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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Dimethylsulphide (DMS) emissions from the West Pacific Ocean: a potential marine source for the stratospheric sulphur layer" *by* C. A. Marandino et al.

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Anonymous Referee #2

Reviewer: 1 General comments The paper is a useful contribution to ACP but needs revision because of misleading conclusions. It is important to present new measurements of DMS and its consequences for the sulphur budget in the upper troposphere and lowermost tropical stratosphere. This includes the HIPPO data not available in the cited website and reference. DMS from tropical convection contributes to lower stratospheric SO2 and sulphate aerosol but is minor compared to the effects of volcanoes and of COS oxidation in contrast to the impression from the abstract and the conclu-

sions. Nevertheless, it is worth to be addressed since it helps to reduce differences between model results and most recent satellite data for SO2 over the tropical Pacific in the UTLS.

General Response to Reviewer 2: We thank the Reviewer for helping to improve the manuscript. The Reviewer is right concerning the HIPPO references. There has been an update since the time of writing. Here is the correct HIPPO reference (it has been added to the manuscript):

Wofsy, S. C., et al.. 2012. HIPPO Combined Discrete Flask and GC Sample GHG, Halo-, Hydrocarbon Data (R_20121129). Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A. http://dx.doi.org/10.3334/CDIAC/hippo_012 (Release 20121129)

The correct website is (and has been added to the manuscript): http://hippo.ornl.gov/

We did not wish to convey that marine derived DMS is as important as volcanoes for stratospheric sulphur loading (see also our detailed answer to Reviewer 1). However, we find it interesting that such a short lived compound has the potential to be transported to the TTL. As we stated in the response to Reviewer 1, we believe that this potential has been largely unaddressed/unexplored by the community and is worth noting. We have gone through the manuscript and revised the title, the abstract, introduction, and conclusions to ensure that we do not overstate the point. Please see also our specific changes highlighted in response to Reviewer 1.

Reviewer: 2 Specific comments In the introduction (page 30545, lines 13f) the references are misinterpreted, they all argue against anthropogenic SO2.

Response: We have changed the first paragraph in the introduction to read (changes highlighted):

"Hofmann et al. (2009) reported that since 2000 there has been an increase in the aerosol backscatter above the tropopause and they propose an increase in sulphur

compounds in the atmosphere as the main cause. It has recently been shown that the influence of minor volcanic eruptions and anthropogenic loading to the atmosphere have an overwhelming global footprint with regard to Junge layer (Bruehl et al., 2012, Bourassa et al., 2012; Vernier et al., 2011). However, it is most likely that a combination of sulphur sources is responsible for the observed increase in stratospheric aerosol, including a natural component that also needs to be investigated. Myhre et al. (2004) have suggested, based on model calculations, that the contribution of sulphur to the stratosphere from marine DMS emissions may also be important."

With respect to the cited references, Vernier et al. says, "In contrast, the convective season of the Northern Hemisphere summer shows an increase in the particle load at the tropopause consistent with a lofting of air rich with aerosols. These aerosols can consist of surface-derived material such as mineral dust and soot as well as liquid sulfate and organic particles." From Bruehl et al., "Considering an anthropogenic fraction of 30% (derived from ice core data), this translates into an over-all direct radiative forcing by COS of 0.003 W m$-$2. The anthropogenic aerosol fraction is made up of sulphates, nitrates, organics and black carbon that are continually produced by the use of fossil fuels, biomass burning and agricultural practices. . ..The atmosphere contains many reduced and partly oxidised sulphur gases, the most important being SO2, hydrogen sulphide (H2S), dimethyl sulphide (DMS), COS and CS2. Most have significant anthropogenic sources, in particular SO2, which is released in large quantities from the combustion of coal."

Reviewer: DMS might contribute to stratospheric sulphur since it is much less soluble than SO2 and can be therefore better transported by convection. Please explain better on page 30546, second paragraph, why the West Pacific is a region which favors penetration of DMS into the stratosphere (convection, low OH etc.).You may cite also Newell and Gould-Stewart (1981).

Response: We added the stratospheric fountain idea by Newell and Gould-Stewart (1981) here.

The paragraph states (changes highlighted): "This oceanic region experiences several meteorological phenomena, such as tropical storms and deep convection, which make it especially significant for transporting climate active trace gases emitted from the surface ocean to the upper troposphere/lower stratosphere. The upper part of the tropical tropopause layer (TTL), between 15 to 17 km altitude, is of specific interest here. The West Pacific region acts as a main entrance region of trace gases into the stratosphere, termed the "stratospheric fountain" based on cold point temperatures at 100 mb (Newell and Gould-Stewart, 1981), throughout the year peaking during boreal winter season with enhanced vertical transport (Fueglistaler and Haynes, 2005; Krüger et al., 2008; 2009). Since the atmospheric DMS lifetime is short, between 11 minutes and 46 hours due to reaction with hydroxyl and nitrate radicals (e.g. Osthoff et al., 2009; Barnes et al., 2005), DMS transport to the TTL is more efficient in the western Pacific Ocean than in other oceanic regions."

OH levels are not discussed because we use a range of DMS lifetimes in the computation. In fact, we were conservative in this estimation (1/2 to 1 day lifetime), reflecting the typical OH levels.

Reviewer: El Nino enhances convection over the East and mid Pacific but reduces it over the West Pacific. Please improve this part in section 2.1.

Response: We added the following (changes in highlight): "The circulation of the Pacific Ocean and atmosphere were affected by a strengthening El Nino event, inducing an increase in sea surface temperature towards the east, which triggered an elevated atmospheric convection towards the east and reduced the convection towards the west (Krüger and Quack, 2012). "

Reviewer: I suppose the DMS flux in paragraph 3 of section 2.2 is estimated from the ship measurements. A remark on the consistency of this number with other cited datasets (Kettle,Lana etc) would be useful already here (or at least a cross reference to next section).

Response: We have modified the sentence in the aforementioned paragraph (changes in highlight), “For these runs an average DMS emission of 1.54 x 10-7 mol m-2 hr-1 was distributed uniformly over the tropical oceans (within 30°S-30°N, see section 3.1 for a discussion of the computed fluxes and comparison to current climatologies) and the atmospheric DMS transport was calculated for November 2009.”

Reviewer: At the beginning of section 3.1 ’marine boundary layer’ should be inserted for clarity (right?).

Response: We added marine boundary layer.

Reviewer: Figure 5b and the discussion on mg of DMS in the Lagrangian parcels on top of page 30554 should be skipped or much better explained concerning units, area and reference time.

Response: The units are kilograms of DMS (stated in the text), which are derived from a simple conversion of the initial flux (moles DMS). The time and area are not different between figure 5a and 5b. We have tried to clarify the discussion (changes in highlight): “Between 20°N and 15°N, as well as around 5°S, enhanced vertical transport, which is connected with intense tropical convection (Krüger and Quack, 2012), is visible in Figure 5b (regions with yellow and red colors extending above 12 km). These events coincide with medium to large DMS emissions (right side axis of panels in Figure 5, black line) resulting in 5 x 10-7 – 1 x 10-6 kg of DMS (equivalent to 3 to 10%) reaching the upper TTL.”

Reviewer: The back of the envelope calculations on pages 30554f and in Table 1 are misleading and appear to be wrong. First, only the area of the tropical oceans (or better the regions with strong convection) should be counted if transport to the TTL is considered; second, what is the meaning of a 1 cm wide track along 6000 km (surface area of cruise track)? Is this related to the inlet device? Due to these strange numbers the scaling factor for DMS at the TTL also given in the conclusions is strongly overestimated.

Response: The reviewer is correct that this is misleading. The manuscript states that the area of the cruise track was used to scale the sulphur loading, when in actuality it should say the area of emissions. This wording was changed in the manuscript in several places (abstract, discussion). The emissions are computed for measurements along the cruise track every 3 hours and are, therefore, not from the entire cruise track region. The computed area is 500 m2 multiplied by 115 hours, which is approximately every 3 hours over the entire time of the cruise with viable measurements (it is stated in the second paragraph of Section 2.2 and figure 5 how the extent and timing of emissions is used by FLEXPART, namely 10000 parcels are released in a 500 m2 area over one hour). Regarding the area to be considered, we did not want to cherry pick our results and therefore ran the model for the entire area of emissions.

Reviewer: What is the meaning of 30 g S/month (page 30554, line 25) also mentioned in the abstract? Please explain better and/or convert to a more reasonable scale, this is very confusing. I suppose, the number is again based on the 1 cm wide track. Since transport to the TTL is dominated by fast deep convection, lifetime of DMS in the boundary layer is secondary here and I’m surprised that it scales almost linear. Are diurnal effects taken into account?

Response: We obtained 30 g S/month just by converting from Tg in the table to g in order to make the number more tangible. It is simply a conversion. However, we do not see where on page 30554 line 25 there is a reference to 30 g S. It is only in the abstract. Please see the comment above for how this number was calculated (it has nothing to do with the length or width of the cruise track). Diurnal effects are not explicitly taken into account but we include different lifetimes to account for changes over the day. 12 and 24 hours are conservative for this study and longer lifetimes have been reported (and of course they would be longer at night). We have added a line to the methods section stating this (changes in highlight), “The amount of DMS carried by each air parcel is reduced at a rate corresponding to its chemical lifetime, which is set to 12 hr and 24 hr to represent typical gas phase values found in the literature (Section 1),

without accounting for diurnal effects (conservative approach as the lifetime is longer at night), for two model scenarios."

Reviewer: What means tropical in Figure 7? It might be useful to show the 'fountain region' over the West Pacific separately. Compared to CCM-results using the Kettle DMS in seawater as lower boundary condition the presented values appear to be at the high end for zonal average but this might be related to the Emanuel convection scheme used in FLEXPART (see Tost et al).

Response: Figure 7 is introduced on pg 30555 line 21-22 where the region is described at 20N-20S. This has been added to the figure caption. We were interested in how these fluxes impact the whole region so therefore did not want to separate only the "fountain". We are not sure what CCM results the Reviewer means, however we would like to note that Lana et al., 2011 is a more recent climatology than Kettle, and we see differences between our results and Lana that could reflect that there are not enough measurements to accurately predict in situ fluxes with climatologies.

Reviewer: 3 Technical corrections PSL is an acronym usually not used for the Junge layer.

Response: The acronym has been changed to the Junge layer throughout the text.

Reviewer: Please use a rectangular projection in Figure 1 for regions on both sides of the equator.

Response: We have carefully considered this suggestion by the Reviewer but have decided that the current projection more accurately depicts the back trajectories included in the map. Therefore we would like to keep our current projection.

Reviewer: On page 30546, line 15, refer to Fig.1.

Response: The reference to figure 1 has been added.

Reviewer: In Figure 2 an additional axis with time would be useful to see possible

diurnal variations.

Response: As mentioned above, it is difficult to see diurnal variability because we were steaming. Therefore, to avoid making the plot more complicated, we would like to keep it in its current configuration.

Reviewer: In Figure 4 a logarithmic scale might be better in the right panel. The vertical axis should be extended to 17km even if there are no HIPPO data.

Response: The Reviewer is absolutely correct. We have changed the plot to a logarithmic scale and have extended the vertical reference.

Reviewer: In the caption of Figure 5 parts a and b are messed up.

Response: The caption has been corrected.

Reviewer: There are several typos in the reference list (e.g. p30559, l.19), also standard abbreviations for journals should be used.

Response: The references have been corrected.

Reviewer: 4 References Newell, R.E. and S. Gould-Stewart: A stratospheric fountain? J.Atmos.Sci. 38, 2789- 2796, 1981.

Response: Yes good suggestion included above.

Second comment from Anonymous Referee #2

Reviewer: Oxidation of DMS leads not only to SO2 but also to MSA (methanesulfonic acid) whichis transported to the TTL by deep convection. MSA was detected in particles by measurementsfrom high altitude aircraft in the lowermost tropical stratosphere (Froyd etal, 2009). This might be worth to be addressed also in the paper. Froyd, K.D., D.M. Murphy, T.J. Sanford, D.S. Thomson, J.C. Wilson, L. Pfister and L. Lait: Aerosol composition of the tropical upper troposphere. Atmos. Chem. Phys. 9, 4363-4385, 2009.

Response: We thank the Reviewer for his/her efforts and the additional information and agree that MSA (and other DMS oxidation products) can be transported to the upper troposphere/lower stratosphere. However, because measurements onboard the ship consisted only of DMS, we do not want to add more speculation regarding the fate of unmeasured DMS oxidation products. We did however add the above reference to the conclusions, “Given that dissolved DMS concentrations observed in the tropical western Pacific Ocean were not considerably high, it is noteworthy that the intense vertical transport in this area can deliver large quantities of DMS and, likely, its oxidation products to the TTL, where they can potentially cross into the stratosphere and (further) oxidize and form sulfate aerosol (e.g. DMS derived methanesulphonic acid found in upper troposphere/lower stratosphere aerosols, Froyd et al., 2009).”

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 30543, 2012.