Global distributions of carbonyl sulfide in the upper troposphere and stratosphere

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[1] We present the first upper tropospheric and stratospheric global distributions of carbonyl sulfide (OCS) observed from space using solar occultation measurements made by the Atmospheric Chemistry Experiment (ACE) satellite Fourier transform spectrometer during 2004–2006. We observe high OCS mixing ratios (>400 pptv) within the tropical stratosphere owing to convected tropospheric air. Stratospheric mixing ratios decrease more rapidly with altitude moving away from the Equator, creating a poleward gradient. Elevated OCS concentrations observed at low southern latitudes are consistent with a significant pyrogenic source. Using coincident ACE measurements of CFC-11 and CFC-12 we determine a global OCS stratospheric lifetime of 64 ± 21 years corresponding to a stratospheric sink of $63-124$ Gg OCS yr^{-1}. **Citation:** Barkley, M. P., P. I. Palmer, C. D. Boone, P. F. Bernath, and P. Suntharalingam (2008), Global distributions of carbonyl sulfide in the upper troposphere and stratosphere, *Geophys. Res. Lett.*, *35*, L14810, doi:10.1029/2008GL034270.

1. Introduction

[2] Carbonyl sulfide (OCS) is the most abundant sulfur-containing gas in the atmosphere. Owing to its long lifetime ($\sim 2-6$ years) OCS is transported to the stratosphere where it is either photodissociated by UV radiation or reacts with atomic oxygen or OH, to ultimately form sulfate aerosol particles [*Crutzen*, 1976] that influence the Earth's radiation budget [*Turco et al.*, 1980] and stratospheric ozone chemistry [*Solomon et al.*, 1993]. The oceans are the main source of OCS via direct outgassing and from the oxidation of emitted precursor gases carbon disulfide (CS_2) and dimethyl sulfide (DMS) [*Kettle et al.*, 2002]. Direct and indirect (CS_2 oxidation) anthropogenic emissions and biomass burning are other significant sources. Uptake by vegetation and soils, and photochemical losses are the main OCS sinks. Recent work has highlighted the potential of atmospheric OCS measurements to constrain Gross Primary Production [*Montzka et al.*, 2007]. However, whilst the OCS mass budget is balanced within (large) uncertainties [*Watts*, 2000; *Kettle et al.*, 2002], modelling studies (P. Suntharalingam et

al., Global 3-D model analysis of the seasonal cycle of atmospheric carbonyl sulfide: Implications for terrestrial vegetation uptake, submitted to *Geophys. Res. Lett.*, 2007) and analysis of global wide OCS measurements [*Montzka et al.*, 2007] demonstrate our incomplete understanding of individual source and sink strengths.

[3] Despite widespread tropospheric OCS observations [*Notholt et al.*, 2006; *Montzka et al.*, 2007], stratospheric OCS measurements are still sparse and limited to a few studies [e.g., *Leifer*, 1989; *Engel and Schmidt*, 1994]. Here we use OCS profile measurements made by the Atmospheric Chemistry Experiment (ACE) satellite Fourier transform spectrometer (FTS) to investigate OCS in the upper troposphere (UT) and stratosphere. We present the first global OCS distributions observed from space and use concurrent measurements of chlorofluorocarbons (CFCs) to estimate the stratospheric lifetime of OCS.

2. OCS Vertical Profile Retrievals From ACE

[4] The ACE satellite mission [*Bernath et al.*, 2005], launched in August 2003, was designed to investigate atmospheric composition in the UT and stratosphere. The main instrument aboard ACE is a high spectral resolution (0.02 cm^{-1}) infrared FTS, covering the $750-4400$ cm^{-1} spectral range. ACE operates in a low Earth circular orbit performing a maximum of 30 solar occultation measurements per day, sampling the atmosphere at $\sim 2-6$ km intervals from about 150 km down to the cloud tops. Vertical trace gas profiles of more than twenty species are retrieved (along with temperature and pressure) from recorded transmittance spectra using a non-linear least squares global-fit approach [*Boone et al.*, 2005]. The OCS results used here are "research products", improving on the ACE-FTS version 2.2 OCS retrievals by using more micro-windows and pushing the retrievals to higher altitude. A total of twelve microwindows in the range $2036-2056$ cm^{-1} are employed. Spectroscopic line parameters are taken from the HITRAN 2004 database [*Rothman et al.*, 2005]. The eight interferences retrieved simultaneously are OCS isotopologue 2 (using the HITRAN labelling scheme that numbers isotopologues in terms of decreasing abundance), O_3 isotopologues 1 and 3, CO_2 isotopologues 1, 2, 3, and 4, and H_2O, with a separate volume mixing ratio profile retrieved for each isotopologue. The retrieval altitude range varies with latitude, extending from 8 to 31 km at the Equator and 6 to 23 km at the poles. We use ACE data between February 2004 and December 2006 and perform a quadratic interpolation from the observed tangent heights to a uniform 0.5 km vertical grid, from $6-30$ km. We filter the

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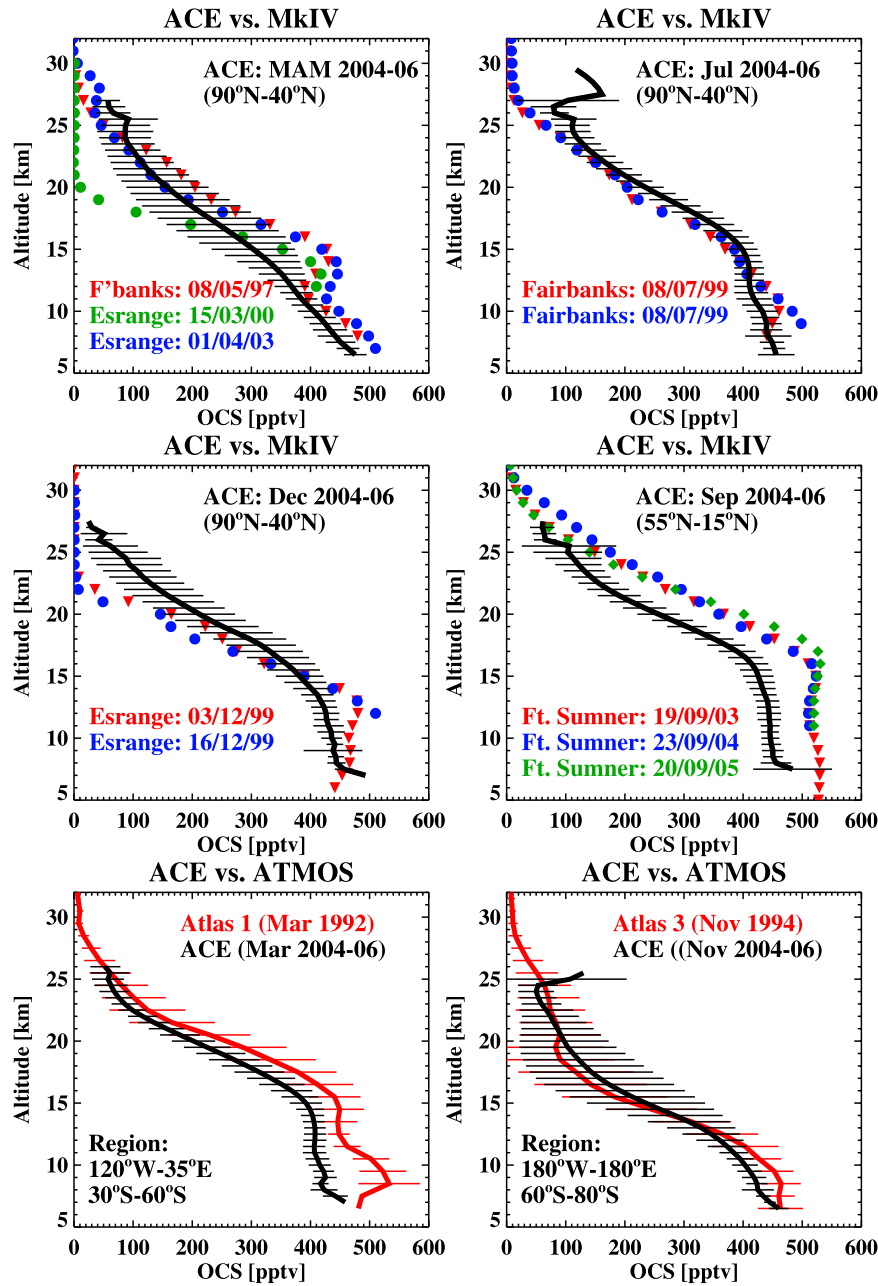[5]School of Engineering and Applied Science, Harvard University, Cambridge, Massachusetts, USA.

Figure 1. Comparison of ACE data with the MkIV OCS measurements. As most of the MkIV measurement times are outside the operational period of ACE, we assemble either a monthly or trimonthly zonal mean ACE profile (averaged over 2004–06) from all observations occurring within ±20° latitude of each site and compare this to data from individual balloon flights over Fairbanks (Alaska), Esrange (Sweden) and Fort Sumner (New Mexico). The bottom two plots show a comparison of ACE OCS profiles (black) with ATMOS OCS measurements (red) from the Atlas-1 (March 1992) and Atlas-3 (November 1994) missions [*Kaye and Miller*, 1996]. One standard deviation uncertainties are shown for the ACE and ATMOS profiles.

measurements discarding anomalous data, reflecting our focus on the mean OCS distribution.

3. Comparison to Other OCS Measurements

[5] Figure 1 shows spatially and temporally averaged ACE OCS profiles compared with OCS occultation measurements made by the balloon-borne MkIV [*Toon et al.*, 1999] and the Shuttle-borne ATMOS [*Farmer et al.*, 1987]

interferometers. In general there is good agreement with the balloon data, with most of the MkIV measurements falling within ±1-σ standard deviation of each ACE profile. The only exception is over Fort Sumner where the ACE profile has a negative bias with respect to the balloon data. However, very few ACE measurements (<20) in the vicinity of New Mexico were used to assemble this mean profile and may account for this difference. The better agreement between the ACE and MkIV OCS profiles at higher

Table 1. Mean OCS Upper Tropospheric and Stratospheric Volume Mixing Ratios and Stratospheric Lifetime[a]

Latitudes	Mean ATMOS VMR [/pptv]		Mean ACE VMR [/pptv]		Lifetime [/yr][c]	
	Troposphere	Stratosphere[b]	Troposphere	Stratosphere[b]	CFC-11	CFC-12
90°N-60°N	-	-	438 ± 29	329 ± 38	56 ± 24	76 ± 32
60°N-20°N	467 ± 36	370 ± 27	438 ± 35	338 ± 43	55 ± 26	67 ± 31
20°N-20°S	470 ± 26	389 ± 19	438 ± 37	356 ± 27	-	-
20°S-60°S	508 ± 32	365 ± 26	419 ± 29	317 ± 46	56 ± 27	70 ± 33
60°S-90°S	463 ± 38	333 ± 19	435 ± 19	310 ± 37	53 ± 23	81 ± 34
Global	477 ± 17	364 ± 12	433 ± 14	330 ± 17	55 ± 14	74 ± 23

[a]Data from all Atlas shuttle missions are used [*Kaye and Miller*, 1996]; ACE data is averaged over 2004–2006. Uncertainties are the one standard deviation of the mean. Global values are the mean and standard error of the latitudinal averages.

[b]Calculated using profiles that have at least 50% of their expected vertical coverage of the stratosphere.

[c]The lifetime is calculated using equation 2 and ACE data with CFC-11 and CFC-12 as reference gases. The estimated error is calculated from the uncertainty in (a) the gradient of the linear correlation, (b) the tropospheric OCS and CFC mixing ratios, and (c) the CFC lifetime. A tropospheric OCS mixing ratio of 500 pptv ±20% is assumed; CFC data is taken from *Clerbaux et al.* [2007] with a 10% error assigned to the tropospheric CFC mixing ratios.

latitudes most likely reflects ACE's greater sampling density. Figure 1 also shows that ACE and ATMOS data (over common SH regions and months but different years) are within one standard deviation of each other, except below 13.5 km during March.

[6] To distinguish between tropospheric and stratospheric OCS we use the average (2004–2006) tropopause height from the NASA Goddard Earth Observing System (GEOS-4) model. The mean tropospheric mixing ratio is calculated as a simple arithmetic mean and the mean stratospheric mixing ratio χ_s is given by

$$\chi_s = \frac{\sum \chi(z)N(z)\Delta z}{\sum N(z)\Delta z} \qquad (1)$$

where $\chi(z)$ and $N(z)$ are the OCS mixing ratio and air density (molecules cm^{-3}) at altitude z respectively, and Δz is the altitude bin (= 0.5 km) [*Chin and Davis*, 1995]. Excluding data within the tropics we find that OCS mixing ratios in the UT and stratosphere are about 11 pptv and 20 pptv higher in the NH than in the SH, respectively (Table 1); the tropical stratospheric mean is significantly higher (>18 pptv) than at other latitudes.

[7] Globally, the tropospheric and stratospheric means are 433 pptv and 330 pptv, slightly lower than previous measurements of free tropospheric mixing ratios of 480–520 pptv [*Notholt et al.*, 2006] and stratospheric mixing ratios of 380 pptv [*Chin and Davis*, 1995]. Analysis of the complete ATMOS dataset yields tropospheric and stratospheric means of 463–508 pptv and 333–389 pptv, about 10% more than ACE. Significant changes in OCS spectroscopic constants between the time of the ATMOS and ACE missions are the origin of (at least most of) the observed differences. For the strongest band in the 5 μm region, intensities in the HITRAN 2004 line list (used in the ACE-FTS retrievals) are more than 5% larger than in the ATMOS line list [*Brown et al.*, 1995]. There is also a weaker OCS band in this region (with intensities about a factor of 10 smaller than in the strongest band), and for this band, the intensities in HITRAN 2004 are more than 15% larger than in the ATMOS line list.

4. Global Distributions and Mean Vertical Profiles

[8] Figure 2 shows the first global OCS distributions observed from space retrieved by the ACE instrument. Elevated OCS (>400 pptv) is generally found throughout the UT and lower stratosphere at low latitudes but decreases with increasing altitude at high latitudes. This distinct latitudinal gradient is more evident in the seasonal zonal distributions (Figure 3) which show relatively high OCS mixing ratios at the Equator extending up to 20–25 km creating a thin ridge of 350–375 pptv that is longitudinally uniform. These features are determined largely by global atmospheric transport, consistent with OCS rich tropospheric air penetrating the stratosphere via deep tropical convection where it is photochemically destroyed as it is transported polewards by the Brewer-Dobson circulation.

[9] Figure 3 shows enhanced OCS at 10–15 km between 0°–30°S particularly during September–November (SON) that correlates with elevated measurements of biomass burning tracers carbon monoxide and hydrogen cyanide, suggesting a strong SH biomass burning source. However, ACE does not observe the high OCS mixing ratios (>600 pptv) attributed to tropical biomass burning previously reported [*Notholt et al.*, 2003], which may reflect year-to-year variability of tropical burning. The ACE observations do not support previous model studies that suggest a large oceanic source of OCS at high SH latitudes [*Kettle et al.*, 2002]. Figure 2 also shows high mixing ratios over the North Pacific and the western US during March–May (MAM) and June–August (JJA). In situ aircraft measurements made over this region during spring and summer also report enhanced OCS which is attributed to anthropogenic OCS originating from Asia [*Blake et al.*, 2004, 2008].

[10] Figure 4 shows the most significant OCS seasonal variations occurs at high NH latitudes where during summer and autumn months the OCS profile is relatively uniform from the UT to 15 km. In contrast, during winter and spring months the decrease with altitude from the UT to the stratosphere is much sharper and corresponding mixing ratios are about 50–100 pptv smaller. At corresponding latitudes in the SH there is an apparent 6 month phase shift but with the greatest differences occurring at 15–20 km instead, suggesting similar seasonal processes (e.g., atmospheric transport) are influencing the stratospheric OCS distributions in each hemisphere. Similar distributions are also observed for other species that are significantly influenced by atmospheric transport [*Grooß and Russell*, 2005]. At mid-latitudes the seasonal differences are smaller and within the tropics they are negligible. Overall, the mean global profile is most similar to that over 60°N–90°N
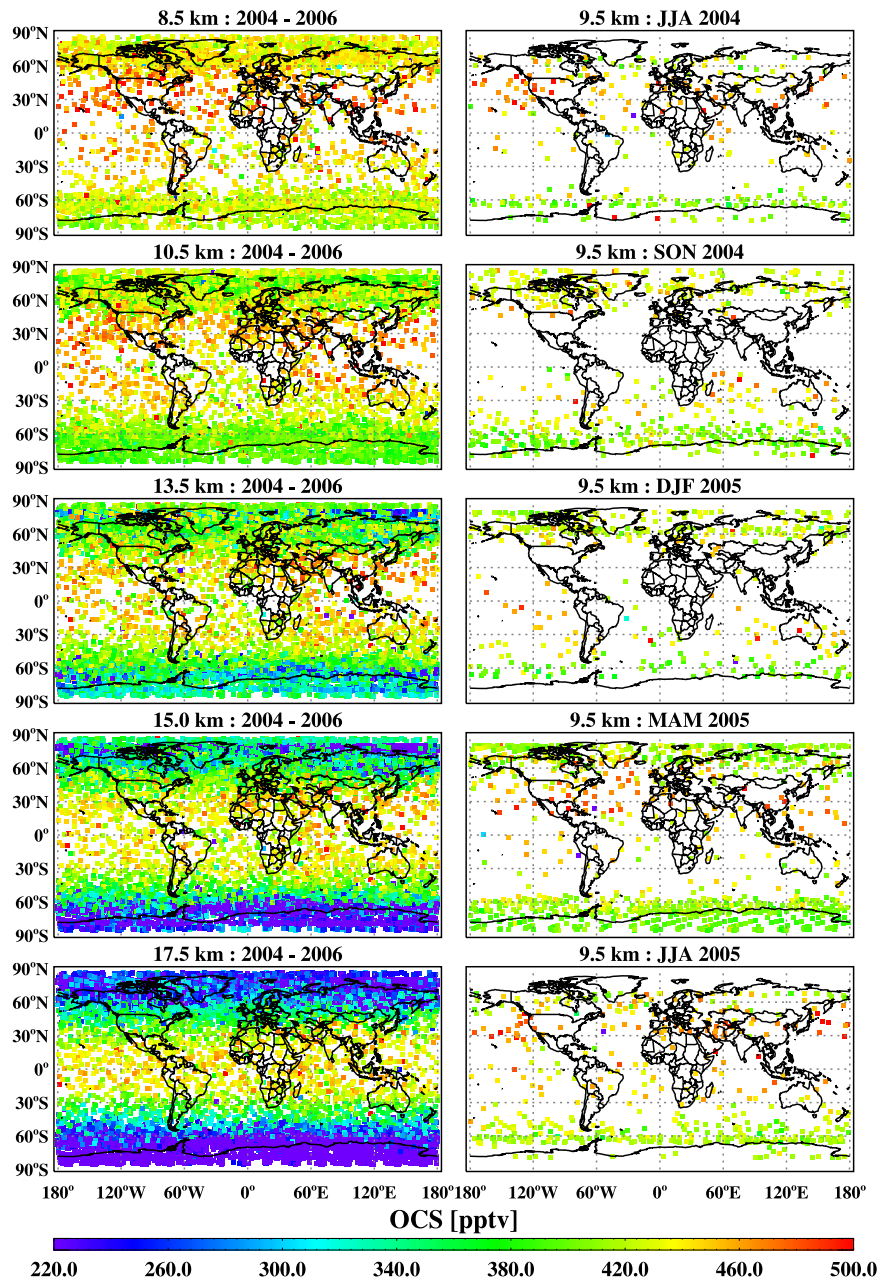
Figure 2. (left) OCS mixing ratios [pptv] at selected altitudes observed by the ACE FTS between February 2004 and December 2006. (right) Seasonal OCS distributions at 9.5 km altitude observed between July 2004 and August 2005.

highlighting the importance of high latitude NH sources/sinks on the global OCS distribution [*Montzka et al.*, 2007].

5. OCS Stratospheric Lifetime

[11] Long-lived stratospheric tracer gases whose lifetimes are long compared to horizontal and vertical transport timescales are linearly correlated in the lower stratosphere, and providing the lifetime of one of the species is known the other can be calculated, assuming tropospheric trends have negligible effect on the slope of the linear correlation [*Plumb and Ko*, 1992]. We use coincident ACE observa-

tions of CFC-11 and CFC-12 to derive the stratospheric lifetime of OCS [*Plumb and Ko*, 1992]:

$$\frac{\tau_1}{\tau_2} = \frac{d\sigma_2}{d\sigma_1}\frac{\sigma_1}{\sigma_2}, \tag{2}$$

where τ_1 and τ_2 are the lifetimes of gas 1 (OCS) and gas 2 (CFC-11 or CFC-12) respectively, and σ_1 and σ_2 are the mixing ratios of OCS and CFC-11 (or CFC-12) within the troposphere and $d\sigma_2/d\sigma_1$ is the gradient of the linear correlation between gas 1 and gas 2. We use CFC-11 and CFC-12 lifetimes of 45 ± 10 and 100 ± 20 years, and
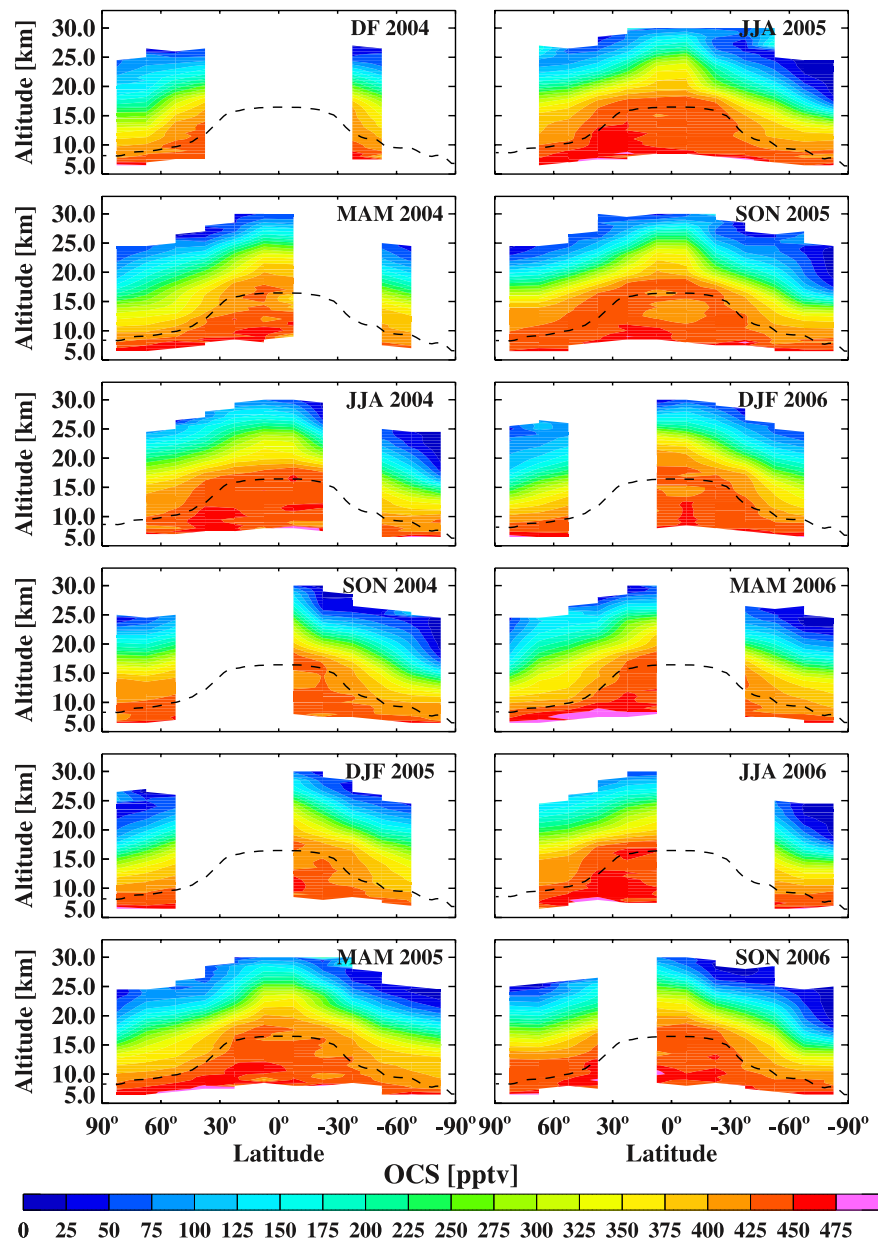
Figure 3. Seasonal zonal distributions observed by ACE during February 2004 and December 2006. The ACE OCS profiles have been grouped together in 15° latitude bins; only bins with a minimum of 10 profiles are plotted. The black dashed line is the average tropopause height from the GEOS-4 model.
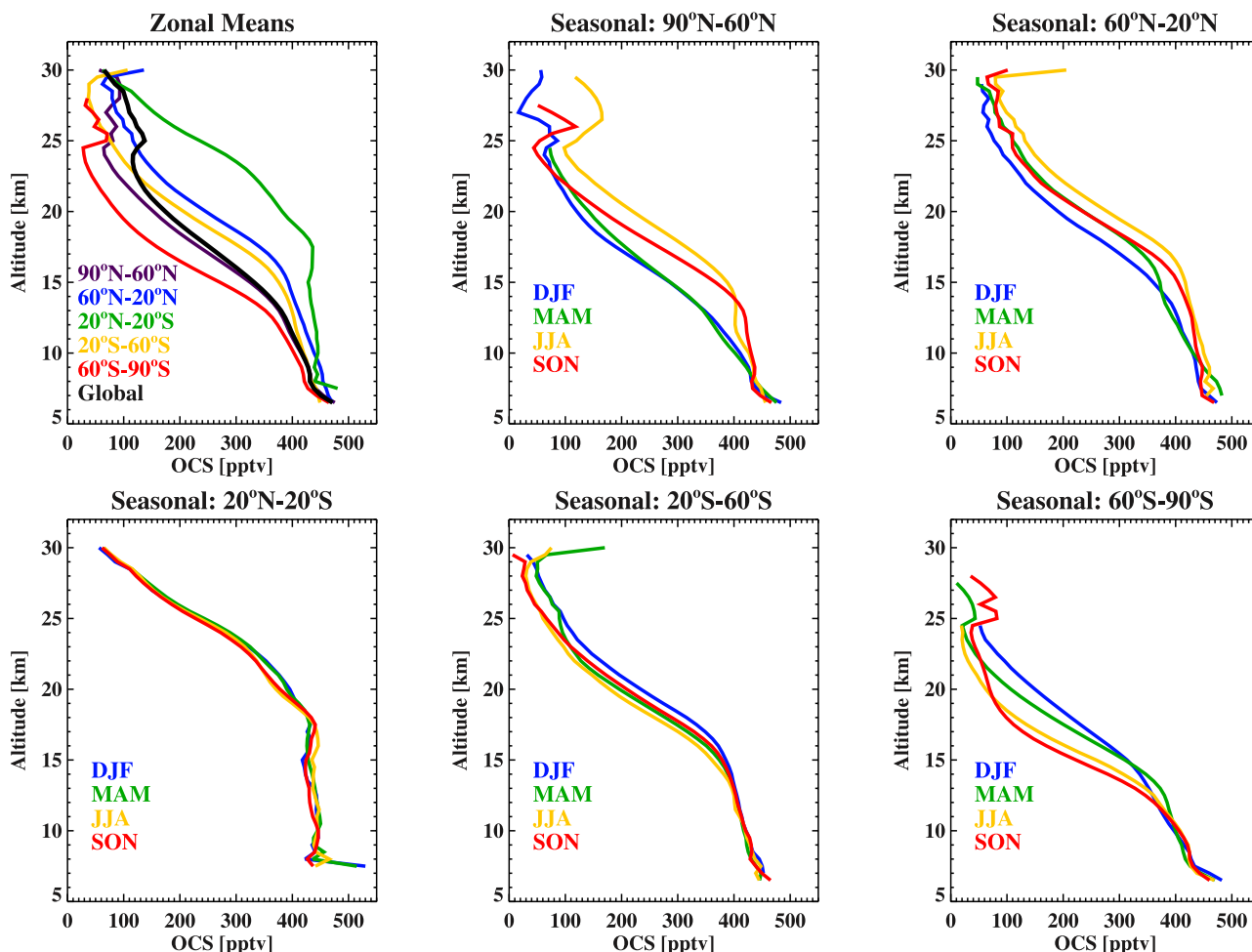
Figure 4. Mean latitudinal OCS profiles measured by ACE interpolated onto a 0.5 km vertical grid and averaged from February 2004 to December 2006.

tropospheric mixing ratios of 254 pptv and 540 pptv, respectively [*Clerbaux et al.*, 2007], and consider only ACE data between the tropopause and 20 km (the upper altitude limit of CFC-12 measurements). We calculate a global OCS lifetime of 55 ± 14 years using CFC-11, and 74 ± 23 years using CFC-12 (Table 1). Combining the lifetimes derived from both gases over all latitudes yields a best estimate of the OCS lifetime of 64 ± 21 years, consistent with a previous estimate of 69 ± 28 years determined from NH balloon measurements [*Engel and Schmidt*, 1994].

[12] The atmospheric burden of a species divided by its stratospheric lifetime yields its stratospheric sink. Assuming a tropospheric OCS mixing ratio of 500 pptv and a total atmospheric mass of 5.148×10^{21} g [*Trenberth and Smith*, 2005], the total mass of OCS in the atmosphere is 5.34×10^{12} g. Using the extremes of our estimate for the OCS stratospheric lifetime, this corresponds to an OCS sink of $63-124$ Gg OCS yr^{-1} ($34-66$ Gg S yr^{-1}). Since the only OCS source in the stratosphere is from tropospheric transport and OCS mixing ratios show no discernible trend, this sink should balance the net OCS flux from the troposphere. Several studies have calculated the tropospheric influx of sulfur required to sustain the stratospheric sulfate aerosol layer to be $30-170$ Gg S yr^{-1} [*Chin and Davis*, 1995, and

references therein]; our estimate of the tropospheric sulfur flux (in the form of OCS) of $34-66$ Gg S yr^{-1} is at the lower end of this range.

References

Bernath, P. F., et al. (2005), Atmospheric Chemistry Experiment (ACE): Mission overview, *Geophys. Res. Lett.*, *32*, L15S01, doi:10.1029/2005GL022386.

Blake, N. J., et al. (2004), Carbonyl sulfide and carbon disulfide: Large-scale distributions over the western Pacific and emissions from Asia during TRACE-P, *J. Geophys. Res.*, *109*, D15S05, doi:10.1029/2003JD004259.

Blake, N. J., et al. (2008), Carbonyl sulfide (OCS): Large scale distributions over North America during INTEX-NA and relationship to CO_2, *J. Geophys. Res.*, *113*, D09S90, doi:10.1029/2007JD009163.

Boone, C. D., R. Nassar, K. A. Walker, Y. Rochon, S. D. McLeod, C. P. Rinsland, and P. F. Bernath (2005), Retrievals for the Atmospheric Chemistry Experiment Fourier-transform spectrometer, *Appl. Opt.*, *44*(33), 7218–7231.

Brown, L. R., M. R. Gunson, R. A. Toth, F. W. Irion, C. P. Rinsland, and A. Goldman (1995), The 1995 Atmospheric Trace Molecule Spectroscopy (ATMOS) linelist, *Appl. Opt.*, *35*(16), 2828–2848.

Chin, M., and D. D. Davis (1995), A reanalysis of carbonyl sulfide as a source of stratospheric background sulfur aerosol, *J. Geophys. Res.*, *100*, 8993–9005.

Clerbaux, C., et al. (2007), Long-lived compounds, in *Scientific Assessment of Ozone Depletion: 2006, Rep. 50*, edited by C. A. Ennis, chap. 1, pp. 7–27, World Meteorol. Organ., Geneva, Switzerland.

Crutzen, P. J. (1976), The possible importance of OCS for the sulfate layer of the stratosphere, *Geophys. Res. Lett.*, *3*, 73–76.

Engel, A., and U. Schmidt (1994), Vertical profile measurements of carbonyl sulfide in the stratosphere, *Geophys. Res. Lett.*, *21*, 2219–2222.

Farmer, C. B., O. F. Raper, and F. G. O'Callaghan (1987), Final report on the first flight of the ATMOS instrument during the Spacelab 3 mission, April 29 through May 6, 1985, *JPL Publ.*, *87-32*.

Grooß, J. U., and J. M. Russell III (2005), Technical note: A stratospheric climatology for O_3, H_2O, CH_4, NO_x, HCl and HF derived from HALOE measurements, *Atmos. Chem. Phys.*, *5*(10), 2797–2807.

Kaye, J. A., and T. L. Miller (1996), The ATLAS series of shuttle missions, *Geophys. Res. Lett.*, *23*, 2285–2288.

Kettle, A. J., U. Kuhn, M. von Hobe, J. Kesselmeier, and M. O. Andreae (2002), Global budget of atmospheric carbonyl sulfide: Temporal and spatial variations of the dominant sources and sinks, *J. Geophys. Res.*, *107*(D22), 4658, doi:10.1029/2002JD002187.

Leifer, R. (1989), Project Airstream: COS measurements in the stratosphere and troposphere, *J. Geophys. Res.*, *94*, 5173–5181.

Montzka, S. A., P. Calvert, B. D. Hall, J. W. Elkins, T. J. Conway, P. P. Tans, and C. Sweeney (2007), On the global distribution, seasonality, and budget of atmospheric carbonyl sulfide (COS) and some similarities to CO_2, *J. Geophys. Res.*, *112*, D09302, doi:10.1029/2006JD007665.

Notholt, J., et al. (2003), Enhanced upper tropical tropospheric COS: Impact on the stratospheric aerosol layer, *Science*, *300*, 307–310.

Notholt, J., H. Bingemer, H. Berresheim, J. Holton, A. Kettle, E. Mahieu, and S. Montzka (2006), Precursor gas measurements, in *SPARC Assessment of Aerosol Processes (ASAP)*, edited by L. Thomason and T. Peter, chap. 2, pp. 36–52, World Clim. Res. Programme, Geneva, Switzerland.

Plumb, R. A., and M. K. W. Ko (1992), Interrelationships between mixing ratios of long-lived stratospheric constituents, *J. Geophys. Res.*, *97*, 10,145–10,156.

Rothman, L., et al. (2005), The HITRAN 2004 molecular spectroscopic database, *J. Quant. Spectrosc. Radiat. Transfer*, *96*, 193–204.

Solomon, S., R. W. Sanders, R. R. Garcia, and J. G. Keys (1993), Increased chlorine dioxide over Antarctica caused by volcanic aerosols from Mount Pinatubo, *Nature*, *363*, 245–248.

Toon, G. C., et al. (1999), Comparison of MkIV balloon and ER-2 aircraft measurements of atmospheric trace gases, *J. Geophys. Res.*, *104*, 26,779–26,790.

Trenberth, K. E., and L. Smith (2005), The mass of the atmosphere: A constraint on global analyses, *J. Clim.*, *18*, 864–875.

Turco, R. P., R. C. Whitten, O. B. Toon, J. B. Pollack, and P. Hamill (1980), OCS, stratospheric aerosols and climate, *Nature*, *283*, 283–286.

Watts, S. (2000), The mass budgets of carbonyl sulfide, dimethyl sulfide, carbon disulfide and hydrogen sulfide, *Atmos. Environ.*, *34*, 761–779.

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