

A long-term record of carbonyl sulfide (COS) in two hemispheres from firn air measurements

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Abstract. Carbonyl sulfide (COS) was measured in polar firn air from one Arctic and two Antarctic locations. The air samples represent atmospheric composition from the early to mid-20th century up to the present day. This provides the longest record to date of atmospheric COS. Southern Hemispheric (SH) concentrations appear to have been almost constant at 482 ± 13 ppt over this period, apart from a slight rise in the earliest part of the record. Northern Hemispheric (NH) concentrations also showed relatively little variation with a mean of 525 ± 17 ppt. Over the last ten years, however, NH concentrations appear to have declined by about $8 \pm 5\%$. Such a decline might be due to decreased carbon disulfide (CS₂) emissions by the viscose-rayon industry. The absence of any large trend in COS concentrations over the last fifty or more years argues against COS being the origin of reported increases in stratospheric sulfate aerosol.

Introduction

Carbonyl sulfide (COS) is the most abundant sulphur gas in the background atmosphere. It is sufficiently long-lived to reach the stratosphere, where it is believed to contribute to sulfate aerosol, with implications for the atmospheric radiation balance, and heterogeneous chemical processes within the stratosphere [Andreae and Crutzen, 1997]. Increases in stratospheric sulfate aerosol have been observed [Hoffman, 1990; Thomason *et al.*, 1997] but the cause remains unexplained. Whilst earlier studies have argued that COS is the dominant source of stratospheric sulphate aerosol [Crutzen, 1976; Engel and Schmidt, 1994], other authors have questioned this appraisal [Chin and Davis, 1995; Kjellstrom, 1998; Weisenstein *et al.*, 1997].

There have been few long-term *in situ* measurements of tropospheric COS trends. Bandy *et al.* [1992] found no significant change in Northern Hemispheric (NH) concentrations between 1977 and 1991. A later update and reanalysis of this data set reported a trend of -1.0 ± 0.6 ppt/yr [Thornton *et al.*, 1996], which the authors deemed insignificant. A spectroscopic measurement of COS profiles in the NH stratosphere from Space Shuttle flights in 1985 and 1994 showed no clear differences [Rinsland *et al.*, 1996].

Long-term records of total column COS have also been reported. No clear trend was discernible above Kitt Peak, Arizona from 1977 to 1991, nor from the Jungfraujoch, Switzerland from 1984 to 1991 [Rinsland *et al.*, 1992]. Similarly

no trend was observed above Lauder, New Zealand between 1993 and 1997 [Griffith *et al.*, 1998]. More recently, however, measurements at the Jungfraujoch have shown a significant decline, variously given as $-0.45 \pm 0.09\% \text{ y}^{-1}$ (1984 – 1995) [Zander *et al.*, 1997] and $-0.28 \pm 0.08\% \text{ y}^{-1}$ (1984 – 1996) [Mahieu *et al.*, 1997].

We have measured COS in air pumped out of deep polar firn representing ages from the early 20th century up to the time of sampling (1998/99). From these measurements we have reconstructed long-term trends of COS in both hemispheres.

Methodology

Firn air was sampled at Devon Island, Canada (75°N, 82°W; 1800 m asl, -23°C mean annual temperature) in April 1998; from Dronning Maud Land, Antarctica (hereafter DML: 77°S, 10°W; 2300 m asl, -35°C) in January 1998; and Dome Concordia, Antarctica (hereafter Dome C: 75°S, 123°E; 3240 m asl; -53°C) in December 1998 – January 1999. A borehole was drilled to successive depths. At each depth a firn air extraction device was let down the hole, inflated to seal the base of the hole, and firn air pumped into various sample flasks [Sturges *et al.*, 2001].

The flasks comprised 3 L and 6 L Restek SilcoCans (fused silica-coated stainless steel), 3 L Meriter Stabilizer electropolished stainless steel (EP-SS), 2 L Max Plank Institute (MPI) custom-made EP-SS, and 2 L National Center for Atmospheric Research (NCAR) custom-made EP-SS flasks. All except the MPI flasks were subject to baking, purging, and humidification cycles to improve internal surface passivation. Repeat analysis of two SilcoCan samples showed COS to have changed by < 1% over three months. Repeat analysis of chemically-dried ambient air placed in two SilcoCans showed COS to have changed by < 1.5% over six months. These compare with the accumulated analytical error of about 2%.

COS and CCl₂F₂ (CFC-12) were measured (amongst other trace gases) by gas chromatography-mass spectrometry (GC-MS) at the University of East Anglia (UEA) [Sturges *et al.*, 2001] and at NCAR [Schauffler *et al.*, 1999]. COS concentrations were referenced to the NCAR scale, based on a comparison of thirteen firn air samples ($1\sigma = 2.4\%$). The NCAR scale is in turn based on secondary ambient air standards that have been calibrated against a Tunable Diode Laser technique [Fried *et al.*, 1992].

Historical trends were reconstructed using a physical transport model that accounts for gravitational fractionation and gaseous diffusivity [Rommelaere *et al.*, 1997]. This intrinsically inverse model was run in the 'direct' mode using diffusivity profiles obtained from inverse modelling of CH₄ and other gases [Fabre *et al.*, 2000]. Estimates of the age spectrum width at given depths (z) were derived from the model in terms of the response over

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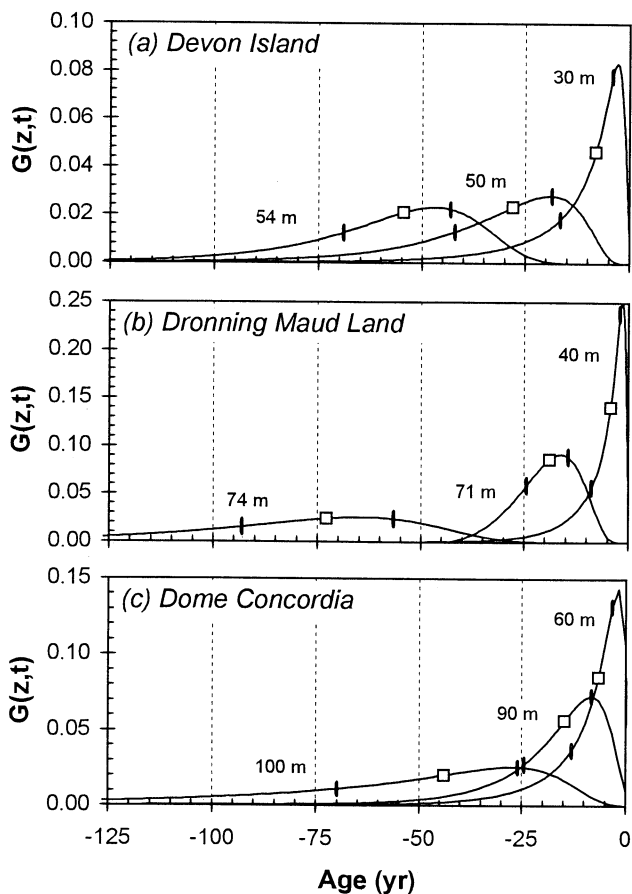


Figure 1. Green probability functions ($G(z, t)$ = solid lines) of the age spectrum of air in firn at selected depths for the three firn drilling sites (panels a to c respectively). Ages are given relative to the drilling date (see text). The open squares mark the mean age of air for each depth shown (i.e. 50% of the area of the probability curve), whilst the solid vertical bars delimit the central 50% of area of the curve.

time (t) to an initial concentration pulse. This is the Green probability function, $G(z, t)$.

Results

Indicative Green probability functions for selected depths are shown in Fig. 1 for the three firn sampling sites. These plots are based on model runs for CH_4 with the apparent ages increased by the ratio of the free air diffusion coefficient of CH_4 to that of COS (1.63). Example profiles are shown at one mid and two lower firn depths, including the lowermost sampled depth in each case. The exception is Devon Island where two deeper sampling depths at 57 and 59 m have been excluded. This is because five of the six samples collected at these depths exhibited a sharp increase both in COS (concentrations of between 606 and 822 ppt) and trichloroethylene (ten-fold increase over concentrations in the overlying firn), as well as increases in other chlorinated solvents, clearly indicating contamination of the samples (such a step-change also cannot be reconciled with the diffusive nature of gas transport through the firn).

Relationships between depth and the mean age of air differed significantly between sites. This is due to differences in porosity and tortuosity profiles. The age distributions were in all cases wide and increased in width with depth, spanning several decades in the lowermost samples. At shallower depths the samples all included variable proportions of present-day air. This decrease in temporal resolution with depth should be borne in mind in the ensuing discussion.

Figs. 2a and 2b show the results from the Antarctic and Arctic

firn air measurements respectively. COS is plotted against CFC-12 rather than against depth. CFC-12 is long-lived (100 yr lifetime) and thus well mixed in the atmosphere, with a long history of emissions to the atmosphere beginning in the 1930s, and no seasonal variation. It therefore provides a pseudo age-normalised scale that allows comparison between sites, and is also consistent with earlier publications on trace gases in firn [Butler *et al.*, 1999; Sturges *et al.*, 2001].

Both Antarctic sites showed almost constant COS concentrations (Fig. 2a) over most of the profile, although there was a small decrease apparent in the oldest air from DML. The mean concentration of COS was 482 ± 13 ppt for CFC-12 > 50 ppt. Modelling this as a constant concentration yielded the thick grey line in Fig. 2a. This line is almost horizontal, rising only slightly with depth due to gravitational fractionation. Other notable features are the good agreement between sample container types, and the good agreement between sites despite

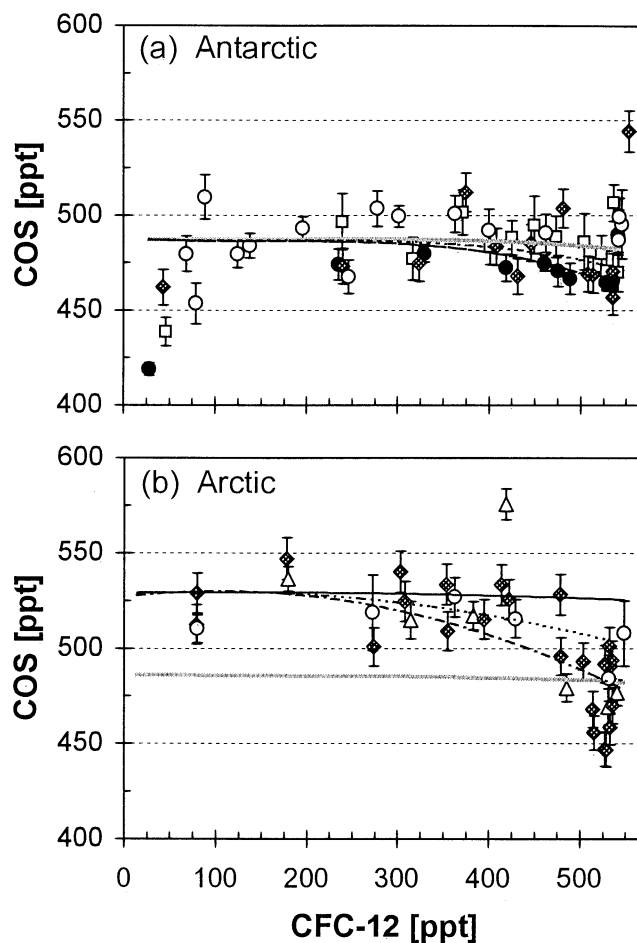


Figure 2. COS in firn air plotted against CFC-12 for (a) the two Antarctic sites combined (DML and Dome C) and (b) the Arctic site (Devon Island). Symbols represent flask types and locations. Dome C samples were collected in SilcoCans (filled circles), DML samples were collected in SilcoCans (open circles), MPI flasks (open squares), and NCAR flasks (shaded diamonds). Devon Island samples were collected in SilcoCans and NCAR flasks (same symbols), and also in Stabilizer flasks (open triangles). Error bars are $1-\sigma$ accumulated analytical errors of individual measurements, except for the NCAR flasks where a separately determined analytical precision of $\pm 2\%$ has been applied. The lines show results from the firn diffusion model. The thick grey line shown in both panels is for a constant COS concentration of 482 ppt. The thin solid line (panel b) is for a constant COS of 525 ppt. The broken lines allow for declining concentrations based on reported reductions (see text) in column COS (dotted line), and for twice this rate (dash-dot line).

the very different firn conditions (no statistical differences between means). These observations give us confidence that there was insignificant sample degradation during storage, that COS was conserved in the firn air column, and that these profiles are representative of the Antarctic lower atmosphere.

The measurements at Devon Island (Fig. 2b) also showed little variability for most of the record. Again there was good agreement between measurements from different sample containers. The same scenario of constant 482 ppt COS was modelled for Devon Island conditions (thick grey line in Fig. 2b). The actual measurements, however, were mostly higher than this model line. In the upper firn (CFC-12 > 450 ppt) there was evidence for a small reduction in concentrations. The mean COS concentrations for CFC-12 concentrations between 50 and 450 ppt was 526 ± 17 ppt. This gives an interhemispheric ratio (IHR) for this time period of 1.08 ± 0.05 . An independent group analysis (equal variance t-test) showed a high probability that the Arctic and Antarctic means were indeed different ($p \ll 0.001$). In contrast, in the most recent firn air (CFC > 450 ppt) COS at Devon Island averaged 481 ± 22 ppt, giving an IHR of 1.00 ± 0.05 for this period. A t-test showed high probability that the means were the same ($p = 0.93$).

A number of authors have reported IHRs for COS, with a wide range of values from 0.96 to 1.25; these discrepancies being variously attributed to geographic differences, altitude, seasonality, and contributions from polluted or COS-depleted air masses [Bingemer et al., 1990; Griffith et al., 1998; Johnson et al., 1993; Mihalopoulos et al., 1991; Notholt et al., 2000; Thornton et al., 1996; Torres et al., 1980; Weiss et al., 1995]. Significantly, the more recent measurements report low IHRs, e.g. 1.01 from an October 1996 Atlantic cruise [Notholt et al., 2000], and 1.03 and 0.96 for boreal spring and winter Pacific cruises respectively in 1993 [Weiss et al., 1995].

Discussion

One of the more remarkable findings of this study is that changes in global COS during the 20th century have been relatively small compared with the dramatic trends in anthropogenic trace gases during the same period [Battle et al., 1996; Butler et al., 1999]. These findings are in agreement with - but extend back in time - previous studies showing little or no detectable change in COS since the late 1970's (see above).

Watts [2000] estimated the rapid atmospheric oxidation of carbon disulfide (CS₂) to be the single largest source (32%) of COS, with 52% of this CS₂ being of industrial origin. Direct anthropogenic emissions of COS account for 9%, and biomass burning 5%, giving a minimum of 31% of global COS arising from anthropogenic sources. (The other sources include open and coastal oceans, wetlands, soils, volcanism, precipitation, and DMS oxidation.) Some effect of 20th century industrialisation on COS levels would, therefore, be anticipated, particularly via changes in industrial emissions of CS₂. Production of viscose-rayon, the first commercially available synthetic fibre, is the principal anthropogenic source of CS₂ [Chin and Davis, 1993]. Viscose-rayon production began in 1910. It is known that production was essentially constant at 3.4 Tg yr^{-1} between at least 1970 and 1990, but then dropped by 24% by 1999 (source: Acordis company). There has also been a recent dramatic shift in regional production. Eastern Europe accounted for more than one third of global output in the 1970s, but this dropped to just 7% in the 1990s. Meanwhile Asian synthetic fibre production has flourished, rising from 24% to 65% of world production in the twenty years to 1997 (source: Fiber Economics Bureau, Inc.).

A small number of Antarctic samples, notably from DML (Fig. 2a), did seem to suggest lower concentrations in the oldest air, although any changes in atmospheric COS early in the 20th century will tend to be highly damped in the firn record, due to

the very broad age spectra at depth (Fig. 1). Lower concentrations at depth were not observed at Devon Island, although the age distribution for the deepest sample tailed less towards older ages than those from the Antarctic (Fig. 1). We cannot, in any case, rule out the possibility that non-conservative effects at the firn-ice transition resulted in the observed downturn in COS at depth at DML.

The apparent recent small decline in NH COS also requires some explanation. Intra-annual cycles can be propagated into the firn [Sturges et al., 2001], and seasonal amplitudes of COS in the NH of up to 10% (spring/summer maxima) have been reported [Rinsland et al., 1992; Weiss et al., 1995]. Firn model runs (not shown), however, indicated that such cycles are both in antiphase and of insufficient magnitude to produce the observed change in COS. Even a 25% seasonal cycle with a summer *minimum* underestimated the required decrease.

We instead considered the implications of the reported recent decline in COS column observed at the Jungfraujoch (see above). We took the more conservative published decrease rate of $-0.28 \pm 0.08\% \text{ y}^{-1}$ between 1984 and 1996, but noted that earlier reports on the same measurement series showed no detectable change up to 1991. We therefore applied the total quoted decrease to the period from 1991 to give a COS trend of $-0.56\% \text{ y}^{-1}$. This was used in the firn model along with a constant COS concentration of 525 ppt up to 1990. As a sensitivity study the model was run with twice the above rate of decrease, and also with no decrease. Fig. 2b shows that the scenarios with decreasing concentrations fit the actual measurements well.

If NH COS has, in fact, declined due to reduced NH emissions, then a more muted response in the SH would be expected, depending on the atmospheric turn-over time of COS. The latter is poorly known due to uncertainty in the global sink terms [Watts, 2000]. Lifetime estimates based on the variability of observational data range from 1 to 7 yr [Griffith et al., 1998; Mihalopoulos et al., 1991; Thornton et al., 1996; Torres et al., 1980], whereas a 3-D model study returned a global turn-over time of 3.5 yr [Kjellstrom, 1998]. We have considered a simplistic example whereby half of COS emissions from northern mid-latitudes reach the Antarctic troposphere, with a 2 yr lag in concentration trends between the two polar regions. The resulting scenarios, with a constant COS of 482 ppt up to 1992, were used in the firn model with conditions appropriate for DML. The resulting modelled profiles all fell within the scatter of the actual measurements (Fig. 2a).

Assuming that 17% of global COS does indeed originate from industrial CS₂, and that the latter originates entirely from the viscose-rayon industry (see above), then the 24% fall in industrial CS₂ emissions would translate into a 4% decline in NH COS. This is numerically half, and statistically indistinguishable, from the $8 \pm 5\%$ decline observed in the upper firn at Devon Island. A geographical shift in industrial emissions from Europe to Asia might also contribute to a negative change in COS concentrations at northern high latitudes, given the strong terrestrial sinks for atmospheric COS (estimated as 89% of all known global sinks [Watts, 2000]).

Conclusions

The main outcome of this study is the demonstration that global COS levels have changed little over the last century. It is unlikely, therefore, that COS could be a major contributor to reported observations of increased stratospheric sulfate aerosol. It has also been shown that the long-term pole-to-pole IHR over most of this period was about 1.08, confirming previous studies that showed mostly higher COS concentration in the NH (except in recent years).

Less certain is the evidence for lower COS in the early part of the 20th century, and a possible recent decline in NH

concentrations to give a present day IHR close to unity. Although we cannot be fully confident that these changes are real, and not due to some non-conservative behaviour of COS in the firn column, they are at least qualitatively in agreement with possible changes in anthropogenic sources, principally oxidation of CS₂ emitted by the viscose-rayon industry. In this respect it supports previously published budgets in which anthropogenic sources of COS are a significant term. Firn air measurements at additional sites, particularly in the NH, would be advantageous to confirm the Devon Island findings, and to examine older air for evidence of lower pre-industrial concentrations.

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