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Interactive Comment

# Interactive comment on "Atmospheric carbonyl sulfide (OCS) variation from 1992–2004 by ground-based solar FTIR spectrometry" by N. M. Deutscher et al.

N. M. Deutscher et al.

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We thank the anonymous reviewers for their comments and suggestions.

Generally, we now intend to provide a more in-depth discussion of the data presented.

To address the points raised:

Anonymous Referee #1:

Specific comments: "The authors present the partial columns at the four stations. One of the most interesting results for me is the apparent decrease of OCS between 4 and 12 km above Arrival Heights. This is not discussed in the paper. Interestingly, the 4-12 km above Hawaii seem to increase throughout that time-span. This is also not

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discussed."

This decrease in OCS 4-12 km partial column has its largest effect in the Arrival Heights data (-1.40 \u00e9 0.25 %/yr), but is also present at the other SH sites (-0.77 \u00e9 0.30 %/yr - Wollongong; -0.27 \u00e9 0.13 %/yr - Lauder). In the context of the entire time base of the data, this "trend" appears to have sinusoidal components with periods of several years (can this also be quantified?), but the relatively short time series of all the solar data precludes any conclusions of possible mechanisms at this point in time. The NH site at Mauna Loa does not appear to have any trend in the 4-12 km layer. However Rinsland et al, (2002) report a 0.25% per year decrease in the 2-12 km partial column above Kitt Peak over a 24 year timespan and no obvious long period sinusoidal dependencies.

Note also the strong seasonal dependence in the Arrival Heights stratospheric column is caused by seasonal downward descent of air in the polar vortex; the local tropopause above arrival heights is at times below 8 km, so the use of the 12 km limit for the mean altitude of the tropopause is not necessarily appropriate for all sites.

Smaller seasonality at Lauder: Please note that we are not trying to suggest that we can observe changes in OCS concentration from local ocean sources at Lauder. Instead we are suggesting that the time of travel of air masses from distant warm ocean sources is sufficiently long that (days to week) that any large fluctuations become well mixed, and hence we observe less variation.

Common OCS and water source: Back trajectory analysis is now being performed. Initial looks appear to confirm our postulation.

Surface pressure corrections: Are done simply using the mean pressure for all years, for comparison between mean total columns. A similar correction has not been applied to the 0-4km partial column, hence why the Hawaii column (the site is already at 3.5 km altitude) is much lower in this altitude range than the other sites.

Citations: Further consideration will be given to the relevant papers suggested.

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### Anonymous Referee #2:

Seasonal variation interpretation: We will include further analysis of the detrended seasonality (by partial column and fraction of year) for all sites in an expanded tabular form, and therefore give a more detailed description, and where possible, explanation of the relationships apparent in the data.

Water and OCS correlation: note that to address referee #1's concerns, we are performing back trajectory analyses to determine if there is a common source and hence correlation between OCS and water. We will also investigate more quantitative measures (correlation coefficients) in line with the analysis of seasonal dependencies etc.

Hawaiian SST: The conjecture concerning the relationship between high OCS columns and SST's with Wollongong data, was meant to imply that the airmasses would have to originate from the direction of the ocean (i.e. the eastern sector with respect to the observation site at Wollongong); the SST influence would not be seen with transport from other directions. In Hawaii on the other hand, with a surrounding ocean, any potential warm ocean source of OCS should be apparent regardless of the direction from which the observed OCS column originated. Hence the influence of SST around Hawaii should be evident regardless of meteorology. We will look further at the seasonality at the differing times of day. At present, the seasonality conclusions are based on all data.

OCS correlation with SST: We believe that greater outgassing from the oceans would occur with warmer temperature. This would not only occur with OCS, but the precursors DMS and CS2, particularly DMS, which has a large oceanic source. Hydrolysis occurs in the upper ocean, along with outgassing, so OCS can be destroyed and/or lost from the ocean, but Flock and Andreae (1996) have shown that the temperature dependence of OCS hydrolysis is not strong enough to override oceanic OCS photochemical or dark production. Greater discussion of these points will be made for clarification.

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Technical issues: We will attempt to clarify what we mean by confirmed. It was referring to the fact that we used a different algorithm and still derived the same seasonal pattern.

We are aware of the limitations of using the IHR - in fact we had considered using a latitudinal gradient as an alternative. I think the statement that it agrees with previous (low) values is still valid - given a N-S gradient, and the NH represented by a low latitude site, the IHR would be expected to be in the low range.

We were not trying to contend that we had new evidence of decreased anthropogenic emissions, merely suggest that the NH decrease is presumably due to this. Montzka et al (2004) quote that anthropogenic S gas emissions have decreased by ~30%.

The results are based on the mean of fits to 2 spectral microwindows, one of which included a single OCS absorption line, and the other included 3 lines (we assume this is where the figure of 4 came from).

The difference between the RMS of a spectral fit and the uncertainty on individual monthly mean data points obviously caused some misunderstanding. The RMS refers to the ability of the spectral fitting algorithm to simulate a spectrum to fit the measured spectrum. The error ranges on the individual points are the standard errors calculated from determining the mean of a number of measurements. This is more indicative of the variation from measurement to measurement, while the RMS could be considered to represent the uncertainty of a single measurement introduced by the retrieval (or more correctly due to the limitations of the retrieval).

The wording of the introduction in the discussion of long-term trends has been adapted for further clarification.

#### References:

Flock, O. R. and Andreae, M. O.: Photochemical and non-photochemical formation and destruction of carbonyl sulfide and methyl mercaptan in ocean waters, Marine

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Chemistry, 54, 11-26, 1996

Montzka, S. A., Aydin, M., Battle, M., Butler, J. H., Saltzman, E. S., Hall, B. D., Clarke, A. D., Mondeel, D. and Elkins, J. W.: A 350 year atmospheric history for carbonyl sulfide inferred from antarctic firn air and air trapped in ice, J Geophys Res, 109, 2004

Rinsland, C. P., Goldman, A., Mahieu, E., Zander, R., Notholt, J., Jones, N. B., Griffith, D. W. T., Stephen, T. M. and Chiou, L. S.: Ground-based infrared spectroscopic measurements of carbonyl sulfide: Free tropospheric trends from a 24-year time series of solar absorption measurements, J Geophys Res, 107, 4657-4665, 2002

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 1619, 2006.

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