Sulphur compounds, methane, and phytoplankton: interactions along a north-south transit in the western Pacific Ocean

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Abstract

Here we present results of the first comprehensive study of sulphur compounds and methane in the oligotrophic tropical West Pacific Ocean. The concentrations of dimethylsulphide (DMS), dimethylsulphoniopropionate (DMSP), dimethyldisulphoxide (DMSO), and methane (CH$_4$), as well as various phytoplankton marker pigments in the surface ocean were measured along a north-south transit from Japan to Australia in October 2009. DMS (0.9 nmol l$^{-1}$), dissolved DMSP (DMSP$_d$, 1.6 nmol l$^{-1}$) and particulate DMSP (DMSP$_p$, 2 nmol l$^{-1}$) concentrations were generally low, while dissolved DMSO (DMSO$_d$, 4.4 nmol l$^{-1}$) and particulate DMSO (DMSO$_p$, 11.5 nmol l$^{-1}$) concentrations were comparably enhanced. Positive correlations were found between DMSO and DMSP as well as DMSP and DMSO with chlorophyll $a$, which suggests a similar source for both compounds. Similar phytoplankton groups were identified as being important for the DMSO and DMSP pool, thus, the same algae taxa might produce both DMSP and DMSO. In contrast, phytoplankton seemed to play only a minor role for the DMS distribution in the western Pacific Ocean. The observed DMSP$_p$ : DMSO$_p$ ratios were very low and seem to be characteristic of oligotrophic tropical waters representing the extreme endpoint of the global DMSP$_p$ : DMSO$_p$ ratio vs. SST relationship. It is most likely that nutrient limitation and oxidative stress in the tropical West Pacific Ocean triggered enhanced DMSO production leading to an accumulation of DMSO in the sea surface. Positive correlations between DMSP$_d$ and CH$_4$, as well as between DMSO (particulate and total) and CH$_4$, were found along the transit. We conclude that both DMSP and DMSO serve as substrates for methanogenic bacteria in the western Pacific Ocean.
1 Introduction

Oceanic dimethylsulphide (DMS) is the most important source of biogenic sulphur to the atmosphere and, thus, the oceanic DMS flux constitutes a significant component of the global sulphur cycle (see e.g. Vogt and Liss, 2009). The oceanic distributions of DMS and its major precursor dimethylsulphoniopropionate (DMSP) result from a complex interplay of biological and non-biological pathways, such as formation by phytoplankton and microbial cleavage of DMSP to DMS on the one hand, and microbial consumption as well as photochemical oxidation of DMS and its loss to the atmosphere on the other hand (Simó, 2004; Stefels et al., 2007; Vogt and Liss, 2009; Schäfer et al., 2010). Although dimethylsulphoxide (DMSO) is recognized as an important reservoir of sulphur in the ocean, its production and consumption pathways are poorly understood. The principal production mechanisms for DMSO are the photochemical and bacterial oxidation of DMS, as well as direct synthesis in marine algae cells (Lee and De Mora, 1999; Lee et al., 1999a). Bacterial consumption, reduction to DMS, further oxidation to dimethylsulphone (DMSO$_2$) and export to deep waters via sinking particles are possible sinks for DMSO in the euphotic zone (Hatton et al., 2005). It is well-known, that DMS, DMSP and DMSO play important roles in the oceanic nutrient cycle. They are ubiquitous in the ocean and are responsible for the transfer and cycling of sulphur and carbon between different trophic levels in plankton (Kiene et al., 2000; Simó, 2004; Simó et al., 2002; Yoch, 2002). DMSP, for example, can completely satisfy the sulphur demand for bacterioplankton and can deliver 48% of the sulphur requirement for microzooplankton (Kiene and Linn, 2000; Simó, 2004). Additionally, DMSP can supply between 8 and 15% of carbon for bacteria and can serve as an energy source, which makes it the most important single substrate for marine bacterioplankton (Kiene et al., 2000; Simó et al., 2002). DMSO seems to be an important substrate for specialized bacteria which use DMSO as carbon or electron source (Lee et al., 1999a; Simó et al., 2000).
Methane (CH$_4$) is an atmospheric trace gas which contributes significantly to the greenhouse effect and chemistry of the Earth’s atmosphere (IPCC, 2007). CH$_4$ is mainly produced by methanogenesis as part of the microbial decomposition of organic matter (Cicerone and Oremland, 1988; Ferry, 2010). Despite the fact that methanogenesis requires strictly anaerobic conditions (see e.g. Ferry, 2010), CH$_4$ concentrations above the equilibrium concentration with the atmosphere are usually found in the ventilated (i.e. oxic) open ocean surface layer (see e.g. Reeburgh, 2007). This indicates that the open ocean is indeed a source of CH$_4$ to the atmosphere. Several explanations for this obvious “oceanic CH$_4$ paradox” have been suggested. For example, methanogens might live in anoxic micro-niches such as found in sinking organic particles and inside of zooplankton guts (De Angelis and Lee, 1994; Karl and Tilbrook, 1994). Only recently Karl et al. (2008) suggested an aerobic CH$_4$ production pathway by Trichodesmium which can use methylphosphonate under phosphate depletion. Moreover, DMSP and its degradation products (methanethiol, methylmercaptopropionate and DMS) have been suggested as important methylated substrates for marine CH$_4$ production (Damm et al., 2008, 2010; Finster et al., 1992; Tallant and Krzycki, 1997). Several bacteria groups have been identified that have the ability to metabolize DMSP and/or its degradation products by producing CH$_4$ (Kiene et al., 1986; Oremland et al., 1989; Van der Maarel and Hansen, 1997). Elevated CH$_4$ production, dependent on the DMSP consumption in the surface ocean, has been observed under oligotrophic conditions as well as in a phytoplankton bloom (Damm et al., 2010).

This study presents measurements of the surface ocean distributions of DMS, DMSP, DMSO, CH$_4$ and phytoplankton pigments in the western Pacific Ocean, an area that is considerably undersampled for all of the listed compounds. By using statistical methods we investigated (i) the interactions and links between the different sulphur compounds and how these might control their distributions, (ii) the role of phytoplankton community composition in determining the surface distributions of the sulphur compounds and (iii) the role of sulphur compounds as potential precursors for CH$_4$ in the surface ocean.
All data were retrieved during a north-south transit cruise in October 2009 (Krüger and Quack, 2012) as part of the “TransBrom” project.

2 Methods

Water samples were collected aboard the R/V Sonne from 9 to 24 October 2009 during a transit cruise from Tomakomai (Japan) to Townsville (Australia) in order to analyse the sea surface concentrations of DMS, DMSP, DMSO, CH4 and phytoplankton composition (Fig. 1). Samples were collected every three or twelve hours from approximately 5 m depth using the underway pump system installed in the hydrographic shaft.

2.1 Analysis of sulphur compounds and CH4

Three replicates from the sample bottles were taken for DMS, dissolved DMSP (DMSPd) and DMSO (DMSOd), as well as particulate DMSP (DMSPp) and DMSO (DMSOp) analysis. Samples were measured immediately after collection, with the exception of DMSO. DMSO samples were stored in the dark and analysed later in the GEOMAR laboratory directly after the cruise. It has been shown that storage of DMSO in hydrolysed samples with gas tight closure does not alter the DMSO concentration (Simó et al., 1998). DMS, DMSPd and DMSPp samples were analysed by purge and trap coupled to a gas chromatograph-flame photometric detector (GC-FPD), as described in Zindler et al. (2012). Two minor modifications were made: (i) replacement of the previously used Tenax with trapping in liquid nitrogen, (ii) injection onto the GC by immersion in hot water. DMSOd and DMSOp were analysed out of the same samples used for analysing DMSPd and DMSPp, respectively. DMSO was converted into DMS by adding cobalt dosed sodium borohydride (NaBH4) and analysed immediately with the same technique as mentioned above. The final DMSOp values were calculated by subtracting DMSOd from the total DMSO concentration. The mean analytical errors were ±0.2 nmol l−1 (±20 %) for DMS, ±0.4 nmol l−1 (±23 %) for DMSPd,
and $\pm 0.5 \text{nmol l}^{-1} (\pm 20\%)$ for particulate DMSP$_p$. For DMSO$_p$ and DMSO$_d$ a mean analytical error of $\pm 2.3 \text{nmol l}^{-1} (\pm 15\%)$ and $\pm 0.5 \text{nmol l}^{-1} (\pm 12\%)$ was determined, respectively. Calibrations were conducted every second day during the cruise and during the analysis in the lab. The precision and accuracy of the system was tested in the lab prior the cruise as described in Zindler et al. (2012). No blanks were found for DMSO, which was tested in 18 M$\Omega$ MilliQ water with and without sodium hydroxide addition.

Concentrations of dissolved CH$_4$ were measured with a static equilibration method as described in detail in Bange et al. (2010). Triplicate water samples for the determination of CH$_4$ were taken from the same underway seawater supply in parallel to the sampling of the sulphur compounds and phytoplankton pigments every twelve hours. The samples were analysed immediately after the cruise in the GEOMAR laboratory. The mean analytical error of dissolved CH$_4$ was $\pm 17\%$.

### 2.2 Phytoplankton analysis

#### 2.2.1 Phytoplankton pigments and group composition

Water samples for pigment and absorption analysis were filtered on GF/F filters, shock-frozen in liquid nitrogen, stored at $-80^\circ\text{C}$ and analysed in the AWI laboratory right after the cruise. According to Taylor et al. (2011), the analysis of phytoplankton pigments with High Performance Liquid Chromatography (HPLC) was performed. Particulate and phytoplankton absorption was determined with a dual-beam UV/VIS spectrophotometer (Cary 4000, Varian Inc.) equipped with a 150 mm integrating sphere (external DRA-900, Varian, Inc. and Labsphere Inc., made from Spectralon (TM)) using a quantitative filter pad technique.

Table 2 in Taylor et al. (2011) summarizes the pigments analysed in this study and provides the information about which pigments have been allocated as marker pigments for the different phytoplankton groups. According to a procedure proposed by Vidussi et al. (2001) which was modified by Uitz et al. (2006) and most recently by
Hirata et al. (2011), we estimated the contributions of three phytoplankton size classes (i.e. micro-, nano- and phytoplankton representing the size classes of 20–200 µm, 2–20 µm and <2 µm, respectively) and seven phytoplankton groups based on the measured concentrations of seven diagnostic pigments (DP) to the biomass. The DP, the calculation procedure of the weighted relationships of these marker pigments and the determination of their biomasses are described in the Supplement.

2.2.2 Identifying phytoplankton assemblages with hierarchical cluster analysis

In order to identify clusters of phytoplankton community composition, an unsupervised hierarchical cluster analysis (HCA) according to Torrecilla et al. (2011) was applied. The HCA groups the pigment measurements from the individual stations into different clusters according to their phytoplankton pigment compositions. The results were evaluated with an additional clustering of hyperspectral phytoplankton absorption coefficients (described in detail in the Supplement).

2.3 Statistical analysis

Linear regression analysis performed with the statistical computing software by RStudio™ (R Development Core Team, 2010; http://www.rstudio.org/) was used to identify significant correlations between sulphur compounds as well as between sulphur compounds and CH₄. Prior to the regression analysis, data were tested for Gaussian distribution and transformed if necessary. The F-statistic, the p-value and the $R^2$ were calculated.

Multiple linear regression models (MLRM) computed with RStudio™ were used to identify how the sulphur compounds might influence each other and which phytoplankton pigments might influence the sulphur compounds (for more details about the analytical procedure see the Supplement). The MLRM were performed for the entire north-south-transit and again for the two main sub-regions referred as cluster 2 and cluster 4, which were demarcated according to the phytoplankton composition (Fig. 1, Sect. 3.1).
No statistical analysis could be performed for cluster 1 and cluster 3 due to the lack of a sufficient amount of data in these clusters.

3 Results and discussion

3.1 Phytoplankton community structure in the western Pacific Ocean

In total, 106 surface stations along the north-south transit were measured. Phytoplankton biomass given as total chlorophyll $a$ ($T\text{Chl} \, a$ concentration in mg m$^{-3}$) was very low (0.05–0.25 mg m$^{-3}$), except for north of 36° N ($T\text{Chl} \, a > 1$ mg m$^{-3}$) where colder waters (16–20°C) of the Oyashio Current were observed, in the vicinity of islands (which were passed at 4° S, 8° S, 10° S and 12° S) and in the region of the Great Barrier Reef (Fig. 1b). Figure 2 shows the measured concentrations of marker pigments and chlorophyll $a$ (chl $a$) along the transit which were used to calculate the biomass of the major phytoplankton groups (Fig. 3). The phytoplankton biomass was generally dominated by picoplankton (sum of biomass of prochlorophytes and other cyanobacteria), with at least 50% contribution by the group of prochlorophytes, except in the Oyashio Current. At the stations with elevated $T\text{Chl} \, a$ values, haptophytes contributed significantly to the phytoplankton biomass. Diatoms and chlorophytes only made a significant contribution (between 20 and 30%) to the biomass in the Oyashio Current.

Four phytoplankton clusters were identified in both the normalized pigment concentrations and the hyperspectral phytoplankton absorption coefficients data (Fig. 4). The resulting cluster trees are presented in Figs. 1 and 2 of the Supplement. The high cophenetic index of 0.712 (see Supplement) between the two cluster trees indicates a very good agreement between the two data sets used to identify the phytoplankton clusters.

The stations located in the Oyashio Current (north of 36° N) belong to cluster 1 which is characterized by high phytoplankton biomass ($T\text{Chl} \, a \sim 1$ mg m$^{-3}$) and a dominance of eukaryotic algae (mainly chlorophytes and haptophytes, and a smaller contribution
from diatoms) and an absence of prochlorophytes. The majority of the stations belong to cluster 2 with low $T\text{Chl}a$ (0.05–0.3 mg m$^{-3}$). Prokaryotic algae are dominating cluster 2, with prochlorophytes contributing more than other cyanobacteria. Cluster 2 stations are mainly found between 36 and 25° N (associated with the Kuroshio Current waters) as well as south of the equator. Cluster 3 stations were found between 36 and 25° N (the Kuroshio Current) and south of 10° S. They are mingled with cluster 2 stations. At cluster 3 stations waters are elevated in $T\text{Chl}a$ (0.4–0.6 m$^{-3}$) and prokaryotic algae, mainly prochlorophytes, are dominating. Haptophytes were identified as the second largest group. Cluster 4 stations are mainly found in waters between 25° N and the equator and are characterized by a very low biomass ($T\text{Chl}a < 0.15$ m$^{-3}$). Prokaryotic algae are dominating cluster 4 almost exclusively with prochlorophytes and other cyanobacteria contributing equally. The spatial distributions of the clusters roughly reflect the biogeographic provinces as defined by Longhurst (1998) (Fig. 4).

3.2 DMS, DMSP and DMSO concentrations in the western Pacific Ocean

Over the entire transit the average surface seawater (i.e. 5 m) concentrations for DMS as well as for dissolved DMSP ($\text{DMSP}_d$) and DMSO ($\text{DMSO}_d$) were 0.9, 1.6 and 4.4 nmol l$^{-1}$, respectively. The average values for particulate DMSP ($\text{DMSP}_p$) and DMSO ($\text{DMSO}_p$) were 2 and 11.5 nmol l$^{-1}$, respectively (Table 1). Highest concentrations for all sulphur compounds were measured when approaching the coasts of Japan and Australia (Fig. 1). The concentrations measured during this cruise were lower than the average surface measurements of DMS (1.8 nmol l$^{-1}$), $\text{DMSP}_d$ (5.9 nmol l$^{-1}$), and $\text{DMSP}_p$ (16.2 nmol l$^{-1}$) based on data collected between 1987 and 2004 in the upper 6 m of the western Pacific Ocean (data retrieved from the Global Surface Seawater DMS Database: http://saga.pmel.noaa.gov/dms). The climatology of DMS concentrations published by Lana et al. (2011) shows a lack of October data from the tropical West Pacific (i.e. Longhurst provinces NPTW and WARM, see Fig. 4). For the Longhurst provinces KURO, ARCH and AUSE (see Fig. 4) the mean October
concentrations of DMS are given as $\sim 1$ nmol l$^{-1}$, $\sim 5$ nmol l$^{-1}$ and $\sim 4$ nmol l$^{-1}$, respectively (Lana et al., 2011). The differences between the climatological data and the data from our cruise might be caused by interannual variability and a general mismatch between climatological means and in-situ data.

The DMSO concentrations presented here are in agreement with the few published measurements of DMSO from the open Pacific Ocean, which range from 4 to 20 nmol l$^{-1}$ and DMSO measurements from the coastal areas of the Pacific Ocean which can reach values up to 181 nmol l$^{-1}$ (see overview in Hatton et al., 2005). More recently Yang and Yang (2011) reported mean surface DMSO$_d$ and DMSO$_p$ concentrations of 61.9 nmol l$^{-1}$ and 21.3 nmol l$^{-1}$, respectively, from the East China Sea in December 2009. The concentration range of surface DMSO$_p$ in the East China Sea (2.4–80 nmol l$^{-1}$) reported by Yang and Yang (2011) is similar to the range as measured in our study (1–72 nmol l$^{-1}$). However, the DMSO$_d$ concentrations in the East China Sea (up to 357 nmol l$^{-1}$) were much higher than those measured during our western Pacific Ocean transit and were caused by the Yangtze River plume (Yang and Yang, 2011).

3.3 Linear regressions between sulphur compounds

We found a positive correlation between DMSP$_t$ and DMSO$_t$ ($R^2 = 0.47$, $n = 104$, $p = < 0.001$, Fig. 5) as well as DMSP$_p$ and DMSO$_p$ ($R^2 = 0.41$, $n = 85$, $p = < 0.001$, Fig. 5). This is in agreement with the finding of Simó and Vila-Costa (2006a) who also reported a correlation between DMSP$_p$ and DMSO$_p$ and concluded that both compounds have the same source, namely phytoplankton. A strong link between the DMSP and DMSO pool were also found in several studies elsewhere by Lee and De Mora (1999). They referred to a possible direct biosynthesis of DMSO in algae cells and doubt the DMS oxidation as solely DMSO source in the ocean.

No correlation was found between DMS and DMSO which is in contrast to the finding by Hatton et al. (1999, 2005) who attributed the correlation to photochemical and/or
bacterial oxidation of DMS to DMSO in the water column (Hatton, 2002). However, the oxidation of DMS as a source for DMSO in the western Pacific Ocean cannot be excluded in general: A significant positive correlation was found between DMSP$_d$ and DMSO$_p$ ($R^2 = 0.35$, $n = 102$, $p = < 0.001$, Fig. 5) as well as between DMSP$_d$ and DMSO$_t$ ($R^2 = 0.33$, $n = 105$, $p = < 0.001$, Fig. 5) which may suggest that DMS, as an intermediate of the transformation of DMSP$_d$ to DMSO, is rapidly oxidised. A direct oxidation of DMSP to DMSO has not been reported yet and thus we suggest that DMS had a very short turnover time, most probably caused by stress factors (e.g. oxidative stressors, solar ultraviolet radiation and nutrient limitation) encountered during our measurements (Sunda et al., 2002).

### 3.4 Relationship between sea surface temperature and DMSP$_p$ : DMSO$_p$ ratio

A negative correlation between sea surface temperature (SST) and DMSP$_p$ : DMSO$_p$ ratio was found by Simó and Vila-Costa (2006b) based on a compilation of data from various oceanic regions (mainly from the North Atlantic Ocean and its adjacent marginal seas). On the basis of the data listed in Simó and Vila-Costa (2006a), we recalculated mean DMSP$_p$ : DMSO$_p$ ratios as well as mean SST for the various campaigns. In addition, we added other data: from the East China Sea (ratio: 0.27, 17.2°C) (Yang and Yang 2011), the northern Baffin Bay (ratio: 0.20, estimated 0°C) (Bouillon et al., 2002) and the average DMSP$_p$ : DMSO$_p$ ratio (0.22 ± 0.27) and the average SST (28.3 ± 2.7°C) computed from the measurements during the transit presented here (see Fig. 6). In agreement with Simó and Vila-Costa (2006a) we found a significant negative linear correlation between DMSP$_p$ : DMSO$_p$ ratios and SST for the temperature range 5 to 28°C. Moreover, a positive trend was also visible in the SST range < 10°C indicating that there seems to be a maximum of DMSP$_p$ : DMSO$_p$ ratios at approximately 5–10°C. This is in line with the observations that blooms of coccolithophorids (major DMSP producers, Simó, 2001) usually occur in high (subpolar) latitudes at SST around 9°C (3–15°C) (Iglesias-Rodriguez et al., 2002).
Our findings are in line with the argumentation of Simó and Vila-Costa (2006a) who proposed that (i) in warm waters DMSO enriched nano- and picoplankton is dominating the phytoplankton community (indeed we found that nano- and picoplankton was dominant during the transit, see Sect. 3.1), and (ii) high SST could be associated with surface waters receiving a high solar radiation dose which triggers a cascade reaction system, including enhanced DMSO production, as a reply to nutrient limitation and oxidative stress (Sunda et al., 2002).

### 3.5 Interactions between sulphur compounds explained by multiple linear regression models (MLRM)

In order to find further statistically significant interactions between the different sulphur compounds, MLRM were used. The MLRM calculations were performed either with the entire data set or with a subset of cluster 2 and cluster 4 data, respectively. Both cluster 2 and 4 were characterized by low biomass and were mainly dominated by prokaryotic algae, namely prochlorophytes and other cyanobacteria, which are not known to be DMSP producers (Keller et al., 1989). This resulted in low DMS and DMSP concentrations (see Sect. 3.2, Fig. 1). In the following sections we discuss the main results of the MLRM (see Table 2). The complete MLRM results are listed the Supplement.

#### 3.5.1 DMS

Over the entire transit, the DMS concentration could be roughly estimated by the DMSP$_p$ and DMSO$_p$ distribution ($R^2 = 0.32$, Table 2, a). It is possible that the DMS concentration was coupled to particulate DMSP and DMSO through the antioxidation system in algae cells (Sunda et al., 2002). It is most likely that in the tropical waters of the western Pacific Ocean the radiative stress on phytoplankton was enhanced. Within the clusters 2 and 4 all sulphur compounds have an influence on the DMS pool (Table 1, Supplement).
3.5.2 DMSP

A link between DMSP$_d$ and the DMSO pool for the entire transit could be found \((R^2 = 0.32, \text{Table 2, d})\). In the individual clusters 2 and 4 and also for DMSP$_p$ all sulphur compound could be identified which had a significant influence (Table 1, Supplement). A direct production of DMSP from DMSO, however, can be excluded because this pathway has not been observed yet. However, a same source for both compounds in certain algae species might explain the close link between these compounds. The MLRM showed, especially in the clusters 2 and 4, that all sulphur compounds correlated with the DMSP$_{d/p}$ pool (Table 1, Supplement). This is in line with several studies which referred to the fast cycling, within a few hours, between the different sulphur compounds (Simó, 2004; Stefels et al., 2007).

3.5.3 DMSO

The MLRM showed that DMSP$_d$ and DMS slightly influenced the DMSO$_d$ pool for the entire transit \((R^2 = 0.19, \text{Table 2, i})\). It is most likely that DMSO$_d$ is directly produced due to the oxidation of DMS in the water column (Hatton et al., 2005). DMSP$_d$ might be used by free living bacteria in the water column as a substrate to produce DMSO. Additionally, DMSP$_d$ could be converted to DMS by bacteria which can contribute to the DMS pool. However, these processes might be of minor importance because it only explains 19% of the DMSO$_d$ distribution. Thus, other factors are probably more important for the DMSO$_d$ production, such as direct synthesis in algae cells and release into the water column (Simó et al., 1998) or photo-oxidation of DMS to DMSO (Hatton et al., 1996).

In cluster 2, DMSO$_d$ seemed to be dependent only on the DMSP pool \((R^2 = 0.28, \text{Table 2, j})\), while in cluster 4, DMSP$_p$ and DMSO$_p$ were significant contributors \((R^2 = 0.35, \text{Table 2, k})\). The findings within the clusters confirm the assumption of direct biosynthesis of DMSO in the phytoplankton. Due to the ability of DMSO to permeate easily through membranes, a coupling of DMSO$_d$ and DMSO$_p$ is reasonable. However,
a direct correlation could not be observed due to the different fates of these compounds in surface waters.

DMSO$_p$ was directly dependent on DMSP$_{d/p}$ ($R^2 = 0.43$, Table 2, l) over the entire transit and in the region of cluster 4 ($R^2 = 0.46$, Table 2, n) comparable to DMSO$_d$. The same result was also confirmed by the direct correlation (see Sec. 3.3). These findings again underline the possible same source of DMSO$_p$ and DMSP$_p$ in algae cells. The production of DMSO$_p$ from DMSP$_d$ can be explained by bacteria that are attached to particles and use DMSP$_d$ as a substrate. The statistical analysis underlines the importance of DMSO for the sulphur cycle and the tight coupling especially between DMSO and DMSP.

3.6 Influence of phytoplankton on the DMS, DMSP and DMSO distributions in surface seawater

Only weak linear positive correlations between $T_{Chl}a$ and DMSO$_p$, DMSO$_t$, DMSP$_d$ as well as DMSP$_p$ were found for the entire dataset ($R^2 = 0.25$, $n = 94$; $R^2 = 0.22$, $n = 96$; $R^2 = 0.29$, $n = 99$; and $R^2 = 0.23$, $n = 87$, for all $4 < 0.001$, respectively). The weak correlations may result from a dependency on certain algae taxon and not on phytoplankton in general for both DMSP and DMSO. In contrast, Lee et al. (1999b) found a negative correlation between DMSO$_p$ and chl $a$ in a Canadian Fjord. They explained this observation with an increase in photosynthetic activity and, therefore, an increase in free radicals which reacted with DMSO. Low $T_{Chl}a$ concentrations were observed during the north-south transit, indicating that enhanced radical production due to high photosynthetic activity most likely did not occur.

The DMSO$_p$ : chl $a$ ratio of 75 nmol $^{-1}$ (Table 1) was higher than measurements in the East China Sea of 49 nmol $^{-1}$ in December 2009 (Yang and Yang, 2011). Both ratios were in the upper range of measured DMSO$_p$ : chl $a$ ratios (0.03–8 nmol $^{-1}$) in different oceanic regions (Yang and Yang, 2011). The West Pacific Ocean as well as the East
China Sea showed low chl $a$ and elevated DMSO concentrations compared to other oceanic regions (see discussion in Sect. 3.4).

### 3.6.1 DMS and phytoplankton groups

The influence of a variety of phytoplankton groups on the different sulphur compounds for the entire transit and within the clusters 2 and 4 were also tested by using the MLRM. The following phytoplankton groups were tested (characteristic marker pigments are given in parenthesis): diatoms (fucoxanthin, diatoxanthin, diadinoxanthin), dinoflagellates (peridinin), cryptophytes (alloxanthin), haptophytes (19’-hexanoyloxyfucoxanthin), chrysophytes (19’-butanoyloxyfucoxanthin), prasinophytes (prasinoxanthin), chlorophytes (violaxanthin), cromophytes (anthraexanthin) and cyanobacteria (zeaxanthin). Chlorophyll pigments were not used for the calculations due to their occurrence in all phytoplankton groups.

The model showed that algae groups played a minor role for the DMS distribution over the entire transit. Only in cluster 2, diatoms, haptophytes and dinoflagellates were tested significantly for DMS ($R^2 = 0.32$, Table 3, a). Bürgermeister et al. (1990) and Merzouk et al. (2008) found increased DMS concentrations triggered by diatoms in the Atlantic Ocean. Elevated abundance of haptophytes and dinoflagellates were measured together with enhanced DMS concentrations in different oceanic regions in general. Additionally, all these algae groups were identified as important contributors to the DMSP$_{d/p}$ pool with the MLRM in this study (see below), which indicated that DMS was probably only indirectly dependent on these algae via bacteria. This finding is in line with Yoch (2002), Kiene et al. (2000) and Schäfer et al. (2010), reporting that DMS is mainly controlled by the activity of bacterioplankton. It is most likely that only a minor part of algae-DMSP contributes to DMS reflected in the low DMS concentrations, which explains the lack of correlations between algae and the DMS along the western Pacific Ocean transit. In addition, as stated previously, the DMS pool may undergo rapid cycling that would lead to low concentrations.
3.6.2 DMSP and phytoplankton groups

Over the entire transit, the main phytoplankton groups which influenced the DMSP\textsubscript{d} distribution were chrysophytes, dinoflagellates and cyanobacteria, although cyanobacteria are not considered to be important DMSP producers (Keller et al., 1989). Additionally, diatoms were only important in conjunction with other phytoplankton groups ($R^2 = 0.44$, Table 2 in Supplement, b). In contrast, diatoms appear to be the most important algae group in cluster 2 ($R^2 = 0.61$, Table 3, c). In cluster 4 no statistical significances could be found.

Similar results were obtained for DMSP\textsubscript{p}. Dinoflagellates, chrysophytes, and diatoms appeared to be the most important contributors to the DMSP\textsubscript{p} pool ($R^2 = 0.37$, Table 3, d) for the entire transit while in cluster 2 the diatoms were dominant. Also, haptophytes and cyanobacteria seemed to influence the DMSP\textsubscript{p} concentration ($R^2 = 0.73$, Table 3, e) in this cluster. In cluster 4, again, no pigment was found that contributed significantly to DMSP\textsubscript{p}.

Belviso et al. (2001) showed a clear relationship between DMSP\textsubscript{p} and haptophytes as well as chrysophytes with over 200 samples from different regions (Atlantic Ocean, Mediterranean Sea and Southern Ocean) by using linear regression. Although haptophytes were only important for DMSP\textsubscript{p} in cluster 2 chrysophytes were identified as important algae group for all DMSP pools in this study. Dinoflagellates were identified as producers for all DMSP pools in the Pacific Ocean, which is in agreement with findings in other marine regions (Keller et al., 1989; Stefels, 2000; Steinke et al., 2002). Surprisingly, diatoms and cyanobacteria influenced DMSP, although these algae groups are thought to be minor DMSP producers in general (Keller et al., 1989). The diatoms and cyanobacteria were distributed in similar patterns to the DMSP producing taxa, possibly causing the model to identify them as contributors to the DMSP pool. It should also be considered that cyanobacteria were dominating the main part of the West Pacific Ocean transit and were mainly responsible for the $T$Chl\textsubscript{a} concentration, which correlated slightly with DMSP. In addition, some specialized diatom species in the Pacific
Ocean may also be able to produce a sizable amount of DMSP. Keller et al. (1989) showed that certain species of diatoms can be significant for the DMSP pool. Thus, this alga taxon cannot be dismissed as DMSP contributor in general. Although a direct linear correlation between DMSP\text{p} and DMSP\text{d} could not be found, the pigments influencing both pools are the same, underlining the common origin but the different fates of DMSP\text{p} and DMSP\text{d}.

**3.6.3 DMSO and phytoplankton groups**

Diatoms, haptophytes and chrysophytes correlated significantly with DMSO\text{d} ($R^2 = 0.42$, Table 3, i). In cluster 2, dinoflagellates, diatoms and chrysophytes were the most important pigments for the DMSO\text{d} distribution ($R^2 = 0.45$, Table 3, j). For cluster 4 no significant correlations could be identified.

Diatoms, cyanobacteria and dinoflagellates seemed to influence the DMSO\text{p} distribution ($R^2 = 0.54$, Table 3, k). In the region of cluster 2, instead of cyanobacteria, chrysophytes contributed to the DMSO\text{p} pool ($R^2 = 0.84$, Table 3, l). Again, cluster 4 contained no significant correlations. The same phytoplankton groups especially in cluster 2 for DMSO\text{d} and DMSO\text{p} indicated also for DMSO the same origin but different fates for both compounds.

For DMSP and DMSO the same algae groups were identified as important sulphur producers but in different compositions dependent on sulphur compound and region. Field measurements conducted by Lee et al. (1999b) and culture experiments with dinoflagellates and haptophytes which showed high DMSO\text{p} production (Simó et al., 1998) suggested that DMSO\text{p} might be produced by a broad range of phytoplankton comparable to that of DMSP producing algae groups. The authors did not exclude that other species, which are not known as DMSP producers, might also be responsible for a significant amount of DMSO. In this study, we also found that DMSO\text{p} correlated with phytoplankton pigments of known DMSP producers. However, the pigment analysis did not show direct correlations between DMSO and pigments from non-DMSP producing
phytoplankton. In addition, the phytoplankton groups which have an influence only due to their interactions were the same for DMSP and DMSO (Table 2 in Supplement). The results of the MLRM, as well as the direct correlations, show the close link between DMSP and DMSO and their similar sources in the north-south transit of the western Pacific Ocean. Additionally, the MLRM’s showed similar phytoplankton groups influencing DMS as well as DMSP and DMSO but the models also emphasized that other sources might be more important for the DMS pool indicated by the absence of correlations in large regions. Cryptophytes, prasinophytes, chlorophytes and cromophytes showed no or a negligible influence on the sulphur distribution in the western Pacific.

Interestingly, the smallest number of correlations was found in cluster 4. This cluster included mainly the oligotrophic warm waters of the West Pacific Ocean dominated by cyanobacteria. The distribution pattern of phytoplankton is similar to cluster 2. However, cluster 4 was different from other clusters by its particularly low biomass, as well as the lowest sulphur concentrations of the entire transit (Fig. 1). It seems that the very low biomass was the main factor governing the concentrations of sulphur in this region, with a minor influence of the algae composition. Thus, large regions in the subtropical and tropical western North Pacific Ocean were of minor importance for the sulphur cycle in the surface ocean.

### 3.6.4 Sulphur compounds as precursors for methane

The CH$_4$ concentrations during the cruise were in the range from 1.8 to 4.8 nmol l$^{-1}$ with an average of 2.5 ± 0.8 nmol l$^{-1}$. The highest CH$_4$ concentrations (3.8–4.8 nmol l$^{-1}$) were measured at the beginning of the cruise in the cold waters of the Oyashio Current (north of 36° N), followed by a drop in CH$_4$ concentrations to 2.8 nmol l$^{-1}$ when the warm Kuroshio Current was crossed (between 36 and 25° N). The lowest CH$_4$ concentrations were measured between the equator and 28° N and, thus, they were roughly associated with cluster 4 (see Sect. 3.1, Fig. 1). Comparable mean surface CH$_4$ concentrations of 2.5 ± 0.3 nmol l$^{-1}$ and 2.2 ± 0.02 nmol l$^{-1}$ were measured along 165° E between 40° N...
and 5° S and in the Kuroshio Current waters (27–30° N, 133–142° E), respectively, by Watanabe et al. (1995). Rehder and Suess (2001) measured CH$_4$ surface concentrations in the range from 2.5 to 5 nmol l$^{-1}$ between 38.6 and 42° N in the Tsugaro Current outflow/Oyashio Current mixing region and a drop in CH$_4$ concentrations to 2.3 nmol l$^{-1}$ when Kuroshio Current waters were measured in the coastal waters off Honshu further south. Moreover, Bates et al. (1996) reported CH$_4$ concentrations between 1.6 and 3.6 nmol l$^{-1}$ for a series of five latitudinal transects in the Pacific Ocean.

We found a significant positive correlation between TChl$\alpha$ and CH$_4$ surface concentrations ($R^2 = 0.69$, $p = < 0.001$, $n = 36$, Fig. 7). There are only a few other studies which report a correlation between chl $\alpha$ and CH$_4$ (Owens et al., 1991; Damm et al., 2008). Watanabe et al. (1995) found a general trend but no significant correlation along 165° E. Since the majority of the studies did not find a correlation between chl $\alpha$ and CH$_4$ and direct evidence from lab experiments with (axenic) algae cultures has not been published yet, it is widely accepted that the accumulation of CH$_4$ in the upper open ocean is not related to a direct production by algae.

In our study, significant positive linear correlations were found between DMSO$_p$ and CH$_4$ ($R^2 = 0.37$, $p = < 0.001$, $n = 31$) and DMSO$_t$ and CH$_4$ ($R^2 = 0.42$, $p = < 0.001$, $n = 33$), as well as between DMSP$_d$ and CH$_4$ ($R^2 = 0.57$, $p = < 0.001$, $n = 35$) for the entire north-south transit (Fig. 8). Additionally, we found a good correlation between CH$_4$ and the marker pigment for chrysophyceae ($R^2 = 0.76$, $p = < 0.001$, $n = 36$, Fig. 7), which are known as DMSP producers (Belviso et al., 2001) and which were well correlated with DMSP$_d$ and DMSO$_t$ in our study (see Sects. 3.4.2, 3.4.3). Therefore, we conclude that algae derived DMSP and DMSO might serve as important substrates for methanogens in the western Pacific Ocean.

Damm et al. (2008) showed a significant negative correlation between DMSP$_t$ and CH$_4$ ($R^2 = 0.55$) in the surface waters of an Arctic shelf region (Storfjorden, Svalbard Archipelago), which is in contrast to the positive correlation with DMSP$_d$ found in our study. Moreover, we could not find any correlation between DMSP$_t$ and CH$_4$ in our
data from the western Pacific Ocean. Thus, there are obvious differences between the results from the Storfjorden and the West Pacific Ocean (despite the fact that the conclusions are identical): The algal community in the West Pacific Ocean during our cruise was very likely suffering from continuous oxidative stress and nutrient limitation which could have led to a continuous production of DMSP (Sunda et al., 2002). This, in turn, implies a continuous formation of CH₄ from DMSP via the demethylation pathway (Moran et al., 2012) and may explain the positive correlation between the DMSP and CH₄. In contrast, a bloom situation was encountered in the Storfjorden which implies that the algae did not suffer from oxidative stress and/or nutrient limitation and therefore a continuous production of DMSP was not necessary. The negative correlation found in Storfjorden might have been caused by the fact that CH₄ has been produced from a DMSP pool which was not replenished at the time of the bloom. Additionally, it is remarkable that Damm et al. (2008) observed CH₄ production when DMSPₜ concentrations were in the range from 5 to 30 nmol l⁻¹ but could see no effect on the CH₄ production when DMSPₜ levels were < 5 nmol l⁻¹. In our study, however, a correlation between DMSPₙ and CH₄ was found although the concentrations for both compounds were much lower. This reflects less intensive biological activity, perhaps due to different assemblages of bacterioplankton, physiological stages of the bacteria and/or nutrient limitation and oxidative stress compared to the Storfjorden.

A negative correlation between CH₄ and DMSPₜ was also found in phosphate enriched, but nitrogen depleted, oligotrophic Arctic Sea waters originating from the Pacific Ocean. This indicates that CH₄ production from DMSPₜ in oligotrophic Arctic waters seems to be mainly depending on the availability of phosphate (Damm et al., 2010). Despite the fact that nutrient data are not available for the TransBrom cruise, it is reasonable to assume that the surface waters in the western tropical Pacific Ocean during TransBrom were depleted in both phosphate and nitrate (see e.g. World Ocean Atlas of the National Oceanographic Data Center: http://www.nodc.noaa.gov/OC5/SELECT/woaselect/woaselect.html). Thus, the CH₄ production from DMSP in the west Pacific Ocean seems to be driven by a different mechanism than the one found...
in Arctic waters. Moreover, we found no correlation between cyanobacteria and CH$_4$, suggesting that the CH$_4$ production by *Trichodesmium*, which has proposed for phosphate depleted regions (Karl et al., 2008), seemed to have been negligible during the time of our cruise.

In a microcosm experiment conducted in the central Arctic, three main proteobacteria groups were identified as possible CH$_4$ producers which used DMSP as a carbon and energy source (Damm et al., 2010): *Rhodobacter*, *Sulfitobacter* (both in the family: *Rhodobacteraceae*) and *Mesorhizobium* types. It is noteworthy that bacteria of *Rhodobacteraceae* are widespread in the oligotrophic oceans and have genes that metabolize DMSP (Curson et al., 2008; Moran et al., 2003, 2007) and therefore we may conclude that they could have been responsible for the CH$_4$ production along the north-south transit in the Pacific Ocean.

For the first time a correlation between DMSO and CH$_4$ could be observed in surface ocean waters. There are two possible pathways: (1) DMSO was reduced into DMS, which, in turn, acted as precursor for methane, and (2) DMSO was directly taken up by methanogenic bacteria. Additionally, if DMSO is a potential substrate for the marine CH$_4$ production, the influence of DMSO on the CH$_4$ pool in the deep oceans is underestimated because of the widespread distribution of DMSO throughout the entire water column (Bouillon et al., 2002; Hatton et al., 1999).

4 Summary

Along the north-south transit of the TransBrom cruise, the western Pacific Ocean contained low biomass except in the cold Oyashio Current waters, in coastal regions in the vicinity of islands and the Great Barrier Reef. The low biomass regions were dominated by picoplankton with prochlorophytes dominating. In high $T$Chl $a$ regions, haptophytes contributed significantly to the biomass.

For the first time a DMSO distribution pattern was presented in surface seawater along a north-south transit in the western Pacific Ocean. Correlations between DMSO
and DMSP, as well as DMSO and DMSP with TChl a, were observed for the entire transit, suggesting a similar source for both sulphur species, namely biosynthesis in specialized algae. Several algae groups were identified as contributors to the DMSP and DMSO pool, mostly haptophytes, chrysophytes and dinoflagellates. Diatoms were also identified although they are not known to be significant sulphur producers. DMSP and DMSO seemed to be influenced by largely the same algae species, indicating that DMSP producing algae might have the potential to synthesis DMSO as well.

The observed DMSP$_p$ : DMSO$_p$ ratios were extremely low and generally < 1. They seem to be characteristic for oligotrophic tropical waters representing the extreme endpoint of the global DMSP$_p$ : DMSO$_p$ ratio vs. SST relationship. It is most likely that nutrient limitation and oxidative stress in the tropical West Pacific Ocean triggered enhanced DMSO production.

DMSP$_d$ and DMSO$_p/t$ were positively correlated with CH$_4$ for the entire north-south transit, although the concentrations of both sulphur compounds and CH$_4$ were low. We conclude that DMSP could be considered as a potential substrate for methanogenic bacteria in the western Pacific Ocean. For the first time we could show that DMSO might act as a substrate for CH$_4$ production as well. However, further studies are necessary to understand how sulphur compounds are converted into CH$_4$.

Supplementary material related to this article is available online at: http://www.biogeosciences-discuss.net/9/15011/2012/bgd-9-15011-2012-supplement.pdf.

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Table 1. DMS, DMSP and DMSO [nmol l$^{-1}$] and total chl $a$ [mg m$^{-3}$] concentrations as well as DMS, DMSP and DMSO versus total chl $a$ [nmol mg$^{-1}$] for the entire transit and for cluster 2 and 4.

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<th>DMSP$_p$ average</th>
<th>DMSP$_t$ average</th>
<th>DMSO$_d$ average</th>
<th>DMSO$_p$ average</th>
<th>DMSO$_t$ average</th>
<th>T Chl $a$ average</th>
<th>T Chl $a$ range</th>
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<td>cluster 4</td>
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Values are given in nmol l$^{-1}$ and mg m$^{-3}$.
Table 2. Significant multiple linear regressions between DMS, DMSP and DMSO (d = dissolved, p = particulate, t = total) for the entire data set and within the cluster 2 and 4. Single coefficients and p-values of each multiple linear regression model as well as $R^2$, F-statistic and p-value of each entire model are given. The response variable is given under the model number. The independent variable squared shows a quadratic relationship to the response variable. The complete output of all models is given in the Supplement.

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Abbr.: st.: statistic; e.m.: entire model; e.d.s.: entire data set; a–m: number of models.
Table 3. Significant multiple linear regressions between DMS, DMSP and DMSO (d = dissolved, p = particulate, t = total) and phytoplankton marker pigments for the entire data set and within the cluster 2 and 4. Single coefficients and p-values of each multiple linear regression model as well as \( R^2 \), F-statistic and p-value of each entire model are given. The response variable is given under the model number. The independent variable squared shows a quadratic relationship to the response variable. The complete output of all models is given in the Supplement.

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</table>

Abbr.: st.: statistic; e.m.: entire model; e.d.s.: entire data set; fuco: fucoxanthin; hex: 19'-hexanoyloxyfucoxanthin; peri: peridinin; diato: diatoxanthin; dia: diadinoxanthin; diato: diatoxanthin, but: 19'-butanoyloxyfucoxanthin; zea: zeaxanthin.
Fig. 1. Distribution of (a) DMSO [nmol l\(^{-1}\)], (b) total chl a [mg m\(^{-3}\)] (HPLC in-situ measurements), DMS, and methane [nmol l\(^{-1}\)], and (c) DMSP [nmol l\(^{-1}\)] along the cruise track. The middle line in each panel shows the exact position of the cruise track. The dashed lines show the approximate location of cluster 2 and 4.
Fig. 2. Surface water phytoplankton major pigment concentration ([ng l$^{-1}$], upper level) used as marker pigments to calculate the chl $a$ concentration for eight phytoplankton groups over the north-south transit. Also shown are monovinyl-chl and div-a which were used to calculate total chl $a$. 

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Fig. 3. Chl a concentration of main phytoplankton groups [mg m\(^{-3}\)] as derived from major pigment composition (shown in Fig. 2) sampled from surface waters over the cruise track.
Fig. 4. Distribution of clusters among pigment stations with the Longhurst provinces shown underneath. Yellow indicates cluster 1, green is cluster 2, blue is cluster 3, and red is cluster 4.
Fig. 5. Left panel: linear regression between DMSP$_d$ and DMSO$_t$: $y = 6.66x + 5.06$, $R^2 = 0.33$, p-value: $1.414e^{-10}$, F-statistic: 50.86, $n = 105$ and between DMSP$_d$ and DMSO$_p$: $R^2 = 0.35$, $y = 6.41x + 1.42$, p-value: $6.493e^{-11}$, F-statistic: 53.53, $n = 102$, both regressions for the entire data set.

Right panel: linear regression between DMSP$_t$ and DMSO$_t$: $y = 2.84x + 4.28$, $R^2 = 0.47$, p-value: $9.613e^{-16}$, F-statistic: 90.87, $n = 104$ and between DMSP$_p$ and DMSO$_p$, $y = 2.84x + 5.68$, $R^2 = 0.41$, p-value: $5.849e^{-11}$, F-statistic: 56.54, $n = 85$, both regressions for the entire data set.
Fig. 6. Average DMSP$_p$ : DMSO$_p$ ratios vs. SST. Mean ratios for individual campaigns are recalculated from the data listed in Simó and Vila-Costa (2006a). We added data points consisting of the mean DMSP$_p$ : DMSO$_p$ and SST (given in parenthesis) from the East China Sea (0.27, 17.2°C) (Yang and Yang, 2011), the northern Baffin Bay (0.20, estimated 0°C) (Bouillon et al., 2002) and the western Pacific Ocean (0.22, 28°C) (this study). The linear correlations are $y = -0.445x + 12.96$ ($R^2 = 0.61$, open circles) and $y = 1.312x + 1.44$ ($R^2 = 0.67$, solid circles).
Fig. 7. Linear regression between total chl-a and methane ($y = 0.0027x + 1.82$, $R^2 = 0.69$, F-statistic: 63, p-value < 0.001, $n = 36$, open diamonds) and between chrysophytes (indicated by marker pigments $19'$-butanoyloxyfucoxanthin) and methane ($y = 0.044x + 1.92$, $R^2 = 0.76$, F-statistic: 80, p-value: < 0.001, $n = 36$, solid circles).
Fig. 8. Relationship between the sulphur compounds (DMSP$_d$, DMSO$_p$, DMSO$_t$ [nmol l$^{-1}$]) and methane [nmol l$^{-1}$] in the surface water of the north-south transit in the Western Pacific Ocean. DMSP$_d$ vs. methane: $y = 0.55x + 1.54$, $R^2 = 0.57$, F-statistic: 43.08, p-value: $1.85e^{-7}$, $n = 36$; DMSO$_p$ vs. methane: $y = 0.06x + 1.72$, $R^2 = 0.37$, F-statistic: 17.25, p-value: $2.64e^{-4}$, $n = 31$; DMSO$_t$ vs. methane: $y = 0.06x + 1.48$, $R^2 = 0.42$, F-statistic: 22.49, p-value: $4.5e^{-05}$, $n = 33$. 