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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 (∼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 (CS₂) and dimethyl sulfide (DMS) [Kettle et al., 2002]. Direct and indirect (CS₂ 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 ∼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), O₃ isotopologues 1 and 3, CO₂ isotopologues 1, 2, 3, and 4, and H₂O, 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
measurements discarding anomalous data, reflecting our focus on the mean OCS distribution.

3. Comparison to Other OCS Measurements

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 Lifetimea

<table>
<thead>
<tr>
<th>Latitudes</th>
<th>Mean ATMOS VMR [pptv]</th>
<th>Mean ACE VMR [pptv]</th>
<th>Lifetime [yr]b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Troposphere</td>
<td>Stratosphere</td>
<td>Troposphere</td>
</tr>
<tr>
<td>90°N–60°N</td>
<td>-</td>
<td>-</td>
<td>438 ± 29</td>
</tr>
<tr>
<td>60°N–20°N</td>
<td>467 ± 36</td>
<td>370 ± 27</td>
<td>438 ± 35</td>
</tr>
<tr>
<td>20°N–20°S</td>
<td>470 ± 26</td>
<td>389 ± 19</td>
<td>438 ± 37</td>
</tr>
<tr>
<td>20°S–60°S</td>
<td>508 ± 32</td>
<td>365 ± 26</td>
<td>419 ± 29</td>
</tr>
<tr>
<td>60°S–90°S</td>
<td>463 ± 38</td>
<td>333 ± 19</td>
<td>435 ± 19</td>
</tr>
<tr>
<td>Global</td>
<td>477 ± 17</td>
<td>364 ± 12</td>
<td>433 ± 14</td>
</tr>
</tbody>
</table>

aData 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.

bCalculated using profiles that have at least 50% of their expected vertical coverage of the stratosphere.

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.

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 \( \chi_s \) is given by

\[
\chi_s = \frac{\sum \chi(z)N(z)\Delta z}{\sum N(z)\Delta z} \tag{1}
\]

where \( \chi(z) \) and \( N(z) \) are the OCS mixing ratio and air density (molecules cm\(^{-3}\)) at altitude \( z \) respectively, and \( \Delta z \) 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.

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 \( \mu m \) 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

Figure 2 shows the first global OCS distributions observed from space retrieved by the ACE instrument.
highlighting the importance of high latitude NH sources/sinks on the global OCS distribution [Montzka et al., 2007].

5. OCS Stratospheric Lifetime

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

\[
\frac{\tau_1}{\tau_2} = \frac{\sigma_2}{\sigma_1} \frac{\text{d}\sigma_2}{\text{d}\sigma_1}
\]

where \(\tau_1\) and \(\tau_2\) are the lifetimes of gas 1 (OCS) and gas 2 (CFC-11 or CFC-12) respectively, and \(\sigma_1\) and \(\sigma_2\) are the mixing ratios of OCS and CFC-11 (or CFC-12) within the troposphere and \(\text{d}\sigma_2/\text{d}\sigma_1\) 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 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.
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.
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].

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.

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References


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