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Dimethylsulphide (DMS) emissions from the West Pacific Ocean: a potential marine source for the stratospheric sulphur layer

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Abstract

Sea surface and atmospheric measurements of dimethylsulphide (DMS) were performed during the TransBrom cruise in the West Pacific Ocean between Japan and Australia in October 2009. Air-sea DMS fluxes were computed between 0 and 30 µmol m^{-2} d^{-1}, which are in agreement with those computed by the current climatology, and peak emissions of marine DMS into the atmosphere were found during the occurrence of tropical storm systems. Atmospheric variability in DMS, however, did not follow that of the computed fluxes and was more related to atmospheric transport processes. The computed emissions were used as input fields for the Langrangian dispersion model FLEXPART, which was set up with actual meteorological fields from ERA-interim data and different chemical lifetimes of DMS. A comparison with aircraft in-situ data from the adjacent HIPPO2 campaign revealed an overall good agreement between modeled versus observed DMS profiles over the tropical West Pacific ocean. Based on observed DMS emissions and the meteorological fields over the cruise track region, the model projected that up to 30 g S per month in the form of DMS can be transported above 17 km in this region. This surprisingly large DMS entrainment into the stratosphere is disproportionate to the regional extent of the cruise track area and mainly due to the high convective activity in this region as simulated by the transport model. Thus, 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.

1 Introduction

Dimethylsulphide (DMS) is the most abundant naturally produced sulphur compound emitted from the sea surface. DMS has been the focus of much research since Charlson et al. (1987) proposed that DMS produced in the sea surface by phytoplankton may affect the atmospheric radiative budget via its role in aerosol and cloud formation.

In addition, because DMS is rapidly oxidized when emitted to the atmosphere, studies have been conducted showing that certain DMS oxidation products can be transported above the tropopause and contribute to the persistent stratospheric sulphur layer (PSL), e.g. carbonyl sulphide (Crutzen, 1976), sulphur dioxide (SO_2) (Chatfield and Crutzen, 1984), and sulphur species in general (Gondwe et al., 2003; Lucas and Prinn, 2003). Recent work has shown that an underestimation of the radiative effect of the PSL can lead to an overestimation of global warming (Solomon et al., 2011). 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. The importance of naturally occurring sulphur containing trace gases as a source to the stratosphere is currently debated, since minor volcanic eruptions and anthropogenic sulphur dioxide (SO_2) seem to have an overwhelming global footprint (Bruehl et al., 2012; Bourassa et al., 2012; Vernier et al., 2011). Nonetheless, 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 be important.

Typically surface ocean DMS emissions (F, flux) are calculated using $F = k \Delta C$, where k is a wind speed based parameterisation of the gas transfer coefficient and ΔC is the measured bulk air-sea concentration difference. Because DMS is almost always supersaturated in the surface ocean, seawater concentrations are the main component of the concentration difference. Regarding k values, there is currently no consensus on the functionality of the wind speed dependence of the gas transfer coefficient. Thus, several different parameterisations have been proposed and used frequently in the literature, which lead to considerable variability in computed surface ocean trace gas fluxes (see Ho et al., 2006 for an overview). Furthermore, although remotely sensed wind speeds, with high spatial and temporal resolution, are readily available for flux calculations, it is still difficult to parameterise surface ocean DMS concentrations on

similar scales. Therefore, it is necessary to use archived in situ measurements to calculate DMS emissions. Unfortunately, there is a considerable lack of high spatial and temporal resolution data for oceanic DMS. It is important to build up the current Global Surface Seawater DMS Database (http://saga.pmel.noaa.gov/dms), in conjunction with
5 ancillary data, in order to better understand the controls on oceanic DMS and predict future air-sea fluxes. Lana et al. (2011), in the footsteps of Kettle et al. (1999, 2000), has used the existing database to compile a current surface ocean DMS climatology and compute air-sea fluxes. However, the influence of DMS hotspots and high wind speed events, such as typhoons and tropical storms, on the DMS flux is hard to deter-
10 mine from such climatology. Therefore, it is important to compare in situ calculations to those in the climatology, not only to make the database more robust, but also to determine the importance of such events relative to "normal" conditions.

In this paper, we use in situ measurements of ΔC and wind speed (U) with three different k parameterisations to compute DMS emissions during the TransBrom cruise
15 in October 2009 in the western Pacific Ocean. 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
20 West Pacific region acts as a main entrance region of trace gases into the stratosphere 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 min and 46 h due to reaction with hydroxyl and nitrate radicals (e.g. Osthoff et al., 2009; Barnes et al., 2006), DMS transport to the TTL
25 is more efficient in the western Pacific Ocean than in other oceanic regions. Computed DMS sea-to-air in situ fluxes from the TransBrom cruise to the West Pacific Ocean were used to initiate the high resolution Lagrangian transport model FLEXPART to determine the importance of surface DMS emissions for stratospheric sulphur loading in this region.

2 Data and model

2.1 Ship measurements

Underway surface water samples for DMS and air samples for DMS were collected aboard the R/V *Sonne* from the 9 to 24 October 2009 during a transit from Tomakomai (Japan) to Townsville (Australia). A detailed description of the TransBrom cruise including the meteorological background is given by Krüger and Quack (2012). Three tropical storms (Melor, 9 October; Nepartak, 12 October; Lupit, 14 October) passed the transit and were responsible for wind speeds up to $18\,\mathrm{m\,s^{-1}}$ (see also Figs. 1 and 2). The circulation of the Pacific Ocean and atmosphere were affected by a strengthening El Niño event, inducing an increase in sea surface temperature towards the east, which triggered an elevated atmospheric convection. The analyses of water samples, taken every three hours, from this cruise using gas chromatography coupled to flame photometric detection are described in detail by Zindler et al. (2012). Atmospheric measurements of DMS were performed according to Schauffler et al. (1999), also with samples taken at three hour intervals. Air and water samples were not always taken simultaneously. When this occurred, the distance between the sample locations was used to determine the air and water pairs. The mean analytical errors were estimated to be ±20 % for dissolved DMS (Zindler et al., 2012) and ±10 % for atmospheric DMS.

The DMS oceanic and atmospheric data were used for the flux calculation. Sea surface temperature and wind speed data from ship sensors at one minute resolution were selected dependent on time and latitude of the DMS samples (Fig. 2). Flux calculations were performed by applying three different gas transfer coefficient parameterisations at a Schmidt number of 720, that of DMS in seawater at 25 °C according to Saltzman et al. (1993): Marandino et al. (2007) – UCI; Wanninkhof (1992) – W92; Liss and Merlivat (1986) – LM. The parameterisations were chosen to reflect the different theories of wind speed dependence and measurement techniques for k, where UCI is linear and derived from eddy covariance measurements, W92 is quadratic and derived from the

[14]C ocean inventory, and LM contains three different linear parameterisations based on tracer studies and wind-wave tank measurements.

2.2 Model runs

The atmospheric transport of DMS from the oceanic surface into the upper troposphere and the TTL is simulated with the Lagrangian particle dispersion model FLEXPART (Stohl et al., 2005). This model has been widely applied to simulate long-range and mesoscale transport (e.g., Spichtinger et al., 2001; Stohl et al., 2003; Forster et al., 2004) and extensively validated based on measurement data from three large-scale tracer experiments (Stohl et al., 1998) and on intercontinental air pollution transport studies (e.g. Stohl and Trickl, 1999; Forster et al., 2001). FLEXPART is an off-line model driven by meteorological fields from the European Centre for Medium-Range Weather Forecast (ECMWF) numerical weather prediction model. It includes the simulation of chemical decay based on a prescribed atmospheric lifetime, parameterisations for moist convection (Forster et al., 2007), turbulence in the boundary layer and free troposphere (Stohl and Thompson, 1999), dry deposition and in-cloud, as well as below-cloud, scavenging.

In order to quantify the amount of DMS transported into the upper TTL for the observations during the TransBrom campaign, we simulate the transport pathways (trajectories) of a multitude of air parcels starting at the ship measurement time and location. For each computed DMS in situ sea-to-air flux a separate FLEXPART run is launched where 10 000 air parcels were released over one hour from a $0.0002° \times 0.0002°$ grid box ($\sim 500\,m^2$) at the ocean surface centered at the measurement location. Based on the computed DMS in situ flux, the total amount of DMS emitted from this grid box over one hour is calculated and uniformly distributed over all air parcels. The amount of DMS carried by each air parcel is reduced at a rate corresponding to its chemical lifetime, which is set to 12 h and 24 h to represent typical gas phase values found in the literature (Sect. 1), for two model scenarios. The FLEXPART runs are driven by

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the ECMWF reanalysis product ERA-Interim (Dee et al., 2011) using 6-hourly meteorological data. The input fields of horizontal and vertical wind, temperature, specific humidity, convective and large scale precipitation, among other parameters, are given at a horizontal resolution of 1° × 1° on 60 model levels.

For the validation of the FLEXPART runs, we compare simulated DMS abundances with available aircraft observations from the HIAPER Pole to Pole Observations (HIPPO) 2 campaign, which were collected during several flight missions over the Pacific Ocean during October/November 2009 (http://catalog.eol.ucar.edu/hippo2/index.html; Wofsy et al., 2011). For this intercomparison, additional FLEXPART runs were launched applying the actual meteorological fields for the time of the HIPPO2 campaign during November 2009, but using the DMS emissions from the TransBrom cruise during October 2009 since we do not have observed DMS emissions for November 2009. For these runs an average DMS emission of $1.54 \times 10^{-7} \, \mathrm{mol \, m^{-2} \, h^{-1}}$ was distributed uniformly over the tropical oceans (within 30° S–30° N) and the atmospheric DMS transport was calculated for November 2009. Additionally, the same global runs were carried out for October and December 2009 to estimate temporal (month-to-month) variations of the DMS entrainment into the stratosphere.

The level above which no significant washout is expected is of special importance for the transport of DMS to the stratosphere. DMS and its oxidation products reaching this altitude can be assumed to contribute to the stratospheric sulfur loading irrespective of their remaining chemical lifetime. While the exact vertical extent of the region where significant washout is expected is still under debate (Fueglistaler et al., 2009), we have chosen the cold point temperature at around 17 km as upper estimate of this level. Additionally, we evaluate DMS entrainment above 15 km which is well above the main convective outflow regions and close to the level of zero radiative heating. 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 (∼ 11 km altitude) in the tropics than

other convection schemes used. Therefore, it is possible that FLEXPART may show increased injected mass across ∼ the 17 km altitude surface in the tropics. However, the representation of convection in FLEXPART has been validated with tracer experiments and ^{222}Rn measurements in Forster et al. (2007).

For the surface air mass origin, one-day backward trajectories have been calculated online with the HySplit model using the meteorological fields from National Centers for Environmental Prediction – Global Data Assimilation System (NCEP-GDAS). Detailed technical information about the trajectory model version 4 can be found in Draxler and Hess (2004).

3   Results and discussion

3.1   Atmospheric concentrations and computed DMS air-sea fluxes

Atmospheric mixing ratios of DMS ranged between 2 and 200 ppt (76.2 ± 52.2 ppt), which are in the low to average range for open ocean background mixing ratios of DMS (Fig. 2). Previous measurements of atmospheric DMS around the area of the TransBrom cruise track are in general agreement, 26.6 ± 16.1 ppt, 19.3 ± 14.7 ppt, 42.4 ± 26.9 ppt, and 59.3 ± 16.8 ppt, but were measured during May–June (Kato et al., 2007; Marandino et al., 2007). DMS values measured in the marine boundary layer, during the adjacent HIPPO2 aircraft campaign (discussed in Sect. 3.2), were between 0 and 100 ppt during November 2009. One day back trajectory analysis shows that the first 5 days of the ship cruise were influenced by continental air masses from Asia, the next 6 days experienced back trajectories from the open ocean (the 11th day, just south of the equator had air masses originating over the Soloman Islands), and the air in the last 4 days originated from eastern Australia or the Tasman Sea (Fig. 1). The largest atmospheric DMS abundances were observed at approximately 16° N, when the cruise encountered the tropical storm Nepartak. However, the highest values that

were not influenced by major storm events were found towards the end of the cruise track, in the air regime influenced by the Tasman Sea.

DMS fluxes were computed using the shipboard measurements of atmospheric and surface ocean concentrations (discussed by Zindler et al., 2012), sea surface temperature, and horizontal wind speed (Fig. 2). Three different parameterisations were applied to compute the gas transfer coefficient: Marandino et al. (2007) – UCI; Wanninkhof (1992) – W92; Liss and Merlivat (1986) – LM. The computed fluxes vary between 3 and 30 $\mu mol\,m^{-2}\,d^{-1}$. The range of the fluxes reflects the range in the computed k values, e.g. W92 employs a quadratic and UCI a linear wind speed dependence. The diversity of gas exchange parameterisations causes approximately a factor of three difference in the computed fluxes. In this study, the highest values were computed during the tropical storm Nepartak, during which the highest wind speeds (up to 18 $m\,s^{-1}$) were experienced. The fluxes shown here are in the general range reported in the Lana et al. (2011) DMS climatology for October in this region. However, there are some spatial distribution differences. Lana et al. (2011) compute values between 0 and 15 $\mu mol\,m^{-2}\,d^{-1}$, with a maximum of approximately 30 $\mu mol\,m^{-2}\,d^{-1}$ in the Tasman Sea. Our maximum values are similar to those of Lana et al. (2011) but were observed northward of the equator between 20 and 40° N, directly related to storm events. The Tasman Sea values reported here did not reach the values in the Lana et al. (2011) climatology and are approximately 5 $\mu mol\,m^{-2}\,d^{-1}$.

The computed fluxes in all cases correlate more with wind speed than with the seawater concentrations of DMS, especially for fluxes computed with k values more strongly dependent on wind speed (Fig. 3). This may point to the fact that the gas transfer coefficient parameterisation disproportionately influences the computed fluxes. Eddy correlation measurements of DMS flux have indicated that the surface seawater DMS concentrations explain more of the variability in the directly measured fluxes than horizontal wind speed by a factor of approximately 2 (Marandino et al., 2007). Another complication surrounding the use of wind speed based parameterisations and measured concentrations was determined by Marandino et al. (2008). They found that

directly measured emissions were up to 5 times higher than those computed using the flux equation alone, possibly reflecting a disparity between the concentration of DMS at the interface and that of the bulk water. However, Marandino et al. (2008) hypothesise that this finding may be specific to regions with high biological activity and, therefore, may be not be not applicable here.

Interestingly, atmospheric values of DMS do not follow the same pattern as the computed fluxes or seawater DMS concentrations over the cruise track (Fig. 2). It is evident that the seawater concentrations of DMS do not have the same level of variability as the air values. It is very likely that the atmospheric values measured over the cruise track were more influenced by horizontal advection than by in situ fluxes. The highest fluxes were computed for the Nepartak storm event, at which time there is only a secondary maximum in the atmospheric mixing ratio. This may indicate that DMS was rapidly transported away and replaced with continental air, since back trajectories indicate a continental influence in this region. Conversely, there was a maximum peak in atmospheric values during the next tropical storm Lupit, which was at the secondary flux maximum. During this time, back trajectory analysis indicates that air masses originated from the open ocean. There may have been a larger source region upwind, which resulted in more DMS in the atmosphere that was rapidly transported by the storm toward the cruise track.

3.2 Implications for atmospheric sulphur loading

The measured levels of surface ocean DMS in the western Pacific Ocean are not above the mean level of the global open ocean (Zindler et al., 2012). Considering that the patterns of atmospheric DMS mixing ratios do not follow the surface ocean concentration patterns, nor do the flux values, transport processes seem to have an important influence on DMS derived sulphur loading to the atmosphere. In order to investigate the role of transport in more detail, the high resolution transport model FLEXPART was used to track the fate of DMS after its emission from the ocean. As a test, the tropical DMS distribution based on average TransBrom emissions was calculated for

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November 2009, where in-situ aircraft measurements of the HIPPO2 campaign were available above the tropical West Pacific Ocean (see Sect. 2.2 for details). FLEXPART simulations use an atmospheric DMS lifetime of 1/2 day and the output is given on a 1° × 1° grid. Figure 4 shows the locations of the tropical HIPPO2 measurements color coded by day. Coincident data points between the tropical HIPPO2 measurements and the FLEXPART output were identified, if their distance in latitude/longitude space is less than 0.5° and their altitude distance is less than 500 m. A comparison of all identified coincidences is shown in the right panel of Fig. 4. Large parts of the vertical DMS distribution observed during the HIPPO2 campaign can be reproduced by the FLEXPART simulation. DMS values are high in the boundary layer and low above, reaching mixing ratios between 0 and 2 ppt in the lower TTL (12–14 km). Some fragment of the HIPPO2 observations shows very large values (around 200 ppt) at around 8 km altitude that are not reproduced by the FLEXPART simulations. It is very likely that these large DMS mixing ratios resulted from local convective events lifting DMS rich air from the boundary layer into the upper troposphere. These large DMS values seem to be due to an atmospheric feature that is narrow in horizontal extent. It is very likely that such small scale features can only be reproduced using the true emission fields, which are not available for the present FLEXPART runs. The overall good agreement provides confidence in the simulated oceanic DMS contribution to the upper atmosphere using the in situ emissions from the TransBrom cruise.

In the next step, the amount of DMS transported into the TTL and to the top of the TTL was calculated using the emissions computed with the UCI air-sea gas flux approach as input for the FLEXPART simulations (Sect. 2.2). Figure 5 shows the vertical DMS distribution given as a total quantity [kg] and as a relative quantity [%] with respect to the amount of originally emitted DMS for the 1/2 day lifetime case. This vertical DMS distribution was determined for each emission event as the accumulated amount of DMS reaching the respective altitudes given on the y-axis. Figure 5a illustrates that in most cases less than 30 % of the originally emitted DMS leaves the boundary layer. With increasing altitude less DMS is found in the atmosphere and above 12 km more

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than 10 % of the originally emitted DMS can only be detected for a few isolated cases. Less than 1 % DMS in nearly all cases reaches the level of 17 km. The total amount of DMS transported from the ocean surface along the TransBrom cruise track is given in kg in Fig. 5b. Between 20° N and 15° N, as well as around 5° S, enhanced vertical trans-
5   port, which is connected with intense tropical convection (Krüger and Quack, 2012), can be observed. These events coincide with medium to large DMS emissions result-ing in 5×10^{-7}–1×10^{-6} kg of DMS (equivalent to 3 to 10 %) reaching the upper TTL. These same events also demonstrate that more than 30 % of emitted DMS can reach 8 to 9 km altitude, where peak mixing ratios of 50 to 180 ppt were detected by the
10   HIPPO2 aircraft campaign (Fig. 4). It is noteworthy, however, that the pattern in emis-sions, namely the peak emissions, does not entirely follow the pattern of entrainment to the TTL. On the first half of the cruise, until around 10° S, we can surmise that the storm events that triggered the large emissions do not always coincide with the high en-trainment events. South of 10° S, the pattern of sea-to-air fluxes is more closely linked
15   to the pattern of entrainment. Similar results were observed for $CHBr_3$ transport during the TransBrom cruise (Tegtmeier et al., 2012). Figure 6 shows tropical estimates of the amount of DMS transported above the level of 17 km for two different atmospheric DMS lifetimes (1 day and 1/2 day). As expected, the amount of DMS reaching 17 km is considerably smaller for the shorter lifetime.
20   These estimates of DMS entrained above 17 km, summed over the whole Trans-Brom campaign, are compared to the required global annual sulphur source com-puted by Hofmann et al. (2009) to maintain the PSL during volcanically quiescent periods (Table 1). For DMS with a one day lifetime, the average quantity trans-ported above 17 km over the cruise track is approximately 6.37×10^{-6} kg DMS h^{-1}
25   or 2.37×10^{-11} Tg S month^{-1}. The value changes to 3.84×10^{-6} kg DMS when FLEX-PART is run with the more conservative assumption of a DMS lifetime of 12 h. The monthly mean calculation for DMS transport above 17 km assumes that the DMS emis-sion field and convective processes are constant for the entire month, which is reason-able given that the cruise and FLEXPART runs extended over a 2 week period. Hoffman

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et al. (2009) calculates that 0.01–0.02 Tg S yr^{-1} is required globally, from all the different sulphur sources, including anthropogenic sulphur and minor volcanic eruptions, to maintain the increase in the PSL after 2000. A value of 2.0×10^{-13} Tg S month^{-1} is obtained when this value is scaled down by surface area to the region of the cruise track, i.e. the surface area of cruise track (5.75×10^4 m^2) divided by the surface area of world ocean (3.6×10^{14} m^2). The amount of DMS projected to be transported above the TTL is approximately 75–119 times higher than the required amount of sulphur from Hoffman et al. (2009). This computed sulphur loading does not take into account the oxidation products of DMS that may also be transported above the TTL. Myhre et al. (2004) projected that natural sulphur emissions on a global scale contribute significantly to the PSL source, however they also conclude that anthropogenic emissions are the dominant factor. While their conclusions are obvious for the global scale, the regional importance of marine sulphur has been overlooked. The value computed here from the TransBrom cruise highlights that oceanic emissions of DMS in regions of fast vertical uplift play a disproportionately (when evaluated by regional size) important role in the radiative budget of the atmosphere. Modest increases in marine emissions coupled to enhancements of vertical transport or tropical cyclone activity in the tropics may easily be a main factor, on a regional scale, contributing to the higher source of sulphur discussed by Hofmann et al. (2009) to the PSL.

Additionally, the entrainment rates modeled by FLEXPART for the month of October are not constant over the entire year. Figure 7 illustrates the change in tropical (20° S–20° N) DMS entrainment above 15 and 17 km over time, from October to December 2009, based on the conservative lifetime projection of 1/2 day. The FLEXPART runs use the same emission fields over the entire period, but variability in entrainment is clearly evident. This variability is only due to changes in the meteorology and hence in vertical transport processes (i.e. deep tropical convection) over time. On average, October shows lower DMS abundances at 15 and 17 km altitude than November and December, as would be expected from the pronounced and fast TTL transport during the boreal winter season over the West Pacific Ocean (Fueglistaler and Haynes, 2005;

Krüger et al., 2009). These runs are of course only representative for 2009 and interannual variability may be even more pronounced. However, during the TransBrom period from 9 to 24 October 2009, the DMS model values can be as high as during other short-term periods for November and December months. Thus, we conclude that given the very short lifetime of DMS the TTL entrainment is mainly determined by synoptic-scale processes such as tropical deep convective events rather than large-scale seasonal effects. The Lana et al. (2011) flux climatology shows increased DMS emissions in the tropics seasonally, especially from December to February. The emissions increase approximately 5 times over that time period, while entrainment above 17 km stays in the same order of magnitude and can be large for short-term periods (Fig. 7). Scenarios, in which several factors related to both emissions and meteorology background conditions (e.g. wind speed and direction, sea surface temperature) change, need to be investigated in order to understand how increased marine emissions coupled with increased transport to the stratosphere may impact sulphur loading to the free troposphere as well as to the PSL.

4 Conclusions

Ship measurements of seawater and atmospheric DMS, wind speed, and sea surface temperature from October 2009 in the western Pacific Ocean, on board the TransBrom cruise, were used to compute marine emissions of DMS. The emissions were employed to model the amount of DMS that is transported above the tropical tropopause layer (17 km) in October applying the high resolution Lagrangian transport model FLEXPART. The resulting amount of DMS in the stratosphere is notable, 75–119 times greater than the required stratospheric source when scaled by region. 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 deliver large quantities of DMS and its oxidation products

into the stratosphere, where they can (further) oxidize and form sulfate aerosol. Additional focused studies on DMS seawater concentrations and emissions are required in regions, such as the western tropical Pacific Ocean, in order to better quantify the full impact of marine DMS emissions on the radiative budget of the atmosphere, now and in a future climate.

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Table 1. Calculation of sulphur loading above the TTL relative to the $0.015\,\mathrm{Tg\,S\,yr^{-1}}$ required globally to maintain PSL after 2002 (Hofmann et al., 2009).

DMS lifetime	DMS above 17 km ($\mathrm{Tg\,S\,month^{-1*}}$)	Area of emissions ($\mathrm{m^2}$)	Area of global ocean ($\mathrm{m^2}$)	Required Tg S $\mathrm{month^{-1*}}$	Marine contribution (multiplying factor)
12 h	1.43×10^{-11}	5.75×10^{4}	3.60×10^{14}	2.00×10^{-13}	71.5
24 h	2.37×10^{-11}				119

[*] Scaled to the area of emissions.
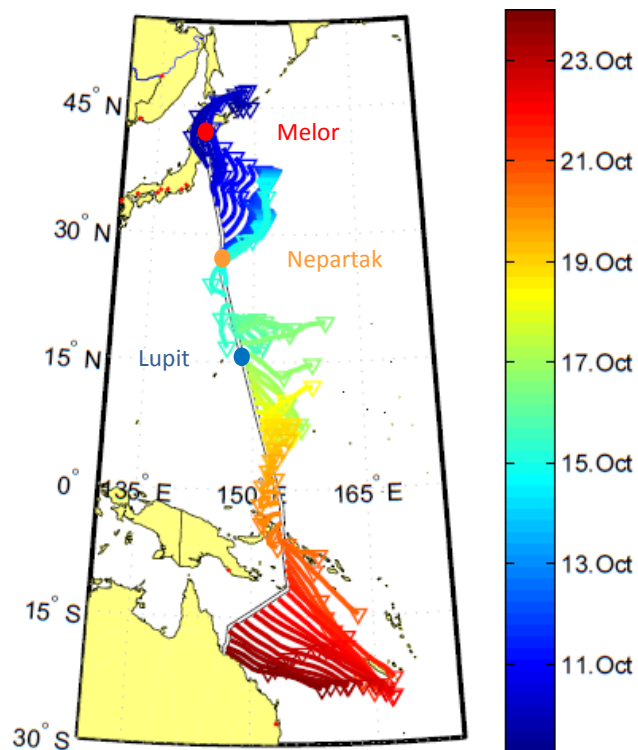
Fig. 1. TransBrom cruise track from Japan to Australia in October 2009. Colored lines indicate one day back trajectories for each day shown in the colorbar. Dots on the cruise track indicate the three storm events that occurred during the cruise.

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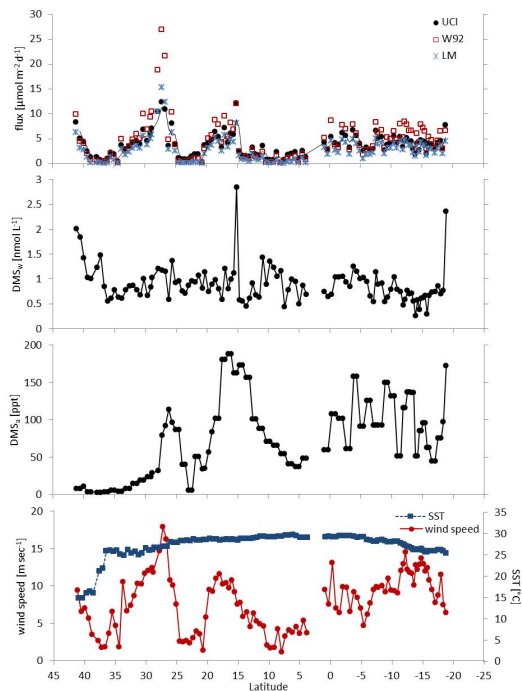
Fig. 2. Shipboard measurements and subsequent flux calculations over the TRANSBROM cruise track (by latitude, positive denotes northern latitudes and negative southern), from top: **(a)** computed DMS fluxes using the UCI k parameterisation (UCI-solid circle), the Wanninkhof, 1992 parameterisation (W92-open square), and the Liss and Merlivat(1986) parameterisation (LM-asterix); **(b)** measured seawater DMS concentrations from Zindler et al.(2012); **(c)** measured atmospheric DMS mixing ratios; **(d)** measured horizontal wind speed (solid circle) and sea surface temperature (solid square).
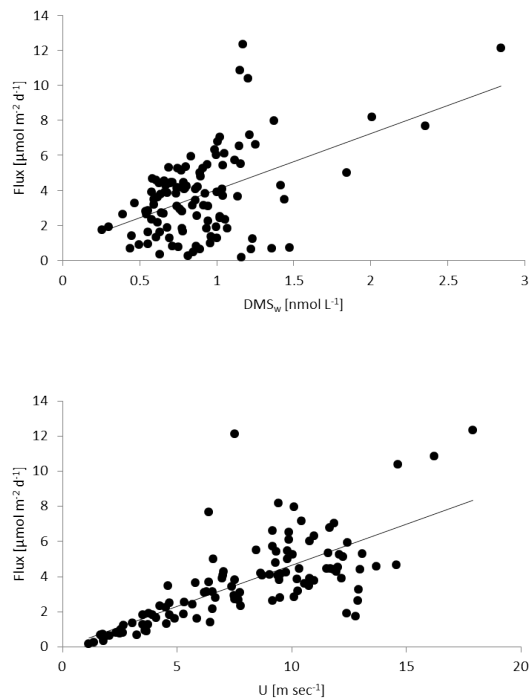
Fig. 3. (Top) Computed flux regressed against seawater concentration of DMS ($y = 3.20x + 0.84$, $r^2 = 0.24$). (Bottom) Computed flux regressed again horizontal wind speed ($y = 0.47x - 0.00$, $r^2 = 0.52$).
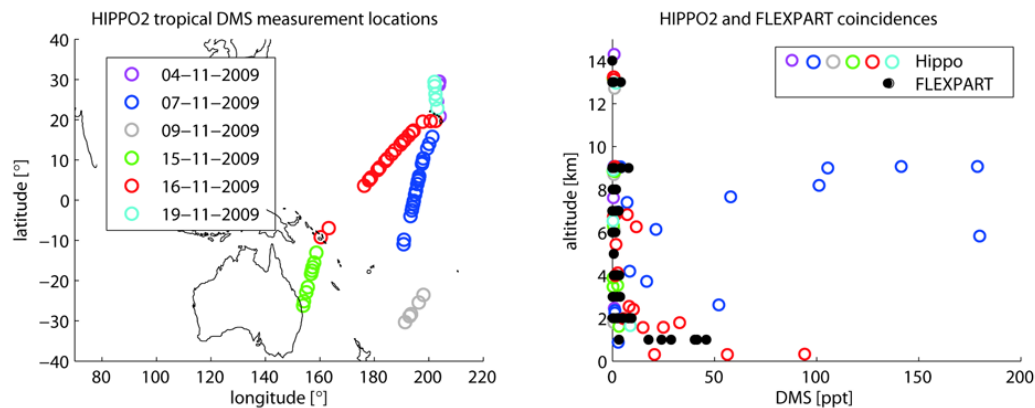
Fig. 4. Comparison between HIPPO2 atmospheric DMS observations and FLEXPART DMS simulations (1/2 day atmospheric lifetime). Measurement locations for HIPPO2 (left panel) and comparison between HIPPO2 and FLEXPART coincidences (right panel) are shown.
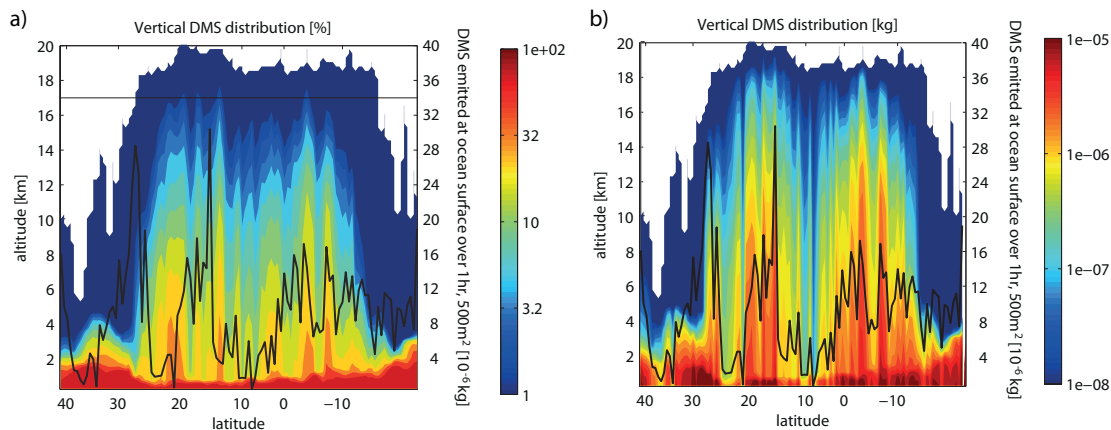
Fig. 5. Atmospheric vertical DMS distribution computed along the TransBrom cruise track given as **(a)** total amount [kg] and **(b)** amount relative to DMS emission from the sea surface [%]. Atmospheric DMS distribution is based on FLEXPART simulations with a 1/2 day atmospheric lifetime. DMS emission at the ocean surface over $500\,\text{m}^2$ and one hour is given as the black line corresponding to the right y-axis.
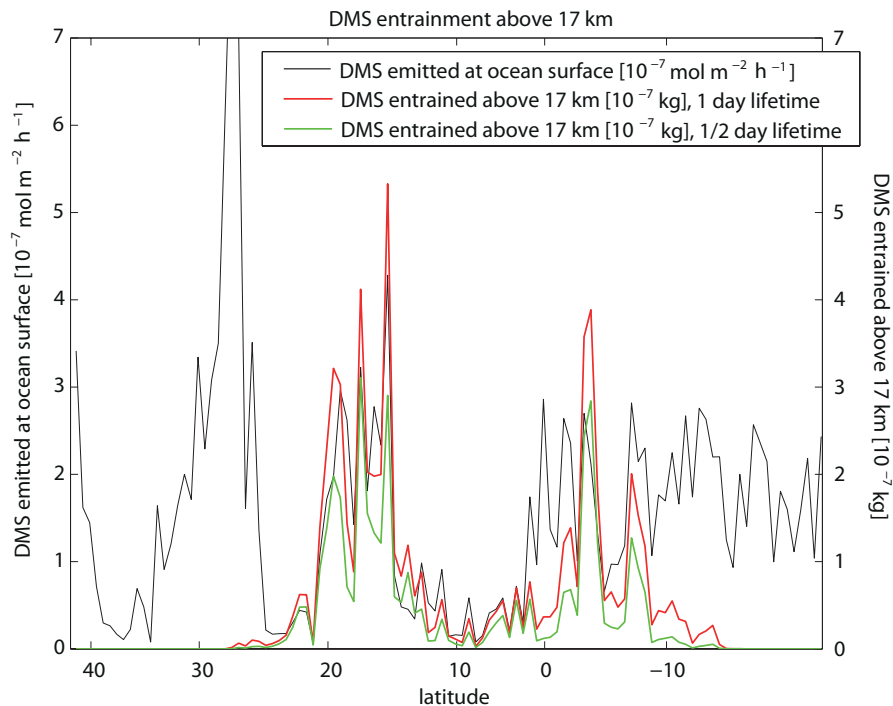
Fig. 6. Observed emissions of DMS at the ocean surface (black line), and total amount of DMS entrained above 17 km based on FLEXPART simulations with 1 day (red line) and 1/2 day (green line) atmospheric lifetimes are shown.
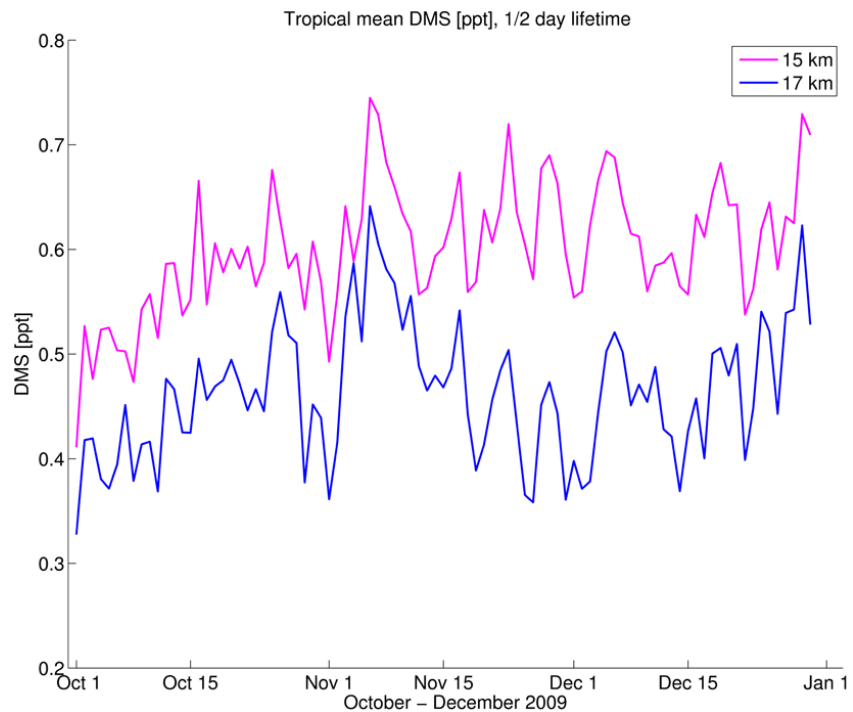
Fig. 7. Time series of tropical mean DMS VMR at 17 km and 15 km for October to December 2009. The time series is based on FLEXPART model simulations using TransBrom average emissions for the tropcial oceans and 1/2 day atmospheric lifetime for DMS.

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