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A reanalysis of carbonyl sulfide as a source of stratospheric background sulfur aerosol

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Abstract. This study investigates the importance of carbonyl sulfide (OCS) in the formation of stratospheric background sulfur aerosol. Specific questions examined include the loss rate in the stratosphere, the net flux into the stratosphere, and the contribution of OCS to the stratospheric background sulfur aerosol. From an analysis of current atmospheric measurements of OCS, the total amount of OCS in the atmosphere is evaluated to be 5.2 Tg. Of this total, 4.63 Tg is in the troposphere and 0.57 Tg in the stratosphere. Based on the estimated global OCS source strength of 1.2 Tg yr^{-1}, the global atmospheric lifetime of OCS is estimated to be 4.3 years. Using a one-dimensional photochemical model, the stratospheric photochemical lifetime of OCS is estimated to be 10 years, more than 2 times longer than its global atmospheric lifetime. These results suggest that most of the OCS transported into the stratosphere returns to the troposphere where it is mainly taken up by surface vegetation. The production of stratospheric background sulfur aerosol from OCS oxidation is calculated to be 3.0×10^{10} gS yr^{-1}, 2 to 5 times smaller than the most recent estimates of the amount of sulfur required to maintain the stratospheric background aerosol level. Possible explanations for this difference include (1) an overevaluation of the nonvolcanic background aerosol burden; (2) an underevaluation of the lifetime of stratospheric background aerosol; (3) the presence of other sulfur sources such as high-altitude aircraft emissions; or (4) that the stratospheric OCS database used in our analysis is flawed with a substantial yet unidentified systematic error.

1. Introduction

The existence of a stratospheric aerosol layer containing a substantial component of sulfate was first reported in the early 1960s [*Junge et al.*, 1961; *Junge and Manson*, 1961]. Since its discovery, extensive work has been done to study the origin and mechanisms of formation of this aerosol layer [*Castleman et al.*, 1974; *Lazrus and Gandrud*, 1974; *Hofmann et al.*, 1976; *Turco et al.*, 1979, 1982; *Sedlacek et al.*, 1983; *Hofmann*, 1990].

On the basis of numerous observations of stratospheric aerosol over the past 30 years, volcanic emissions have been shown to be a major source of this aerosol, most of which appears to be sulfate in its chemical composition. However, even during volcanic quiescent periods, observations have revealed the presence of a persistent aerosol layer with a maximum at 20 km. Under the latter conditions the size range was found to be several tenths of a micrometer in radius and the mass loading ranged from a few hundredths to a few tenths of a micrometer per cubic centimeter [*Junge et al.*, 1961; *Castleman et al.*, 1974; *Hofmann and Rosen*, 1981; *Sedlacek et al.*, 1983].

The origin and variability of the background stratospheric aerosol level has drawn considerable attention during the past two decades since changes in its level could have long-term planetary climate effects. The importance of carbonyl sulfide (OCS) as a potential source of stratospheric aerosol was first proposed by *Crutzen* [1976]. This trace gas is now recognized as the most abundant sulfur compound in the atmosphere. Because it is nearly chemically inert in the troposphere, much of it is transported into the stratosphere where it can be photodissociated as well as oxidized via reaction with $O(^3P)$ atoms and OH radicals. The most immediate gaseous sulfur product resulting from this chemistry, SO_2, is subsequently converted to sulfate aerosol.

Long term measurements of stratospheric aerosol seem to suggest that the background aerosol level has been increasing. For example, from their measurements of SO_4^{2-} obtained during the volcanic quiescent periods of 1973-

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Table 1. Observed Carbonyl Sulfide (OCS) Mixing Ratios in the Troposphere

Location	Time	OCS, pptv	Reference
England, surface	fall 1975	506±56	*Sandalls and Penkett* [1977]
70°N-57°S, aircraft, Pacific Ocean	spring 1978	515±67, NH[a] 495±45, SH	*Torres et al.* [1980]
28°N-42.5°N, aircraft	summer 1982	517±65	*Carroll* [1985]
40°N-11°S, aircraft, Atlantic Ocean	summer 1990	475±50, NH 437±45, SH	*Johnson et al.* [1990]
Philadelphia, surface	1980-1989	524±170	*Bandy et al.* [1992]
26°N-56°N, aircraft, Middle East	spring 1991	528±39	*Bandy et al.* [1992]
51°N-37°, surface, Atlantic Ocean	spring 1991	609±96, NH 460±46, SH	*Bingemer et al.* [1991]
54°N-4°S, surface, Pacific Ocean	spring 1982 and spring 1983	508±84	*Johnson and Harrison* [1986]
Europe, aircraft	fall 1984 and fall 1985	569±76	*Ockelmann et al.* [1987]
Britainy Coast surface	summer 1988	563±41	*Mihalopoulos et al.* [1989]
37°S, Amsterdam Island, surface	March 1987 to Feb. 1988 April 1989 to Feb. 1990	475±47	*Mihalopoulos et al.* [1991]
50°S-70°S, surface	Nov.-Dec. 1990	481±73	*Staubes and Georgii* [1993]
0-61°N, aircraft	9/91-10/90	493±20	*Blomquist et al.* [1992]
62°N-7°S, aircraft	1980-1983	410±53	*Leifer* [1989]

[a] NH, northern hemisphere; SH, southern hemisphere.

1974 and 1979, *Sedlacek et al.* [1983] suggested that there might be an anthropogenic contribution, possibly the release of OCS in the troposphere. These authors have interpreted their data as indicating that the annual increase in the background aerosol level could be as high as 6-8%. In yet another study covering the time period 1971-1989, *Hofmann* [1990] reported stratospheric balloon-borne measurements of aerosol over Laramie, Wyoming, which indicated that the background aerosol mass mixing ratio had increased at the rate of 5±2% per year during the decade of 1979-1989. The latter author also speculated at that time that increases in anthropogenic emissions of OCS in the troposphere might be largely responsible for these increases in sulfate aerosol. However, in a subsequent paper *Hofmann* [1991] presented new arguments, based in part on the absence of any significant long term trend in the mixing ratio of OCS, suggesting that stratospheric sulfur sources other than OCS might be responsible for the observed sulfate increases.

There have been several modeling studies which have examined the stratospheric OCS/sulfate aerosol hypothesis [*Turco et al.*, 1979, 1980; *Sze and Ko,* 1979, 1980]. All of these studies showed that the flux of OCS into the stratosphere was sufficient to sustain the background sulfur aerosol layer. One of these studies also suggested that anthropogenic emissions of OCS had the potential for having a large impact [*Turco et al.*, 1980]. These earlier studies, however, were based on both limited atmospheric measurements of OCS as well as photochemical/kinetic laboratory studies of this species. During the past 15 years a rather extensive atmospheric OCS database has become available. Considerable progress has also been made in laboratory studies of OCS reaction rates, cross sections, and photolytic quantum yields. In addition, considerable updating has occurred in several rate coefficients for stratospheric processes, many of which have impacted on model-calculated levels of key reactive species like the hydroxyl radical. The net effect of the aforementioned changes has been to significantly alter the earlier estimates of the stratospheric OCS loss rate.

Presented here is a one-dimensional modeling study of atmospheric OCS which utilizes the newer field measure-

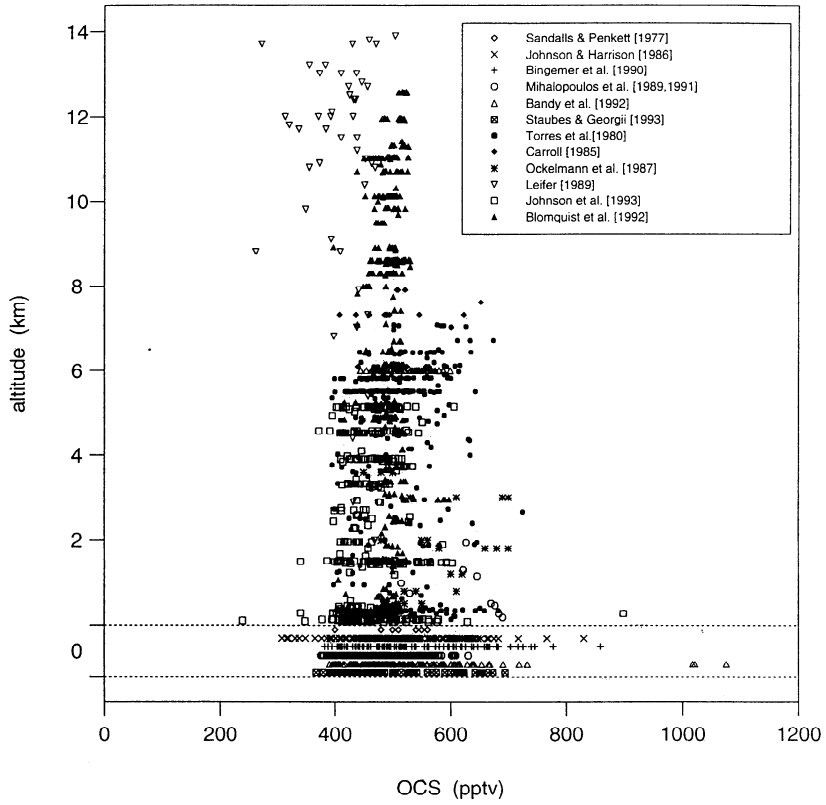

Figure 1. Tropospheric carbonyl sulfide (OCS) measurements as a function of altitude. For purposes of clarity the surface measurements are shown between the dashed lines.

ment data as well as updated laboratory photochemical/kinetic data. The major objective of this study has been to reevaluate the question of the possible contribution of OCS to the stratospheric background sulfur aerosol loading.

The organization of this paper is as follows: In section 2 we briefly review the available atmospheric measurements of OCS, in both the troposphere and the stratosphere, and estimate the total mass of OCS in the atmosphere as well as its lifetime. Section 3 provides a description of the one-dimensional model used in this study; and in section 4 we present our results for the total OCS loss rate in the stratosphere as well as the net flux. Section 5 compares the results from this study with previous work; and section 6 discusses the contribution of OCS to the stratospheric background aerosol loading.

2. Atmospheric Distribution of Carbonyl Sulfide (OCS)

2.1. Tropospheric OCS

The OCS mixing ratio is nearly constant throughout the entire troposphere at approximately 500 parts per trillion by volume (pptv), having almost no vertical gradient. Latitudinal gradients in OCS have been reported by several investigators, with the finding that typical ratios for the northern to southern hemisphere range from 1 to 1.3. Of the numerous OCS data sets now in the literature, all but one appear to be in reasonably good agreement [*Sandalls and Penkett*, 1977; *Torres et al.*, 1980; *Carroll*, 1985; *Johnson and Harrison*, 1986; *Ockelmann et al.*, 1987; *Leifer*, 1989; *Bingemer et al.*, 1990; *Bandy et al.*, 1992; *Mihalopoulos et al.*, 1989, 1991; *Blomquist et al.*, 1992; *Staubes and Georgii*, 1993; *Johnson et al.*, 1993]. These measurements are summarized in Table 1.

Most of the available tropospheric measurements have been reported for latitudes between 60°N and 60°S and at altitudes below 8 km. Figure 1 shows the observed OCS mixing ratio as a function of altitude. As seen from this figure, the data reported by *Leifer* [1989] are consistently lower than all other tropospheric observations. From Leifer's measurements the average tropospheric mixing ratio for OCS is given as 410 pptv with 400 pptv being observed at the tropopause. Other investigators have reported average tropospheric OCS mixing ratios of 440 to 600 pptv with an average value of approximately 490 pptv. More recent high-altitude OCS measurements by *Blomquist et al.* [1992], recorded during NASA's Global Tropospheric Experiment (GTE) Pacific Exploratory Measurements-West(A) expedition, reported seeing almost no vertical variation in OCS mixing ratios from the surface to the tropopause. The average value was again approximately 490 pptv. Collectively, the available information suggests the strong possibility that a systematic error exist in the

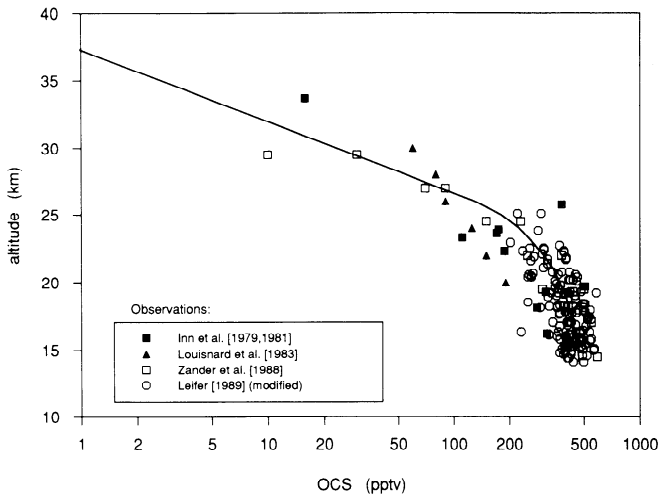

Figure 2. Stratospheric mixing ratio of OCS. The measurement data are shown as symbols and have been normalized to a tropopause height of 14 km (*Leifer's* [1989] data have been modified as per text). The solid curve represents the average OCS vertical profile obtained from averaging the measurement data binned every 2 km intervals below 25 km and is extrapolated for altitudes above 25 km (see text).

Leifer data set. However, since Leifer's measurements are the only ones currently available in the literature that cover altitudes ranging from the upper troposphere to the stratospheric altitudes of 25 km, we have chosen to use the data but have adjusted all values upward by 20%. This adjustment brings the Leifer data into reasonably close agreement with other reported tropospheric OCS mixing ratios. The same adjustment has also been applied to Leifer's stratospheric data.

Most of the OCS field data reported in the literature are based on aircraft or ship measurements; thus the observations have involved relatively short calendar sampling times. The only relatively longterm observations are those reported by *Bandy et al.* [1992] in Philadelphia for the time period 1977-1991 and by *Mihalopoulos et al.* [1991] for Amsterdam Island (located in the southern Indian Ocean) involving a 2-year observational period. The mean OCS mixing ratio at Philadelphia was reported to be near 520 pptv, but large fluctuations were sometimes observed due to the influence of local sources [*Bandy et al.*, 1992]. By contrast, the measurements at Amsterdam Island showed a mean OCS value of 475±48 pptv [*Mihalopoulos et al.*, 1991] with little seasonal variation. The Philadelphia and Amsterdam Island OCS data combined with all other OCS data going back to 1977 suggest that the atmospheric mixing ratio of OCS has remained relatively stable since the first measurements reported by *Sandalls and Penkett* [1977]. More recently, *Rinsland et al.* [1992] have also reported long term monitoring of OCS but in this case the authors were observing the total overhead column abundance. Their observations were made in Arizona from 1977 to 1991 and in the Swiss Alps from 1984 to 1991. This study showed that the OCS total column growth rate has been near zero at both places over the last decade. This is consistent with the historical data on industrial releases going back to 1977 which indicate that anthropogenic industrial sources have been relatively stable for both OCS and its precursor CS_2 over the last 15 years (e.g., see *Chin and Davis* [1993]). The fact that OCS sources and concentrations have remained constant in the atmosphere suggests that OCS is an unlikely explanation for the reported increases in stratospheric background aerosol. *Hofmann* [1991], based on a more limited OCS database, arrived at a similar conclusion.

2.2. Stratospheric OCS

In the stratosphere the OCS mixing ratio is found to decrease rapidly with altitude, decreasing from near 500 pptv at the tropopause to less than 10 pptv at about 30 km [*Inn et al.*, 1979, 1981; *Louisnard et al.*, 1983; *Zander et al.*, 1988; *Leifer*, 1989]. Most stratospheric measurements have been reported for the northern hemisphere only. However, the one measurement that was reported for the southern hemisphere did show a lower OCS mixing ratio than for the northern hemisphere [*Zander et al.*, 1988]. Shown in Figure 2 are the currently available stratospheric OCS measurement data; here we have normalized all observations to a tropopause height of 14 km. Based on these limited observations, we have been unable to extract any meaningful seasonal or latitudinal variations in the OCS mixing ratio within the northern hemisphere. The most representative OCS vertical profile is shown as a solid curve in Figure 2. This profile was obtained by averaging all available data binned every 2-km intervals for altitudes below 25 km. For the altitudes above 25 km, where the measurements were sparse or nonexistent, the OCS profile was extrapolated by assuming a linear relationship between the logarithm of the OCS mixing ratio and the altitude. It is this OCS vertical profile that is used later in the text to calculate the OCS lifetime in the stratosphere (i.e., see section 4). The average stratospheric OCS mixing ratio, χ_s, can be calculated from the expression:

$$\chi_s = \frac{\sum_z \chi(z)[M](z)\Delta z}{\sum_z [M](z)\Delta z} \qquad (1)$$

where [M](z) is the number density of the air (molecules cm^{-3}) and $\chi(z)$ is the OCS mixing ratio at the altitude z. Based on a Δz value of 2-km, the average stratospheric OCS mixing ratio was estimated from equation (1) to be 380 pptv.

2.3. Total Mass and Lifetime of OCS in the Atmosphere

On the basis of the average mixing ratios of OCS in the troposphere and stratosphere the total mass of OCS in the atmosphere W_{ocs} is obtained from the expression

$$W_{OCS} = \left(\frac{W_{air,t}}{M_{air}} \chi_t + \frac{W_{air,s}}{M_{air}} \chi_s \right) M_{OCS} \quad (2)$$

where $W_{air,t}$ is the mass of air in the troposphere (4.56×10^{21} g); $W_{air,s}$ is the mass in the stratosphere (7.2×10^{20} g), χ_t (490 pptv) and χ_s (380 pptv) are, respectively, the average OCS mixing ratios in the troposphere and stratosphere, M_{air} is the molecular weight of air (28.9 g mol^{-1}); and M_{OCS} is the molecular weight of OCS (60 g mol^{-1}). Thus the total mass of OCS is estimated at 5.2 Tg. Of this total, 4.63 Tg can be assigned to the troposphere and 0.57 Tg to the stratosphere.

In a recent study by *Chin and Davis* [1993] the global source strength of OCS was estimated at 1.2 (0.83-1.7) Tg yr^{-1}. As noted above, since no evidence has been found for a secular trend in OCS, this suggests that the global source is very nearly balanced by a similar magnitude sink. Under these conditions the atmospheric OCS lifetime can be estimated by dividing the total OCS mass by its source strength, e.g., 4.3 years. The latter value is nearly twice as long as the previous estimated OCS lifetime of 2 years by *Khalil and Rasmussen* [1984]. This difference can be primarily attributed to the higher total OCS source strength used in the earlier study (see detailed discussion of OCS sources as provided in *Chin and Davis*, 1993).

3. Model Description

3.1. General

A one-dimensional photochemical model was used to evaluate the loss rate of OCS in the stratosphere and, subsequently, to evaluate the OCS stratospheric lifetime. Vertical profiles of temperature, pressure and ozone for 30° latitude and equinox conditions were taken from *Anderson et al.* [1986] to represent the global average condition for our calculations. The atmosphere was divided into 25 layers (7 tropospheric and 18 stratospheric) with an even spacing of 2-km (troposphere, 0-14 km and stratosphere, 14-50 km).

3.2. Chemistry

Carbonyl sulfide is photodissociated by solar UV radiation according to

(R1) $OCS + h\nu \rightarrow CO + S$

For this photochemical process to occur requires radiation having a wavelength of 388 nm or shorter. The other two important processes that can lead to the oxidation of OCS are reactions (R2) and (R3):

(R2) $OCS + O(^3P) \rightarrow CO + SO$

(R3) $OCS + OH \rightarrow CO_2 + HS$

The products from these reactions, S, SO, and HS are further oxidized to SO_2 via gas phase reactions with O_3, OH, and/or HO_2 and, subsequently, to H_2SO_4 either by reaction with OH or by heterogeneous processes involving O_3 or H_2O_2. In the troposphere the reaction rates for processes (R1), (R2), and (R3) are extremely slow, resulting in an OCS mixing ratio that is nearly constant throughout the troposphere. In the stratosphere, processes (R1), (R2), and (R3), in conjunction with reduced vertical mixing, lead to a significant vertical gradient in the OCS profile. Details concerning these chemical processes as related to the stratosphere are discussed in the text below.

3.2.1. Photodissociation of OCS. The photodissociation rate, J_1, is defined by equation (3):

$$J_1 = \int_\lambda F_\lambda \sigma_\lambda \phi_\lambda \, d\lambda \quad (3)$$

where F_λ is the actinic flux, σ_λ is the OCS absorption cross section at wavelength λ, and ϕ_λ is the quantum yield for production of CO and S from the photolysis of OCS. In our evaluation of J_1, equation (3) was integrated over the wavelength range of 185 to 388 nm, wavelengths that are available in the middle and lower stratosphere and are energetic enough to break the C=S bond in OCS. Details concerning each term in equation (3) are given below.

Actinic flux: The actinic flux, F_λ, is the total photon flux from direct, scattered, and reflected solar radiation which can be defined as the integral of the solar radiance over a sphere [*Madronich*, 1987; *Stamnes and Tsay*, 1990]. In the short wavelength part of the spectral range of interest, i.e., 186-201 nm, only direct radiation was considered in our calculations. This reflects the fact that absorption of UV radiation by molecular oxygen is the dominant process in this spectral region and scattering is negligible. At longer wavelengths, however, the diffuse solar radiation from multiple scattering becomes important; this was computed here using a discrete-ordinate radiative transfer model developed by *Stamnes et al.* [1988].

The total extinction optical depth at altitude z was defined by the sum of the optical depths of absorbing species (in this case, O_2 and O_3) and molecular scattering (scattering by clouds and aerosol was not considered). The major absorption feature of molecular oxygen for $\lambda < 200$ nm is the Schumann-Runge band. The transmission of solar radiation in this region was calculated on the basis of a line-by-line description of Schumann-Runge band cross sections as given by *Minschwaner et al.* [1992]. The cross section of O_2 in the Herzberg continuum (e.g., 194-243 nm) was taken from the formula recommended by *Yoshino* [1988]. The cross section for O_3 at 273 K was

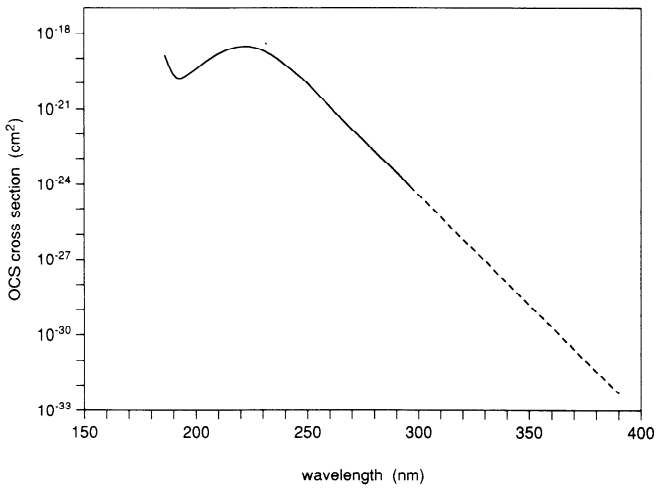

Figure 3. OCS cross sections for the wavelength range of 185-390 nm. The solid curve has been defined from measurement data; whereas, the dashed line represents extrapolated values. See text for explanation.

taken from *DeMore et al.* [1992] and that for Rayleigh scattering was taken from a compilation of the *World Meteorological Organization (WMO)* [1985]. Extraterrestrial solar irradiance data were taken from a recent compilation by *Nicolet* [1989]. The surface albedo (i.e., 0.05) was taken from *Demerjian et al.* [1980] as the "best estimate" value for the wavelength region of 290-388 nm.

OCS cross section: There are several OCS cross section measurements that have been reported for the spectral region 185-300 nm [*Breckenridge and Taube,* 1970; *Chou et al.*, 1979; *Rudolph and Inn*, 1981; *Molina et al.*, 1981; *Locker et al.*, 1983]. In general, the results from these studies are in good agreement for those regions where they overlap. The cross section values obtained by *Molina et al.* [1981] between 185 and 300 nm at 225 K were the principal ones used in this study for purposes of evaluating J_1 in the stratosphere. However, even though Molina et al. estimated the OCS cross section to be less than 1×10^{-24} cm^2 at 300 nm, we have assumed that the OCS cross section for wavelengths above 300 nm could still be important. Thus in this study the values for the OCS cross section were extrapolated to 388 nm assuming a linear relationship between the logarithm of the cross section and the wavelength in the wings of the broad OCS UV absorption band [*Molina et al.*, 1981]. The measured cross sections and our extrapolations are shown in Figure 3. In fact, the absorption of solar radiation longer than 300 nm dominates the OCS photolysis rate in the lower stratosphere due to the strong attenuation of UV solar radiation by ozone in the wavelength region of 220-290 nm.

OCS photolytic quantum yields: The discrete structure overlying the OCS continuum absorption spectrum [*Rudolph and Inn*, 1981; *Molina et al.*, 1981] suggests that OCS absorbs into a discrete, stable state that could lead to processes other than photodissociation. If so, the quantum yield for reaction (R1) would be less than unity. *Sidhu et al.* [1966] obtained a quantum yield for the production of CO from the photodissociation of OCS of 0.91 at wavelengths of 253.7 and 228.8 nm, but these investigators could not rule out that the less than unity quantum yield was not due to experimental error. *Rudolph and Inn* [1981] reported a significantly lower value of 0.72±0.08 for the primary quantum yield for CO at wavelengths between 214.0 and 253.7 nm. The latter value has been recommended by *DeMore et al.* [1992] for the entire OCS absorption region. Still more recently, a new study by *Zhao et al.* [1994] has reported a quantum yield for CO production from OCS photolysis at 248 nm of unity.

Considering the uncertainties that exist in the extrapolation of the OCS cross section to longer wavelengths (λ=300-388 nm) and the uncertainties associated with the quantum yield for the production of the primary species S and CO, we have set the upper and lower limits for the OCS photodissociation rate as follows: The upper limit for J_1 was estimated by integrating equation (3) from 185 to 388 nm based on an extrapolated cross section for OCS for the wavelength range of 300 to 388 nm and a quantum yield of unity for the entire range of 185 to 388 nm. The lower limit was estimated by integrating equation (3) over the wavelength range 185-300 nm using Molina et al.'s OCS cross sections and assuming a quantum yield of 0.7. The "best estimate" of J_1 was taken as the average of the upper and lower limits.

3.2.2. Reaction rates of OCS with $O(^3P)$ and OH. The temperature dependent rate coefficients for reactions (R2) and (R3) have been compiled by *DeMore et al.* [1992]. The diurnally averaged concentrations of $O(^3P)$ atoms were calculated from the steady state approximation equation:

$$[O(^3P)] = \frac{J_{O_3}[O_3]}{k_{O,O_2}[O_2]} \quad (4)$$

where J_{O3} is the O_3 photodissociation rate and $k_{O,O2}$ is the rate coefficient for the reaction $O(^3P) + O_2 + M \rightarrow O_3 + M$. The values of J_{O3} were calculated in our model using O_3 cross sections from *DeMore et al.* [1992]. The diurnally averaged OH concentrations were obtained from the Harvard stratospheric photochemical model (R. Salawitch, personal communication, 1994).

4. Results and Discussion

4.1. Stratospheric Loss Rate of OCS

The calculated 24-hour-averaged OCS photodissociation rate, J_1, is shown in Figure 4 together with those calculated by *Crutzen* [1976] and *Turco et al.* [1979]. (For comparison purposes Crutzen's J_1 values are shown here diurnally averaged, i.e., one half of the value in the work of *Crutzen* [1976].) The total loss rate for OCS (molecules cm^{-3} s^{-1}) at altitude z can be expressed as

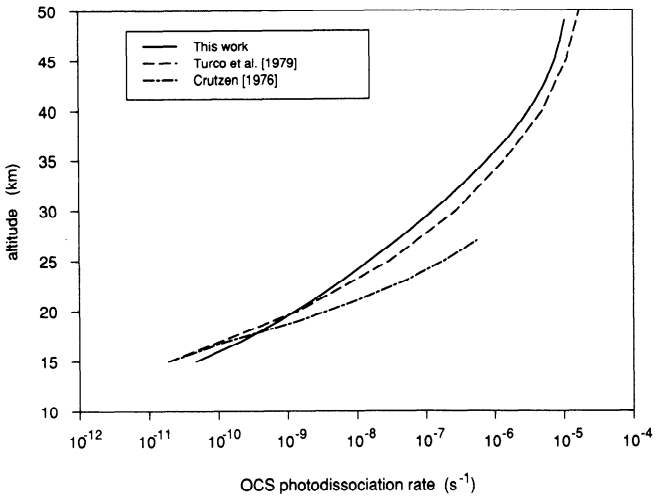

Figure 4. Diurnally averaged OCS photodissociation rate J_1 from this study and from two other investigations.

$$\text{loss rate} = L(z)\chi(z)[M](z) \quad (5)$$

where [M] is the number density of air (molecules cm^{-3}), χ is the OCS mixing ratio, and L is the OCS first-order loss frequency factor defined as

$$L(z) = J_1(z) + k_2(z)[O(^3P)](z) + k_3(z)[OH](z) \quad (6)$$

In Figure 5 the total loss rate as well as the loss rates for the individual stratospheric processes (R1), (R2) and (R3) are plotted versus altitude. On the basis of these loss rates and integrating over all altitudes (14-50 km), we have found that the total amount of OCS lost in the stratosphere is 5.6×10^{10} g OCS yr^{-1}. Approximately 71% of this total is lost by photolysis, 22% due to reaction with O atoms, while only 7% is lost via reaction with OH radicals.

Since the only known OCS source in the stratosphere is transport from the troposphere and as shown in section 2 there is no evidence of OCS growth in the atmosphere, it follows that the net flux of OCS into the stratosphere should be balanced by the total amount of OCS lost there. Thus it can be concluded that the net flux of OCS into the stratosphere is 5.6×10^{10} g OCS yr^{-1}, which is equivalent to 3.0×10^{10} gS yr^{-1}. Slightly more than 50% of this total is destroyed at altitudes below 25 km and about 95% below 35 km. When this stratospheric net flux is compared to the estimated global OCS source of 1.2×10^{12} g OCS yr^{-1} or 6.6×10^{11} gS yr^{-1} [*Chin and Davis*, 1993], the fraction of OCS transported into the stratosphere and chemically converted to sulfur aerosol is seen to comprise only 5% of the total OCS source in the troposphere.

The major uncertainties in calculating the OCS loss rate from equation (5) arise from the combination of uncertainties in the OCS vertical profile $\chi(z)$ and the loss frequency factor, L(z). Although the OCS profile above 25 km was extrapolated from measurement data at lower altitudes, the impact of any error in this extrapolation is relatively small because most of the OCS mass in the stratosphere is located below 25 km. For example, if the absolute value of the slope for OCS above 25 km (Figure 2) is increased by 50% (more negative), the total OCS flux would decrease by only 18%. The values of $\chi(z)$ below 25 km have somewhat larger uncertainties considering the relatively large variance in the measurement data. Thus we estimate that the uncertainty associated with the OCS vertical profile is in the range of 20-30%. Based on the uncertainties in the OCS cross section, quantum yield, and reaction rate coefficients k2 and k3, we also estimate that the loss frequency factor has an uncertainty of approximately 30%. Combining these errors in quadrature, the overall uncertainty in the calculated stratospheric OCS flux is estimated at 35 to 42%.

4.2. Stratospheric Lifetime and Global Budget of OCS

The inverse of the loss frequency factor, L(z), in equation (6) can be used to define the photochemical lifetime of OCS, τ_s, in the stratosphere, e.g.,

$$\tau_s = \frac{1}{\bar{L}} = \frac{\sum_{14\,km}^{50\,km} \chi(z)[M](z)\Delta z}{\sum_{14\,km}^{50\,km} L(z)\chi(z)[M](z)\Delta z} \quad (7)$$

From equation (7) τ_s for OCS is estimated at 10 years, or more than 2 times as long as its estimated global atmospheric lifetime of 4.3 years (section 2). This relatively long photochemical lifetime for OCS in the stratosphere suggests that only a small fraction of the OCS transported into the stratosphere is destroyed. A more quantitative estimate of this "fraction destroyed" can be obtained using the recent tropospheric-stratospheric mass transport/exchange results by *Rosenlof and*

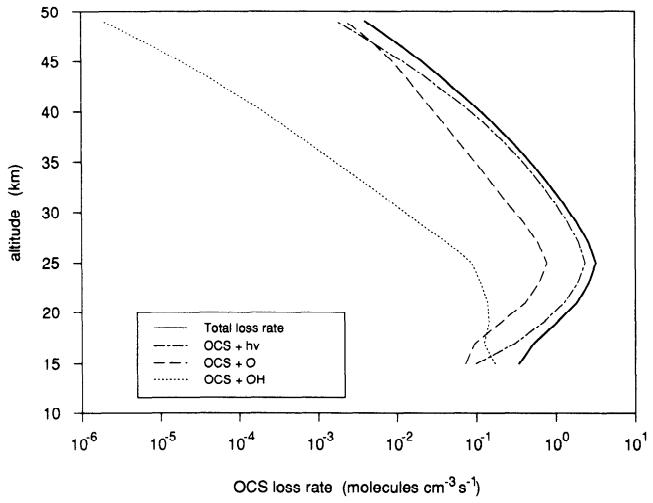

Figure 5. Calculated stratospheric OCS loss rates.

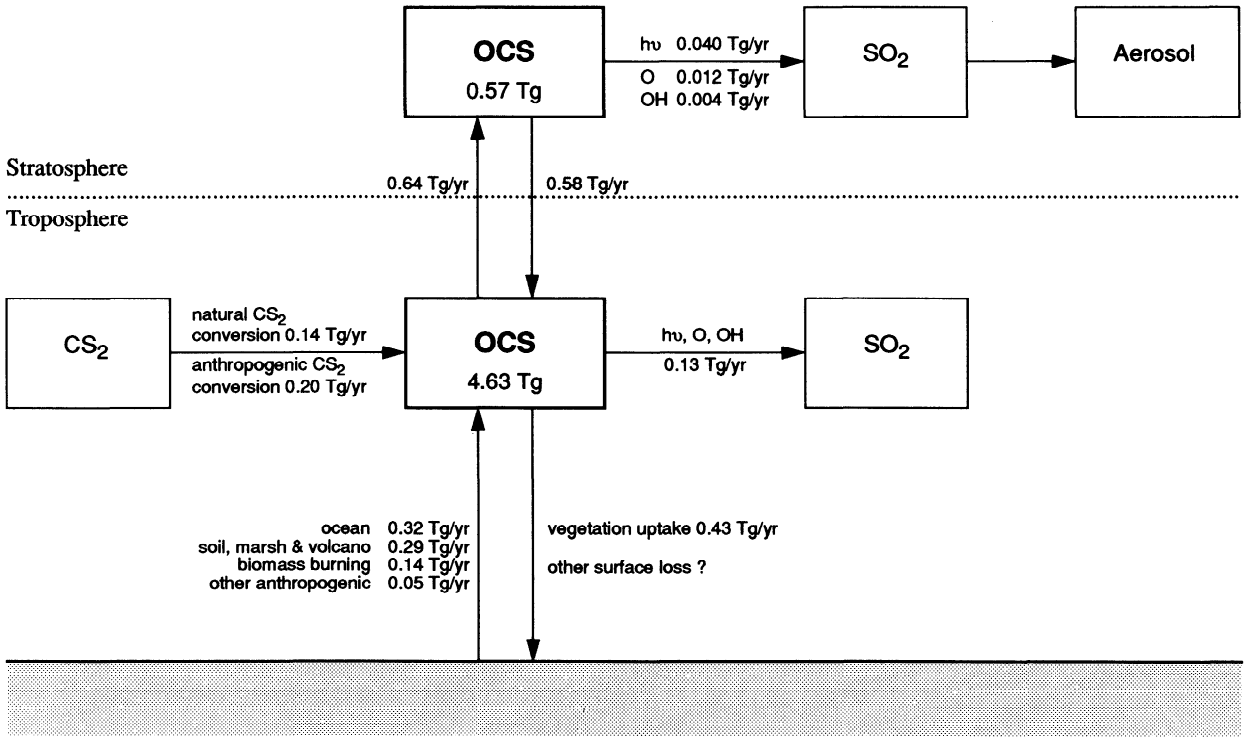

Figure 6. A schematic diagram of the atmospheric budget of OCS.

Holton [1993]. These authors have calculated the total mass transport from the troposphere to the stratosphere in terms of the sum of the tropical upward mass flow across the tropopause (typically between ±15° latitude) and the horizontal exchange through the tropopause break. This troposphere-stratosphere mass exchange was given as 6.5×10^{20} grams of air per year. Using Rosenlof and Holton's mass exchange estimate and taking our estimated average OCS mixing ratio of 475 pptv at the tropopause, the amount of OCS transported into the stratosphere is evaluated to be 6.4×10^{11} g OCS yr^{-1}. If this value is combined with our earlier estimates of the OCS stratospheric chemical loss rate (i.e., 5.6×10^{10} g OCS yr^{-1}), the fraction of OCS oxidized in the stratosphere is given as approximately 9% of the total OCS transported.

Combining the results from this study with our previous work involving estimates of the global source and sink strengths of OCS [*Chin and Davis*, 1993], a global OCS budget has been configured, as shown in Figure 6. The key features and/or conclusions that can be drawn from this budget are as follows: (1) the reservoir of OCS in the troposphere is 8 times larger than that in the stratosphere; (2) there is 0.06 Tg OCS yr^{-1} which is removed in the stratosphere to form sulfur aerosol while 0.13 Tg OCS yr^{-1} is chemically removed in the troposphere, yielding an overall OCS "chemical" lifetime of 27 years; (3) the global lifetime of OCS in comparison to its "chemical" lifetime is 4.3 years; and (4) of the estimated annual OCS source strength, 1.2 Tg, the anthropogenic component (due to direct release and CS_2 chemical conversion) is 34% of this total.

5. Comparison With Previous Work

Table 2 compares the net flux of OCS into the stratosphere (as sulfur) as estimated from this study with values given in previous studies. For purposes of this discussion we have used the unit grams of sulfur per year to represent the sulfur flux. In *Crutzen's* [1976] study the net OCS flux

Table 2. Comparison of Calculated OCS Flux Into the Stratosphere

Investigator	OCS, Tropopause pptv	Flux, gS yr^{-1}
Crutzen [1976]	475 (200)[a]	1.2×10^{11} (5×10^{10})
Turco et al. [1980]	500	1.5×10^{11}
Sze and Ko [1979, 1980]	500	1.0×10^{11}
This work	475	3.0×10^{10}

[a] Values in parentheses are originally from *Crutzen* [1976]. See text for explanation.

into the stratosphere was computed to be 5×10^{10} gS yr^{-1}, based on a boundary condition of 200 pptv OCS at the tropopause. If, however, the boundary condition at the tropopause is assigned the same value as used in this work (i.e., 475 pptv), Crutzen's flux is shifted to 1.2×10^{11} gS yr^{-1}. *Turco et al.* [1980] calculated a net OCS flux of 1.5×10^{11} gS yr^{-1} (tropopause mixing ratio of 500 pptv), and *Sze and Ko* [1979, 1980] estimated a value of 1.0×10^{11} gS yr^{-1}. Although details from the earlier studies are in many cases lacking, in general the discrepancy between the present study and the earlier investigations can be attributed to two factors: (1) differences in the OCS vertical distribution and (2) differences in the estimated values of the loss frequency factor.

In earlier modeling studies, because of the limited amount of stratospheric OCS data, the vertical profile of OCS was computed from one-dimensional models where the stratospheric transport process was parameterized using effective vertical transport coefficients, commonly referred to as "eddy diffusion" coefficients. For example, the transport coefficients from *Ehhalt et al.* [1975] and from *Wofsy and McElroy* [1973] were used, respectively, in the modeling calculations by *Crutzen* [1976] and *Turco et al.* [1979]. These vertical transport coefficients were determined from the best fit to observed mean profiles of long-lived species such as methane and/or nitrous oxide. However, as other investigators have pointed out, these coefficients should also reflect horizontal transport and be dependent on the photochemical lifetime of the species. Thus a transport coefficient based on a single species (e.g., methane or nitrous oxide) may not, in many cases, satisfactorily reproduce observed trace gas distributions for other species [*WMO*, 1982; *Holton*, 1986]. As discussed in section 2.2, the OCS profile used in this study was obtained from averaging all available measurement data. In principle, therefore, it should come closer to reflecting the overall physical and chemical processes controlling OCS in the stratosphere without the complication of parameterizing the stratospheric transport within the one-dimensional model. For purposes of comparison, however, we have used the transport coefficients from *Ehhalt et al.* [1975] and *Wofsy and McElroy* [1973] in combination with the loss frequency factors obtained here to estimate the OCS vertical profile. These respective profiles resulted in estimated OCS fluxes from our model that were a factor of 2.1 and 1.3 times larger than our original estimate. Both calculated OCS profiles were found to underestimate the observed OCS concentration profile at altitudes below 25 km and significantly overestimate the OCS mixing ratio, relative to our extrapolated OCS profile, for altitudes above 25 km.

As noted above, the second reason for the lower OCS flux estimated in this study is reflected in lower OCS loss rates relative to earlier studies. As shown in Figure 4, the diurnally averaged photodissociation rate for OCS (J_1) from this study is about a factor 1.2 to 2 times smaller than that used by *Turco et al.* [1979] for altitudes >20 km. Nearly half of this discrepancy can be attributed to the higher OCS photolysis quantum yield (unity) used by *Turco et al.* By contrast, at altitudes below 20 km our J_1 values are a factor of 1.2-3 times larger than Turco et al.'s values. We believe that the latter discrepancy is largely a result of the extrapolation of the OCS photolysis cross section in this study to wavelengths longer than 300 nm, as discussed in section 3.2. As shown in Figure 4, the J_1 obtained by *Crutzen* [1976] is in agreement with ours only at an altitude of 17 km, being much larger than our value above this altitude and lower than this study when below 17 km. The reason for the discrepancy is not clear. Even when we use the same solar zenith angle (45°) and OCS photolysis quantum yield (1.0) as used by Crutzen and limit the integration of equation (3) to the wavelength interval 186-300 nm, our calculated J_1 is still twice as high as Crutzen's at 15 km and more than a factor of 8 times smaller than Crutzen's at 27 km.

Turco et al.'s estimated stratospheric values for O and OH were also much higher than those calculated here (e.g., about 2 times more [O] and up to 10 times more [OH]). In addition, the latter investigator used a rate coefficient for reaction (R3) that was 1 to 2 orders of magnitudes higher than currently recommended by *DeMore et al.* [1992]. Collectively, these differences result in an estimated total stratospheric OCS loss rate in Turco et al.'s work of 1.5×10^{11} gS yr^{-1} as compared to our value of 3.0×10^{10} gS yr^{-1}. No values for the OCS photodissociation rate, and vertical profiles of O, OH, or diffusion coefficients were provided in the work reported by *Sze and Ko* [1979, 1980], thus making it impossible to further assess any differences between our respective results.

More recently, a two-dimensional modeling study of stratospheric OCS was completed at Atmospheric Environmental Research Incorporated in which the total stratospheric OCS loss rate was estimated at 3.75×10^{10} gS yr^{-1}. The latter rate resulted in an estimated OCS global chemical lifetime of 24 years (D. Weinsenstein, personal communication, 1994), in good agreement with our results of 27 years.

6. Contribution of OCS to Stratospheric Background Sulfur Aerosol

Earlier in this text we evaluated the total amount of OCS oxidized in the stratosphere. We now examine the following question: Is this amount large enough to explain the stratospheric sulfur aerosol level during volcanic quiescent periods?

In past studies, one of the more common methods employed to estimate this flux has been that labeled here the "mass/lifetime" method. In this approach the sulfur flux is obtained from the ratio of the total stratospheric sulfur mass to the estimated stratospheric sulfur lifetime.

Table 3. Summary of Sulfur Flux Estimates Required to Sustain the Stratospheric Background Sulfur Aerosol Layer

Investigator	Method	Flux, gS yr^{-1}
Crutzen [1976]	total mass and lifetime	4.3×10^{10}
Servant [1986]	total mass and lifetime	1.3×10^{11}
Hofmann [1991]	total mass and lifetime	6.3×10^{10}
Lazrus and Gandrud [1974]	profile and transport rate	7.0×10^{10}
Hofmann et al. [1976]	deduced from observation	1.7×10^{11}
Turco et al. [1982]	model calculation	1.6×10^{11}

For example, based on *Junge's* [1974] assessment of the stratospheric aerosol budget and an assumed average stratospheric sulfur residence time of 2 years, *Crutzen* [1976] estimated that a sulfur flux of 4.3×10^{10} gS yr^{-1} was required to sustain the stratospheric background sulfur aerosol. *Servant* [1986] estimated a value for this flux of 1.3×10^{11} gS yr^{-1}; however, the latter author assumed an average stratospheric removal time of 14 months and based his estimate on the stratospheric SO_4^{2-} measurements of *Sedlacek et al.* [1983]. In still another evaluation, *Hofmann* [1991] estimated that a sulfur source of 6.25×10^{10} gS yr^{-1} was required to sustain background sulfate aerosol levels based on his observations of background aerosol levels as measured over Laramie, Wyoming. Hofmann assumed a 1-year lifetime for stratospheric aerosol.

An earlier work by *Hofmann et al.* [1976], involving 1 year's worth of observations over a latitude range of 85°N to 90°S, led to the conclusion that 1.6×10^{10} gS yr^{-1} was required to maintain background aerosol levels. Other modeling calculations by *Lazrus and Gandrud* [1974] and *Turco et al.* [1982] have resulted in estimates of 7.0×10^{10} gS yr^{-1} and 1.7×10^{11} gS yr^{-1}, respectively. All estimates are summarized here in Table 3.

Although estimates of the magnitude of sulfur flux required to maintain background stratospheric aerosol levels remain highly uncertain, it is of some interest to compare the OCS stratospheric flux estimated from this study with those cited in Table 3. From Table 3, for example, it can be seen that the amount of required sulfur ranges from 4.3×10^{10} to 1.7×10^{11} gS yr^{-1}. Thus within our stated uncertainty the amount of sulfur from OCS oxidation (3.0×10^{10} gS yr^{-1}) overlaps only the lower end of the required background sulfur flux; and it is a factor of 2 to 5 times smaller than the more recently estimated values in Table 3.

Given the level of disagreement between our analysis and previous estimates and making the initial assumption that there are no large unidentified systematic errors in our OCS stratospheric database, we have further explored this disagreement in terms of two questions: (1) is it possible that previous evaluations have significantly overestimated the required sulfur flux? and (2), are there still missing sulfur sources that could contribute to the background aerosol? For example, recognizing that the secular trends in tropospheric OCS could not account for the stratospheric background aerosol growth, *Hofmann* [1991] has recently suggested that high-altitude aircraft emissions might represent a significant sulfur source. This author has estimated the magnitude of this stratospheric source at 4×10^{10} gS yr^{-1}. If true, it would be comparable to the OCS source in terms of stratospheric background sulfur. More work clearly needs to be done to quantify this source.

As related to question 1, at least two potential problems would appear to exist: (1) overestimating the total background sulfur aerosol level and (2) underestimating the lifetime of the "very fine particulate" sulfur aerosol. Recall that the sulfur aerosol lifetime values used by *Servant* [1986] and *Hofmann* [1990] were 14 months and 1 year, respectively. These values were inferred from lifetimes assigned to nuclear test debris and from volcanic aerosols injected into the lower stratosphere. By comparison, *Crutzen* [1976] used a lifetime of 2 years. Considering the persistence of the stratospheric aerosol layer, one may, in fact, speculate that the lifetime of the very fine particulate sulfur aerosol could be similar to that of the turnover time for stratospheric air. In this context, *Rosenlof and Holton* [1993] have recently estimated that the exchange time for air above 100 mbar and that below this level is approximately 2 years.

Concerning the level of stratospheric background aerosol, the issue here is: can one reliably define a baseline value for an environment that is periodically being disturbed by volcanic injections of sulfur? During *Hofmann's* [1990] 18 years of observations of stratospheric aerosol at Laramie, Wyoming (time period 1971 to 1989), only the years of 1979 and 1989 could be identified as background aerosol periods. By comparison, *Sedlacek et al.* [1983] reported measurements of stratospheric sulfate over the time period of 1971 to 1981; based on these measurements, the latter authors designated the time periods May 1973 to April 1974 and October 1978 to November 1979 as stratospheric background periods. For both investigations the long-term background level for the total observation period was defined by connecting the data measured during the two labeled "volcanic quiescent" periods. In neither case, however, was it possible to demonstrate that the aerosol or SO_4^{2-} levels observed during the quiescent

periods were in fact free of any significant volcanic influence. For example, if the stratospheric sulfur decay time (1/e time) of volcanic-originated sulfur is taken to be 1 year, it would take over 4.6 years to reach a sulfur level that was 1% of the maximum level. (Typically, the maximum aerosol level is not observed until several months after a major volcanic eruption).

Much related to the issue of background aerosol levels is the observation that even during the "volcanic quiescent" periods volcanic eruptions have been reported. In these cases there appears to be very little information available about the amount of material injected into the lower stratosphere other than it was not large enough to cause a major perturbation to the preexisting aerosol level. Considering the remoteness of many active volcanoes, it is also quite likely that still other eruptions have gone unrecorded in the scientific literature. Overall, therefore, there still remains a serious question whether a true background sulfur aerosol level (i.e., one largely uninfluenced by volcanic emissions) has as yet been observed.

7. Conclusions

The available observations of OCS during the past 15 years have shown that the concentration of OCS has been stable with an average tropospheric mixing ratio of 490 pptv and stratospheric mixing ratio of 380 pptv. From an analysis of atmospheric observations of OCS, the total amount of OCS in the atmosphere is estimated at 5.2 Tg, with 4.63 Tg in the troposphere and 0.57 Tg in the stratosphere. The global atmospheric lifetime of OCS is estimated to be 4.3 years.

We have calculated from our analyses that the stratospheric photochemical lifetime of OCS is 9.5 years; this is more than twice as long as its estimated global atmospheric lifetime of 4.3 years. These results indicate that most of the OCS transported into the stratosphere is returned to the troposphere and most likely is destroyed at the surface via loss to vegetation. Emissions of OCS into the troposphere do not appear to explain reported increases in the levels of stratospheric background sulfur aerosol.

The net flux of OCS into the stratosphere is estimated to be 5.6×10^{10} g OCS yr^{-1} or 3.0×10^{10} gS yr^{-1}, which is 5% of the total OCS source strength in the troposphere. On the basis of other investigators' estimates of the amount of sulfur required to sustain the stratospheric background sulfur aerosol, the OCS flux is too low to explain these estimates by factors of 2 to 5. Possible explanations for this include: (1) an overevaluation of the nonvolcanic background aerosol burden; (2) an underevaluation of the lifetime of stratospheric background aerosol; (3) the presence of other sulfur sources such as high-altitude aircraft emissions [*Hofmann*, 1991]; or (4) that the stratospheric OCS database used in our analysis is flawed with a substantial, yet unidentified, systematic error.

Clearly, new evaluations of the stratospheric background aerosol level and its lifetime are needed. Critical to any future analyses of defining the role of OCS in forming stratospheric sulfur aerosol will be the further elucidation of the volcanic component of the so-called "background" aerosol.

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