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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

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The authors present an interesting set of measurements that adds substantially to the long-path measurement records of atmospheric OCS. They provide important new results pertaining to nearly decade-long trends and seasonality. As such, the results are ripe for comparing to one another and to those published previously to reveal insights into the variables that influence OCS atmospheric abundance and seasonality. The discussion of the results, however, is cursory and a bit disappointing. Correlations are claimed when they aren't apparent, seasonality is suggested when it is difficult to discern from the data as displayed, and speculation as to causes of variability and in abundance is sometimes not consistent with our general understanding of the predom-

inant OCS fluxes.

Specific comments:

Much insight might be obtained from a intercomparison of seasonal variation magnitudes and phase for OCS observed at these different sites. The authors make some interpretations of their measurements in this regard, but it is very difficult for the reader to affirm their conclusions with the figures currently included. For example, the conclusions that “the seasonal cycle observed occurred largely in the 0-4 and 4-12 km partial columns” (p. 1629, line 1) and that the seasonality does “not fit a sinusoidal cycle well” are not at all clear from a glance at figure 1. It would help tremendously if some effort were made to express seasonal variations as a function of altitude bin in a table or figure with multiple panels–and to provide some indication of how consistent this seasonality is interannually. Please consider a figure of total and partial columns vs fraction of year (perhaps plot residuals to running annual means for sites where a trend is observed). Persistent seasonal changes, if they exist, should become apparent (what is the interannual variability in the p-p amplitudes observed?); the phase of the seasonality should also become apparent–it might be interesting to compare this between the different hemispheres; the vertical dependence of the seasonality should become apparent, which would be useful in assessing the role of the ocean in influencing the seasonal changes (one might expect any oceanic influence to be largest in the lowest layer).

It is concluded based upon the Wollongong results displayed in Figure 2 that ‘high water vapor total columns highly correlated with the high OCS columns’. I agree that both water vapor and OCS were highest in 1996-1997, but a perusal of the results for other years doesn’t suggest to me a high correlation. What is the r2 correlation coefficient and is it significant? The authors may wish to assess the correlation during months of Dec-March (i.e., are the yearly peak magnitudes in water and OCS correlated?).

It is curious that while no correspondence is apparent between OCS and SST at the

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coastal Wollongong site, the authors contend that the results from Hawaii (high altitude site) are likely influenced by SSTs. There is very little oceanic influence in downslope air (8:00 am) to Hawaii–it would seem a comparison of the seasonality observed at 8:00am and 5:00 pm might shed some light on their speculation, provided the influence of the volcanic emissions don't overwhelm any signal. Are the conclusions regarding seasonality solely based upon the 5:00pm results?

A discussion as to why one might expect OCS to correlate with SST is not given–based upon my reading of the literature I might expect the opposite! In fact much of the discussion is made without a careful consideration of our understanding of OCS sources and sinks. OCS hydrolysis is more rapid at higher temperatures–OCS production from aqueous photochemistry is thought to be enhanced during summer (see Kettle et al papers), this may be a point to consider in this regard. Kjellstrom (1998) calculated that some of the highest surface mixing ratios across the globe might be expected for COS near Arrival Heights (owing to slower hydrolysis perhaps)–so that comments suggesting that this site is a long 'distance from sources' might be reconsidered.

Technical issues:

Wollongong peak-to-peak seasonality 'confirmed'–please define this clearly in the abstract and text. I presume you mean that the same data were interpreted with a refined algorithm and seasonality was still derived–not that you have performed an independent measurement and found a similar result?

Please consider that calculations of IHR from a few sites in each hemisphere rely on results from those sites to be representative of the entire hemisphere. One potential reason that past estimates of IHR vary substantially (you have only quoted those that are somewhat similar to what you have estimated–others exist) is just this. I would urge you to consider adding some comment to remind the reader that your NH is represented entirely by 1 high altitude site at only 19N. Furthermore, what new evidence do you bring to bear on the discussion that allows the conclusion that "The NH abun-

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dances are higher than those in the SH due to larger anthropogenic emissions."?

Please be clear, are the OCS results based on a mean of fits to the 4 spectral microwindows? Spectra with rms residuals of $<$0.4% were retained–but the uncertainty ranges on individual data points in the figures look much larger–please indicate why this is so. Can you remind the reader what potential biases or uncertainties (and their magnitudes) are introduced with the assumption of a vertical profile as in Griffith et al., 1998?

Note that the OCS trends reported by Sturges et al. (2001) for the 1990s were inferred from the analysis of firn-air results, and were not from ongoing atmospheric sampling and analysis.

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