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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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Response to Reviews: Dimethylsulphide (DMS) emissions from the West Pacific Ocean: a potential marine source for the stratospheric sulphur layer C. A. Marandino et al.

Anonymous Referee #1

Reviewer: The paper addresses the question of the possible contribution of biogenic DMS emission to the formation of stratospheric aerosols as suggested by Crutzen in 1976. From simultaneous measurements of oceanic and atmospheric DMS during a research vessel cruise from Japan to Australia in October 2009, the authors are

showing that DMS emissions are reinforced up to 200 ppt during storms high wind episodes. The same DMS concentration reported occasionally by the HIPPO2 aircraft at 8 km altitude is very consistent with a fast uplift from the PBL by meso-scale convective systems (although poorly captured by the ERA-Interim global model). The vertical and horizontal transport of the DMS rich layer is further explored using the FLEXPART Lagrangian model with ERA-Interim winds, suggesting that large amounts of sulphur could be transported up to 17 km altitude in this region and thus that DMS might be an important source of sulphur for the stratospheric aerosols.

General Response to Reviewer 1: We thank the reviewer for providing helpful comments. It is important to highlight here that no one has really considered DMS itself as being transported to the tropopause region, but more so the DMS oxidation products (such as OCS, Crutzen et al., 1976). Therefore, the model results presented here are unique and unconventional. However, we do not think that marine DMS, in any way, competes with volcanic sulphur loading to the stratosphere. In addition, we want to make it clear that this study is very regional in its scope. We are only stressing the tropical West Pacific delivery, which is clearly reflected in our title, and, again, do not want to convey that marine DMS is of global importance. We revised the following sentence in our abstract:

"Thus, if DMS can cross the TTL, we conclude that the considerably larger area of the tropical West Pacific Ocean can be an important source of sulphur to the stratospheric persistent sulphur layer, which has not been considered as yet." We have also revised the introduction (e.g. in the last sentence we added "...of surface DMS emissions for potential stratospheric sulphur loading in this region."). Additional detailed comments are below.

Reviewer: General Comments The analysis of ship and aircraft DMS measurements and the demonstration of the reinforced emissions in high wind conditions is a nice piece of work which by no doubt will deserve publication. But the conclusion that oceanic DMS emissions could be an important source of stratospheric aerosol is far

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less convincing. There are several reasons for that: a) The 17 km altitude over the West Pacific during the boreal winter is in the upper troposphere and not in the lower stratosphere. It is below the cold point tropopause.

Response: While aboard the TransBrom cruise, radiosondes measurements were performed. They show that the height of the tropical cold point tropopause lies at 17 km altitude (Quack and Krüger, IFM-GEOMAR Cruise Report No. 37, 2010). This sentence has been added to section 2.2, "The cold point tropopause altitude was confirmed during TransBrom with regular 6-hourly radiosonde measurements (see text above)." In addition, for clarification, the TransBrom cruise was performed during October, which is NH fall season.

Reviewer: b) the ERA-Interim vertical wind in the Tropical Troposphere Layer (TTL) derived from the horizontal wind divergence is a very poor measure of vertical velocity. It leads to a strong overestimation of the DMS flux reaching 17 km. As shown for example by Corti et al (GRL 2005), Yang et al. JGR (2008) or Fueglistaler (2009), the vertical transport above the neutral buoyancy layer (NBL) around 14 km altitude is due (at least above oceanic areas) to the radiative heating of the air-masses, a very slow process of 0.4 mm/s (1 km/month) which do not permit very short lived species like DMS to reach the stratosphere.

Response: Recent studies have shown that the meteorological assimilation ERA-Interim has improved vertical velocities, leading to a much better representation of the Brewer Dobson Circulation (e.g. Ploeger et al., 2010; Monge-Sanz et al., 2012; Diallo et al 2012) in contrast to previous available assimilation data (e.g. Meijer et al., 2004; Corti et al., 2005; Monge-Sanz et al., 2007; Scheele et al., 2005; Krüger et al., 2008; Wohltmann and Rex, 2008). Ploeger et al (2010) has shown that the residence time of ERA-Interim using the kinematic versus dynamic approach reveals only small differences in contrast to previous studies relying on the too high and noisy vertical velocities fields (Fueglistaler et al 2004 and ff). Next to this, we are not using the ERA-Interim vertical velocities provided by ECMWF, but vertical wind fields calculated

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in hybrid coordinates mass-consistently from spectral data using a pre-processor. This information has been added to the methods section (Section 2.2 second paragraph): "The vertical wind input data retrieved from ECMWF is calculated in hybrid coordinates mass-consistently from spectral data using a pre-processor." Additionally, as Krüger et al (2009) have shown with the diabatic approach using opECMWF/ ERA40 heating rates, the residence time above the tropical West Pacific can be significantly lower than in the rest of the TTL.

However, we agree with the reviewer that vertical velocities (no matter if derived from diabatic heating rates or from the horizontal wind divergence) cannot explain TTL residence times short enough to deliver a 1-day life time tracer to the stratosphere. Here, we think that convective overshooting is the crucial mechanism enabling transport of such short lived species. In our case, only 0.48% of DMS reaches the 17 km level and, due to the ongoing discussion of the impact of deep convective overshooting, it is not easily possible to reject such entrainment as unrealistic. For example, Vernier et al (2011, ACP) states, "The CALIPSO aerosols observations suggest that convective overshooting might be a major contributor of troposphere-to-stratosphere transport, . . ."We moved the discussion of Tost et al., from the methods to the results and added the following discussion:

Tost et al. (2010), using different convective parameterisation schemes in a global CTM, showed that the choice of the convection parameterisation has an influence on trace gas distributions. It is shown that the Emanuel parameterisation, used by FLEXPART, injects more mass across the 250 mb surface ($\sim$11 km altitude) in the tropics than other convection schemes used. Therefore, it is possible that FLEXPART may show increased injected mass across $\sim$ the 17 km altitude surface in the tropics. However, the representation of convection in FLEXPART has been validated with tracer experiments and 222Rn measurements in Forster et al. (2007). While observational evidence for direct convective injections into the lower stratosphere exists (e.g., Ricaud et al., 2007; Corti et al., 2008), it is not clear yet how frequent such convective over-

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shooting events are and what their relative impact on the stratospheric composition is. The importance of convective overshooting for troposphere-stratosphere exchange has been highlighted recently by Vernier et al. (2011), and with regard to regional importance by Sassen et al. (2008) and Nazaryan et al. (2008). Additionally, Romps and Kuang (2009) discuss the enhanced likelihood of deep convection during tropical storms, three of which were encountered on the TransBrom cruise (Krüger and Quack, 2012). On the other hand studies based on satellite data from Gettelman et al. (2002), Liu and Zipser (2005), and Rossow and Pearl (2007) argue for only little impact of deep convective overshooting with less than 1% of storms penetrating the stratosphere. Note that our model results suggest that 0.48% of the DMS emitted into the marine boundary layer will reach the stratosphere corresponding to a delivery of 30 g S per month. Such a scenario suggests a mechanism where deep convection, although not important for the overall mass flux, could surprisingly enable DMS to act as a regional source for stratospheric sulfur.

Reviewer: c) As shown by Vernier et al. (GRL 2011) the stratospheric aerosol increase since 2003 reported by Hofmann (2009) is not resulting from anthropogenic sulphuric pollution from China as suggested by Hofmann but to a series of relatively small volcanic eruptions.

Response: We acknowledge the reviewer's point that Vernier et al. (2011) quite convincingly argues for minor volcanic eruptions to be the major contributor to the sulphur loading to the stratosphere (and again, we in no way think marine DMS rivals this source). However, there has been an evolution in thinking with regard to the important processes contributing to stratospheric sulphur loading that should not be ignored. In addition, no study to date, except perhaps Myrhe et al. (2004) but likely only with respect to silent degassing by volcanoes, has attempted to assess the role of all likely contributing factors to stratospheric sulphur loading. We have rewritten a part of the introduction reflecting the major importance of volcanoes but still refer to the other possible sources:

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"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 the 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."

Again, we think it is interesting and largely unexplored that changes in marine derived DMS fluxes in the tropics may have (or could in the future) contributed to changes in the stratospheric sulphur layer.

Reviewer: d) In the absence of volcanic eruption between 1996-2003, the background aerosol concentration is reducing considerably (Vernier et al. 2011 Fig. 1) showing that DMS and anthropogenic sources of sulphur are very small compared to volcanoes,

Response: We agree with the reviewer that marine sulphur is a small source compared to volcanoes. As stated above, we are not trying to argue for a greater importance for marine sulphur, rather to note that it can be regionally important. However, we would like to respectfully point out there is a bit of debate related to the Reviewer's comment. Solomon et al. (2011) states that both anthropogenic and volcanic sources are important. In addition, Solomon et al. (2011) also show in their Figure 2 that there have been increases in the aerosol optical depth at Mauna Loa from late 1990s to 2000. They compare the data presented to three other observations and conclude they all say the same thing. She also cites an additional paper (Deshler et al., 2006, reference 15 within Solomon et al.) that argues that the apparent increasing/decreasing trend in stratospheric aerosols is influenced by the way the time period for analysis is chosen. They discuss a bit about how in 2000 there is controversy surrounding the trend in aerosol optical depth in the literature (page 867 last column last paragraph).

Reviewer: e) There is no signature of aerosol increase during the DMS boreal winter in the tropics but exactly the opposite: a cleansing of the aerosols by injection of clean air

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in the lower stratosphere (mainly above continental regions) (Vernier et al. ACP 2011).

Response: We see the Reviewer's concern here, but we are not sure that the information from Vernier is contradictory to this paper. If more "clean" air is delivered to the lower stratosphere that is in keeping with the possibility of more open ocean West Pacific ("clean air") DMS delivery (provided it is still gaseous DMS). We were in the region during October and the drop in aerosols from Vernier is from November to January. It is unclear to us, what the conversion time from DMS to sulphate aerosol would be in the stratosphere (it is possible the aerosols are formed before November). In addition, if we believe climatologies, DMS fluxes should be high from September to March, and maybe are influential in September, October, February, and March. Or maybe the conversion time is slow and DMS emissions January – March are influential in a few months time. Given all the uncertainties, we are not prepared to make any concrete statements as to whether or not it is possible for DMS to contribute to stratospheric aerosols. The possibility still exists and should be further studied.

Reviewer: In summary, it cannot be concluded from FLEXPART/ERA-Interim simulations that DMS could penetrate the stratosphere and that sulphur from DMS could represent a significant contribution to stratospheric aerosols. However, providing the conclusions are revised, the analysis of the DMS ship and aircraft measurements showing that high DMS levels can be reached in the mid-troposphere near convective systems is very valuable and deserves publication. I fully understand that the authors might be disappointed by the above comments. But the conclusion that DMS cannot reach the stratosphere will be also very valuable and useful. This already happened with another oceanic VSLS, Iodine oxide IO, which was suggested by S. Solomon et al. (JGR 1994) to be responsible for ozone depletion in the lower tropical stratosphere, but shown later to be of insignificant concentration there (Pundt et al. JAC, 1998).

Recommendations My recommendation is to publish the paper but after deep revision of the discussion and the conclusions by taking into account the above comments. If meso-scale model simulations, which could reproduce the DMS entrainment up to the

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altitude of the HIPPO2 aircraft, are not available which is fully understandable, I would recommend to add a discussion on the limitation of the FLEXPART/ERA-Interim simulations to reproduce the convective lifting of PBL air-masses in the mid-troposphere, particularly above the neutral buoyancy level, and add some comments on the very slow ascent velocity above the zero radiative heating level. Otherwise, the paper is nicely written and technically fully acceptable.

Response: Given the aircraft data and the model simulation we can conclude that DMS reaches the TTL, the assumption that it reaches the stratosphere however can only be concluded by the model itself. Thus, we adapt our main conclusion to this statement (changes are highlighted): "The emissions were employed to model the amount of DMS that is transported to the tropical tropopause layer (12-17 km) in October applying the Lagrangian transport model FLEXPART. The resulting amount of DMS to 17 km altitude is notable, 75-119 times greater than the required stratospheric source when scaled by the area of emissions. This amount could also increase with season, during times of higher emission, tropical cyclone or deep tropical convection activities. 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 to form sulfate aerosol (e.g. DMS derived methanesulphonic acid found in upper troposphere/lower stratosphere aerosols, Froyd et al., 2009)." To reflect this statement better we have added a question mark now to our ms title and changed the last sentence of our abstract to read, "Thus, if DMS can cross the TTL, we conclude that the considerably larger area of the tropical West Pacific Ocean can be an important source of sulphur to the stratospheric persistent sulphur layer, which has not been considered as yet.' Regarding aircraft data and model comparison, there are not very many datasets available. According to our co-author, E. Atlas, aircraft that can reach above tropical deep convection like to avoid these areas. Tropical missions, such as PEM-TROPICS A&B, had an altitude limit of 12 km. Data from the PEM missions showed non-zero

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DMS values at the 11 - 12 km region (range from a few to >10 pptv). For the TC-4 mission, no DMS above active convection (well above the main outflow) was observed, but this mission was largely over Southern US/Central America. Strong overshooting convection might have a chance to inject DMS directly (see detailed comments above). We estimate that 0.48% DMS reach the 17 km level and due to the ongoing discussion of the impact of deep convective overshooting it is not easily possible to reject such an entrainment as unrealistic.Also, please see our revised figure 4 according to the second reviewer's suggestions (below), which has now been plotted on a logarithmic scale. It is now evident that > 0 ppt DMS mixing ratios at altitudes above 8 km exist.

Regarding the limitations of FLEXPART, please see the detailed discussion related to point b).

Cited References:

Corti, T., Luo, B. P.,de Rues, M., Brunner, D., Cairo, F., Mahoney, M. J., Martucci, G., Matthez, R., Mitev, V., dos Santos, F. H., Schiller, C., Shur, G., Sitnikov, N. M., Spetlen, N., Vössing, J. J., Borrmann, S. and Peter, T.: Unprecedented evidence for deep convection hydrating the tropical stratosphere, Geophys. Res. Lett., 35, L10810, doi:10.1029/2008GL033641, 2008. Diallo, M., Legras, B. and Chédin, A.: Age of stratospheric air in the ERA-Interim, Atmos. Chem. Phys., 12, 12133-12154, doi:10.5194/acp-12-12133-2012, 2012. Deshler, T., Anderson-Sprecher, R., Jäger, H., Barnes, J., Hofmann, D. J., Clemesha, B., Simonich, D., Osborn, M., Grainger, R. G. and Godin-Beekmann, S.: Trends in the nonvolcanic component of stratospheric aerosol over the period 1971–2004, J. Geophys. Res., 111, D01201, doi:10.1029/2005JD006089, 2006.

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. Fueglistaler, S., Wernli, H. and Peter, T.: Tropical troposphere-to-stratosphere transport inferred from trajectory calculations, J. Geophys. Res., 109,

ACPD

12, C13448–C13459, 2013

D03108, doi:10.1029/2003JD004069, 2004. Gettelman, A., Salby, M. and Sassi, F.: Distribution and influenceof convection in the tropical tropopause region, J. Geophys. Res.-Atmos., 107(D10), 4080, doi:10.1029/2001JD001048, 2002

Liu, C. T. and Zipser, E. J.: Global distribution of convection penetrating the tropical tropopause, J. Geophys. Res.-Atmos., 110, D23104, doi:10.1029/2005JD006063, 2005 Monge-Sanz, B. M., Chipperfield, M. P., Untch, A., Morcrette, J-J., Rap, A. and Simmons, A. J.: On the uses of a new linear scheme for stratospheric methane in global models: water source, transport tracer, and radiative forcing, Atmos. Chem. Phys. Discuss., 12, 479–523, 2012

Meijer, Y. J., Swart, D. P. J., Allaart, M., Andersen, S. B., Bodeker, G., Boyd, I., Braathen, G., Calisesi, Y., Claude, H., Dorokhov, V., von der Gathen, P., Gil, M., Godin-Beekmann, S., Goutail, F., Hansen, G., Karpetchko, a., Keckhut, P., Kelder, H. M., Koelemeijer, R., Kois, B., Koopman, R. M., Kopp, G., Lambert, J.-C., Leblanc, T., McDermid, I. S., Pal, S., Schets, H., Stubi, R., Suortti, T., Visconti, G., Yela, M.:Pole-to-pole validation of Envisat GOMOS ozone profiles using data from ground-based and balloon sonde measurements, J. Geophys. Res., 109, D23305, doi:10.1029/2004JD004834, 2004.

Monge-Sanz, B. M., Chipperfield, M. P., Simmons, A. J. and Uppala, S. M.: Mean age of air and transport in a CTM: Comparison of different ECMWF analyses, Geophys. Res. Lett., 34, L04801, doi:10.1029/2006GL028515, 2007.

Nazaryan, H., McCormick, M. P. and Menzel, W. P.: Global characterization of cirrus clouds using CALIPSO data, J. Geophys. Res.-Atmos., 113, D16211, doi:10.1029/2007JD009481, 2008

Ploeger, F., Konopka, P., Günther, G., Grooß, J.-U. and Müller, R.: Impact of the vertical velocity scheme on modeling transport in the tropical tropopause layer, J. Geophys. Res., 115, D03301, doi:10.1029/2009JD012023, 2010.

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12, C13448–C13459, 2013

Ricaud, P., Barret, B., Attié, .-L., Motte, E., Le Flochmoën, E., Teyssèdre, H., Peuch, V.-H., Livesey, N., Lambert, A. and Pommereau, J.-P.: Impact of land convection on troposphere-stratosphere exchange in the tropics, Atmos. Chem. Phys., 7, 5639-5657, doi:10.5194/acp-7-5639-2007, 2007.

Romps, D. M. and Kuang, Z.: Overshooting convection in tropical cyclones, Geophysical Research Letters, 36(9), L09804, doi:10.1029/2009GL037396, 2009. Rossow, W. B. and Pearl, C.: 22-Year survey of tropical convection penetrating into the lower stratosphere, Geophys. Res. Lett., 34, L04803, doi:10.1029/2006GL028635, 2007

Sassen, K., Wang, Z. and Liu, D.: Global distribution of cirrus clouds from CloudSat/CloudAerosol Lidar and Infrared Pathfinder Satellite Observations (CALIPSO) measurements, J. Geophys. Res.-Atmos., 113, D00A12, doi:10.1029/2008JD009972, 2008

Scheele, M. P., Siegmund, P. C. and Velthoven, P. F. J.: Stratospheric age of air computed with trajectories based on various 3D-Var and 4D-Var data sets, Atmos. Chem. Phys., 5, 1-7, doi:10.5194/acp-5-1-2005, 2005.

Vernier, J.-P., Pommereau, J.-P., Thomason, L. W., Pelon, J., Garnier, A., Deshler, T., Jumelet, J. and Nielsen, J. K.: Overshooting of clean tropospheric air in the tropical lower stratosphere as seen by the CALIPSO lidar, Atmos. Chem. Phys., 11, 9683-9696, doi:10.5194/acp-11-9683-2011, 2011.

Wohltmann, I. and Rex, M.: Improvement of vertical and residual velocities in pressure or hybrid sigma-pressure coordinates in analysis data in the stratosphere, Atmos. Chem. Phys., 8, 265-272, doi:10.5194/acp-8-265-2008, 2008.

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

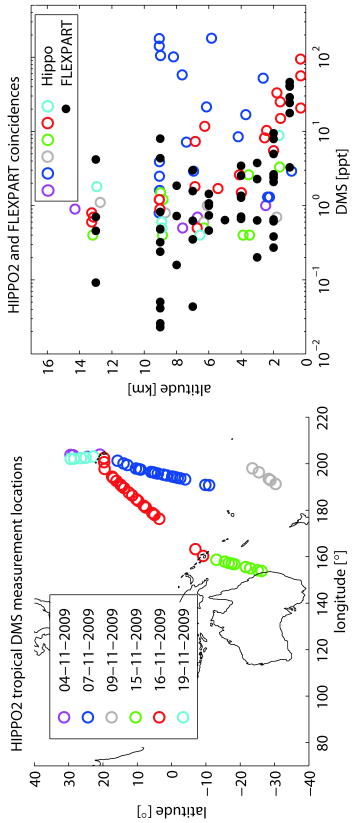

Fig. 1.

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