Anonymous Referee #2

We have an additional short response to the following comment, based on our recent analysis of the CS_2 lifetime (Khan et al. 2017).

Comments

If the lifetime of CS_2 was 12 days, it might make sense to model CS_2 separately, since the associated OCS will not show up in the air parcel until it has traveled nearly around the globe. However, more recent evidence suggested that the lifetime is much shorter than that. For example, see the 3D atmospheric transport study performed by Anwar Khan which focusses only on CS_2 and estimates a lifetime of less than 4 days at maximum: 10.3934/environsci.2017.3.484.

We thank the reviewer for pointing out this more recent paper regarding the CS_2 lifetime. We implemented the CS_2 + OH chemistry using the rate quoted in (Khan et al. 2017). As a result, we spotted a mistake in the rate constant of the CS_2 + OH reaction in the Khan et al. (2017) paper. According to (Khan et al. 2017), the rate constant of CS_2+OH is (their Table 1):

$$rate\ constant\ 1 = \frac{1.25 \times 10^{-16} e^{\frac{4550}{T}}}{(1 + 1.81 \times 10^{-13} e^{\frac{3400}{T}})}$$

However, the rate constant (Sander et al., 2006, Hynes et al., 1988) should read:

$$rate\ constant\ 2 = \frac{1.25 \times 10^{-16} e^{\frac{4550}{T}}}{(T + 1.81 \times 10^{-3} e^{\frac{3400}{T}})}$$

We verified with the authors of Khan et al. (2017) that this is a typo and that the rate constant is correctly implemented in their model. We also implemented the Sander et al. (2006) rate constant in our simulations. Results are shown in Figure 1.

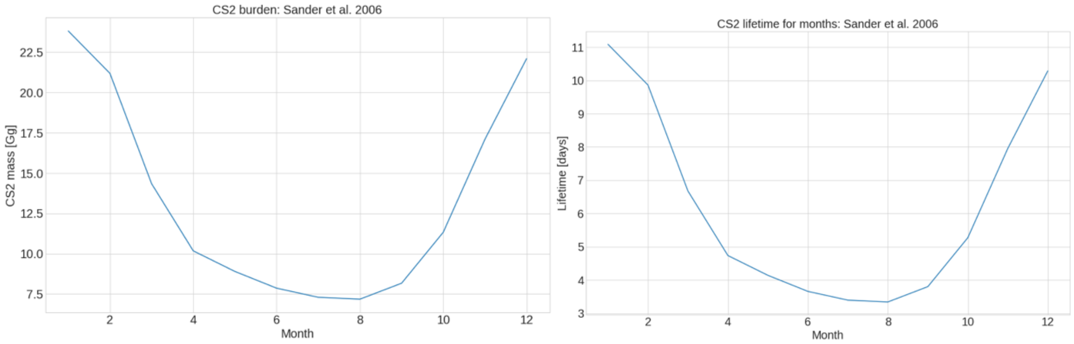

Figure 1: Monthly averaged burden (left) and atmospheric lifetime (right) of CS2, calculated in TM5 with the rate constant of Sander et al. (2006) implemented.

As can be seen in Figure 1, the burden and lifetime vary considerably over the year. The yearly average lifetime (burden/loss) amounts to 6.2 days, substantially larger than the value quoted in Khan et al. (2017): 2.8-3.4 days. Possible reasons are (1) our burden is higher due to larger emissions and possibly lower OH (2) no deposition has been implemented in our simulations. In Khan et al. (2017) loss through deposition in their standard run account for ~15% of the CS_2 removal. Note also that their standard model simulation underestimated CS_2 mole fractions, specific over large emission regions.

For comparison, Figure 2 shows the results from our standard run, with a constant CS_2 + OH rate from Jones et al. (1982): $2.0\text{x}10^{-12}$ cm^3 molecules^{-1} s^{-1}.

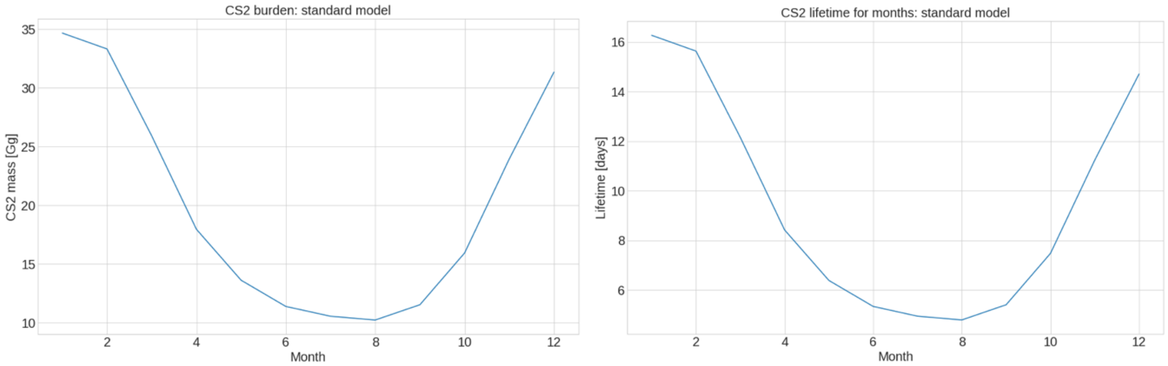

Figure 2: Monthly averaged burden (left) and atmospheric lifetime (right) of CS2, calculated in TM5 with the rate constant of Jones et al. (1982) implemented.

As can be seen, the lifetime and burden are slightly larger using this rate. The yearly average lifetime amounts to 9.4 days. Figures 3 and 4 show the January and July COS mole fraction difference at the surface between our standard model and the Sander et al. (2006) rate. It can be seen that the differences are relatively small and remain smaller than 10 pmol mol^{-1}.

Since the lifetime in TM5 is relatively long (> 10 days in the Northern Hemisphere winter), we would argue that it is necessary to simulate CS_2 as a separate tracer, to model the delayed COS production from CS_2 oxidation. To highlight this further, we will (in the Supplement of the revised paper) show results from a simulation in which we emit CS_2 directly as COS.

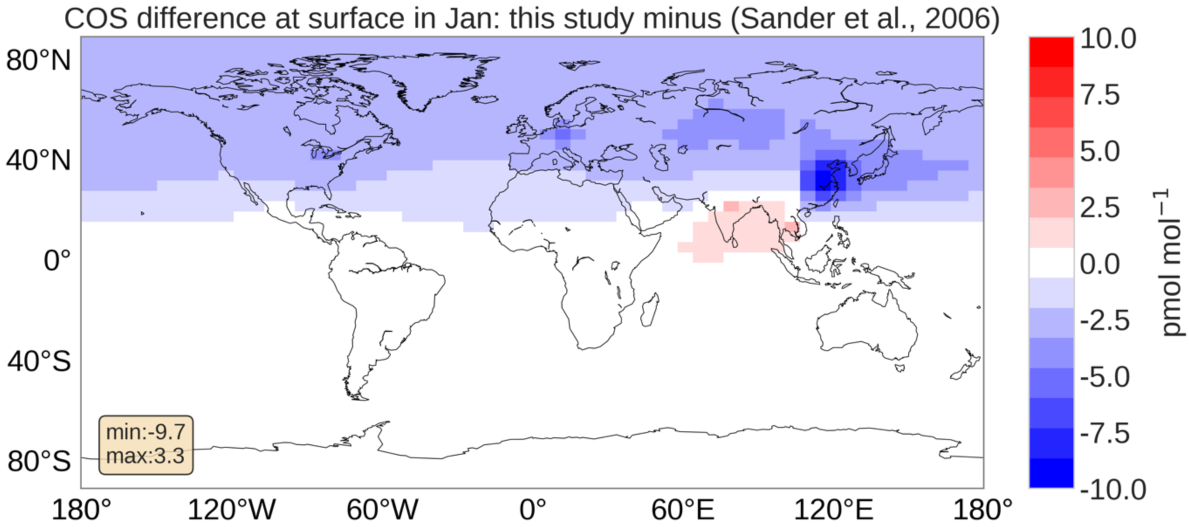

Figure 3. COS mole fractions difference between this study and the rate as (Sander et al., 2006). This is the average COS mole fraction difference in January 2008-2010. The maximum and minimum values of the difference are marked in the left bottom corner.

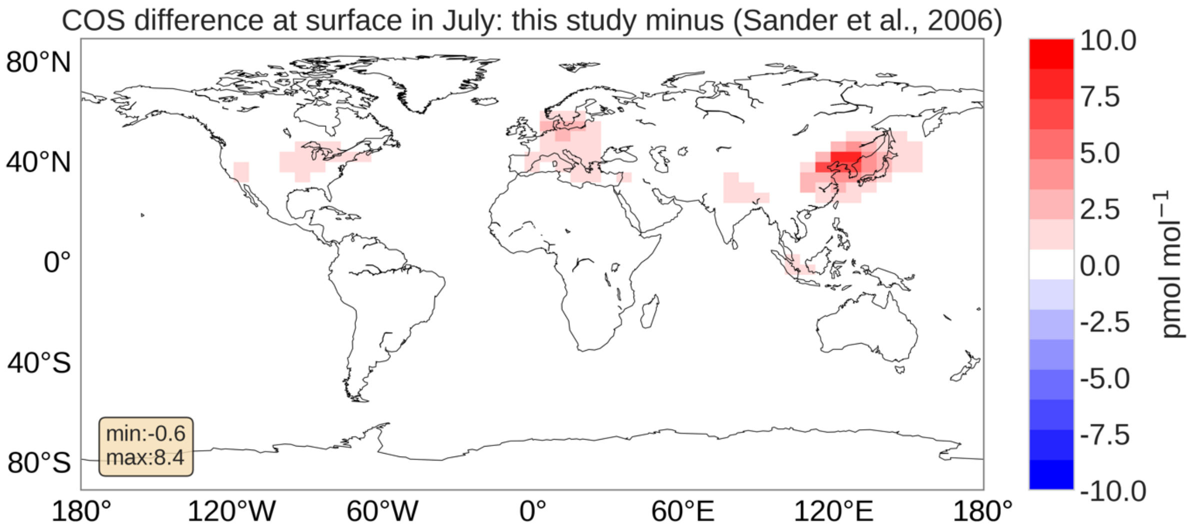

Figure 4. The same as Figure 3 but for July 2008-2010.

Reference:

Khan, Anwar, et al. "Global analysis of carbon disulfide (CS2) using the 3-D chemistry transport model STOCHEM." Aims Environ. Sci 4 (2017): 484-501.

Sander, S. P., et al. Chemical kinetics and photochemical data for use in atmospheric studies evaluation number 15. Pasadena, CA: Jet Propulsion Laboratory, National Aeronautics and Space Administration, 2006.

Hynes, Anthony J., P. H. Wine, and J. M. Nicovich. "Kinetics and mechanism of the reaction of hydroxyl with carbon disulfide under atmospheric conditions." The Journal of Physical Chemistry 92.13 (1988): 3846-3852.

Khalil, M. A. K., and R. A. Rasmussen. "Global sources, lifetimes and mass balances of carbonyl sulfide (OCS) and carbon disulfide (CS2) in the earth's atmosphere." Atmospheric Environment (1967) 18.9 (1984): 1805-1813.

Jones, B. M. R., et al. "OCS formation in the reaction of OH with CS2." Chemical Physics Letters 88.4 (1982): 372-376.