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Abstract

Solar absorption spectra recorded over a 24-year time span have been analyzed to retrieve average free tropospheric mixing ratios of carbonyl sulfide (OCS). The measurements were recorded with the Fourier transform spectrometer located in the U.S. National Solar Observatory McMath solar telescope facility on Kitt Peak (altitude 2.09 km, lat. 31.9°N, long. 111.6°W), southwest of Tucson, Arizona, and were obtained on 167 days between May 1978 and February 2002, typically at 0.01-cm⁻¹ spectral resolution. A best fit to the time series shows an average mixing ratio of 566 pptv (1 pptv = 10⁻¹² per unit volume) between 2.09 and 10 km, a small but statistically significant long-term decrease equal to $(-0.25 \pm 0.04)\% \text{ yr}^{-1}$, 1 sigma, and a seasonal variation with a summer maximum, a winter minimum, and a peak amplitude of $(1.3 \pm 0.4)\%$, 1 sigma, relative to the mean. Although a statistically significant decline and seasonal variation have been detected, both are exceedingly small. The present results confirm and extend earlier studies showing that the OCS free tropospheric abundance at northern midlatitudes has remained nearly constant over the last decades.

Keywords

absorption, solar, time, year, 24, ground, free, sulfide, carbonyl, infrared, trends, series, measurements, tropospheric, spectroscopic, GeoQuest

Disciplines

Medicine and Health Sciences | Social and Behavioral Sciences

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Ground-based infrared spectroscopic measurements of carbonyl sulfide: Free tropospheric trends from a 24-year time series of solar absorption measurements

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[1] Solar absorption spectra recorded over a 24-year time span have been analyzed to retrieve average free tropospheric mixing ratios of carbonyl sulfide (OCS). The measurements were recorded with the Fourier transform spectrometer located in the U.S. National Solar Observatory McMath solar telescope facility on Kitt Peak (altitude 2.09 km, lat. 31.9°N, long. 111.6°W), southwest of Tucson, Arizona, and were obtained on 167 days between May 1978 and February 2002, typically at 0.01-cm⁻¹ spectral resolution. A best fit to the time series shows an average mixing ratio of 566 pptv (1 pptv = 10⁻¹² per unit volume) between 2.09 and 10 km, a small but statistically significant long-term decrease equal to $(-0.25 \pm 0.04)\% \text{ yr}^{-1}$, 1 sigma, and a seasonal variation with a summer maximum, a winter minimum, and a peak amplitude of $(1.3 \pm 0.4)\%$, 1 sigma, relative to the mean. Although a statistically significant decline and seasonal variation have been detected, both are exceedingly small. The present results confirm and extend earlier studies showing that the OCS free tropospheric abundance at northern midlatitudes has remained nearly constant over the last decades. **INDEX TERMS:** 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 4857 Oceanography: Biological and Chemical: Pollution; **KEYWORDS:** long-term trends, carbonyl sulfide, infrared spectroscopy, troposphere, remote sensing

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1. Introduction

[2] Carbonyl sulfide (OCS) is the predominant sulfur-bearing gas in the remote troposphere with a global average concentration of about 500 parts per trillion by volume (pptv or 10⁻¹² ppv) [e.g., Sandalls and Penkett, 1977; Maroulis *et al.*, 1977; Torres *et al.*, 1980; Rasmussen *et al.*, 1982a, 1982b; Carroll, 1985; Johnson and Harrison, 1986; Johnson *et al.*, 1993; Mihalopoulos *et al.*, 1991; Thornton *et al.*, 1996; Notholt *et al.*, 2000] and a lifetime of about 4 years [Chin and Davis, 1995; Watts, 2000], though estimates from measurements and models range from 1–7 years. Despite a high tropospheric abundance, its low reactivity and limited

knowledge of the strengths of its sources and sinks have resulted in an uncertainty in its chemistry and long-term trend. Higher net emission fluxes than sinks in most models [e.g., Chin and Davis, 1993, 1995; Krellström, 1998] should lead to an increase in OCS tropospheric concentrations as a function of time. However, measured trends near zero have been reported from analyses of multiyear tropospheric and stratospheric mixing ratio [Chin and Davis, 1995; Bandy *et al.*, 1992; Mihalopoulos *et al.*, 1991; Thornton *et al.*, 1996], ground-based total column abundance [Rinsland *et al.*, 1992; Mahieu *et al.*, 1997; Griffith *et al.*, 1998], and lower stratospheric mixing ratio [Zander *et al.*, 1998; Rinsland *et al.*, 1996] data sets. The discrepancy may be explained by an enhanced role for atmospheric removal by soils [Castro and Galloway, 1991; Kuhn *et al.*, 1999; Kesselmeier *et al.*, 1999; Simmonds *et al.*, 1999] and a revision in the net influence by open and coastal oceans [Watts, 2000], though large uncertainty remains in both the OCS source and sink budgets.

[3] The upward flux of sulfur through the tropical tropopause to the stratosphere provides an in situ source of aerosol through its photooxidation to form SO₂, which is photochemically destroyed to form aerosol particles that contribute to the background stratospheric aerosol layer [Crutzen, 1976; World Meteorological Organization (WMO), 1986]. Estimates of the OCS flux from the tropical

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tropopause to the stratosphere vary widely [Klellström, 1998, section 3.4, Table VII], but the range suggests its contribution to the stratospheric aerosol loading is less than initially estimated [Crutzen, 1976]. As the stratospheric aerosol layer plays a significant role in the Earth's radiative balance and climate [e.g., Lacis *et al.*, 1992] and provides a surface for heterogeneous chemistry with an important influence on ozone [Hofmann and Solomon, 1989; Rodriguez *et al.*, 1994], changes in tropospheric OCS loading or vertical transport through the tropical tropopause could lead to changes in OCS concentrations and other key lower stratospheric species such as NO_2 and HNO_3 (see the results of Hofmann and Solomon [1989]) as a result of heterogeneous chemistry and sulfate aerosol production. Although an increase in the background stratospheric sulfuric acid aerosol mass at northern midlatitudes was reported [Hofmann and Rosen, 1980; Hofmann, 1990], the observed increase rate is too rapid to be due to OCS alone [Hofmann, 1991]. It was hypothesized that additional sources, particularly sulfur emitted by jet aircraft flying in the 11–12 km region, must be responsible for most of the increase [Hofmann, 1991]. However, a study comparing aerosol trends during 1979 and 1989–1991 concluded that the 1989–1991 period, though low, still contained a significant volcanic signature that could not be completely attributed to non-volcanic sources [Thomason *et al.*, 1997].

[4] In view of these studies, precise, long-term sets of tropospheric and stratospheric OCS measurements are needed for trend evaluation and to obtain insights into source and sink strengths and their geographic locations. As most previous studies were limited in time duration to about one decade, an extended time series might reveal a previously undetected trend or seasonal changes. Although a previous analysis suggested that the main sources of OCS are natural, with oceans, microbial processes in soils, and the conversion of CS_2 (also predominately natural) contributing about 30, 20, and 30%, respectively [e.g., Khalil and Rasmussen, 1984], these estimates are quite uncertain. Khalil and Rasmussen [1984] inferred a northern-to-southern interhemispheric ratio (IHR) of 1.05 from published OCS measurements [Torres *et al.*, 1980], and used this result to deduce that only about 25% of the OCS in the atmosphere results from direct and indirect (CS_2 to OCS conversion) anthropogenic activities. The largest anthropogenic source was attributed to emissions from biomass burning, about 10%, followed by releases from coal-fired power plants (about 4%), and automobiles, chemical industry, and sulfur recovery processes (about 3%) [Khalil and Rasmussen, 1984]. However, Turco *et al.* [1980] concluded that as much as 50% of OCS emissions might originate from anthropogenic emissions. Other estimates of the mean IHR are as high as 1.25 [Bingemer *et al.*, 1990], though most estimates are lower [Carroll, 1985; Johnson and Harrison, 1986; Mihalopoulos *et al.*, 1991; Griffith *et al.*, 1998; Xu *et al.*, 2001; Sturges *et al.*, 2001].

[5] In this investigation we report OCS average free tropospheric mixing ratios derived from the analysis of high-spectral resolution ground-based infrared solar absorption spectra recorded with the Fourier transform spectrometer operated at the U.S. National Solar Observatory facility on Kitt Peak in southern Arizona, a remote high-altitude station located in a semi-arid region with a sparse popula-

tion. The time series covers May 1978 to February 2002 and extends the results reported previously [Rinsland *et al.*, 1992] by more than a decade. With respect to the previous work which dealt with total vertical column abundances, the analysis has been performed with an improved retrieval algorithm and an updated set of spectroscopic parameters with the goal of providing a more accurate and extended time series of tropospheric abundances, long-term, trends and seasonal variations.

2. Observations and Analysis

[6] The Kitt Peak solar spectra were recorded with the custom-made folded Michelson Fourier transform spectrometer (FTS) [Brault, 1978] located in the McMath solar telescope complex of the U.S. National Solar Observatory (altitude 2.09 km, lat. 31.9°N , long. 111.6°W), southwest of Tucson, Arizona. Individual spectra were recorded with two InSb detectors and a KCl or CaF_2 beam splitter with a weak apodizing function, mostly at 0.01-cm^{-1} resolution, where the unapodized spectral resolution is defined as $1/2\Delta_{\text{max}}$ and Δ_{max} is the maximum optical path difference. Retrievals were derived by fitting 3 spectral regions in the OCS ν_3 fundamental band, which is 2 orders of magnitude stronger than any other OCS IR band [cf. Kagann, 1982]. The typical signal-to-noise in an individual spectrum is 2000. The number of measurement days per year ranged from 1 to 13 with more frequent observations obtained during the last five years as a consequence of an increased commitment to the Network for the Detection of Stratospheric Change (NDSC) [Kurylo, 1991] (available at <http://www.ndsc.ws>) of which Kitt Peak is an official complementary site.

2.1. Analysis Method

[7] The measurements were analyzed with version 3.8 of the SFIT2 algorithm [Pougatchev *et al.*, 1995; Rinsland *et al.*, 1998], based on a semi-empirical application [Parrish *et al.*, 1992; Connor *et al.*, 1995] of the optimal estimation method [Rodgers, 1990]. Volume mixing ratio profiles of one or more molecules are retrieved by simultaneously fitting one or more narrow spectral intervals (microwindows) in one or more solar spectra. Examples of its use have been reported in recent papers [Jones *et al.*, 2001; Rinsland *et al.*, 2000, 2001a, 2001b].

[8] Profiles were retrieved with a 29-layer forward model that extended from the surface to 100 km with a layer vertical thickness of less than 1 km in the lowest layer, 1 km between 3 and 14 km, increasing to 2 km in the lower stratosphere, and even thicker above. Refractive ray-tracing, air masses, and density-weighted effective pressures in each layer were performed with an algorithm based on the FSCATM program [Gallery *et al.*, 1983] modified and updated for ground-based retrievals from NDSC stations with a set of a priori profiles consistent with typical recent measurements [Meier *et al.*, 2002].

[9] The stratospheric portion of the a priori OCS mixing ratio profile was an average of ATMOS (Atmospheric Trace Molecule Spectroscopy) version 3 measurements recorded during the final November 1994 mission between latitudes of 22°N to 42°N [Irion *et al.*, 2002]; it was extended below 13.5 km assuming a constant volume mixing ratio of 495 pptv based on the mean of measurements of background

Table 1. Microwindows, Primary Target Lines, Principal Interferences, and OCS Spectral Parameters Adopted in the Analysis^a

Microwindow	Interfering Molecules	OCS Line Position	Spectroscopic Assignment	Intensity	$\gamma(\text{air})$	E''	$n(\text{air})$
2045.30–2045.67	CO ₂ , O ₃ , solar CO	2045.578488	P(37)	7.058E-19	0.0876	285.1308	0.60
2051.18–2051.48	O ₃ , CO ₂ , H ₂ O	2051.331394	P(25)	1.008E-18	0.0919	131.8385	0.82
2055.64–2055.96	solar CO, O ₃ , CO ₂	2055.860551	P(15)	9.075E-19	0.0964	48.6831	0.88

^aStandard HITRAN database units [Rothman *et al.*, 1998, Table 3]. Positions and lower state energies (E'') are in cm^{-1} , intensity are $\text{cm}^{-1}/(\text{molecule cm}^{-2})$ at 296 K, air-broadening coefficients $\gamma(\text{air})$ are in $\text{cm}^{-1}\text{atm}^{-1}$ at 296 K, and $n(\text{air})$, the coefficient of the temperature dependence of the air-broadening coefficient is dimensionless. All target OCS lines are in the ν_3 vibrational-rotational band.

marine air in the tropical north Pacific in September–October 1991 covering 0–40°N latitude [Thornton *et al.*, 1996]. The assumption of a constant tropospheric mixing ratio is consistent with previous measurements [e.g., Rasmussen *et al.*, 1982b, Figure 2] and its long tropospheric lifetime. A priori vertical profiles of other gases were taken mostly from reference profiles, as tabulated by [Meier *et al.*, 2002].

[10] Temperature profiles assumed in the analysis were daily mean compilations performed by the National Centers for Environmental Prediction (NCEP) for the location of Kitt Peak and the measurement dates. They were smoothly connected to the *U.S. Standard Atmosphere* [1976] above 65 km.

[11] Table 1 lists the spectral ranges and retrieval parameters for the three microwindows fitted simultaneously in the analysis. Retrievals were performed from solar spectra recorded at astronomical zenith angle of 85° or less. The OCS mixing ratio uncertainty normalized to the a priori value was assumed to increase with altitude from 0.15 near the surface to 1.5 in the stratosphere and above. The vertical profile of O₃ was also retrieved from the spectra. The OCS covariance matrix was assumed diagonal. Total columns of H₂O and CO₂ were both retrieved by scaling the a priori profile of each molecule by a single factor. In addition, 4 parameters were adjusted to model the absorption by solar

CO lines [Rinsland *et al.*, 1998, section 3.2.2], which is important for the present investigation because of the strong absorption by solar CO in two of the 3 microwindows used here.

2.2. Spectroscopic Parameters

[12] Spectroscopic parameters adopted in the present study originated from several sources. Parameters for H₂O were taken from HITRAN 2001 (available from <http://www.hitran.com>). The bands of O₃ at 4.7 μm are about one third as strong as those at 10 μm and hence are important absorbers, with significant absorption by the rare O₃ isotopes in the regions used to retrieve OCS [Arlander *et al.*, 1994; Goldman *et al.*, 1998, 2000, 2002]. Line parameters for the $\nu_1 + \nu_3$ bands of $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ [Flaud *et al.*, 1994] and $^{16}\text{O}^{17}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{16}\text{O}^{17}\text{O}$ [Perrin *et al.*, 2001] were included in the database; absorptions by the latter two isotopes are weak but observable in some regions of high spectral resolution balloon-borne and ground-based infrared atmospheric spectra [Goldman *et al.*, 2002]. Spectral parameters for OCS from HITRAN 2000 were adopted with a total of 5 isotopic species and additional hot bands in the 5- μm region as compared to earlier lists [Goldman *et al.*, 2000]. The air-broadening coefficients for OCS at 296 K are based on a fit to the measurements in Table II of Bouanich *et al.* [1987]. The temperature dependence of the air-broadening

Figure 1. Volume mixing ratio (VMR) averaging kernels for merged layers from 2.09–10 km and 10–100 km altitude vs. height.

Figure 2. Simulation of the transmittance of solar CO, individual atmospheric molecules (O3666 = $^{16}\text{O}_3$, O3686 = $^{16}\text{O}^{18}\text{O}^{16}\text{O}$, O3668 = $^{16}\text{O}^{16}\text{O}^{18}\text{O}$) obtained with the a priori volume mixing ratio profiles, and a Kitt Peak solar spectrum (bottom trace) in the microwindow selected for fitting the OCS ν_3 band P(25) line at $2051.331394\text{ cm}^{-1}$ (upper panel) and the P(15) OCS line at $2055.860551\text{ cm}^{-1}$ (lower panels). Each spectrum has been normalized and offset vertically for clarity. The arrow beneath the atmospheric spectrum marks the location of the target OCS line. The measured spectrum was recorded at 0.01-cm^{-1} resolution and an astronomical zenith angle of 70.82° on the afternoon of 4 January 2000.

coefficients was taken from the HITRAN 2002 file without modification. The pressure-shift coefficient and its temperature dependence were assumed equal to zero for all OCS lines. Note that this band is sometimes labeled ν_1 rather than ν_3 [e.g., Wells *et al.*, 1990]. The spectroscopic parameters described above constitute a consistent set of the best currently available spectroscopic parameters for the target and interfering lines to be fitted in the selected microwindows. Solar CO lines were simulated with a single layer model assuming an effective temperature of 4500 K with adjustable parameters to fit the depths of the solar CO features [Rinsland *et al.*, 1998, section 3.1].

2.3. Retrieval Characterization

[13] Averaging kernels provide a direct assessment of the theoretical altitude sensitivity of the observations in the

absence of errors in the measurements and model parameters [Rodgers, 1990, section 4]. They are a function of the retrieval intervals selected, the spectral resolution of the observations, an assumed signal-to-noise ratio, and the selections of the retrieval parameters, such as the a priori profile and its covariance matrix.

[14] Averaging kernels for mixing ratio profile retrievals of 2.09–10 km and 10–100 km merged layers are plotted in Figure 1. The 10-km limit was selected to provide sampling of the free troposphere with only minor, infrequent contributions from stratospheric layers. The annual average tropopause altitude above Kitt Peak is 14 km [Rinsland *et al.*, 1998]. Daily average tropopause altitudes calculated from a $2.5^\circ \times 2.5^\circ$ NCEP analysis for 2000 and 2001 interpolated to the location of Kitt Peak indicate that the tropopause height is located between 7.6 and 17.5 km, but less than 2%

Table 2. Estimated OCS 2.09–10 km 1-Sigma Uncertainties for Daily Averages

Error Source	Uncertainty, %
<i>Random Errors</i>	
Temperature profile	1
Finite signal-to-noise	<1
Interfering atmospheric lines	2
Zenith angle uncertainty	2
Zero level offsets	<1
RSS total random error	3
<i>Systematic Errors</i>	
Spectroscopic parameters	5
A priori profile relative contribution	5
Forward model approximations	3
Instrument line shape function	<1
Zero transmittance offsets	<1
RSS total systematic error	8

of the occurrences during this two year period were below 10 km (S. Zhou, and A. Miller, NCEP, private communication, 2002).

[15] Calculations were performed for the typical spectral resolution of 0.01 cm^{-1} and the 3 microwindows listed in Table 1 assuming a signal-to-noise of 250. The latter value is lower than the typical signal-to-noise of the solar spectra to empirically account for errors in the spectroscopic database and imperfections in the forward model (e.g., modeling of solar CO absorption), consistent with the semi-empirical retrieval approach adopted in SFIT2. The mixing ratio averaging kernels for the two layers are broad with maximum sensitivity at 4.9 km for the lower layer, the focus of this investigation. Although there is significant stratospheric sensitivity, we limit the focus of this work to the evaluation of the free tropospheric trend and seasonal cycle.

[16] Molecule-by-molecule simulations of the transmittance by the principal absorbing species in two of the three selected microwindows are shown in Figure 2. The simulated transmission spectra of OCS and all interfering gases (offset vertically for clarity) are calculated for the spectral resolution and solar zenith angle of the Kitt Peak measurement shown in the lowest trace in each frame. An arrow beneath the measured spectrum marks the location of the target OCS line. Each absorber in the simulation is identified on the right vertical axis including solar CO. Absorption by $^{16}\text{O}^{16}\text{O}^{17}\text{O}$ and $^{16}\text{O}^{17}\text{O}^{16}\text{O}$ is negligible in both selected intervals, and therefore omitted. Positions and strengths of the features in the measured spectrum and those in the simulated spectra show close correspondence. Note that solar CO absorbs significantly in the bottom microwindow of Figure 2. Molecule-by-molecule simulations for the interval containing the P(37) OCS line have been displayed previously [Rinsland *et al.*, 1992, Figure 4].

[17] Table 2 lists the most important random and systematic sources of error and estimates of their contribution to the error budget for a typical spectrum. Values have been estimated as described previously [e.g., Rinsland *et al.*, 1998, section 6]. Random error has been reduced by averaging mixing ratios from the 4 layers below 10 km to obtain the 2.09–10 km mean mixing ratio and then calculate daily averages from all measurements. The two most important sources of systematic error are uncertainties in the

intensities and air-broadening coefficients of the target OCS lines, which are both estimated as 5%. Additional systematic sources of error are the uncertainty in the retrievals due to forward model approximations, estimated as 3% based on comparisons such as the one described by Goldman *et al.* [1999], and the bias from the a priori profile, 2%.

3. Results and Discussion

[18] Figure 3 displays fits to the 3 OCS microwindows from the same Kitt Peak spectrum shown in Figure 2, which is typical of the time series. The retrieved daily average volume mixing ratios as well as related fits versus time are displayed in Figure 4. The time series spans 24 years, and to our knowledge, it is the longest time period of near continuous OCS measurements reported to date. After excluding noisy spectra and weak absorption by the target lines [Rinsland *et al.*, 1998, Figure 9], the database contains 347 measurements on 167 days between May 1978 and February 2002.

[19] The time series of 2.09–10 km daily average mixing ratios were fitted with the expression

$$C_A = a_0 + a_1(t - t_0) + a_2 \cos(2\pi(t - t_0 - \varphi)), \quad (1)$$

where C_A is the daily average 2.09–10 km mixing ratio at time t , a_0 is the mean 2.09–10 km mixing ratio of the time series, a_1 is the trend, a_2 is the amplitude of the seasonal cycle, and φ is the phase corresponding to the seasonal maximum. The best fit to the 24-year time series shows a long-term 2.09–10 km volume mixing ratio trend of $(-1.41 \pm 0.25)\text{ pptv yr}^{-1}$ and a seasonal cycle with a peak amplitude of $(7.2 \pm 2.2)\text{ pptv}$ with φ equal to $(0.103 \pm 0.09\text{ yr})$, 1 sigma, relative to the first measurement in the time series in May 1978. Normalized to the mean mixing ratio of 566 pptv, the results indicate a statistically significant long-term decrease in the 2.09–10 km average mixing ratio OCS equal to $(-0.25 \pm 0.04)\%\text{ yr}^{-1}$, and a seasonal cycle amplitude of $(1.28 \pm 0.40)\%$ with a June maximum and a December minimum. The best fit long-term trend and seasonal cycle are both displayed in Figure 4.

[20] Sets of multi-year ground-based OCS total column measurements of from high spectral resolution solar absorption measurements were obtained from two northern hemisphere stations, Kitt Peak and the International Scientific Station of the Jungfraujoch, (ISSJ) (46.5°N , 8.0°E , 3.58 km altitude) [Rinsland *et al.*, 1992; Mahieu *et al.*, 1997] and from two midlatitude southern hemisphere stations, Lauder, New Zealand (45.0°S , 169.7°E , 0.37 km altitude) and Wollongong, Australia (34.45°S , 150.88°E , 30 m altitude) [Griffith *et al.*, 1998]. Although a statistically significant decline of $(0.3 \pm 0.1)\%\text{ yr}^{-1}$ was found from a fit to the 1984–1995 ISSJ measurements, large variability led to the conclusion that no unambiguous evidence existed for either a seasonal variation or a long-term trend above that site. The southern hemisphere studies also found no statistically significant long-term OCS total column trend over time periods as long as 4 years. However, after correcting for the seasonal variation in the tropopause height above Wollongong, a statistically significant 12% seasonal variation was identified with a late summer/early autumn maximum (March), which was tentatively attributed to the effects of

Figure 3. Sample fitting results for the OCS P(37) line at $2045.578488\text{ cm}^{-1}$ (top), the P(25) line at $2051.331394\text{ cm}^{-1}$ (middle), and the P(15) line at $2055.860551\text{ cm}^{-1}$ (bottom). The measured spectrum was recorded at an astronomical zenith angle of 70.82° on the afternoon of 4 January 2000 (same spectrum as in Figure 2) and is displayed in the lower panel with a vertical arrow marking the location of the target OCS lines and the strongest interferences. The upper panel shows the residuals (measured minus simulated values) on an expanded vertical scale.

lower tropospheric air transported from the warm nearby ocean by the prevailing winds towards the station [Griffith *et al.*, 1998, Figure 5]. More recent solar absorption measurements remain consistent with the earlier Wollongong observations and this interpretation (D. W. T. Griffith, unpublished results, 2002).

[21] The relative amplitude of the seasonal variation in the present study is less than reported previously from sites distant from strong sources and sinks. The seasonal variation found from the Kitt Peak time series fit may result from a residual influence of tropopause height changes, as the tropospheric kernel is broad (Figure 1), as already mentioned, or real variations in source or sink strengths. The summer maximum and winter minimum obtained from the time series fit is consistent with that expected from uptake by soils, now recognized as a strong OCS sink. No significant seasonal changes in the OCS total column above 12 km were found from aircraft solar absorption measure-

ments recorded during aircraft flights between 2°N to 48°N latitude during summer and winter time periods in 1978, [Mankin *et al.*, 1979], though additional measurements are needed to confirm this conclusion in view of their limited spatial, temporal and seasonal sampling.

[22] Long-term firm air measurements in an Arctic location (72°N , 82°W , 1800m altitude) and two Antarctic stations (77°S , 10°W , 2300m altitude and 75°S , 123°E , 3240m altitude) have been reported recently [Sturges *et al.*, 2001]. The air samples were analyzed by gas chromatography-mass spectrometry to derive OCS mixing ratios spanning atmospheric composition from the early through the mid-20th century up to the time of the sampling (1998/1999). Although the concentrations in Antarctica were found to be almost constant with time, the Arctic measurements appear to have declined over the last 10 years by $8 \pm 5\%$, leading to a present interhemispheric ratio (IHR) close to unity. The authors hypothesized that the decline origi-

Figure 4. Daily average 2.09–10 km mean mixing ratios of carbonyl sulfide above Kitt Peak (plus symbols) plotted versus measurement date. A solid line and curve show fits to the time series for the long-term trend and seasonal cycle with equation 1, respectively.

nated from a reduction in CS₂ emissions by the viscose-rayon industry, its principal anthropogenic source, though a shift of industrialized CS₂ emissions from Europe to Asia was also cited as a possible cause of the recent decline. An unpublished time series of OCS total columns from ground-based solar spectra obtained by one of us (J. Notholt) between 1993 and 2001 at the NDSC station in Ny Ålesund (78.9°N, 11.9°E, 10/20 m altitude) in Spitzbergen between days 140 and 270 of each year (selected to avoid time periods with perturbed chemistry and transport) also show evidence for a small OCS long-term total column decline with time. The Kitt Peak measurements are recorded sufficiently far south that no instances of perturbed winter-spring stratospheric chemistry are observed (e.g., elevated winter/spring ClONO₂).

[23] As mentioned earlier [Rinsland *et al.*, 1992, section 3], it is reasonable to assume the maximum seasonal change in the free tropospheric OCS concentration is no more than a few percent in the absence of strong local sources or sinks as the lifetime of OCS is several years. The present results are consistent with that limit.

[24] Our measurements over a 24-year time span place a strong constraint on the long-term OCS growth rate with a higher vertical resolution than the previous solar absorption measurements, which only reported total columns. Our mean 2.09–10 km mixing ratio of 566 pptv is slightly higher than most northern hemisphere measurements [Sandalls and Penkett, 1977; Maroulis *et al.*, 1977; Torres *et al.*, 1980; Rasmussen *et al.*, 1982a, 1982b; Carroll, 1985; Johnson and Harrison, 1986; Sturges *et al.*, 2001], but consistent within our estimated 6% total systematic error.

4. Summary and Conclusions

[25] A 24-year time series of solar absorption spectra recorded typically at a spectral resolution of 0.01 cm⁻¹ has been analyzed to retrieve carbonyl sulfide average free tropospheric mixing ratios for the 2.09–10 km altitude

region. The time series was recorded from the U.S. National Solar Observatory and analyzed with the SFIT2 algorithm based on a semi-empirical implementation of the Rodgers [1990] optimal estimation method. A fit to the 167 daily averages from 347 measurements between May 1978 to February 2002 yields a mean mixing ratio of 566 pptv, a long-term trend of $(-0.25 \pm 0.04)\% \text{ yr}^{-1}$, 1 sigma, superimposed on a seasonal cycle with a peak amplitude of $(1.28 \pm 0.40)\%$, 1 sigma, relative to the mean, with a June maximum and a December minimum. The present database reduces the impact of seasonal changes in the tropopause height by restricting the measurements to 2.09 to 10 km, significantly below the 14 km mean tropopause height above Kitt Peak. The results are consistent with previous shorter duration studies that found no significant long-term change in the free tropospheric concentration of OCS at northern midlatitudes, though the small statistically significant decline detected by fitting the extended time span is consistent with other recently reported long-term time series.

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