



## RESEARCH LETTER

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## Key Points:

- First in situ measurements of SO<sub>2</sub> in the tropical UT/LS
- Typical SO<sub>2</sub> at the tropical tropopause is near 5–10 pptv
- Flux of SO<sub>2</sub> across the tropopause is a minor source of stratospheric aerosol

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








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## The role of sulfur dioxide in stratospheric aerosol formation evaluated by using in situ measurements in the tropical lower stratosphere

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**Abstract** Stratospheric aerosols (SAs) are a variable component of the Earth's albedo that may be intentionally enhanced in the future to offset greenhouse gases (geoengineering). The role of tropospheric-sourced sulfur dioxide (SO<sub>2</sub>) in maintaining background SAs has been debated for decades without in situ measurements of SO<sub>2</sub> at the tropical tropopause to inform this issue. Here we clarify the role of SO<sub>2</sub> in maintaining SAs by using new in situ SO<sub>2</sub> measurements to evaluate climate models and satellite retrievals. We then use the observed tropical tropopause SO<sub>2</sub> mixing ratios to estimate the global flux of SO<sub>2</sub> across the tropical tropopause. These analyses show that the tropopause background SO<sub>2</sub> is about 5 times smaller than reported by the average satellite observations that have been used recently to test atmospheric models. This shifts the view of SO<sub>2</sub> as a dominant source of SAs to a near-negligible one, possibly revealing a significant gap in the SA budget.

### 1. Introduction

Stratospheric aerosols (SAs) are an important component of the Earth's radiative balance. Because SA lifetimes are on the order of 100 times those of tropospheric aerosols [Crutzen, 2006], the relatively small sources of SAs are disproportionately significant for climate. SAs also provide surfaces for catalytic chemistry that can efficiently destroy stratospheric ozone [Solomon, 1999]. A number of proposals suggest that it may become necessary to attempt to mitigate global warming (i.e., climate intervention (CI), solar radiation management, or geoengineering) by enhancing SAs through direct injection of sulfur dioxide gas (SO<sub>2</sub>) into the lower stratosphere [Shepherd, 2012; McNutt et al., 2015]. For all of these reasons the chemistry and source gases that control the SA burden in both current and future climates are of wide interest.

Filter measurements [Junge et al., 1961], volatility measurements [Rosen, 1971; Borrmann et al., 2010], and mass spectrometer measurements [Arnold et al., 1998; Murphy et al., 2014] all point to SA being dominated by sulfuric acid (H<sub>2</sub>SO<sub>4</sub>)-water mixtures, although recent work has shown that in the upper troposphere and lower stratosphere (UT/LS) organic material may sometimes be a significant fraction of the mass [Brühl et al., 2012; Murphy et al., 2014; Yu et al., 2016]. Crutzen [1976] originally proposed that oxidation of carbonyl sulfide (OCS) to form H<sub>2</sub>SO<sub>4</sub> might play a dominant role as a source of SAs because of its ubiquitous tropospheric mixing ratio of ~500 parts per trillion by volume (pptv) and its efficient photolytic destruction in the stratosphere. While subsequent modeling studies have agreed that OCS plays an important role [Chin and Davis, 1995; Thomason and Peter, 2006; Brühl et al., 2012; Sheng et al., 2015], the fraction of the SA burden that can be explained by OCS oxidation during volcanically quiescent periods remains unclear.

Other than OCS, the only gas-phase stratospheric sulfur source that is thought to potentially be a major term in the background SA budget is SO<sub>2</sub>. Because SO<sub>2</sub> is completely converted to H<sub>2</sub>SO<sub>4</sub> and then SA on a time scale of ~1 month in the lower stratosphere, the flux of SO<sub>2</sub> into the stratosphere can be considered to be an equivalent source of sulfate aerosol. With the current global anthropogenic emission of SO<sub>2</sub> near

60,000 GgS yr<sup>-1</sup> [Smith *et al.*, 2011], even a very small fraction entering the stratosphere would be significant compared with the approximately 100 GgS yr<sup>-1</sup> estimated as necessary to maintain the SA burden. Recent positive trends in SA have been suggested to potentially result from increased anthropogenic emissions, particularly in Asia where the summer Asian Monsoon anticyclone efficiently transports pollutants including SO<sub>2</sub> to the lower stratosphere [Hofmann *et al.*, 2009; Randel *et al.*, 2010]. Others have shown that the apparent trend can be mostly explained by a series of minor volcanic eruptions [Vernier *et al.*, 2011; Neely *et al.*, 2013; Brühl *et al.*, 2015; Mills *et al.*, 2016]. In situ measurements of SO<sub>2</sub> at the tropical tropopause where the majority of species enter the stratosphere have, however, not previously been available, and this has long been recognized as leaving significant uncertainty in the relative importance of this stratospheric sulfur source [Kremser *et al.*, 2016]. Unlike OCS, SO<sub>2</sub> processes in the troposphere are complex. A large suite of natural and anthropogenic SO<sub>2</sub> point sources and the SO<sub>2</sub> reactivity with hydroxyl radicals (OH) and oxidants dissolved in cloud droplets result in a heterogeneous SO<sub>2</sub> distribution in the UT. Transport into the UT through deep convection is particularly uncertain due to the sensitivity of aqueous-phase sulfur oxidation chemistry to parameters such as pH and the availability of hydrogen peroxide. Therefore, having confidence in modeled UT/LS SO<sub>2</sub> abundances requires direct validation.

To understand the tropospheric SO<sub>2</sub> contribution to the SA budget, we performed the first in situ SO<sub>2</sub> measurements at and above the tropopause in the tropics. Here we present these measurements and compare the in situ measurements to calculations by using two chemistry-climate models. We then use the models as a form of transfer standard to evaluate the accuracy of the retrievals of background SO<sub>2</sub> mixing ratios from the MIPAS satellite instrument (Michelson Interferometer for Passive Atmospheric Sounding) [Höpfner *et al.*, 2013, 2015], as well as those from the ACE-FTS satellite instrument (Atmospheric Chemistry Experiment Fourier transform spectrometer) [Doeringer *et al.*, 2012]. Finally, we provide an estimate of the global annual flux of SO<sub>2</sub> into the stratosphere and discuss its contribution to the SA budget.

## 2. Methods

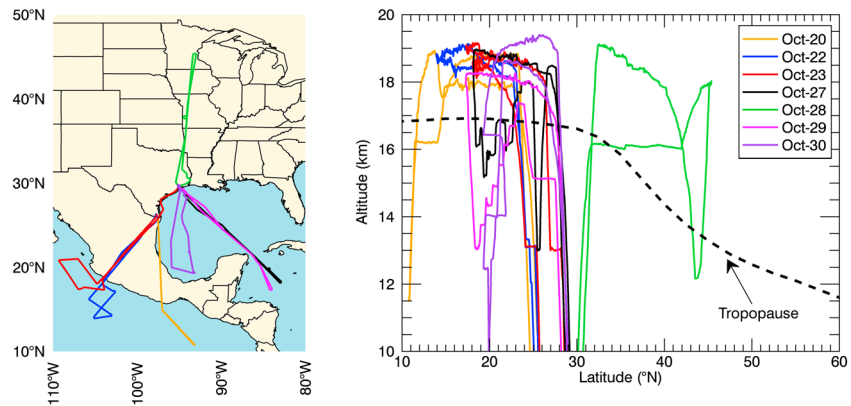
### 2.1. In Situ Measurements

An in situ instrument based on a laser-induced fluorescence (LIF) technique was used in this study to achieve the desired sensitivity for SO<sub>2</sub> mixing ratios on the order of 1 part per trillion (pptv, 10<sup>-12</sup> number mixing ratio) and to afford operation onboard the NASA WB-57F high-altitude research aircraft [Rollins *et al.*, 2016]. The instrument excites SO<sub>2</sub> by using a tunable laser near 216.9 nm and detects the resulting red-shifted fluorescence at 240–400 nm. Typical precision (1σ) during aircraft operation with 10 s of integration is 2 pptv. For the present analysis the LIF data were averaged to 1 min, reducing the uncertainty due to instrument noise to <1 pptv. Systematic uncertainty in the measurement is ±16% + 0.9 pptv.

During the NASA VIRGAS experiment (Volcano-plume Investigation Readiness and Gas-phase and Aerosol Sulfur) in October 2015, the instrument acquired over 18 h of SO<sub>2</sub> measurements in the UT/LS with flights based from Houston, TX, spanning 10.8°N–45.4°N latitude at altitudes up to 19.4 km (Figure 1). The in situ temperature and ozone measurements indicated that the tropopause in the tropical regions during these flights was typically near 17 km (Figure 2). No large volcanic eruptions are known to have occurred immediately prior to or during the sampling period that might have significantly affected our measurements. A number of effusive volcanoes in Mexico and Central America, however, were active during that time, and some isolated plumes that were encountered in the UT can be traced back as likely having originated from those sources.

### 2.2. CESM1(WACCM)

We conducted detailed calculations of the sulfur budget and transport across the tropopause, using the Community Earth System Model version 1 (CESM1) with the Whole Atmosphere Community Climate Model (WACCM) [Marsh *et al.*, 2013]. Mills *et al.* [2016] describe the development of the CESM1(WACCM) version used here. Sources of sulfur-bearing gases are included in the model as either time-varying lower boundary conditions, as for dimethyl sulfide (DMS) and OCS, or direct emissions from natural and anthropogenic sources, as for SO<sub>2</sub> from pollution and volcanoes [Dentener *et al.*, 2006]. This includes effusive volcanoes in Mexico and Central America. The model includes a prognostic treatment of aerosols, including sulfate in the troposphere and stratosphere. CESM1(WACCM) is run at 1.9° latitude × 2.5° longitude horizontal

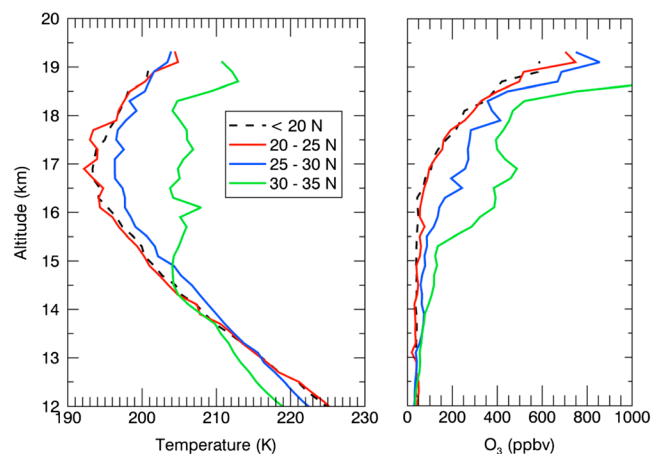


**Figure 1.** Flight tracks from the VIRGAS experiment during October 2015.

resolution, with 88 vertical levels from surface to  $6 \times 10^{-6}$  hPa. The vertical resolution near the tropopause is about 1 km. Horizontal winds and temperatures are nudged to specified dynamics (SD) from the Goddard Earth Observing System Model (GEOS-5) by using a 50 h relaxation time. We initialized SD-WACCM for 1 January 2015, with conditions generated by the volcanic simulation described in Mills *et al.* [2016]. We ran SD-WACCM from 1 January to 31 October 2015, including the input of 0.4 Tg SO<sub>2</sub> from the eruption of Calbuco (72.614°W, 41.326°S) on 23 April 2015.

**2.3. GEOS-5**

During VIRGAS the NASA GEOS-5 model [Rienecker *et al.*, 2007; Molod *et al.*, 2015] provided near-real time (NRT) global forecasts and analyses of meteorological and chemical fields. GEOS-5 comprises an atmospheric general circulation model coupled to a 3-DVar data assimilation system for meteorological fields and incorporates assimilation of bias-corrected aerosol optical depth observations from Moderate Resolution Imaging Spectroradiometer [Buchard *et al.*, 2015]. The NRT GEOS-5 products (available here: <https://gmao.gsfc.nasa.gov/forecasts/>) were provided at a global 0.25° latitude × 0.3125° longitude horizontal resolution, with 72 vertical levels from the surface to 0.01 hPa and vertical resolution of about 1 km near the tropopause. The chemistry module used here is based on the Goddard Chemistry, Aerosol, Radiation, and Transport module, as described in Colarco *et al.* [2010], and includes simulation of dust, sea salt, sulfate, and carbonaceous aerosols. SO<sub>2</sub> inputs to the model are derived from anthropogenic and volcanic sources including effusive volcanoes in Mexico and Central America. SO<sub>2</sub> is also produced from oxidation of DMS, and conversion to sulfate occurs in gas phase and aqueous processes using prescribed oxidant inventories based on the Global Modeling Initiative chemical transport model [Duncan *et al.*, 2007; Strahan *et al.*, 2007].

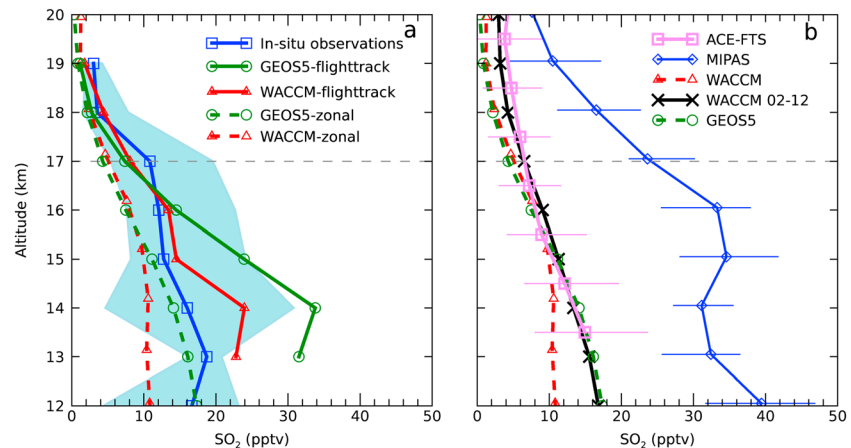


**Figure 2.** (left) Mean temperature and (right) ozone (O<sub>3</sub>) profiles for four latitude ranges sampled during VIRGAS. Similarities of temperature and O<sub>3</sub> from 10 to 25°N suggest that data up to 25°N are representative of tropical air masses on these flights.

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**2.4. Satellites**

Retrievals of SO<sub>2</sub> volume mixing ratios have been performed by using spectra from ACE-FTS [Doeringer *et al.*, 2012] and MIPAS [Höpfner *et al.*, 2013, 2015]. Retrievals of SO<sub>2</sub> are available from ACE-FTS for the time range covering January 2004 until September 2010 and from MIPAS from July 2002 until April 2012. For MIPAS, we use monthly means of the single-radiance SO<sub>2</sub> retrievals (data versions V5R\_SO2\_20,



**Figure 3.** Measured and modeled  $\text{SO}_2$  profiles in the tropical ( $10\text{--}25^\circ\text{N}$ ) UT/LS. (a) The blue line and the shaded region show the VIRGAS in situ measurement median and interquartile range. WACCM and GEOS-5 have been adjusted upward by 1 km to match the aircraft ozone and thermal tropopause level. Two profiles each are shown for WACCM and GEOS-5: one for the zonal mean for 2015 (dashed lines) and another showing data sampled from the models along the flight track locations/times (solid lines). (b) ACE-FTS median and interquartile range (2004–2010). MIPAS median and interquartile range of monthly means (2002–2012). Data during periods affected by major volcanic events were omitted from the ACE-FTS and MIPAS data [Höpfner *et al.*, 2013]. WACCM and GEOS-5 profiles are the same zonal mean profiles shown in Figure 3a. WACCM 02-12 profile (black) shows the mean profile obtained by sampling the WACCM run during the 2002–2012 MIPAS period [Mills *et al.*, 2016] from the same times and locations as the MIPAS data that are averaged to derive the blue MIPAS profile.

V5R\_SO2\_220, and V5R\_SO2\_221) [Höpfner *et al.*, 2015]. While the MIPAS single-radiance retrievals provide global daily coverage, the precision of these data at low  $\text{SO}_2$  mixing ratios is 70–100 pptv, necessitating significant averaging to quantify background  $\text{SO}_2$  in the UT/LS. To compare the satellite retrievals with our in situ measurements we use zonally averaged satellite profiles from 10 to  $25^\circ\text{N}$  during the periods when enhancements due to significant volcanic activity appear to be minor as described in Höpfner *et al.* [2013]. For the profiles in Figure 3, we show the median and interquartile range of the individual ACE-FTS retrievals and of the MIPAS monthly means to provide a measure of the variability of the retrieved  $\text{SO}_2$  mixing ratios.

### 3. Discussion

The temperature and ozone structure observed during the VIRGAS flights indicates that air sampled south of  $25^\circ\text{N}$  during VIRGAS is representative of tropical air masses (Figure 2). Therefore, we use measurements south of  $25^\circ\text{N}$  to characterize the tropical  $\text{SO}_2$  field. Figure 3 shows statistics of the  $\text{SO}_2$  measurements made from the aircraft in the tropical UT/LS region and compares these with the model calculations (Figure 3a) and satellite retrievals (Figure 3b). We show the median and interquartile range for the 1 min averaged in situ  $\text{SO}_2$  measurements (blue markers and shading). In the lower stratosphere (18 km and above) a narrow distribution centered near 3 pptv was observed and values above 10 pptv were rare. In the tropopause region ( $\sim 17$  km), a broader distribution was observed with a median value of 10.8 pptv. In the upper troposphere (14–17 km) only a minor vertical gradient is observed, likely evidence of vertical mixing related to the extensive convection in this region.

Figure 3a presents two profiles produced by using both the WACCM and GEOS-5 models. For each model an average  $\text{SO}_2$  profile is derived by sampling the model along aircraft flight tracks (Figure 3a solid lines). In addition, an annual zonal mean profile from each model for 2015 is calculated to estimate typical tropopause  $\text{SO}_2$  levels (Figures 3a and 3b, dashed lines). Because the models include all known volcanoes globally, the zonal average model profiles estimate the effects of volcanoes outside of the sampling region. At the tropopause ( $\sim 17$  km), the flight-track sampled models show  $\text{SO}_2$  values that are lower than the aircraft observations of 10.8 pptv by 25% (WACCM, 8.1 pptv) and 31% (GEOS-5, 7.5 pptv), although both models are well within the range of the observations (5.4–19.5 pptv). The tropopause zonal mean values from both

WACCM (5.1 pptv) and GEOS-5 (4.3 pptv) are somewhat lower than the flight-track sampled model SO<sub>2</sub> mixing ratios. We expect that this is due to influence of local emissions from effusive volcanoes in Mexico and Central America, which were active during this time and were also included by the models.

The differences between the zonal average and flight-track-sampled model outputs suggest that the aircraft measurements are somewhat high relative to the zonal mean values due to spatial and temporal sampling biases. Thus, comparing the zonal means from the models with those from satellite retrievals is arguably the most reliable way to evaluate the consistency of satellite retrievals with the more spatially and temporally limited in situ observations. The UT/LS model-satellite comparisons in Figure 3b for nonvolcanic periods show strong agreement between models and ACE-FTS but large overestimates from MIPAS. For example, at the tropopause the WACCM zonal mean (5.1 pptv) is a factor of 4.6 smaller than the MIPAS mean (23.6 pptv). It is important to note that the MIPAS  $\pm 2\sigma$  uncertainty range ( $-7.4$  pptv to 54.6 pptv, not shown in Figure 3 [see Höpfner *et al.*, 2015]) and the variability at shorter time scales do include the WACCM value. As discussed in Höpfner *et al.* [2015], the MIPAS systematic uncertainties are quite significant relative to background SO<sub>2</sub> mixing ratios. In addition, the potential influence of volcanic SO<sub>2</sub> emissions during the MIPAS period (2002–2012) that differ from those during 2015 cannot be completely excluded. To further address this issue we sampled WACCM at the times and locations of the individual MIPAS profiles by using a WACCM run that includes explosive volcanoes and reproduces the historic SA burden during the MIPAS 2002–2012 period [see Mills *et al.*, 2016]. Figure 3b shows that the mean of these WACCM profiles exhibits a slightly higher but very similar profile to that for 2015. Overall, the in situ/model/satellite comparison suggests that MIPAS mean values are not useful for characterizing background UT/LS SO<sub>2</sub> without considering the full range of stated uncertainty and temporal variability. This is an important conclusion because MIPAS mean values have been used as an absolute point of reference for recent global model simulations in the LS [Brühl *et al.*, 2015; Sheng *et al.*, 2015].

A primary objective surrounding the various measurements of SO<sub>2</sub> in the LS is whether they suggest that the chemical and transport processes controlling SO<sub>2</sub> in this region are understood well enough to have confidence in the role of SO<sub>2</sub> in maintaining SA mass and, ultimately, in SO<sub>2</sub>-based geoengineering simulations. For example, the in situ observations of the SO<sub>2</sub> vertical gradient in the lower stratosphere are consistent with destruction of SO<sub>2</sub> by OH in conjunction with slow ascent. Assuming a lower stratosphere ascent rate of 0.4 mm s<sup>-1</sup> [Schoeberl *et al.*, 2008], the transit time between 17 km and 18 km is 29 days. The SO<sub>2</sub> lifetime (*e*-folding) in this region due to reaction with OH is estimated to be about 30 days [Höpfner *et al.*, 2015]. Therefore, if the chemistry and dynamics in the LS are well simulated in models, then the SO<sub>2</sub> mixing ratio at 18 km should be about 38% of that at 17 km. This fraction is in reasonable agreement with the in situ measured ratio (33%) and simulated ratios of 50% (both GEOS-5 and WACCM). The larger equivalent ratios from MIPAS (70%) and ACE-FTS (80%) are likely due at least in part to insufficient vertical resolution in the satellite retrievals (~3 km).

An estimate of the annual flux of SO<sub>2</sub> into the stratosphere can be derived by taking the product of the annual mass flux across the tropical tropopause and the mean tropical tropopause SO<sub>2</sub> mixing ratio. Rosenlof and Holton [1993] calculated a flux through the tropical tropopause (15°S–15°N) of  $6.5 \times 10^{11}$  Gg air yr<sup>-1</sup>. As reasoned above, the modeled zonal mean provides the most representative values of the SO<sub>2</sub> zonal mean mixing ratio in the LS. Assuming a zonally averaged value of 5.1 pptv SO<sub>2</sub> ( $5.6 \times 10^{-12}$  sulfur mass mixing ratio) at the tropopause, a flux of 3.6 GgS yr<sup>-1</sup> is derived. In contrast, the SOCOL-AER modeling study [Sheng *et al.*, 2015] shows SO<sub>2</sub> mixing ratios close to those retrieved by MIPAS and calculates a flux of 50.9 GgS yr<sup>-1</sup> due to SO<sub>2</sub> alone, which is a factor of 14 times higher than our derived flux. That study shows an average tropical tropopause mixing ratio of about 30 pptv SO<sub>2</sub> at 17 km for September/October/November, which accounts for a factor of about 6 difference relative to our 5.1 pptv. The remaining factor of 2.3 in the flux is likely due to differences in the assumed troposphere/stratosphere exchanges. Stenke *et al.* [2013] show that the tropical water vapor tape recorder produced in the SOCOL version used by Sheng *et al.* (SOCOLv3T31) implies modeled tropical upwelling that is about 1.85 times as fast as that observed by the HALOE satellite, suggesting that the modeled flux through the tropical tropopause is likely high by a similar factor. This may also imply that the SOCOL-AER stratospheric aerosol lifetime is too short due to an overestimated Brewer-Dobson circulation speed. After the differences in tropopause SO<sub>2</sub> and tropical upwelling, the small remaining difference between our flux estimate and the SOCOL-AER flux is likely due

to extratropical transport that is neglected in our analysis and uncertainties in the tropical upwelling. Given that SOCOL-AER does not include eruptive volcanic SO<sub>2</sub> sources and that the continuous emissions at the surface are quite similar to those used in the WACCM and GEOS-5 simulations, this implies that SOCOL-AER brings about 5.9 times (30 pptv/5.1 pptv) as much of the surface SO<sub>2</sub> to the tropopause.

Many studies have used various techniques to calculate the flux of sulfur into the stratosphere (in the form of sulfate or its precursors) that would be required to maintain the observed stratospheric aerosol burden [Chin and Davis, 1995, and references therein; Thomason and Peter, 2006; Brühl et al., 2012; Sheng et al., 2015]. These studies typically either estimate the stratospheric aerosol burden and divide this by the estimated lifetime of the aerosols or derive the required flux by using a more detailed chemical transport model to reproduce the observed aerosol burden. Sheng et al. [2015] used SOCOL-AER to calculate an aerosol burden of 109 GgS, and Mills et al. [2016] used WACCM to calculate a burden of 138 GgS. These are both in reasonable agreement with the measured burden using the Stratospheric Aerosol and Gas Experiment satellite 4<sub>λ</sub> technique [Arfeuille et al., 2013] of 115 GgS during the volcanically quiescent 2000–2001 period.

While most of the recent estimates of the total sulfur flux (i.e., SO<sub>2</sub> + OCS + DMS + SO<sub>4</sub> + ...) derive numbers greater than 100 GgS yr<sup>-1</sup>, the full range of reported estimates is from 43 GgS yr<sup>-1</sup> [Crutzen, 1976] to 181 GgS yr<sup>-1</sup> [Sheng et al., 2015]. As a point of reference here we use 181 GgS yr<sup>-1</sup> which is the most recently reported value and has been adopted in the recent review paper [Kremser et al., 2016]. Comparing 181 GgS yr<sup>-1</sup> to the SO<sub>2</sub> flux of 3.6 GgS yr<sup>-1</sup> derived in this work would indicate that the direct stratospheric flux of SO<sub>2</sub> is a near-negligible source of SA at ~2% of the budget. If one compares the Sheng et al. SO<sub>2</sub> flux estimate of 50.9 GgS yr<sup>-1</sup> to our in situ-based estimate of 3.6 GgS yr<sup>-1</sup>, our estimate would leave 47.3 GgS yr<sup>-1</sup>, or approximately 26% of the SA mass budget unaccounted for. This gap cannot be made up by increased OCS flux both because the uncertainty in the OCS contribution is much less than the additional 47.3 GgS yr<sup>-1</sup> required and because OCS is an aerosol source only above ~20 km [Chin and Davis, 1995], while SO<sub>2</sub> is a source of aerosol in the 17–20 km region where the majority of the SA mass resides. To maintain agreement with the vertical distribution of SA that has been observed by using remote sensing and optical particle counters [Thomason and Peter, 2006], a gap in the SA budget could likely be filled by an increased flux of sulfate aerosols, or other aerosols or their precursor gases such as organic compounds, which generally have not been included in SA modeling studies. A second possibility is that the total budget of 181 GgS yr<sup>-1</sup> is significantly overestimated, which could be due to an underestimate of the SA lifetime. As noted above, this may be the case if SOCOL significantly overestimates the tropical upwelling mass flux. Brühl et al. [2012], for example, calculated that about 65 Gg yr<sup>-1</sup> of OCS (34.7 GgS yr<sup>-1</sup>) accounts for at 65–75% of the SA source, implying that the total budget is only 46–53 GgS yr<sup>-1</sup>. Clearly, uncertainties in the SA budget still lie in both the rates of exchange between the troposphere and stratosphere and in the role of spatial and temporal inhomogeneities in SO<sub>2</sub> in the UT. Resolving this issue will require more UT measurements in important convective regions and near regions with unique SO<sub>2</sub> emissions (e.g., Asia).

SO<sub>2</sub>-based CI scenarios suggest that a sustained stratospheric input of 10<sup>3</sup>–10<sup>4</sup> GgS yr<sup>-1</sup> would be required to increase the SA burden to sufficiently offset the radiative forcing from a doubling of preindustrial CO<sub>2</sub> [McNutt et al., 2015]. In such a world, the current budget (~10<sup>2</sup> GgS yr<sup>-1</sup>) of background SA mass becomes irrelevant. However, understanding the present-day chemistry and dynamics that controls the distribution of aerosols in the stratosphere is the key to predicting the effectiveness and consequences of CI scenarios. An accurate assessment of the vertical distribution of SO<sub>2</sub> in the LS, such as is reported here, helps to provide confidence in the chemistry there and should be considered an essential benchmark to test models and satellites that might be used to evaluate CI scenarios.

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