden under nonvolcanic conditions. Uncertainties of the organic contribution to the stratospheric aerosols remain high, and further measurements may be required to confirm the validity of organic contributions in lower stratospheric aerosols. However, existing single-particle

measurements show that the fraction of organic aerosols decreases from more than 50% in the upper tropical troposphere to 10–20% just 1–2 km above the tropical tropopause [Murphy *et al.*, 1998, 2014]. Also, our results do not support the 70% burden due to OCS as suggested by Brühl *et al.* [2012], but rather only 56% and the rest due to short-lived sulfur-containing species. This discrepancy might possibly be due to insufficient surface emissions of short-lived sulfur-containing species, or the lack of penetration into the stratosphere by primary tropospheric aerosols and SO₂ in the EMAC model.

The scenario without anthropogenic SO₂ emissions produces 84% of the stratospheric background burden, which is similar to the scenario without DMS and H₂S emissions (noDMS_H₂S). This is not surprising because these short-lived species contribute roughly one third of the tropospheric SO₂ total source strength (see the budget analysis in Figure 3), and they are transported by convection into the tropical middle and upper troposphere [Chatfield and Crutzen, 1984], serving as more efficient source gases for SO₂ compared to

Figure 11. Comparison of seasonal zonal mean 1020 nm extinctions at the equator for sensitivity experiments of anthropogenic SO₂ emissions. (left) December–February seasons. (right) June–August seasons. Black symbols: SAGE II data averaged over 5 years (2000–2004). Colored lines: SOCOL-AER results. Blue: year 2000 reference conditions. Green: with US and EU emissions enhanced by 13.4 Gg S/yr. Red: with China and India emissions enhanced by 13.4 Gg S/yr.

Figure 12. Comparison of 525 nm extinctions for sensitivity experiments of SO_2 in July at $10\text{--}15^\circ\text{N}$. Gray circles: SAGE II data in July averaged over 5 years (2000–2004). Horizontal bars: natural variability observed by SAGE II (± 1 standard deviation). Colored lines: SOCOL-AER results for different scenarios. Black dashed line: CALIOP data, mean of July 2011, the month after the Nabro eruption.

anthropogenic emissions at the surface (which accounts for more than half of the tropospheric SO_2 total source strength). Sensitivity studies related to volcanic degassing (noVolc and 2Volc) suggest that roughly 10% of the stratospheric aerosol burden originates from volcanic degassing, which is comparable to the impact of anthropogenic emissions, albeit their relatively small emission fluxes. This is mainly due to the geographical distribution and height of volcanic degassing sources [Graf et al., 1998].

Geographical dependence of anthropogenic SO_2 emissions. Doubling the emission in China and India (CH/IN), i.e., $+13.4 \text{ Tg S/yr}$, leads to roughly 9% more stratospheric aerosol burden compared to the reference simulation (see Table 4). When the same additional flux of SO_2 ($+13.4 \text{ Tg S/yr}$) is superimposed on the emissions of the U.S. and Europe (scenario US/EU), this leads to an increase of the stratospheric aerosol burden of only 3% (see Table 4). This weaker response is due to deep convection in the western Pacific region

amplifying the impact of sulfur emissions there, particularly during the summertime, and transporting SO_2 into the middle and upper troposphere, from where it is more readily available for transport into the stratosphere (see Figure 3 in Fueglistaler et al. [2004]). Figure 11 compares the aerosol extinction at 1020 nm wavelength for the CH/IN and US/EU scenarios. The aerosol extinction for CH/IN scenario is about 10–20% higher between 17 and 20 km during the summertime and much less pronounced during other seasons, which are less convective over India or China. Conversely, the US/EU scenario almost overlaps with the reference simulation. These results corroborate the earlier findings by Neely et al. [2013].

Altitude dependence of volcanic SO_2 . Two simulations (VoIT and VoIS) of a Nabro-like eruption have been conducted, where VoIT injects sulfur into the free troposphere (9–14 km), and VoIS into the stratosphere (16–19 km). For details, see the last paragraph of section 3. As listed in Table 4, VoIS doubles the stratospheric background aerosol burden during the first 6 months after eruption, while VoIT contributes

only about 6%, similar to the anthropogenic scenario CH/IN. Figure 12 shows profiles of aerosol extinctions at $10\text{--}15^\circ\text{N}$ in July 2011, 1 month after the eruption. VoIT basically remains at background levels and is close to the results of CH/IN, while VoIS results in a massive increase of extinction in the lower stratosphere. VoIS reaches maximum extinction of about $2 \times 10^{-3} \text{ km}^{-1}$ at 18 km, which is comparable to the Cloud-Aerosol Lidar with Orthogonal Polarization (CALIOP) onboard the CALIPSO satellite. The calculated aerosol extinctions are elevated across a larger altitude range than observed by CALIOP. This might be caused by the insufficient vertical resolution of the model or by an imperfect initial SO_2 distribution in the volcanic injection plume. Our model results

Figure 13. Comparison of the time-space evolutions of CALIOP AOD ($>18 \text{ km}$) at 532 nm and the calculated AOD ($>18 \text{ km}$) at 525 nm from the scenario “VoIS” after the Nabro eruption on 13 June 2011.

suggest that the simulation VoT fails to affect stratospheric aerosols. In contrast, *Bourassa et al.* [2012] indicated, based on the Optical Spectrograph and IR Imaging System observations, that Nabro injected SO₂ into 9 to 14 km and suggested a significant increase in the stratospheric AOD because of deep convection associated with the Asian summer monsoon. This discrepancy might be due to the resolution of convection in SOCOL-AER. However, a recent analysis of the CALIPSO lidar data by *Vernier et al.* [2013] has suggested that Nabro volcanic plume was injected directly into the lower stratosphere, which agrees with our model results. The calculated stratospheric AOD from the scenario VoS is compared with CALIOP observations as shown in Figure 13. SOCOL-AER simulates the evolution of the observed aerosol optical depth reasonably well and peaks at 0.01, which is roughly 4 times the background conditions. However, it should be noted that our experiments cannot rule out that SO₂ injected at or just below the tropopause region could enter the stratosphere via the Asian monsoon given the specific meteorology at the time of the eruption proposed by *Bourassa et al.* [2012, 2013]. Because the SOCOL-AER used free-running dynamics rather than being nudged with analyzed meteorological fields, it has little chance of reproducing the specific winds that carried the observed SO₂ plume from Nabro to the Asian monsoon region.

5. Summary and Conclusions

We have developed the aerosol-chemistry-climate model SOCOL-AER which includes prognostic transport, chemistry, particle-size resolving aerosol microphysics, sedimentation, and interactive aerosol radiative feedbacks. SOCOL-AER accurately reproduces the characteristic features of stratospheric aerosols under nonvolcanic conditions. In a follow-up paper (Sheng et al., manuscript in preparation, 2014), we show that the model provides also accurate prediction of atmospheric and climate effects following large volcanic eruptions, owing to its detailed resolution of individual processes and comprehensive aerosol-chemistry-climate coupling.

Modeled OCS mixing ratios are mostly within the range of ATMOS and MklV measurements. Modeled SO₂ mixing ratios are largely consistent with the ATMOS and MIPAS measurements throughout the atmosphere. At altitudes above 30 km, agreement can only be achieved by including an overtone-induced photolytic conversion of gaseous H₂SO₄ into SO₂ [*Vaida et al.*, 2003]. The model sulfur budget indicates that aerosol particles carrying sulfur flux of approximately 103 Gg S/yr through the tropopause leaves the stratosphere. In terms of upward fluxes through the tropopause, the stratospheric aerosol layer is maintained by about 43% primary tropospheric aerosol, 28% SO₂, 23% OCS, 4% H₂S, and 2% DMS. It is important to note that large amounts of OCS and aerosols enter the stratosphere but leave it again in the same form, i.e., do not contribute to the net sulfur flux. The modeled stratospheric aerosol burden is 109 Gg S, providing excellent agreement with the burden (112.5 Gg S) derived from SAGE II (by means of the retrieval algorithm SAGE 4λ). This largely improves the stratospheric aerosol burden (187.2 Gg S) previously found in the international model comparison ASAP conducted by SPARC [2006]. SOCOL-AER successfully reproduces aerosol extinctions from visible to IR wavelengths (within ±30%, and mostly better than ±10%) compared to SAGE II and HALOE observations in the lower and middle stratosphere. Above ~35 km, close to the upper edge of the Junge layer, SOCOL-AER is not able to match observations, likely due to the lack of meteoritic dust in the model. Model comparisons with in situ measurements by optical particle counters above Wyoming and Lauder [*Deshler et al.*, 2003], and Focused Cavity Aerosol Spectrometers in the Northern Hemisphere verify that the model successfully represents the particle size distribution and particle volume density in the lower and middle stratosphere. Measurements in the UTLS region are necessary for model validation, e.g., to validate modeled sulfur fluxes into the stratosphere in the form of SO₂ and aerosols under volcanically quiescent conditions.

Sensitivity studies reveal that OCS establishes about 56% of the background stratospheric aerosol burden (mostly due to its oxidation at higher altitudes) and 44% provided by shorter-lived gases, mainly SO₂. The model results also suggest that anthropogenic SO₂ emissions in East Asia and India contribute generally more to the lower stratospheric aerosols than emissions in Europe and the U.S., in particular during the summertime. This may be explained by the importance of deep convection and the proximity of the western Pacific region. The model results further suggest that emissions of DMS, H₂S, and volcanic degassing contribute comparably to the stratospheric aerosol burden as do anthropogenic SO₂ emissions and must be taken into account in modeling studies. However, even more important in terms of sulfur input into the stratosphere are small and medium size volcanic eruptions. Simulations of Nabro-like eruptions

demonstrate that even a modest volcanic eruption can dramatically perturb the stratospheric aerosol layer and dominate anthropogenic SO₂ emissions over months-long timescales, provided the volcanic plume reaches the lower stratosphere.

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