From coastal waters to the open ocean: Dimethylated sulfur compounds in the SW Baltic Sea, the SE Pacific Ocean, and the SW Indian Ocean

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Zur Erlangung des Doktorgrades
der Mathematisch-Naturwissenschaftlichen Fakultät
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Tag der mündlichen Prüfung:	20. 01. 2022
Zum Druck genehmigt:	

gez. Prof. Dr.

Eidesstattliche Erklärung

Hiermit erkläre ich, dass ich die vorliegende Doktorarbeit selbständig und ohne unerlaubte Hilfe erstellt habe. Weder diese noch eine ähnliche Arbeit wurde an einer anderen Abteilung oder Hochschule im Rahmen eines Prüfungsverfahrens vorgelegt, veröffentlicht oder zur Veröffentlichung vorgelegt. Ferner versichere ich, dass die Arbeit unter Einhaltung der Regeln guter wissenschaftlicher Praxis der Deutschen Forschungsgemeinschaft entstanden ist.

Kiel, den November. 2021

gez. Yanan Zhao

Acknowledgements

First and foremost, I would like to thank Prof. Dr. Hermann W. Bange, for his patient guidance, encouragement, and positive feedback throughout my doctoral research and thesis. Also, I appreciate Prof. Dr. Arne Körtzinger and Prof. Dr. Anja Engel to be my ISOS committee members for helping me understand the bigger picture in their scientific views. Special thanks to Dr. Christa A. Marandino; without her precious dataset and dedication, it would be unable for me to combine different topics tightly in my doctoral thesis. I also thank Dr. Cathleen Schlundt for her extensive knowledge, pushing me to dive deep into my research. A huge 'Thank you!' goes to Dr. Dennis Booge, who offered me great help in all aspects and was always open to any further questions. I sincerely appreciate Prof. Dr. Astrid Bracher, Dr. Michael Meyerhöfer and Kerstin Nachtigall, all of whom helped my research with regards to the phytoplankton pigments. A big thanks to Dr. Birgit Quack, for accommodating me in her office, which kept me productive in a quiet environment.

The members of the Chemical Oceanography Department at GEOMAR have contributed significantly, whether it was in the lab or life, which made my time more comfortable. Special thanks to Annette and Max, for building my research skills during the early stages of my research. Thank you to the GC-FPD group, Hanna, and Tina, for assisting me in the lab. Also, I acknowledge Prof. Dr. Sinikka Lennartz for her suggestions on the trend analysis.

Here I am grateful to my friends in Kiel, especially Jiajun Wu and Ding Jin; it is their lovely accompany, made me relax from one after another tough research day.

Lastly, I show my particular appreciation to Dr. Fangyuan Xiu and my dear family; without their immense encouragement, support and love, I cannot imagine how difficult my life would be during my doctoral studies.

Acknowledgements

Manuscript contributions

This dissertation is based on the following manuscripts:

1. Manuscript I: **Zhao, Y**., Schlundt, C., Booge, D., and Bange, H. W.: A decade of dimethyl sulfide (DMS), dimethylsulfoniopropionate (DMSP) and dimethyl sulfoxide (DMSO) measurements in the southwestern Baltic Sea, 18, 2161–2179, https://doi.org/10.5194/bg-18-2161-2021, 2021.

Author contributions: YZ, CS, DB, and HWB designed the study and participated in the fieldwork. Sulfur compound measurements and data processing were done by YZ, CS and DB. YZ conducted further data analysis and wrote the article with contributions from all co-authors.

2. Manuscript II: **Zhao, Y**., Booge, D., Marandino, C. A., Schlundt, C., Bracher, A., Atlas, E. L., Williams, J., and Bange, H. W.: Dimethylated sulfur compounds in the Peruvian upwelling system, Biogeosciences Discuss. [preprint], https://doi.org/10.5194/bg-2021-174, in review, 2021.

Author contributions: YZ, DB, CAM, CS, and HWB designed the study. DB, CAM, CS, AB and HWB participated in the fieldwork. Seawater sulfur compound measurements and data processing were done by DB, CS and YZ. Atmospheric DMS data processing was done by ELA and JW. Pigment data processing was done by AB. YZ conducted further data analysis and wrote the article with contributions from all co-authors.

3. Manuscript III: **Zhao, Y**., Booge, D., Marandino C. A., Bracher, A., and Bange, H. W.: Dimethylated sulfur compounds and bromoform in the Southwest Indian Ocean, manuscript in preparation.

Author contributions: YZ, DB, CAM and HWB designed the study. DB, CAM and AB participated in the fieldwork. Seawater sulfur compound measurements and data processing were done by DB and YZ. Pigment data processing were done by AB. YZ conducted further data analysis and wrote the article with contributions from all co-authors.

ABSTRACT

The climate-relevant trace gas dimethyl sulfide (DMS) has received significant attention over the past years as its potential role in affecting the Earth's climate by forming atmospheric sulfate aerosols, which, in turn, can backscatter solar radiation and possibly act as cloud condensation nuclei that form clouds. However, the global significance of this DMS-driven ocean–climate feedback mechanism remains under debate, especially due to the lack of long-term observations in the oceans, with most temporal studies focusing on the seasonal cycles of DMS. Also, despite the intensive DMS research in the spatial domain, some oceanic regions are still sparsely sampled, and hence, the production and consumption processes of DMS are poorly understood there. To address these knowledge gaps, we undertook studies in the southwestern Baltic Sea (the Boknis Eck Time Series station), in the eastern Pacific (the Peruvian upwelling system) and southwestern Indian Oceans. This thesis compiles these studies, which involve measuring water column DMS, dimethyl sulfoniopropionate (DMSP) and dimethyl sulfoxide (DMSO) to identify their temporal or spatial variabilities and to associate these changes with trends in phytoplankton composition and/or environmental factors, contributing new insight into the fates of these biogenic sulfur compounds.

In the first study, a decade of DMS, DMSP and DMSO measurements was conducted in the water column in conjunction with the phytoplankton composition at the Boknis Eck (BE) Time Series Station (Eckernförde Bay, southwestern Baltic Sea) during the period February 2009–December 2018. Our results show considerable interannual and seasonal variability in the mixed-layer concentrations of DMS, total DMSP ($DMSP_t$) and total DMSO ($DMSO_t$). Positive correlations were found between particulate DMSP ($DMSP_p$) and particulate DMSO ($DMSO_p$) as well as $DMSP_t$ and $DMSO_t$ in the mixed layer, suggesting a similar source for both compounds. The decreasing long-term trends observed for $DMSP_t$ and DMS in the mixed layer were linked to the concurrent trend of the sum of 19'-hexanoyloxyfucoxanthin and 19'-butanoyloxy-fucoxanthin, which are the marker pigments of prymnesiophytes and chrysophytes, respectively. Major Baltic inflow events influenced the distribution of sulfur compounds due to phytoplankton community changes, and sediment might be a potential source for DMS in the bottom layer during seasonal hypoxia/anoxia at BE. A modified algorithm based on the phytoplankton pigments reproduces the $DMSP_p$:Chl *a* ratio well during this study and could be used to estimate future surface (5 m) $DMSP_p$ concentrations at BE.

In the second study, oceanic and atmospheric DMS measurements were made during two shipborne cruises between 1–26 December 2012 (M91, on board the R/V Meteor) and 5–22 October 2015 (SO243, on board the R/V Sonne) in the Peruvian upwelling region. DMSP and DMSO were also measured during M91. Relatively low DMS concentrations were measured in surface waters during both cruises compared to those reported previously. Nutrient availability appeared to be the main driver of the observed variability in the surface DMS distributions in the coastal areas (defined as bathymetry < 300 m). DMS, DMSP and DMSO showed maxima in the surface layer, and no elevated concentrations associated with the oxygen minimum zone off Peru were measured. The possible role of DMS, DMSP and DMSO as radical scavengers (stimulated by nitrogen limitation) is supported by their negative correlations with N: P (sum of nitrate and nitrite: dissolved phosphate) ratios. The atmospheric DMS mole fractions were generally low, and the sea-to-air flux was primarily driven by seawater DMS. The Peruvian upwelling region was identified as a source of atmospheric DMS in December 2012 and October 2015; however, in comparison to the previous measurements in the adjacent regions, the Peru upwelling was a moderate source of DMS emissions at either time.

In the third study, DMS, DMSP and DMSO were determined simultaneously in the water column in the southwestern Indian Ocean during two cruises between 8–20 July 2014 (SO234-2, on board the R/V Sonne) and 23 July–8 August 2014 (SO235, on board the R/V Sonne). Significant variation in DMS, $DMSP_t$ and $DMSO_t$ concentrations was observed in surface seawater, with higher concentrations measured during SO235, especially around the Mascarene Plateau, which was be related to the enhanced nutrient concentrations, which might stimulate the production of sulphur compounds by haptophytes. Vertical profiles of sulfur compounds and showed typical oceanic patterns with maxima in the subsurface layer, which paralleled to those of haptophytes and bacteria. In addition, for the first time, we validated the hypothesis that hypobromous acid (HOBr) might be a potential sink for marine DMS by using data set of DMS, $DMSO_t$ and bromoform ($CHBr_3$) in the surface layer.

ZUSAMMENFASSUNG

Das klimarelevante Spurengas Dimethylsulfid (DMS) hat in den letzten Jahren große Aufmerksamkeit erregt, da es möglicherweise das Erdklima beeinflusst, indem es atmosphärische Sulfataerosole bildet, die wiederum die Sonnenstrahlung zurückstreuen und möglicherweise als Wolkenkondensationskerne wirken können, die Wolken bilden. Die globale Bedeutung dieses DMS-bedingten Ozean-Klima-Rückkopplungsmechanismus steht jedoch nach wie vor zur Debatte, insbesondere aufgrund des Mangels an Langzeitbeobachtungen in den Ozeanen, wobei sich die meisten zeitlichen Studien auf die saisonalen Zyklen von DMS konzentrieren. Außerdem sind trotz der intensiven DMS-Forschung im räumlichen Bereich einige Ozeanregionen nach wie vor nur spärlich beprobt, so dass die Produktions- und Verbrauchsprozesse von DMS dort nur unzureichend verstanden sind. Um diese Wissenslücken zu schließen, haben wir Studien in der südwestlichen Ostsee (Zeitserienstation Boknis Eck), im östlichen Pazifik (das peruanische Auftriebssystem) und im südwestlichen Indischen Ozean durchgeführt. Die vorliegende Arbeit fasst diese Studien zusammen, bei denen DMS, Dimethylsulfoniopropionat (DMSP) und Dimethylsulfoxid (DMSO) in der Wassersäule gemessen werden, um ihre zeitlichen und räumlichen Schwankungen zu ermitteln und diese Veränderungen mit Trends in der Zusammensetzung des Phytoplanktons und/oder mit Umweltfaktoren in Verbindung zu bringen, wodurch neue Erkenntnisse über das Schicksal dieser biogenen Schwefelverbindungen gewonnen werden.

In der ersten Studie wurde eine Dekade von DMS-, DMSP- und DMSO-Messungen in der Wassersäule in Verbindung mit der Phytoplanktonzusammensetzung an der Zeitserienstation Boknis Eck (BE) (Eckernförder Bucht, südwestliche Ostsee) im Zeitraum Februar 2009-Dezember 2018 durchgeführt. Unsere Ergebnisse zeigen eine beträchtliche interannuelle und saisonale Variabilität in den Mischschichtkonzentrationen von DMS, Gesamt-DMSP (DMSPt) und Gesamt-DMSO (DMSOt). Es wurden positive Korrelationen zwischen partikulärem DMSP (DMSPp) und partikulärem DMSO (DMSOp) sowie DMSPt und DMSOt in der Mischschicht festgestellt, was auf eine ähnliche Quelle für beide Verbindungen hindeutet. Die für DMSPt und DMS in der gemischten Schicht beobachteten abnehmenden Langzeittrends waren mit dem gleichzeitigen Trend der Summe von 19'-Hexanoyloxyfucoxanthin und 19'-Butanoyloxy-fucoxanthin verbunden, die die

Markerpigmente von Prymnesiophyten bzw. Chrysophyten sind. Größere Inflow-Ereignisse in der Ostsee beeinflussten die Verteilung von Schwefelverbindungen aufgrund von Veränderungen in der Phytoplanktongemeinschaft, und das Sediment könnte eine potenzielle Quelle für DMS in der Bodenschicht während der saisonalen Hypoxie/Anoxie in der BE sein. Ein modifizierter Algorithmus, der auf den Phytoplanktonpigmenten basiert, reproduziert das DMSPp:Chl a-Verhältnis in dieser Studie gut und könnte zur Abschätzung künftiger DMSPp-Konzentrationen an der Oberfläche (5 m) der BE verwendet werden.

In der zweiten Studie wurden ozeanische und atmosphärische DMS-Messungen während zweier Schiffsreisen zwischen dem 1. und 26. Dezember 2012 (M91, an Bord der R/V Meteor) und dem 5. und 22. Oktober 2015 (SO243, an Bord der R/V Sonne) in der peruanischen Auftriebsregion durchgeführt. DMSP und DMSO wurden ebenfalls während M91 gemessen. Während beider Fahrten wurden in den Oberflächengewässern relativ niedrige DMS-Konzentrationen gemessen, verglichen mit den zuvor gemeldeten Werten. Die Nährstoffverfügbarkeit scheint der Hauptgrund für die beobachtete Variabilität in der DMS-Verteilung an der Oberfläche in den Küstengebieten (definiert als Bathymetrie < 300 m) zu sein. DMS, DMSP und DMSO zeigten Maxima in der Oberflächenschicht, und es wurden keine erhöhten Konzentrationen im Zusammenhang mit der Sauerstoffminimumzone vor Peru gemessen. Die mögliche Rolle von DMS, DMSP und DMSO als Radikalfänger (stimuliert durch Stickstofflimitierung) wird durch ihre negativen Korrelationen mit dem N:P-Verhältnis (Summe von Nitrat und Nitrit: gelöstes Phosphat) unterstützt. Die atmosphärischen DMS-Molfraktionen waren im Allgemeinen niedrig, und der Fluss von Meer zu Luft wurde hauptsächlich durch DMS aus dem Meerwasser angetrieben. Die peruanische Auftriebsregion wurde im Dezember 2012 und im Oktober 2015 als Quelle für atmosphärisches DMS identifiziert; im Vergleich zu den früheren Messungen in den angrenzenden Regionen war der peruanische Auftrieb jedoch zu beiden Zeitpunkten eine mäßige Quelle für DMS-Emissionen.

In der dritten Studie wurden DMS, DMSP und DMSO gleichzeitig in der Wassersäule im südwestlichen Indischen Ozean während zweier Fahrten vom 8. bis 20. Juli 2014 (SO234-2, an Bord der R/V Sonne) und vom 23. Juli bis 8. August 2014 (SO235, an Bord der R/V Sonne) bestimmt. Im Oberflächenmeerwasser wurden erhebliche Schwankungen der DMS-, DMSPt- und DMSOt-Konzentrationen beobachtet, wobei während SO235 höhere Konzentrationen gemessen wurden, insbesondere um das Maskarenen-Plateau, was mit den erhöhten Nährstoffkonzentrationen zusammenhängen könnte, die die Produktion von Schwefelverbindungen durch Haptophyten

stimulieren. Vertikale Profile von Schwefelverbindungen und zeigten typische ozeanische Muster mit Maxima in der unterirdischen Schicht, die mit denen von Haptophyten und Bakterien übereinstimmten. Darüber hinaus haben wir zum ersten Mal die Hypothese bestätigt, dass hypobromige Säure (HOBr) eine potenzielle Senke für marines DMS sein könnte, indem wir einen Datensatz von DMS, DMSOt und Bromoform (CHBr3) in der Oberflächenschicht verwendeten.

Contents

1 Introduction

1.1 Atmospheric dimethyl sulfide (DMS) and its potential role in climate

The atmosphere plays an important role in the climate as its composition influences the radiative budget of the Earth (Boucher et al., 2013). Despite their seemingly low abundances, certain trace gases (e.g., methane, tropospheric O_3 and N_2O) critically warm the planet by reducing the loss rate of infrared solar radiation from Earth's surface and hence trap heat (Dickinson and Cicerone, 1986). In contrast to greenhouse gases, atmospheric aerosols affect the radiative balance by directly absorbing/scattering solar radiation or indirectly contributing cloud condensation nuclei (CCN) and, as a consequence, increase the Earth's albedo (Hansen et al., 2007; Sanchez et al., 2018).

Dimethyl sulfide (DMS), the focus of this thesis, is a biogenic sulfur compound mainly produced in the ocean and represents more than half of the natural sulfur emitted to the atmosphere (Andreae, 1990). Once emitted to the atmosphere, DMS is mainly oxidized in the troposphere with a lifetime of 1–2 days (Boucher et al., 2003; Breider et al., 2010). DMS is oxidized to methanesulfonic acid (MSA) and sulfur dioxide (SO_2) by hydroxyl and/or nitrate radicals. DMS-derived SO_2 can be further oxidized to sulfuric acid (H_2SO_4), which plays an important role in natural aerosol formation and growth in the marine boundary layer (MBL). Recently, a previously unobserved DMS oxidation product, hydroperoxymethyl thioformate (HPMTF), was proposed to play a substantial role in aerosol formation and/or growth as well (Veres et al., 2020). Therefore, atmospheric DMS may have a whitehouse effect to counteract the warming potential of greenhouse gases (Schwartz, 1996; Thomas et al., 2010). However, interactions between clouds and natural aerosols (such as those that originate from DMS oxidation) account for a large uncertainty of radiative forcing in climate projections (Carslaw et al., 2013).

DMS started to receive much scientific attention since the 1970s that its emission is proposed to close the global sulfur budget (Lovelock et al., 1972). Moreover, as the proposal of the well-known

CLAW hypothesis (Charlson et al., 1987), DMS captured the imagination and interest of scientists, spurring significant research in this area over the past decades (e.g., Watanabe et al., 1995; Belviso et al., 2004; Deng et al., 2021). The hypothesis suggested an important role of DMS in climate regulation (Fig. 1.1), which is based on the following steps: (1) an increase in biogenic DMS emissions from the ocean would lead to an increase in CCN, (2) an increase in DMS-derived CCN yields an increase in cloud albedo and, thus, a decrease in incoming solar radiation and temperature, and (3) a decrease in surface temperature leads to a reduction in DMS production by altering the speciation and abundance of the phytoplankton in the ocean. However, this hypothesis is still under debate to date, since every step in the proposed feedback loop (e.g., phytoplankton dynamics, air-sea exchange and atmospheric chemistry) requires a strong response to close to the loop (Quinn and Bates, 2011). Nonetheless, DMS emissions might still contribute to a large fraction of aerosol particle formation over remote ocean regions (Quinn et al., 2017). Hence, the influence of DMS on marine stratiform cloud albedo remains in the spotlight (Brooks and Thornton, 2018), and it is necessary to understand its behaviour and distribution from the origin in order to quantify its emissions to the atmosphere accurately.

As the ocean is the most significant source of atmospheric DMS, it is therefore of great importance to understand and determine which factors control the cycling of oceanic DMS and related sulfur compounds. This understanding will assist modellers to better predict future change in DMS variability, especially in view of global warming, ocean eutrophication, and deoxygenation. To this end, DMS and related sulfur compounds will be discussed in detail in the following sections, with respect to their interaction and distribution in response to physical, chemical, and biological ecosystem parameters, as well as their seasonal and spatial characteristics.

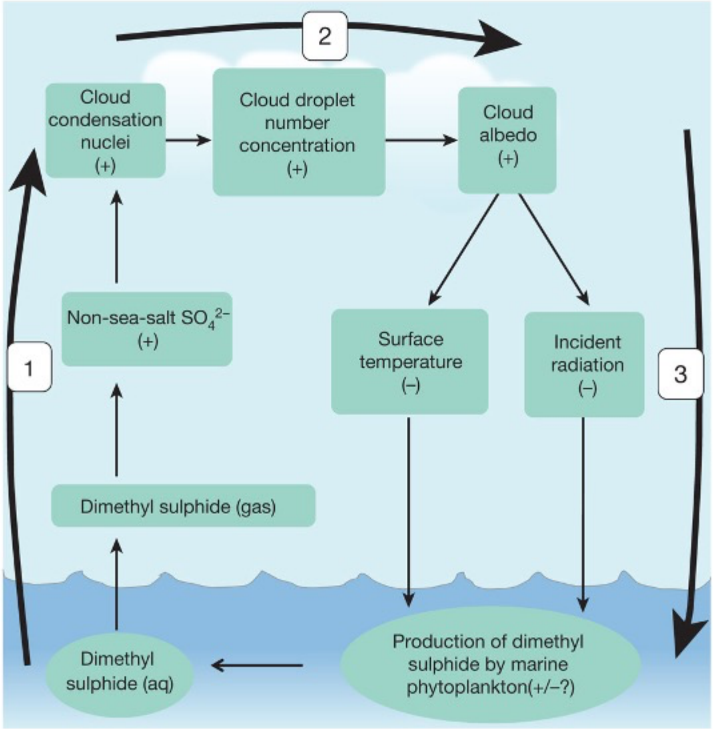

Figure 1.1. Schematic of the CLAW hypothesis proposed by Charlson et al. (1987) (Quinn and Bates, 2011). The main steps are labelled in the figure.

1.2 Cycling of organic sulfur compounds in the ocean

1.2.1 Dimethylsulfoniopropionate (DMSP)

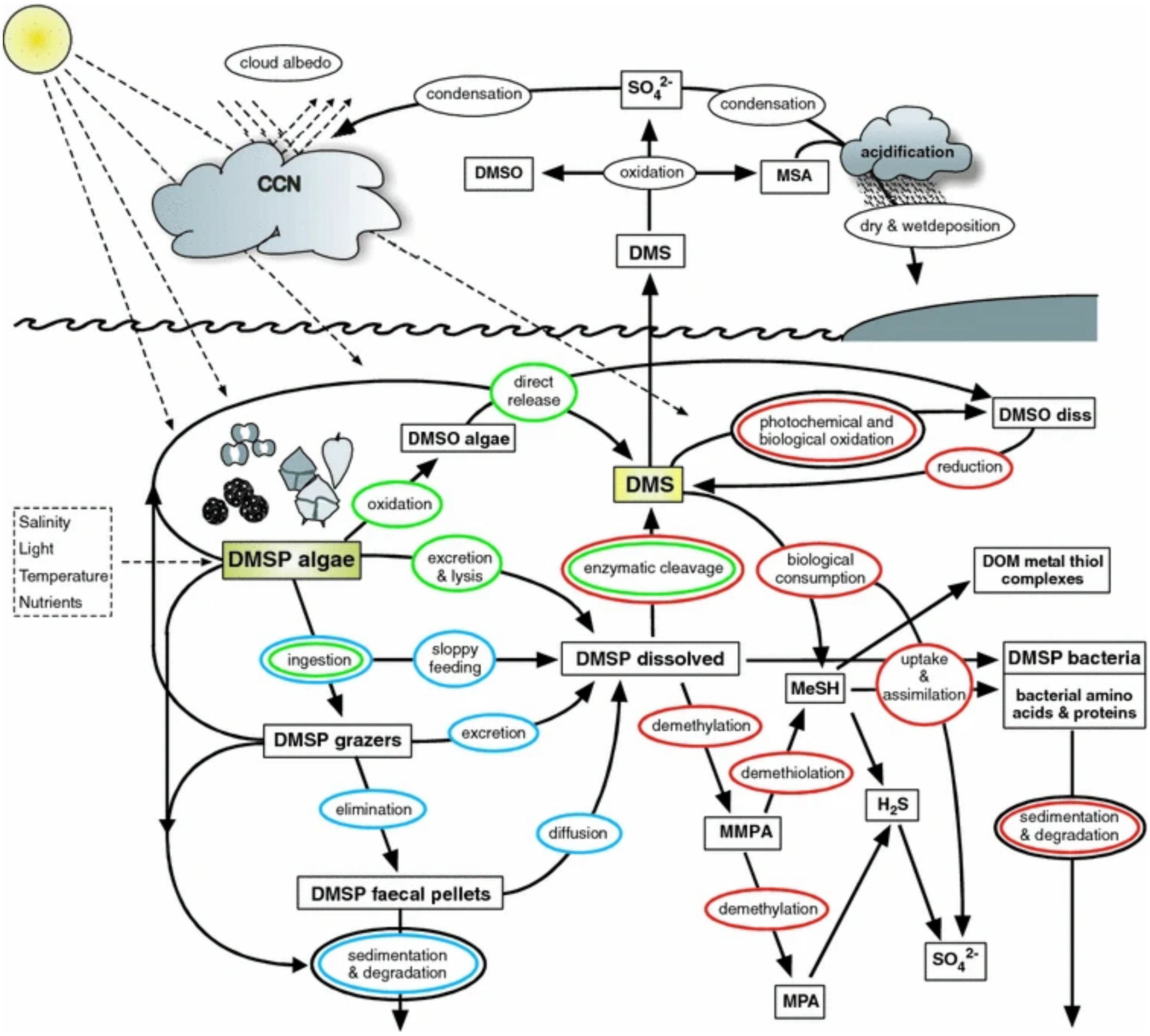

Figure 1.2. Biogeochemical cycling of organic sulfur compounds (Stefels et al., 2007). DOM: dissolved organic matter; MeSH: methanethiol; MPA: mercaptopropionate; MMPA: methylmercaptopropionate; MSA: methanesulfonic acid.

DMS is mainly produced from its precursor, dimethylsulfoniopropionate (DMSP; Fig. 1.2), an organic sulfur compound ubiquitous in each ecosystem. The ocean seems to be a more abundant source than others, such as terrestrial environments, due to the higher sulfate concentrations in seawater (Stefels, 2000). Surface seawater DMSP concentrations generally vary between 1–100 nmol L^{-1} (Dacey et al., 1998; Galí et al., 2015), occasionally increasing to micromolar concentrations during phytoplankton blooms (Speeckaert et al., 2018; Kiene et al., 2019). DMSP can be produced by many marine organisms, such as macroalgae, phytoplankton and corals (Raina et al., 2013; Zhang et al., 2019). Recently, marine bacteria have been identified to contribute to DMSP production (Curson et al., 2017).

On a global scale, it is widely recognized that phytoplankton is the main producer of DMSP, and the estimated annual production by phytoplankton is 2.0 Pg S $year^{-1}$ (Galí et al., 2015). Strains in the classes of dinoflagellates and haptophytes contain high DMSP concentrations, whereas diatoms and cyanobacteria contain low DMSP concentrations (Keller, 1989; Speeckaert et al., 2018; Kiene et al., 2019), with the exception of ice algal communities (e.g., diatoms) (Kirst et al., 1991; Baumann et al., 1994). At present, there are several different pathways identified for DMSP biosynthesis in marine eukaryotes and prokaryotes, such as a methylation pathway in angiosperms (e.g., Kocsis et al., 1998), a decarboxylation pathway in one dinoflagellate (Uchida et al., 1996), and transamination pathways in various phytoplankton (e.g., diatoms, haptophytes and green algae), corals and marine bacteria (e.g., *Alphaproteobacteria*) (Curson et al., 2017, 2018). Despite the subsequent steps vary, each of these proposed pathways for DMSP synthesis starts with methionine (Met) (Zhang et al., 2019). In addition, bacterial studies powered by genomic sequences and molecular tools provided new insights into DMSP biosynthesis at genic scales. Curson et al. (2017, 2018) proposed that the *DSYB* gene, encoding a SAM-dependent methyltransferase, was the key gene to mediate the transamination pathway in marine algae such as diatoms, dinoflagellates and coccolithophores. Recently, one gene *dsyB,* was detected in some marine *Alphaproteobacteria*. It coded a functional 4-dimethylsulfonio-2-hydroxybutyrate (MTHB) and was identified as the key gene in mediating the transamination pathway in bacterial DMSP biosynthesis.

There are several mechanisms of releasing particle DMSP ($DMSP_p$) to the oceanic environments, including active exudation, autolysis, viral lysis and grazing by zooplankton (Fig. 1.2; Stefels et al., 2007). Once released into the water column, the dissolved DMSP ($DMSP_d$) is rapidly utilized by marine organisms, predominant by free-living or attached bacteria, since DMSP can satisfy significant carbon demand (estimated 1–15 %) and almost all the sulfur demand of bacterioplankton (Kiene et al., 2000; Zubkov et al., 2001). The two major pathways of DMSP bacterial degradation are demethylation and cleavage (Fig. 1.2). The usual dominant degradation pathway of DMSP is demethylation (up to 75 %) (Kiene et al., 2000; Moran et al., 2012), and it does not yield DMS, instead, it yields methiolpropionate (MMPA). MMPA can be further demethylated to 3-mercaptopropionate (MPA) or demethiolated to methanethiol (MeSH), with the latter being considered as another important organic compound that can serve as an important sulfur source for bacterioplankton (Kiene et al., 1999). The cleavage pathway yields DMS and acrylate/3-hydroxypropionate, which is considered the primary source of oceanic DMS.

It is hypothesized that the two competing degradation pathways (demethylation and cleavage) are controlled by DMSP availability relative to the carbon and sulfur demands of the marine bacteria. Low $DMSP_d$ availability (e.g., pre-bloom of algae) would lead to a demethylation pathway as this is a more economical way for the assimilatory purpose (Kiene et al., 2000). This is supported by a recent laboratory study finding that strains of *Ruegeria pomeroyi* DSS-3 preferred the demethylation pathway when the $DMSP_d$ concentration was relatively low (> 1 nmol L^{-1}) and then switched to the cleavage pathway when the $DMSP_d$ concentration increased (>35 nmol L^{-1}) (Gao et al., 2020). On a smaller scale, the role of the key enzyme DmdA in the DMSP demethylation pathway (Howard et al., 2006; Moran et al., 2012), and ddd*D*, -*L*, -*Q*, -*W* and -*K* in the DMSP cleavage pathway, have been fully elucidated (Curson et al., 2011; Sun et al., 2016). In addition to bacterial DMSP degradation, it has been known that marine phytoplankton can cleave DMSP into DMS and acrylate via DMSP-lyases (Yoch, 2002). Caruana and Malin (2014) presented a synthesis and analysis of all relevant DMSP intracellular concentrations and DMSP lyase activity measurements within dinoflagellates. Furthermore, a eukaryotic DMSP lyase gene, *Almal*, was identified by Alcolombri et al. (2015) from the haptophyte *Emiliania huxleyi*, which is the first study to prove that DMSP can be directly degraded to DMS and acrylate within algae cells. However, it is still challenging to differentiate the two cleavage pathways between algae and bacteria, which needs more investigation.

1.2.2 Dimethyl sulfide (DMS)

The dominant source of DMS is thought to be the bacteria and/or algae enzymatic cleavage of algal-derived DMSP, although dimethyl sulfoxide (DMSO) reduction could also contribute (Asher et al., 2017; Dixon et al., 2020). Additionally, a handful of grazing studies showed that grazing is also an important mechanism for DMS production (e.g., Archer, 2003; Asher et al., 2017). DMS concentrations are generally less than 10 nmol L^{-1} (Leck et al., 1990; Lana et al., 2011; Dixon et al., 2020) in the oceans, and occasionally greater than 50 nmol L^{-1} associated with peak DMSP concentrations (Turner et al., 1996; Speeckaert et al., 2018). DMS is lost principally via four processes in the surface waters (Fig. 1.2): (i) microbial consumption, (ii) photochemical oxidation, (iii) air-sea exchange and (iv) vertical mixing (Stefels et al., 2007).

Microbial consumption in marine surface waters is often the major sink for DMS, especially under the condition of deep mixing and/or cloudy skies (Kiene and Bates, 1990; Simó and Pedrós-Alió, 1999; Simó, 2004; Lidbury et al., 2016). Simó (2004) estimates that 80 % of DMS concentrations were taken up by bacteria based on data from various oceanic regions. The major microbial degradation pathways of DMS are oxidation to DMSO via DMS dehydrogenase and consumption to MeSH and formaldehyde via DMS monooxygenases/methyltransferases and (Bentley and Chasteen, 2004; Stefels et al., 2007). Both pathways could lead to the formation of sulfate. Some field studies also reported that the microbial community metabolized most DMS to DMSO and/or sulfate in the water column (see e.g., Vila-Costa et al., 2006; del Valle et al., 2007). In contrast to its precursor DMSP, DMS seems only to be utilized as carbon, as only a minor fraction of DMS (~ 2–7 %) is used for bacterial sulfur assimilation (Vila-Costa et al., 2006; del Valle et al., 2007). This is consistent with the observations that DMSP has much higher turnover rates and bacterial consumption rates than DMS (Vila-Costa et al., 2006; Dixon et al., 2020).

Photochemical oxidation is an important loss process for DMS (Kieber et al., 1996), and it could become the dominant sink of DMS under the condition of the shallow upper mixed layer and high-irradiance (e.g., clear skies and summer) (Dacey et al., 1998; Toole et al., 2006). Photochemical oxidation can occur at ultraviolet (UVR) and visible wavelengths via photosensitizers (e.g., nitrate, nitrite, and coloured dissolved organic matter (CDOM)), leading to the production of DMSO or other products (Brimblecombe and Shooter, 1986; Kieber et al., 1996; Brugger et al., 1998; Hatton, 2002; Toole and Siegel, 2004; Bouillon and Miller, 2005). However, considering that nitrate concentrations, CDOM, wavelength, and light intensity can vary with season and depth, more work is required on DMS photolysis to accurately capture this complex process.

Generally, DMS concentrations in the surface ocean have been shown to be orders of magnitude supersaturated relative to those in the atmosphere, suggesting an efflux of the gas from the oceans to the atmosphere (Liss et al., 1994). However, in comparison to biological consumption and photolysis, air-sea exchange is generally considered as a minor sink for oceanic DMS (10%) (Bates et al., 1994; Galí and Simó, 2010), although it could become comparable in a windstorm (Simó and Pedrós-Alió, 1999). The sea-air fluxes of DMS can be either directly measured (e.g., using the eddy correlation technique (e.g., Huebert et al., 2004)) or calculated by parameterization (Liss and Slater, 1974). The calculation of air-sea gas fluxes (*F*) is generally based on the concentration difference (ΔC) between two phases (gas and liquid) and the gas transfer velocity (*k*):

$$F = k \times \Delta C = k \cdot \left(c_{\mathrm{air}} - \frac{c_{water}}{H}\right) \qquad (1.1)$$

where c_{air} and c_{water} are the respective concentrations in air and water, and *H* is Henry's law constant. Since c_{air} is typically orders of magnitude lower relative to c_{water}, c_{air} is usually assumed to be zero, which might lead to an overestimation of DMS fluxes (Turner et al., 1996; Lennartz et al., 2015). In addition, recent publications on *k* parameterizations derived by direct flux measurements suggest that *k* exhibited more of a linear (Marandino et al., 2009; Blomquist et al., 2017) instead of a quadratic (Nightingale et al., 2000) or cubic (Wanninkhof and McGillis, 1999) relationship with wind speed.

Except for the mentioned three main sinks, vertical mixing may also act as a potential mechanism controlling DMS concentration on timescales of hours to days (Stefels et al., 2007). For example, Strong winds induced deepening of the mixed layer would transport DMS into a deeper layer and thus, decrease DMS concentration via dispersion. In contrast, shoaling of mixed layer might trap DMS above the new depth of the pycnocline and hence, increase DMS concentration by inhibiting bacterial activity (microbial consumption) under strong solar radiation dose (SRD) (Vallina et al., 2007). Also, mixing would change phytoplankton community structure by altering nutrient concentrations, which in turn affects DMS production (Yang et al., 2013). Additionally, Müller et al. (2019, 2021) suggested hypobromous acid (HOBr) could react with marine DMS fast to produce DMSO by laboratory experiments, representing a potentially neglected DMS sink; however, it is are not examined in marine environments yet.

1.2.3 Dimethyl sulfoxide (DMSO)

In comparison to DMS and DMSP, dimethyl sulfoxide (DMSO) is a poorly understood organic compound in the marine sulfur cycle. In marine chemistry, it receives scientific attention since its origin and fate are tightly coupled to the biogeochemical cycle of DMS. Generally, surface DMSO concentrations vary from 1 to 50 nmol L^{-1} and are usually higher than DMS (Kwint and Kramer, 1996; Dixon et al., 2020), while its concentration relative to DMSP seems to vary in different regions (Simó and Vila-Costa, 2006). In addition, it appears that the particulate pools are dominated by DMSP on most occasions, and the dissolved pools are dominated by DMSO (Hatton et al., 2004). Unlike DMSP and DMS, which are mainly restricted within the euphotic layer and were only measured at concentrations less than 0.5 nmol L^{-1} or below the detection limit below 200 m (Curran et al., 1998; Zheng et al., 2020), DMSO is ubiquitous throughout the water column and was reported at concentrations greater than 1.5 nmol L^{-1} in the deep ocean (Hatton et al., 1998, 1999), which suggests that DMSO seems to be the biggest organic sulfur pool in the oceans.

The production of particulate DMSO ($DMSO_p$) was observed in laboratory culture studies of some algae groups, such as dinoflagellates and haptophytes (Simó et al., 1998). Moreover, it is suggested that the synthesis of intracellular $DMSO_p$ may be present in a broader range of algae species than those of $DMSP_p$ (Lee et al., 1999; Bouillon et al., 2002). In addition to laboratory experiments, the significant linear relationship between DMSP and DMSO was observed in field studies in the surface layer (Riseman and DiTullio, 2004; Zindler et al., 2012), suggesting a similar source for both sulfur compounds. It is worth noting that the release of $DMSO_p$ into the water column may occur through its ability to permeate cell membranes through passive diffusion, which is not shared by DMSP. In addition to the direct release, dissolved DMSO ($DMSO_d$) can be produced both via DMS oxidation microbially and photochemically, which makes $DMSO_d$ an important sink for DMS in marine environments (Fig. 1.2; Stefels et al., 2007). It is suggested that $DMSO_d$ could also be biologically reduced to DMS and thus, represents a potentially important source for DMS (Hatton et al., 2004; Spiese et al., 2009). Archer et al. (2011) reported that DMSO reduction was a major pathway of DMS production in Antarctic sea ice. Other sinks of $DMSO_d$ include potential oxidation to dimethyl sulfone ($DMSO_2$) (Lee et al., 1999) and bacterial consumption (Simó et al., 2000). A recent study conducted at a temperate coastal site suggested that microbial dissimilation of $DMSO_d$ to CO_2 can be a significant loss pathway, which can address bacterial sulfur and carbon demand (Dixon et al., 2020). In addition, Thume et al. (2018) reported the discovery of an unusual metabolite, dimethylsulfoxonium propionate

(DMSOP), which is an intermediate when forming DMSO from DMSP, and this pathway circumvents DMS production and extends the existing marine organosulfur cycle.

1.3 Physiological and biological functions of sulfur compounds

In addition to the great importance of DMS and its related sulfur compounds (DMSP and DMSO) in the microbial food webs and their potential effects on climate regulation, they have also been proposed to have versatile physiological and biological functions within various marine organisms (Table 1.1).

Numerous studies have been done on a variety of functions of organic sulfur compounds. DMSP is a multifunctional compound proposed to serve as an osmoprotectant, a cryoprotectant, an antioxidant, an overflow mechanism for removing excess reduced sulfur and energy and providing hydrostatic pressure protection (Table 1.1). For instance, the intracellular DMSP concentration of *Hymenomonas carterae* (haptophytes) was measured up to 300 nmol L^{-1}, which can help cells to tolerate osmotic stress induced by increasing salinity (Vairavamurthy et al., 1985; Kirst, 1990). Nishiguchi and Somero (1992) proposed the cryoprotective role based on the observation of improved compatibility of DMSP with protein structure at low temperatures. This was later confirmed by Karsten et al. (1996), extracting the model enzymes from the polar algae *Acrosiphonia arcta* (Chlorophytes). Similarly, it has been postulated that DMSO could act as a cryoprotectant within algae cells (Lee and de Mora, 1999); however, this was dismissed by Lee et al. (2001), who suggested that the low intracellular concentration of DMSO measured in the ice algae were unlikely to have a significant influence on the freezing point depression of intracellular fluids. DMSP may serve as a sink of excess sulfur and energy induced by active photosynthesis, and this mechanism has been well reviewed by Stefels (2000). Recently, Zheng et al. (2020) reported enhanced DMSP production associated with bacteria in the deep ocean (> 8000 m) and attributed this to a bacterial preference to store DMSP against hydrostatic pressure.

The role of antioxidants for DMSP, DMS and DMSO has been well established in laboratory experiments. They can scavenge hydroxyl radicals and other reactive oxygen species (ROS), and hence, may act as efficient antioxidants within algae cells (Sunda et al., 2002, 2007). In addition to the phytoplankton community, Raina et al. (2013) observed increased DMSP concentrations in coral juveniles when they experienced thermal stress and attributed this to the role of DMSP in ROS detoxification. In general, a variety of stressors, including solar UV radiation, nutrient limitation, H_2O_2 and thermal stress, can elevate intracellular DMSP and/or DMS concentrations. This hypothesis is also supported by field data. Riseman and DiTullio (2004) reported increased concentrations of $DMSP_p$ and $DMSO_p$ stimulated by iron limitation and their positive correlations with the antioxidant β-carotene in the Peru upwelling system. Moreover, Simó and Vila-Costa (2006) found a negative correlation between SST and $DMSP_p$:$DMSO_p$ ratio based on a compilation of data from different oceanic regions. They suggested that increased SST could be associated with increased SRD, which would trigger a cascade reaction system (DMSP-DMS-DMSO) against oxidative stress. Later, Zindler et al. (2013) validated this argument by including a broader range of cruise data with their average $DMSP_p$:$DMSO_p$ ratios and SST.

Table 1.1. Functions of DMSP, DMS, and DMSO modified according to Zhang et al. (2019).

Compounds	Functional types	Specific functions	Related organisms	References
DMSP	Physiological functions	Osmoprotectant	Synurophytes Chlorophytes Ulvophytes Rhodophytes Phaeophytes	Vairavamurthy et al. (1985); Kirst (1990)
		Cryoprotectant	Chlorophytes	Karsten et al. (1996)
		Antioxidant	Haptophytes Diatoms Dinoflagellates Corals	Sunda et al. (2002); Lesser (2006); Husband et al. (2012); Raina et al. (2013); Curson et al. (2018)
		Sink of excess sulfur, carbon, and reduced equivalent, saving nitrogen for cell growth and accelerating sulfate uptake from the environment	Photosynthetic marine algae higher plants (e.g., Ulvophytes)	Gage et al. (1997); Stefels (2000); Bullock et al. (2017)
		Hydrostatic pressure protection	Bacteria	Zheng et al. (2020)
	Biological functions	Grazing deterrent	Haptophytes	Wolfe et al. (1997); Strom et al. (2003a, b)
		Chemoattractant	Bacteria Reef fishes Mammals	Miller et al. (2004); Kowalewsky et al. (2006); Debose et al. (2008); Seymour et al. (2010)
		Mediator of bacterial virulence-associated with regulation	Haptophytes and bacteria	Barak-Gavish et al. (2018)
		Bacterial quorum sensing inducer, related to the decomposition of particulate organic matter	Bacteria	Seyedsayamdost et al. (2011); Johnson et al. (2016)

Table 1.1. Continued

Compounds	Functional types	Specific functions	Related organisms	References
DMS	Physiological function	Antioxidant	Haptophytes	Sunda et al. (2002); Lesser (2006)
	Biological function	Chemoattractant	Fishes and seabirds Copepods	Steinke et al. (2006); Debose and Nevitt (2008); Nevitt (2008)
DMSO	Physiological function	Antioxidant	Haptophytes	Sunda et al. (2002)

From the perspective of infochemical signalling, it seems DMSP could act as both 'don't eat' me or 'eat me' cues, which depends on the specific predator-prey interactions (Edgcomb, 2021). For instance, Strom et al. (2003a, b) reported reduced feeding rates of several tested protist grazer species (e.g., ciliates and heterotrophic dinoflagellates) on *Emiliania huxleyi* (haptophytes) with high levels of DMSP lyase activity and/or high DMSP concentrations and suggested that the role of DMSP as predator deterrents (Table 1.1). However, adding the cleavage products of DMS and acrylate has no effect on the tested protist grazers. In contrast, some studies reported phytoplankton-generated DMSP and its breakdown product DMS is used as chemoattractants for a variety of marine organisms, including reef fishes (DeBose et al., 2008), harbour seals (Kowalewsky et al., 2006), specific groups of bacteria (Miller et al., 2004; Seymour et al., 2010), fishes and seabirds (DeBose and Nevitt, 2008; Nevitt, 2008) and copepods (Steinke et al., 2006). These paradoxical findings of DMSP as infochemical needs further investigated. In addition, as a chemical signalling molecule, DMSP is also proposed to mediate *Sulfitobacter* D7 (bacteria) virulence that may regulate the demise of *Emiliania huxleyi* (haptophytes) (Barak-Gavish et al., 2018), to trigger metabolic shifts in specific groups of bacteria and to participate in the particle degradation (Seyedsayamdost et al., 2011; Johnson et al., 2016).

1.4 Distribution characteristics of oceanic DMS and its emissions to the atmosphere

To unravel the link between DMS and climate, it is key to understand DMS distributions on both spatial and temporal (seasonal) scales. Spatially, surface seawater DMS concentrations are higher at the continental margins than those in the pelagic ecosystem and generally decrease from the inshore to the offshore (Fig. 1.3). Lana et al. (2011) estimated that DMS concentrations were less than 2 nmol L^{-1} in around 50% of the global oceans. On a global scale, high-latitude (polar and subpolar) regions are hot spots (high concentrations) of DMS. For instance, high DMS concentrations were measured in the northeast Atlantic (Malin et al., 1993), in the Barents Sea (Matrai and Vernet, 1997), in the Bering Sea (Li et al., 2019), in the Southern Ocean, especially along the coastal Antarctic waters (Gibson et al., 1990; Zhang et al., 2017; Stefels et al., 2018; Webb et al., 2019). Between temperate and subtropical areas, high DMS concentrations coincide with the high primary productivity areas, such as the North Sea, the Mediterranean Sea and the coastal/open ocean upwelling regions (Andreae, 1985; van Duyl et al., 1998; Belviso et al., 2003; Spencer et al., 2005; Shenoy and Kumar, 2007; Speeckaert et al., 2018). Tropical oceans usually presented constantly low DMS concentrations throughout the year (Bates and Quinn, 1997). Seasonally, a clear regional annual cycle could be observed, with elevated DMS concentrations measured during summer in both hemispheres. In polar and subpolar regions, DMS concentrations usually peak approximately in synchrony with phytoplankton biomass, especially linking to the strong DMSP producers, such as haptophytes and dinoflagellates (Iida et al., 2002) and/or sea-ice retreat (Trevena and Jones, 2006). Moving towards temperate and subtropical regions, peak DMS concentrations in the summer tend to lag weeks to months of maxima Chl *a* or its precursor DMSP, a feature so-called the ‘summer paradox’ (Simó and Pedrós-Alió, 1999). Based on a global meta-analysis, Galí (2015) suggested that this could be explained by a short-term dynamic equilibrium, which is driven by gross DMS production rates and various DMS loss rate constants. In the tropical oceans, DMS concentrations are generally invariable due to the reduced seasonality.

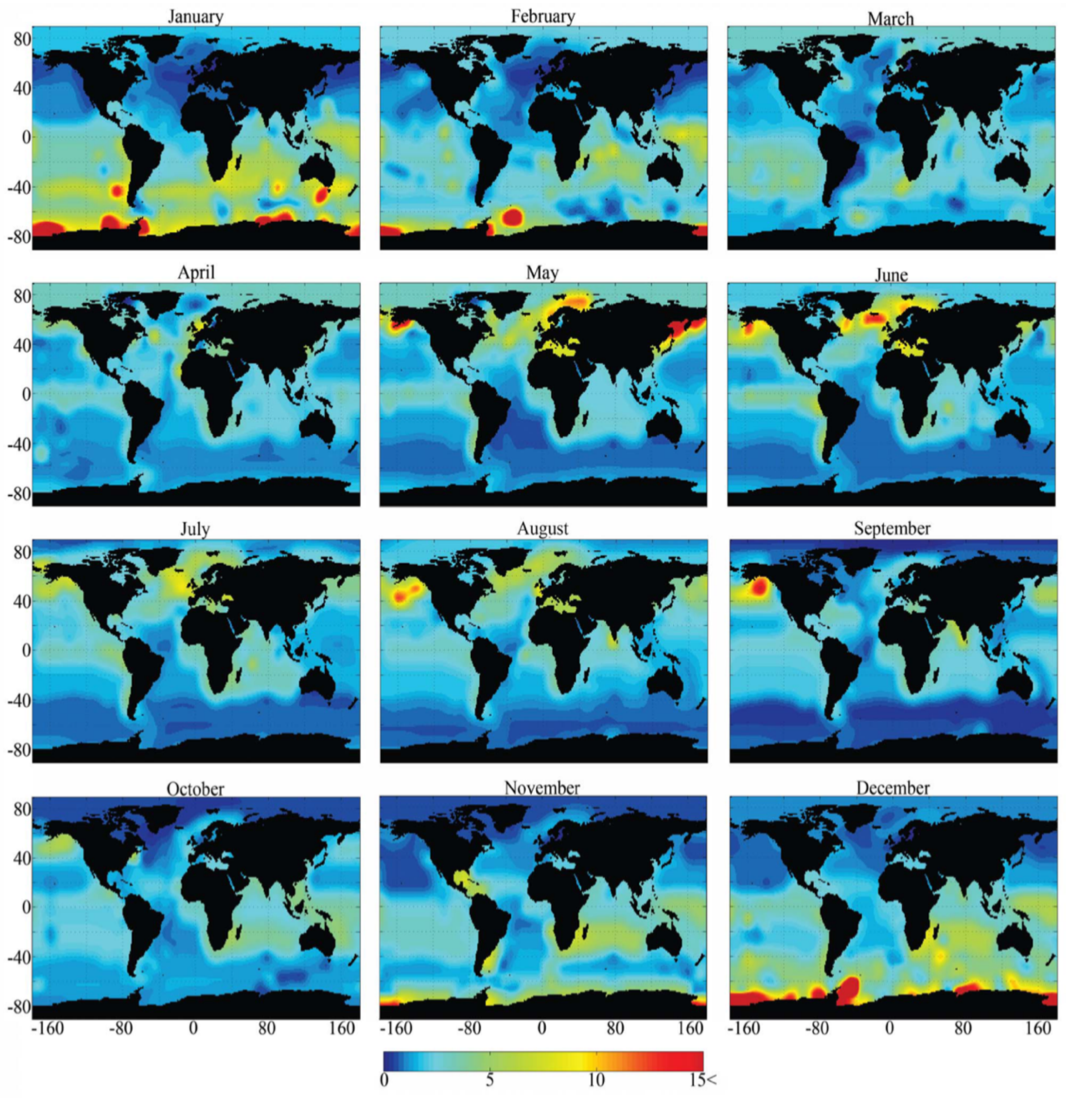

Figure 1.3. Monthly maps of global mean DMS concentrations (nmol L^{-1}) with interpolation/extrapolation created by Lana et al. (2011). Note that the scale is capped at 15 nmol L^{-1} to ensure readability of the plots, although only a few specific regions exceed 15 nmol L^{-1} DMS concentration.

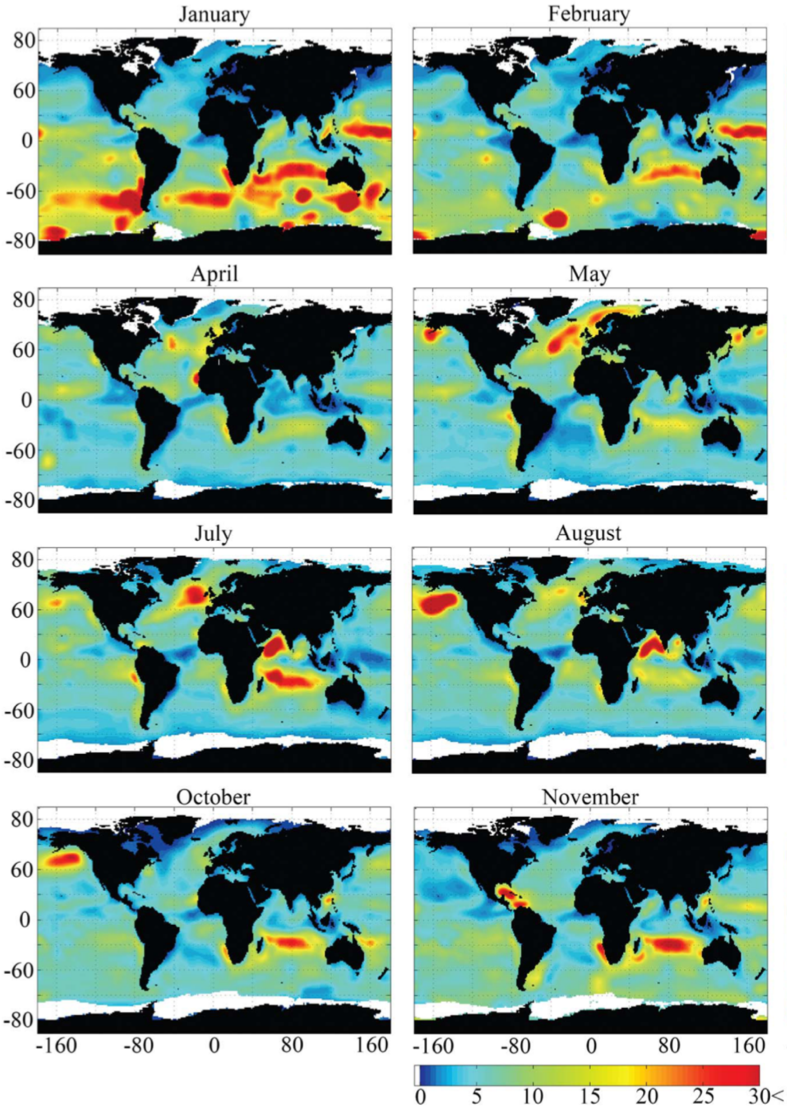

Figure 1.4. Monthly maps of global mean DMS fluxes (µmol S $m^{-2}d^{-1}$) created by Lana et al. (2011). Note that the scale is capped at 30 µmol S $m^{-2}d^{-1}$ to ensure readability of the plots, although only a few specific regions exceed this value.

The typical vertical distribution of DMS shows a subsurface maxima in the euphotic layer and then decreases with the increasing depth (Zhang et al., 2019). However, there are a few studies reporting elevated concentrations of DMS in the bottom layer associated with seasonal low-oxygen events (e.g., Shenoy et al., 2012; Bepari et al., 2020), and this might be attributed to several potential sources, such as DMSP cleavage, DMSO reduction, methylation of MeSH under anoxic conditions and/or sediment release (Kiene, 1988; Nedwell et al., 1994; Song et al., 2020). Therefore, the sediments and their overlying water layer might be a potential source for the upper mixed layer DMS, which needs further investigation.

Oceanic emissions of DMS are important because of their role as a precursor of atmospheric sulfate aerosol. Hulswar et al. (2021) estimated that DMS fluxes were below 10 μmol S $m^{-2}d^{-1}$ in around 93 % of the global oceans. In the northern hemisphere, DMS fluxes generally follow the distribution of seawater DMS concentrations (Fig. 1.4) (Lana et al., 2011; Hulswar et al., 2021). Also, similar to the seasonality of marine DMS, DMS fluxes peak during summer in each hemisphere. It is noted that the subtropical Indian Ocean could be a significant source of DMS emissions because of moderate DMS concentrations and persistent high wind speeds (Zavarsky et al., 2018). In addition, DMS emissions in the Arabian Sea stand out during the southwestern summer monsoon, resulting from the increased wind speeds (Naqvi et al., 2005). The western Pacific Ocean showed strong seasonal DMS fluxes, which is led by the large variability of DMS concentrations and wind speeds (Lana et al., 2011; Marandino et al., 2013). In the southern hemisphere, the coast off Peru and Chile could be a hotspot occasionally for DMS emissions due to the elevated DMS concentrations in this productive region (Andreae, 1985; Marandino et al., 2009). The Southern Ocean is major source of DMS during austral summer and autumn (Kim et al., 2021; Zhang et al., 2021). Overall, it is estimated that the Southern Hemisphere oceans contribute more than half of the global annual DMS emissions (Lana et al., 2011).

1.5 DMS algorithms

In addition to field studies, many attempts have been made to estimate global DMS distributions in the surface ocean by proposing various algorithms. They generally used combinations of variables involved in the DMS cycle to represent the detailed understanding of the process. Anderson et al. (2001) reconstructed global DMS concentrations by using Chlorophyll *a* (Chl *a*), nutrients and light, and it worked well with field DMS data measured in high latitude and productive regions (e.g., coastal upwelling). Belviso et al. (2004) proposed a method using Chl *a* concentrations and phytoplankton community structure (represented by tropical status). It reasonably reproduced DMS observations in the North Atlantic subtropical gyre, where there was a mixture of diatoms and haptophytes. Simó and Dachs (2002) proposed a double algorithm that related DMS concentrations to Chl *a* and mixed layer depth (MLD). These simplified equations had been successfully used to predict the seasonal DMS distribution on a global scale. Vallina and Simó (2007) found a strong relationship between DMS concentrations and the daily averaged SRD index in the open ocean, which emphasized the leading role of sunlight in driving DMS seasonality in the pelagic ecosystem. Galí (2018) applied a two-step remote sensing algorithm, which derived the estimated $DMSP_t$ in the first step and computed DMS with $DMSP_t$ and photosynthetically available radiation (PAR) in the second step. This algorithm reproduced the seasonality of DMS climatology well across contrasting biomes. A recent method used an artificial neural network to extrapolate DMS measurements to the global ocean and suggested that MLD and solar radiation were the strongest predictors of DMS on a global scale (Wang et al., 2020).

The most widely used global DMS climatology is derived from the Global Surface Seawater DMS Database (PMEL; https://saga.pmel.noaa.gov/dms/, last access: 10 October 2021), which consists of DMS(P) data contributed by research groups all over the world and has expanded to more than 80,000 DMS measurements. It is updated nearly every decade (Kettle et al., 1999; Lana et al., 2011), with the third revision under review (Hulswar et al., 2021). It is estimated that the mean global DMS concentration is around 1.9 nmol L^{-1} in the ocean and that roughly 28 Tg of sulfur is transferred annually from the oceans into the atmosphere (Lana et al., 2011), which is pretty similar to the newest result (~ 1.9 nmol L^{-1} and 27 Tg S yr^{-1}, respectively) estimated by Hulswar et al. (2021). Despite the respective shortcoming and limitations (Galí et al., 2018), these parameterization-based, satellite-based, and observation-based algorithms allow for the desired synoptic analysis in the global DMS distribution, which improves our understanding of the complex DMS distribution in view of the big picture instead of only limited to the smaller scale details. Also, they offer the possibility to gauge future DMS variability in changing environmental conditions.

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2 Thesis Outline

The climatically relevant trace gas DMS and related sulfur compounds, DMSP and DMSO, play an important role in climate regulation. During the past decades, extensive field studies have been conducted to investigate their temporal distributions and the controlling factors behind them in the world oceans. However, most of them focus on seasonal and short-term interannual variations, and long-term studies are very sparse, which hinders our understanding of sulfur compound variability under changing climate conditions. Moreover, highly productive coastal regions, such as the Peru upwelling region, are considered as a potentially significant source of DMS emissions, despite the insufficient spatial sampling there. Similarly, the Indian Ocean has been proven to be an important source of DMS emissions during the summer monsoon, as predicted by Lana et al. (2011) and Hulswar et al. (2021) climatology, although the interactions between sulfur compounds and physical, chemical, and biological factors are poorly understood. To address these knowledge gaps, measurements of marine DMS and related sulfur compounds, DMSP and DMSO, were made from three different marine environments (the southwestern Baltic Sea, the southeastern Pacific Ocean, and the southwestern Indian Ocean). Overall, this PhD thesis is divided into the following three chapters, and each one addresses one under-investigated scientific question:

1) What are the long-term trends/seasonal cycles and controlling factors of dimethylated sulfur compounds in the water column?

Chapter 3: A ten-year data set of dissolved and particulate sulfur compounds, as well as various environmental and phytoplanktonic parameters, in the water column at the well-established Boknis Eck time-series station, in the southwest Baltic Sea, are presented. This area is expected to experience significant environmental changes with respect to ongoing global warming, eutrophication, and deoxygenation. The long-term trends and seasonal/interannual variability of sulfur compounds are determined in the mixed layer depth and/or the bottom layer. Furthermore, the influence of hydrographic dynamics on the sulfur compounds is explored.

2) What is the main controlling factor of DMS in the highly productive region (Peruvian upwelling system), and is it a significant source of DMS emissions?

Chapter 4: The Peruvian upwelling system, which is considered a very productive area and expected to be a significant source of DMS emissions. Hence, it might be potentially great importance of global DMS emissions. However, less is known about sulfur compounds in this region due to very limited investigations. Moreover, marine DMS is critically controlled by complex interactions between physical, chemical and biological factors, which are poorly understood there. Therefore, the distribution patterns and the controlling factors of oceanic sulfur compounds and atmospheric DMS are examined based on measurements from two research campaigns. In addition, DMS emissions are evaluated by comparing them to those measured in adjacent regions.

3) Is there a potential relationship between DMS and $CHBr_3$ in the surface waters?

Chapter 5: In this chapter, the distribution patterns of sulfur compounds and $CHBr_3$ are investigated in the water column of the southwest Indian Ocean, which has been proven to be a significant source of DMS and $CHBr_3$ emissions. Although DMS and $CHBr_3$ are both biogenic trace gases, their relationship has not been examined in marine environments. According to lab experiments, HOBr can react with DMS to produce DMSO or DOM to produce $CHBr_3$. Considering HOBr cannot be measured in the seawater, we used the ratio of $CHBr_3$:$DMSO_t$ to represent two end products of the reaction between HOBr and DOM/DMS to explore the potential relationship between the two volatile trace gases.

3 A decade of dimethyl sulfide (DMS), dimethylsulfoniopropionate (DMSP) and sulfoxide (DMSO) measurements in the southwestern Baltic Sea

Published as: Zhao, Y., Schlundt, C., Booge, D., and Bange, H. W.: A decade of dimethyl sulfide (DMS), dimethylsulfoniopropionate (DMSP) and dimethyl sulfoxide (DMSO) measurements in the southwestern Baltic Sea, 18, 2161–2179, https://doi.org/10.5194/bg-18-2161-2021, 2021.

Abstract. Dimethyl sulfide (DMS), dimethylsulfoniopropionate (DMSP) and dimethyl sulfoxide (DMSO) were measured at the Boknis Eck Time Series Station (BE, Eckernförde Bay, SW Baltic Sea) during the period February 2009–December 2018. Our results show considerable interannual and seasonal variabilities in the mixed-layer concentrations of DMS, total DMSP ($DMSP_t$) and total DMSO ($DMSO_t$). Positive correlations were found between particulate DMSP ($DMSP_p$) and particulate DMSO ($DMSO_p$) as well as $DMSP_t$ and $DMSO_t$ in the mixed layer, suggesting a similar source for both compounds. The decreasing long-term trends, observed for $DMSP_t$ and DMS in the mixed layer, were linked to the concurrent trend of the sum of 19′-hexanoyloxyfucoxanthin and 19′-butanoyloxy-fucoxanthin, which are the marker pigments of prymnesiophytes and chrysophytes, respectively. Major Baltic Inflow (MBI) events influenced the distribution of sulfur compounds due to phytoplankton community changes, and sediment might be a potential source for DMS in the bottom layer during seasonal hypoxia/anoxia at BE. A modified algorithm based on the phytoplankton pigments reproduces the $DMSP_p$:Chl *a* ratios well during this study and could be used to estimate future surface (5 m) $DMSP_p$ concentrations at BE.

3.1 Introduction

Dimethyl sulfide (DMS) plays an important role in the sulfur cycle of the Earth's atmosphere (Lovelock et al., 1972): DMS released from the ocean surface may affect the Earth's climate by forming atmospheric sulfate aerosols, which, in turn, can backscatter solar radiation and possibly act as cloud condensation nuclei that form clouds. Both processes have a cooling effect on the atmosphere (Charlson et al., 1987; Vogt and Liss, 2009; Wang et al., 2015). However, the global significance of this DMS-driven ocean–climate feedback mechanism remains elusive (Quinn and Bates, 2011; Green and Hatton, 2014; Wang et al., 2018).

The production and consumption of DMS are affected by complex and interacting processes regulated by environmental and biogeochemical factors (Stefels et al., 2007; Vogt and Liss, 2009; Asher et al., 2011). Marine-derived DMS is produced from its major precursor dimethylsulfoniopropionate (DMSP), mainly by enzymatic cleavage of DMSP into DMS and acrylate (Curson et al., 2011). However, this pathway is only of minor importance for DMSP loss (generally accounting for 10 %), since most of the DMSP is directly consumed by phytoplankton and bacteria (Vila-Costa et al., 2006; Moran et al., 2012). The primary loss processes of dissolved DMS include (i) microbial consumption, (ii) photooxidation, (iii) air–sea gas exchange and (iv) vertical export by mixing (Simo, 2004).

DMSP is mainly produced in the cells of algae and bacteria as a response to multiple environmental stressors (Simo, 2004; Stefels et al., 2007; Schäfer et al., 2009; Alcolombri et al., 2015; Curson et al., 2017). Certain phytoplankton species, such as dinoflagellates and prymnesiophytes, show high DMSP production rates while diatoms are minor DMSP producers (Keller et al., 1989; Kirst et al., 1991). Intracellular DMSP is involved in a variety of physiological functions such as osmoregulation (Vairavamurthy et al., 1985), cryoprotection (Kirst et al., 1991; Lee and De Mora, 1999), antioxidation (Sunda et al., 2002; Simó and Vila-Costa, 2006), methyl donation (Kiene et al., 2000), grazing deterrence (Wolfe et al., 2002) or overflow mechanism during nitrogen-limited conditions (Stefels, 2000). Therefore, DMSP production in phytoplankton is also dependent on the ambient environmental conditions mentioned above. DMSP is released by phytoplankton into the marine environment due to senescence, zooplankton grazing, and virus infections (Stefels, 2000; Stefels et al., 2007).

Although dimethyl sulfoxide (DMSO) is as ubiquitous as DMSP in surface seawater, its formation and consumption pathways are still poorly understood (Green et al., 2011; Hatton et al., 2012). DMSO mainly originates from the photochemical and bacterial oxidation of DMS, as well as direct synthesis in marine algae cells (Lee and De Mora, 1999; Lee et al., 1999). The sinks of DMSO include bacterial consumption and reduction to DMS (Hatton et al., 2004). Only recently was it found by Thume et al. (2018) that dimethylsulfoxonium propionate (DMSOP) is an intermediate when forming DMSO from DMSP, and this alternative DMSO production pathway circumvents DMS production. DMSO possesses similar intracellular functions to DMSP in algae cells (Simo et al., 1998; Sunda et al., 2002).

Long-term observations are a valuable tool for monitoring and deciphering short- and long-term trends in oceanic environments (Ducklow et al., 2009). To this end, several time-series studies of DMS from different open-ocean and coastal sites, such as the North Sea, the Atlantic Ocean and the Indian Ocean, have been conducted during the past years (see e.g., Turner et al., 1996; Dacey et al., 1998; Shenoy and Patil, 2003; Vila-Costa et al., 2008; Dixon et al., 2020)). However, the distributions and cycling of sulfur compounds in the Baltic Sea are still largely unknown, and only a few studies of DMS were carried out in the Baltic Sea (Leck et al., 1990; Leck and Rodhe, 1991; Orlikowska and Schulz-Bull, 2009). Here we present a dataset of long-term observations of DMS, DMSP, and DMSO as well as biotic and abiotic parameters from the Boknis Eck Time Series Station (BE) located in the Eckernförde Bay (southwestern Baltic Sea). To our knowledge, this is the longest and most comprehensive time-series measurement of sulfur compounds so far. The overarching objectives of this study are to decipher (i) seasonal and long-term trends of the sulfur compounds, (ii) the influence of extreme events such as major Baltic inflow (MBI) and low oxygen events on the sulfur cycling and, (iii) how the phytoplankton composition influences the seasonal distributions of the sulfur compounds.

3.2 Sampling area

Sampling was performed at BE (Lennartz et al., 2014), whose site is located at the entrance of the Eckernförde Bay (54° 31.2' N, 10° 02.5' E; Fig. 3.1) in the southwestern Baltic Sea. The BE sampling site has a water depth of 28 m. Monthly sampling at BE started in 1957, making this station one of the longest-operating marine time-series stations worldwide (Lennartz et al., 2014). Riverine inputs are negligible for the Eckernförde Bay which is dominated by the inflow of North Sea water through the Kattegat and the Great Belt. Seasonal stratification at BE is caused by steep density gradients and usually lasts from March to October with a mixed-layer depth (MLD) of 10–15 m (Hoppe et al., 2013; Lennartz et al., 2014). During the stratification period, vertical mixing is restricted and decomposition of organic material by bacteria in the deep layer causes pronounced hypoxia and sporadic anoxia or sulfidic events (Hansen et al., 1999; Lennartz et al., 2014). The main phytoplankton blooms generally occur in spring (February–March). Minor blooms are sporadic in summer (July–August) and always in autumn (September–November) (Smetacek et al., 1984; Smetacek, 1985; Bange et al., 2010). Lennartz et al. (2014) reported an increasingly warming trend of 0.02 °C yr^{-1} (in 1 m and 25 m) at BE for the period from 1957 till 2013. Nutrient concentrations increased until the 1980s in the Baltic Sea, as a result of agricultural over-fertilisation, washing-off and transport via rain and rivers into the Baltic Sea. The nutrient concentration started to decline due to measures which successfully reduced anthropogenically caused marine eutrophication in the Baltic Sea (HELCOM, 2018b). However, low-oxygen events (hypoxia or anoxia) have occurred more frequently within the last decades in the Baltic Sea and so at BE (Lennartz et al., 2014). Probably, climate warming enhances bacterial activities and respiration (Hoppe et al., 2013) and extends the period of stratification (Liblik and Lips, 2019). This overrides the effect of decreasing nutrient inputs in the last decades (Lennartz et al., 2014). Overall, the location of BE is ideal for studying the cycling of sulfur compounds such as DMS, DMSP and DMSO in a productive coastal ecosystem with strong open-ocean influences, which is affected by pronounced changes in salinity and oxygen.

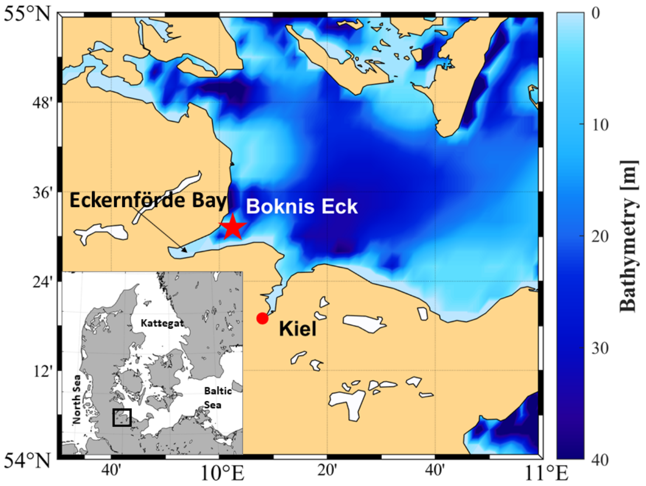

Figure 3.1. Location of the Boknis Eck Time-Series Station near the entrance of Eckernförde Bay in the southwestern Baltic Sea. The location map was created with the m_map package for MATLAB R2019 (Pawlowicz, 2020).

3.3 Material and methods

3.3.1 Sulfur compounds analysis

Monthly sampling of sulfur compounds at BE started in February 2009. Samples were collected bubble-free in 250 mL brown glass bottles. The samples were analysed as soon as possible after returning to GEOMAR's laboratory, usually within a few hours after sampling. Back in the lab, out of the 250 mL water sample, three subsamples (10 mL) were immediately taken and gently filtered through a glass fibre filter (GF/F; Whatman; 0.7 µm) attached to a syringe for DMS and dissolved DMSP (DMSPd) analysis. We used a purge-and-trap technique attached to a gas chromatograph equipped with a flame photometric detector (GC-FPD) to measure sulfur compounds as described in Zindler et al. (2012). After DMS was measured, sodium hydroxide (NaOH; Carl Roth) was added to the subsamples to convert DMSP into DMS. The conversion was allowed to take place at least overnight before analysis of DMSPd. Total DMSP (DMSPt) was measured from the unfiltered alkaline sub-samples, and particulate DMSP (DMSPp) concentrations were calculated by subtracting measured DMS and DMSPd concentrations from measured DMSPt concentrations. Dissolved DMSO (DMSOd) and total DMSO (DMSOt) samples were measured from the same samples of DMSPd and DMSPt measurements by adding cobalt-dosed sodium borohydride (NaBH4; Sigma-Aldrich) right after DMSP analysis to reduce DMSO to DMS. Particulate DMSO (DMSOp) concentrations were calculated by subtracting measured DMSOd concentrations from measured DMSOt concentrations. Calibrations were conducted every measurement day. The mean relative analytical errors for the individual sulfur compounds were generally ≤ 20%. An overview of the methods used for determining oceanographic parameters – such as water temperature, salinity, dissolved O2 and dissolved nutrients – at BE can be found in Lennartz et al. (2014).

3.3.2 Phytoplankton analysis

Pigment samples were collected simultaneously with sulfur compound samples at BE. After returning to the lab, 2 L of seawater was filtered through 0.7 µm GF/F glass fibre filters with a pressure of less than 200 mbar to avoid cell breaking. After filtration, the filters were folded and stored in 2 mL microcentrifuge tubes (Eppendorf cups) at -80 °C for later analysis. Phytoplankton pigment concentrations from April 2009–December 2011 were analysed using a high-performance liquid chromatography (HPLC, Waters 600 Pump, 474 Scanning Fluorometer Detector, 2996 Photodiode Array 717 Autosampler) technique. Fifty microlitres µL of an internal standard (canthaxanthin) and 2 mL of 100 % acetone were added, and the pigments were extracted by homogenisation with glass beads in a cell mill (Bühler). Samples were centrifuged and the supernatant was filtered through 0.2 µm PTFE filters (VWR International). Just prior to analysis, the sample was premixed with 1 mol L^{-1} of ammonium acetate solution in a 1:1 (v/v) ratio in the autosampler and injected onto the HPLC system. The pigments were analysed by reverse-phase HPLC, using a VARIAN Microsorb-MV3 C8 column (4.6 × 100 mm) and HPLC-grade solvents (Baker). The gradient was modified after Barlow et al. (1997). Eluting pigments were detected by absorbance (440 nm). From 2012 on, just prior to analysis, the sample was premixed with 28 mM of tetrabutylammonium acetate solution in a 1:1 (v/v) ratio in the autosampler and injected onto the HPLC system. The pigments were analysed by reverse-phase HPLC, using an Eclipse XDB-C8 column (4.6 × 150 mm) and HPLC-grade solvents (Baker). The gradient was modified after Van Heukelem and Thomas (2001), and eluting pigments were detected by absorbance (440 nm). Both methods showed a good agreement in a pigment analysis, thus data are comparable before and after 2012.

The taxonomic structure of phytoplankton communities was derived from photosynthetic pigment ratios using the CHEMTAX® program (Mackey et al., 1996). The input matrix of Schluter et al. (2000) and Henriksen et al. (2002) applies for all photosynthetic pigments in this study (Table S1 in the supplement). The phytoplankton group composition included diatoms, dinoflagellates, cryptophytes, chrysophytes, chlorophytes, prymnesiophytes and cyanobacteria.

3.3.3 Mixed-layer depth (MLD)

At 28 m water depth, the BE station is a shallow coastal site. Compared to other ocean regions, sea surface salinity is quite variable due to the occasional inflow of saline North Sea water (Lennartz et al., 2014). Therefore, a density-based criterion for calculating the MLD is the best approach (Reissmann et al., 2009). In order to define the MLD, we used the squared buoyancy frequency (N^2), also called stability frequency, which was calculated following Eq. (3.1):

$$\boldsymbol{N^2} = \frac{\boldsymbol{g}}{\boldsymbol{\rho}}\frac{\boldsymbol{d\rho}}{\boldsymbol{dz}}, \tag{3.1}$$

by using the water density (ρ), the water depth (z) and the gravity (g). After calculating N^2 for all depth profiles of this dataset, the MLD was defined as the minimum depth below 4 m where the criterion of $N^2 \geq 10^{-3}\ s^{-2}$ was hold. This N^2 value is low enough to detect a barrier where mixing is mainly suppressed but also high enough not to account for a diurnal surface warm layer, as the MLD is applied for the whole month in which the individual cruises took place.

3.4 Results and discussion

3.4.1 Overview

3.4.1.1 Environmental setting of BE during 2009–2018

The water temperature varied between 0.42 and 22.15 °C (Fig. 3.2a), with a maximum usually in August (14.56 °C; Fig. 3.2b) and a minimum between February (2.88 °C; Fig. 2b) and March (2.51 °C; Fig. 3.2b). The highest water temperature of 22.15 °C was measured at 1 m water depth in August 2018, which was during the warmest summer recorded for the Baltic Sea since 1948 (Naumann et al., 2019) and also the second warmest summer in Germany since 1981 (Zscheischler and Fischer, 2020). The lowest water temperature of 0.42 °C was measured at 15 m water depth in March 2010. In general, the temperature of the water column at BE increased by 0.02 °C yr^{-1} during 1957–2013 due to global warming (Lennartz et al., 2014). The salinity in the bottom layer (25 m) ranged from 13.65 to 25.66, with the highest salinity measured in December 2013 (Fig. 3.2c). In general, the salinity at 25 m water depth reached its maximum in September (23.09; Fig. 3.2d) after the stratification period, and its minimum in April (19.64; Fig. 3.2d), when the water column is well ventilated by wind-driven mixing events. The bottom salinity showed strong fluctuations, which are caused due to the inflow of saline water originating from the North Sea (Lennartz et al., 2014). For instance, in December 2014, a MBI event of highly saline and oxygenated North Sea water occurred after a 10-year stagnation since 2003, as the third-strongest event ever recorded (Fig. 3.2c, marked with the black arrow; Mohrholz, 2018). Occasionally, the break-up of the late-summer/autumn stratification was caused by upwelling events induced by strong winds, leading to the uniform distribution of salinity in the entire water column (e.g., in September 2017).

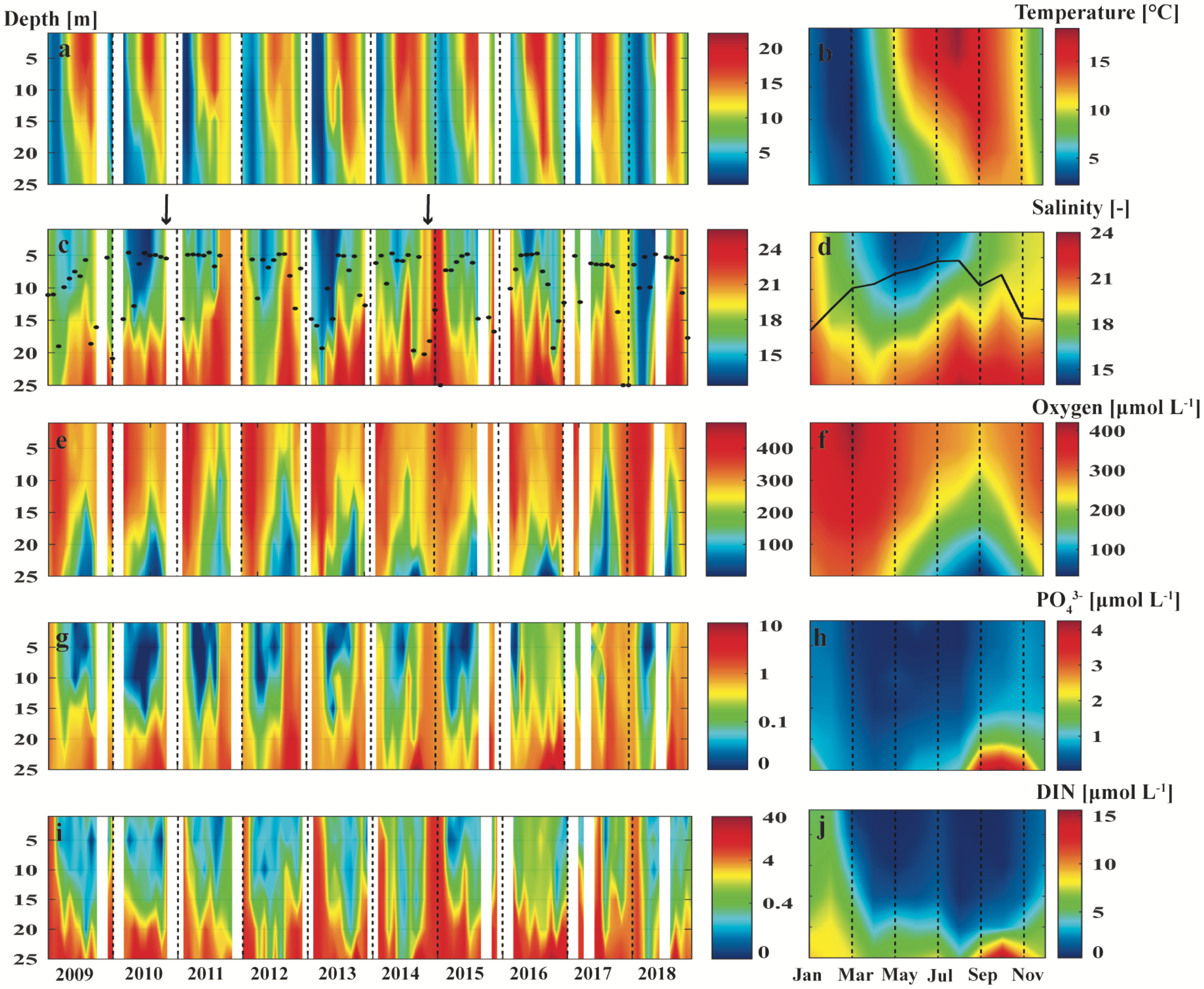

Figure 3.2. Monthly and mean seasonal distributions of temperature (a, b), salinity (c, d), dissolved O_2 (e, f), phosphate (g, h) and dissolved inorganic nitrogen (i, j) at BE during 2009–2018. Please note that in the left panels, the blank areas are due to data gaps caused by cancellations of the research cruises, and the dashed lines indicate January of each year. Black dots (c) and the black line (d) indicate monthly and mean seasonal distributions of the mixed-layer depth, respectively. The black arrows (c) indicate the major Baltic inflow (MBI) events in November 2010 and December 2014. Time–depth Hovmöller Diagrams were generated with MATLAB and note that the colour coding in panels (g) and (i) is shown on a natural logarithmic scale.

Dissolved oxygen concentrations varied significantly from 0 to 479 µmol L^{-1} (Fig. 3.2e), with seasonal hypoxic or anoxic events prevailing in the bottom layer (~ 20–25 m) in autumn at BE (Fig. 3.2f). Dissolved phosphate and total inorganic nitrogen (DIN; the sum of nitrate, nitrite and ammonium) concentrations generally displayed regular seasonal variabilities, with higher concentrations in the upper layers during the winter months (December–February) and in the bottom layer during autumn months (September–November) (Fig. 3.2, g–j). The seasonal variability of chlorophyll a (Chl *a*) concentrations was generally in line with the annual phytoplankton succession at BE previously reported by Smetacek (1985), which is characterised by diatom blooms in spring, minor blooms in summer, dinoflagellate blooms in autumn and a dormancy phase in winter (Fig. 3.3a and 3.3b). During our study, autumn blooms at BE occasionally extended to December, which might have been a result of a longer growing season at higher temperatures in response to climate change (Wasmund et al., 2011). The highest Chl *a* concentration (12.4 µg L^{-1}) was measured in the surface layer (1 m) in October 2017, accompanied by dinoflagellates dominating the autumn bloom.

3.4.1.2 Sulfur compounds

$DMSP_p$ concentrations were up to 103.5 nmol L^{-1} with an average of 9.2 ± 13.3 nmol L^{-1} in the water column, and $DMSP_d$ concentrations reached up to 42.7 nmol L^{-1} with an average of 3.0 ± 4.1 nmol L^{-1}. The highest concentration of $DMSP_p$ was measured at 15 m depth in April 2015. Generally, the seasonal and spatial patterns of $DMSP_p$ and $DMSP_d$ followed that of Chl *a*, which was enhanced in spring (February–April) and autumn (September–October) in the upper layer (~ 1–15 m) and decreased with increasing depth (Fig. 3.3, a–f). The overall mean ratio of $DMSP_p$:$DMSP_d$ was 4.5 ± 8.5, indicating that $DMSP_p$ was generally dominant in the DMSP pool at BE. This is in line with the results reported by Speeckaert et al. (2018) from the coastal areas in the southern North Sea. $DMSO_p$ concentrations were up to 208.4 nmol L^{-1} with an average of 11.3 ± 20.7 nmol L^{-1} in the water column. $DMSO_d$ concentrations were up to 70.3 nmol L^{-1} with an average of 7.9 ± 8.2 nmol L^{-1}. The highest $DMSO_p$ concentration was measured at 1m depth in the same sampling month as $DMSP_p$. The seasonal and spatial distributions of $DMSO_p$ and $DMSO_d$ were similar to DMSP (Fig 3.3. I–l). The mean ratio of $DMSO_p$:$DMSO_d$ was 1.7 ± 2.4, suggesting less dominance of the ratio of $DMSO_p$ to $DMSO_d$ in contrast to DMSP. Overall, our study is consistent with the results reported in Hatton and Wilson (2007) that $DMSP_d$ was very low compared to $DMSP_p$ while $DMSO_d$ could exceed the sum of DMS and $DMSP_d$ concentrations in the seawater. Additionally, significant correlations between $DMSP_p$ and $DMSO_p$ as well as $DMSP_t$ and $DMSO_t$ (Table 3.1) in this study, confirming previous studies that both compounds might share the same source in the seawater and they are subject to close cycling of production and consumption where the composition of the planktonic community, play a prominent role (Simo et al., 1997; Zindler et al., 2013).

The overall mean DMS concentration was 1.3 ± 1.8 nmol L^{-1} in the water column, with the highest concentration of 20.5 nmol L^{-1} measured at 1 m depth in April 2015. The mean concentration of DMS in the mixed layer was 1.7 ± 2.0 nmol $L^{−1}$, which is slightly lower compared to the mean DMS concentration of 2.7 ± 2.0 nmol $L^{−1}$ for the Baltic Sea (53°N–66°N, 10°E–30°E) retrieved from the Global Surface Seawater DMS Database (http://saga.pmel.noaa.gov/dms), including DMS data from Leck et al. (1990) and Leck and Rodhe (1991). DMS concentrations measured at the entrance of Himmerfjärden Fjord (western Baltic Sea) from January 1987 to June 1988 ranged from 0.1 to 6.3 nmol L^{-1} with an average of 1.5 ± 1.3 nmol $L^{−1}$ (Leck et al., 1990), which is in line with our study. Surface DMS was also measured in the Baltic Sea and the Kattegat–Skagerrak (the connection between the Baltic Sea and the North Sea) to be 1.3 ± 0.8 and 2.4 ± 0.9 nmol $L^{−1}$ in July 1988, respectively (Leck and Rodhe, 1991), the former of which was comparable and the latter of which was higher compared to this study. However, statistical results from Leck and Rodhe (1991) indicated that no single factor such as salinity or certain phytoplankton species, could be accounted for these higher concentrations of DMS in the Kattegat–Skagerrak. Leck and Rodhe (1991) suggested that increased eutrophication of coastal regions may result in a net positive effect on DMS production in the Baltic Sea. The study from Orlikowska and Schulz-Bull (2009) in the Bay of Mecklenburg (southern Baltic Sea) showed DMS concentration in the range from < 0.3 nmol L^{-1} in November 2008 up to 120 nmol L^{-1} in May 2008. Considering that the concurrent Chl *a* concentrations from phytoplankton were only 2–4 μg L^{-1}, Orlikowska and Schulz-Bull (2009) proposed that macroalgae could also contribute significantly to the DMS production. A comparison with data from other coastal times-series stations (Table 3.2) reveals that mixed-layer DMS concentrations at BE are generally comparable to those measured at other time-series stations in coastal regions like in the Baltic Sea, the Mediterranean Sea or the Indian Ocean. $DMSP_t$ concentrations from BE are in the same range as the concentrations reported from the NW Mediterranean Sea and the western English Channel, but they are lower than those reported from the southern North Sea (including the Belgian and Dutch coasts), the Revellata Bay (Gulf of Calvi, Mediterranean Sea) and the coast off Goa (eastern Arabian Sea, Indian Ocean). $DMSO_t$ concentrations at BE were generally in the same range as reported from other time-series sites except for the extremely high DMSO$_t$ concentrations measured at the coast of Belgium (southern North Sea). The obvious high variabilities in the range of DMSP(O) concentrations are most probably resulting from the interplay of various factors such as differences in sampling periods/frequency, the prevailing phytoplankton/bacteria community composition and succession, and the eutrophication status as well as the occurrence of anoxic events.

Table 3.1. Spearman's rank correlation coefficients of correlations of all sulfur compounds with several ambient parameters, as well as algae groups in the mixed layer at BE station during 2009–2018. Only datasets were used for which all environmental parameters (n = 85), phytoplankton data (n = 61 for diatoms and dinoflagellates, n = 48 for chrysophytes and n = 35 for prymnesiophytes) were available, and data were averaged for the mixed layer. Bold numbers indicate that a correlation is significant at the 0.01 level (two tailed). Diat, dino, prym and chryso, stand for diatoms, dinoflagellates, prymnesiophytes and chrysophytes, respectively. N:P ratios stand for the ratio of the sum of nitrate, nitrite, and ammonium to phosphate.

	DMS	DMSP$_t$	DMSP$_p$	DMSP$_d$	DMSO$_p$	DMSO$_d$	DMSO$_t$
Chl *a*	**-0.31**	0.19	0.11	0.04	**0.29**	-0.11	0.2
Temperature	**0.41**	0.11	0.14	-0.12	0.26	0.12	0.24
Salinity	-0.19	0.08	-0.04	-0.05	-0.09	-0.11	-0.08
N:P	-0.15	-0.21	-0.08	-0.04	-0.12	-0.04	0.14
Diat	-0.04	-0.05	-0.13	0.16	-0.25	-0.24	-0.27
Dino	0.10	0.09	0.19	-0.26	0.2	0.06	0.19
Prym	0.25	**0.38**	**0.47**	0.14	**0.35**	0.30	**0.34**
Chryso	0.32	**0.44**	**0.37**	0.29	0.28	0.25	0.32
DMSO$_t$	**0.35**	**0.79**	**0.72**	**0.43**	**0.86**	**0.75**	
DMSO$_d$	**0.35**	**0.57**	**0.48**	**0.61**	**0.41**		
DMSO$_p$	0.20	**0.72**	**0.74**	0.26			
DMSP$_d$	**0.26**	**0.53**	**0.27**				
DMSP$_p$	**0.44**	**0.91**					
DMSP$_t$	**0.42**						

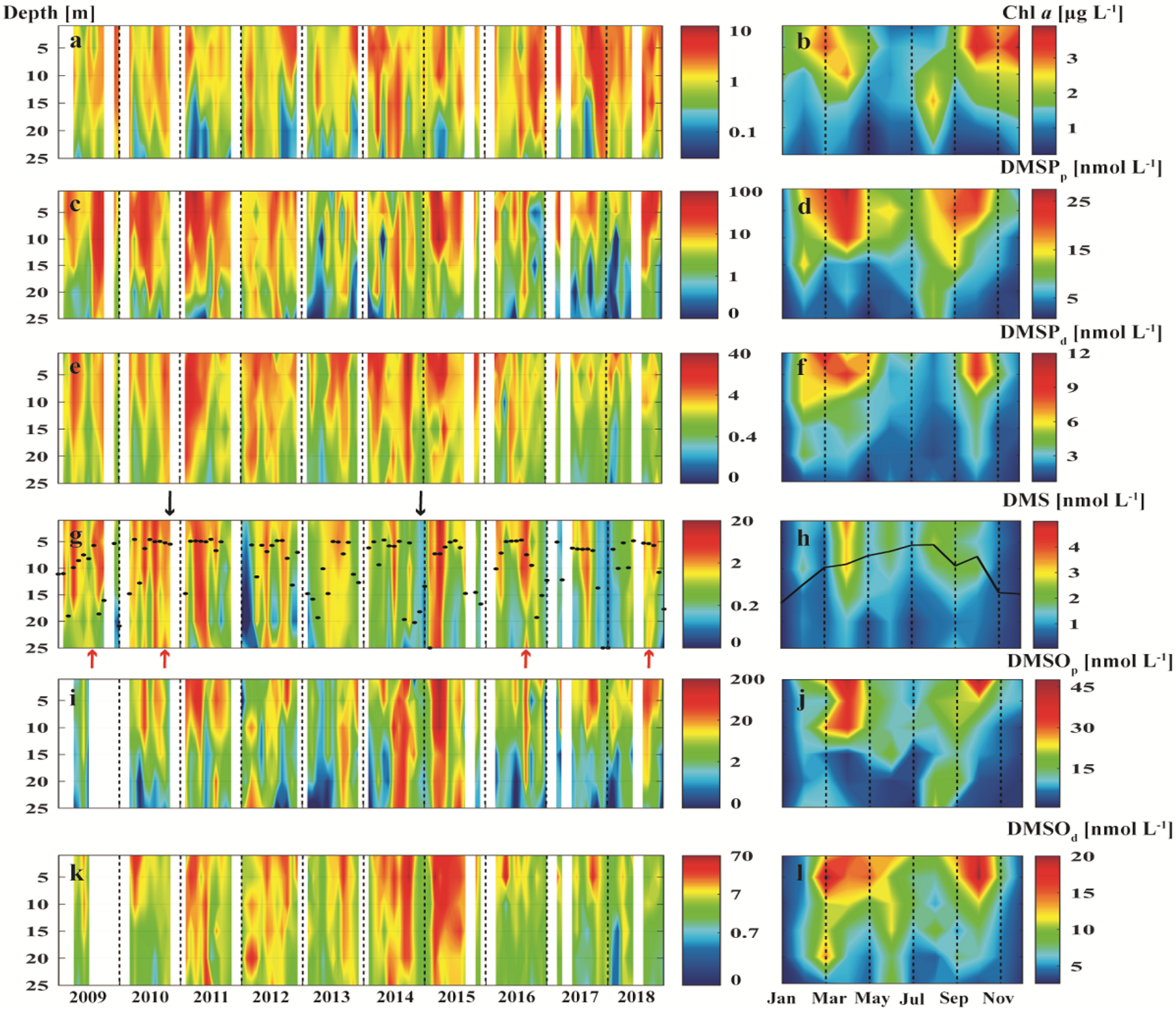

Figure 3.3. Monthly and mean seasonal distributions of chlorophyll a (a, b), DMSP$_p$ (c, d), DMSP$_d$ (e, f), DMS (g, h), DMSO$_p$ (i, j) and DMSO$_d$ (k, l) at BE during 2009–2018. Black dots (g) and the black line (h) indicate monthly and mean seasonal distributions of the MLD, respectively. The black arrows (g) indicate the major Baltic inflow (MBI) events in November 2010 and December 2014. The red arrows indicate elevated concentrations of DMS under hypoxia/anoxia in 2009, 2010, 2016 and 2018. In 2009, DMSO data were only available from April to July. Time–depth Hovmöller diagrams were generated with MATLAB and concentrations shown in the left panels are given on a natural logarithmic scale.

Table 3.2 Surface sulfur compound concentrations from coastal time-series studies.

Region	Period of sampling	Sampling frequency	DMS Avg. Range (min–max)	DMSP_t Avg. Range (min–max)	DMSO_t Range (min–max)	Chl *a* Avg. Range (min–max)	Reference
Boknis Eck Time-Series Station, the Southwest Baltic Sea	Apr 2009–Dec 2018	monthly	1.7(a) 0.1–12.2(a)	18.5(a) 1.4–85.4(a)	31.1(a) 2.5–209.8(a)	2.1(a) 0.3–10.8(a)	This study
Station B1, Himmerfjärden Fjord, the West Baltic Sea	Jan 1987–Jun 1988	weekly in spring, biweekly in summer and monthly in winter	1.51 0.1–6.3	nm	nm	ng < 1–12	Leck et al. (1990)
Heiligendamm station, Bay of Mecklenburg, the Baltic Sea	Jan–Nov 2008	weekly	ng up to ~ 120	nm	nm	ng ~ 1–7	Orlikowska and Schulz-Bull (2009)
The Southern North Sea	Feb–Oct 1989	monthly	3.92 0.1– > 50	ng up to 450	nm	ng up to 35	Turner et al. (1996)
The Belgian Coastal Zone, the North Sea	Jan–Dec 2016	bimonthly from Feb to Jun and monthly for the rest	ng up to 250	ng up to 1740(b)	ng up to 620	ng up to 36	Speeckaert et al. (2018)
Coast of Den Helder, The Netherlands	Nov 1991–Nov 1992 and Jan–Jun 1993	Biweekly in 1991 and 1992, more frequent in 1993	ng 0–18	ng 7– > 1500(b)	nm	ng 0–65	Kwint and Kramer (1996)
Station L4, the Western English Channel	May–Oct 2014	weekly	5.1 up to 17	ng ~ 10–100	ng 2.3–102	ng ~ 0.1–2.4	Dixon et al. (2020)
Toulon Bay, the NW Mediterranean Sea	Jan–Dec 1997	monthly	9.8 3.6–21.03	nm	nm	ng 0.2–2.5	Despiau et al. (2002)

The NW Mediterranean Sea	Jan 2003–June 2004	monthly	ng ~ 0.5–19	ng ~ 10–71.7$^{(b)}$	ng ~ 0–24.2$^{(b)}$	ng ~ 0.4–2.8	Vila-Costa et al. (2008)
The Zuari estuary off Goa	Dec 1999–Jan 2001	monthly	5.8 0.3–15.4	68.3 0.8–415.9	nm	ng up to ~ 10	Shenoy and Patil (2003)
Candolim Time-Series station, coast off Goa	Sep 2009–Dec 2013	monthly	22.5 0.5–442	24 0.4–252	27.8 0.6–185.9	ng 0.1–14.4	Bepari et al. (2020)
Rothera Time-Series Station, Ryder Bay, West Antarctic	Sep 2012–Mar 2017	2–3 times per week	3.7 0.1–170	ng	ng	ng	Webb et al. (2019)

$^{(a)}$averaged for the mixed layer; $^{(b)}$ given as DMSP$_p$ or DMSO$_p$; ng and nm stand for not given and not measured, respectively. $^{(c)}$ given as μmol.g$_{fw}$$^{-1}$. The units of sulfur compounds and Chl a are given as nmol L^{-1} and μg L^{-1}, respectively.

3.4.2 Temporal trend analysis

Temporal trend analysis was calculated by anomaly detection via subtracting the overall monthly mean (2009–2018) from the individual monthly mean, followed by smoothing with a 12-point moving average, which was used to reduce the effects of the seasonal as well as annual cycles on the temporal trend. Temperatures showed increasing trends in the mixed layer and the bottom layer (Fig. 3.4a) during our study. The trends were 0.2 °C yr^{-1} and 0.1 °C yr^{-1} (Table 3.3) in the mixed layer and the bottom layer, respectively. Our result is consistent with the study by Belkin (2009), who reported a post-1987 warming rate in the Baltic Sea exceeding 1.0 °C decade^{-1}. A less pronounced trend of 0.02 °C yr^{-1} (at 1 m and 25 m) during 1957–2013 was reported by Lennartz et al. (2014). This disagreement may arise from the fact that the result reported by Lennartz et al. (2014) covers a much longer study period and there might be an acceleration trend of increasing temperature started around 2014 (Rahmstorf et al., 2017). Salinity in the bottom layer (25 m; Fig. 3.4b) did not show significant trends in our study, which is in agreement with Lennartz et al. (2014). Additionally, there is no trend of dissolved oxygen in the bottom layer (Fig. 3.4b), which is different to the trend computed by Lennartz et al. (2014), who reported bottom O_2 concentrations were decreasing over 56 years. Again, this difference is attributed to the much shorter observation period of our study compared to Lennartz et al. (2014). Dissolved inorganic nitrogen (DIN; Fig. 3.4c) and phosphate (Fig. 3.4d) showed slightly increasing trends of 0.5 µmol L^{-1} yr^{-1} and 0.2 µmol L^{-1} yr^{-1} (Table 3.3) in the bottom layer, but similar trends were not observed or apparent in the mixed layer. The decreasing trends for nutrients (at 1 m and 25 m) at BE reported by Lennartz et al. (2014) are due to a reduction of nutrient inputs to the Baltic Sea to improve the eutrophication status of the Baltic Sea (HELCOM, 2018a). This is consistent with Kuss et al. (2020) who reported a decline in DIN from 1995–2004 and TP (total phosphate) from 2005–2009 in the Belt Sea with no significant changes thereafter. In our study, the increasing trends of nutrients at 25 m coincided with increasing temperature as well as more frequent hypoxic/anoxic events (i.e. ongoing deoxygenation) at 25 m. Increasing temperature favoured bacteria decomposing actives beneath the thermocline due to more pronounced water column stratification, supporting their remineralisation and, thus, leading to more consumption of dissolved oxygen, and releasing more nutrients in the bottom layer (Hoppe et al., 2013; Lennartz et al., 2014). Thus, the increasing nutrient concentrations are not a general eutrophication of the water column, but a natural effect limited within the bottom layer. Chl *a* concentration (Fig. 3.4e) showed an increasing trend of 0.2 µg L^{-1} yr^{-1} (Table 3.3) in the mixed layer, which is primarily driven by high concentrations in 2017, similar to the variability of the sum of fucoxanthin (a marker pigment for diatoms) and peridinin (a marker pigment for dinoflagellates; Fig. 3.4i).

$DMSP_t$ concentrations (Fig. 3.4f) showed a slightly decreasing trend both in the mixed layer (−0.9 nmol L^{-1} yr^{-1}) and in the bottom layer (−0.3 nmol L^{-1} yr^{-1}; Table 3.3), as opposed to the upward trends of Chl *a* in the mixed layer and temperature both in the mixed and bottom layer. A similar decreasing trend in the mixed layer (−9.2 ng L^{-1} yr^{-1}) was detected for the sum of the pigments 19′-hexanoyloxyfucoxanthin (19'-hex, a marker pigment for prymnesiophytes) and 19′-butanoyloxy-fucoxanthin (19'-but, a marker pigment for chrysophytes; Fig. 3.4i). This indicates that the general trend of $DMSP_t$ concentrations in the mixed layer might be primarily controlled by the productivity of chrysophytes and prymnesiophytes (see also Table 3.1). The decreasing trend for DMS (−0.1 nmol L^{-1} yr^{-1}; Fig. 3.4g) generally followed the pattern of $DMSP_t$ in the mixed layer and indicates that DMSP cleavage might play a dominant role in the production of DMS (see Table 3.1). Although no significant trend was observed for $DMSO_t$ (Fig. 3.4h), its general variability over time was similar to those of $DMSP_t$ and DMS in the mixed layer. The decreasing trend observed for $DMSP_t$ at 25 m might be mainly attributable to the corresponding sinking particles from the mixed layer, as no trends were observed for Chl *a* or other algae groups at 25 m.

As a statistical test to decipher significant monotonic long-term trends in time series, the Mann−Kendall test (MKT) was also applied to detect the temporal trends of the individual months. However, no significant trends were observed for any of the dimethylated sulfur compounds by the MKT test in our study.

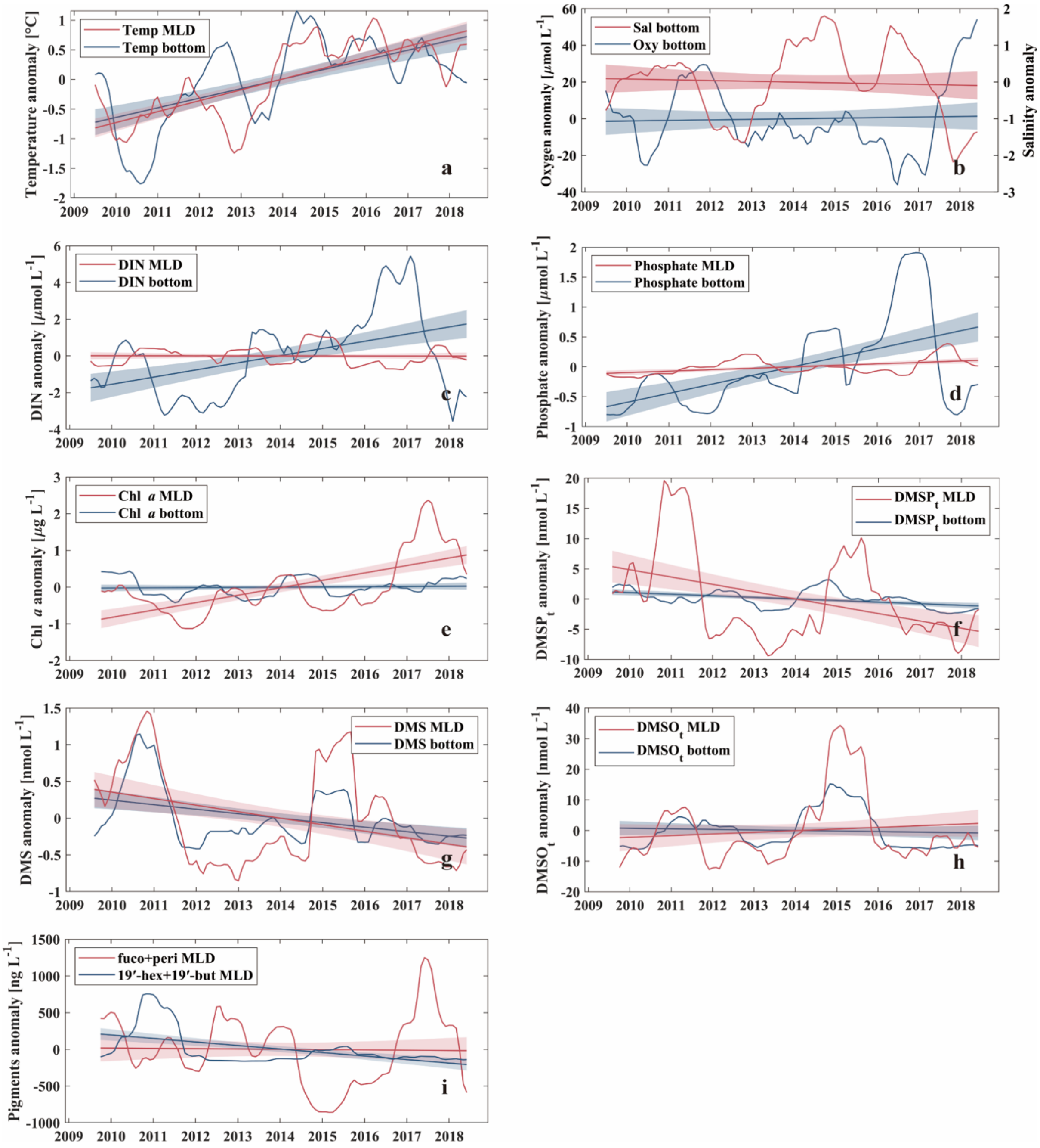

Figure 3.4: Temporal trends of anomalies of temperature (°C), dissolved oxygen (µmol L^{-1}), salinity, dissolved inorganic nitrogen (DIN; µmol L^{-1}), phosphate (µmol L^{-1}), Chl *a* (µg L^{-1}), DMSP$_t$ (nmol L^{-1}), DMS (nmol L^{-1}), DMSO$_t$ (nmol L^{-1}), the sum of pigment concentrations of fucoxanthin (fuco) and peridinin (peri) (ng L^{-1}), 19′-hexanoyloxyfucoxanthin (19′-hex) and 19′butanoyloxy-fucoxanthin (19′-but) (ng L^{-1}). Fuco stands for fucoxanthin, peri stands for peridinin, 19′-hex stands for 19′-hexanoyloxyfucoxanthin and 19′-but stands for 19′-butanoyloxy-fucoxanthin. The shaded areas indicate 95 % confidence intervals. Note that gaps were filled by linear interpolation in the case of one or two missing months in a row and large gaps between August and December 2009 in DMSO$_t$ (h) were filled by replacement with the median of the corresponding month.

Table 3.3. Statistics of the linear regression of the temporal trends for the anomalies of temperature (°C), dissolved oxygen (µmol L^{-1}), salinity, dissolved inorganic nitrogen (DIN; µmol L^{-1}), phosphate (µmol L^{-1}), Chl *a* (µg L^{-1}), $DMSP_t$ (nmol L^{-1}), DMS (nmol L^{-1}), $DMSO_t$ (nmol L^{-1}), the sum of pigments of fucoxanthin (fuco) and peridinin (peri) (ng L^{-1}), 19′-hexanoyloxyfucoxanthin (19′-hex) and 19′-butanoloxy-fucoxanthin (19′-but) (ng L^{-1}). r^2: coefficient of determination in the simple linear regression calculated by the monthly individual parameters. Sen's slope: median slope present in time series (yr^{-1}) according to Sen (1968).

	Mixed layer				Bottom layer (25 m)			
	r^2	*p* value	Sen's slope	n	r^2	*p* value	Sen's slope	n
Temperature	0.54	< 0.01	0.2	108	0.35	< 0.01	0.1	108
Oxygen	0.14	< 0.01	-1.3	108	< 0.01	0.67	-1.2	108
Sal	< 0.01	0.58	0.1	108	0.03	0.07	0	108
DIN	< 0.01	0.89	0	108	0.21	< 0.01	0.5	108
Phosphate	0.27	<0.01	0	108	0.22	< 0.01	0.2	108
Chl *a*	0.40	< 0.01	0.2	105	< 0.01	0.53	0	105
$DMSP_t$	0.17	< 0.01	-0.9	107	0.21	< 0.01	-0.3	107
DMS	0.12	0.01	-0.1	107	0.17	< 0.01	0	107
$DMSO_t$	0.01	0.23	0.3	105	< 0.01	0.45	-0.2	105
fuco + peri	0.02	0.18	-33.3	105	0.07	0.06	-30.2	*105*
19′-hex + 19′-but	0.23	< 0.01	-9.2	105	*NA*	*NA*	*NA*	*43*

3.4.3 Influence of extreme events at BE on the sulfur compounds

3.4.3.1 The major Baltic inflow events

MBI carry large amounts of oxygen-rich saline North Sea water into the Baltic Sea (Mohrholz et al., 2015) and can transport phytoplankton species originating from the North Sea into the Baltic Sea (Olenina et al., 2010). A MBI event lasted for one month in 2014 and was detected in the Eckernförde Bay by elevated sea levels after an outflow period, which indicated that its inflow began on 10 December 2014 (Ma et al., 2020). Therefore, the sampling at BE on 16 December 2014, took place during the MBI period. Our results show that the sulfur compound concentrations in the water column in December 2014 and in January 2015 were low and similar to the overall mean concentrations of sulfur compounds in December/January for the period 2009–2018, indicating that the MBI in December 2014 did not influence the concentrations of sulfur compounds at BE directly. Relatively higher DIN and dissolved phosphate concentrations (Fig. 3.2g and 3.2i) were measured in December 2014, and this would be assumed to trigger a more significant spring bloom in the next year and therefore, higher sulfur compounds concentrations. Indeed we measured higher concentrations of sulfur compounds in March and April 2015; however, this is probably attributable to the unusually higher proportion of prymnesiophytes of the phytoplankton community (see. Sect. 3.4.4), and this high fraction of prymnesiophytes was not supposed to be caused by the rich nutrients accumulated in December 2014. The peak of the spring bloom in 2015 could not be identified considering moderate Chl *a* concentrations in February (1.0 µg L^{-1}) and March (2.0 µg L^{-1}), but a substantial decrease of nutrients occurred between February and March 2015. Concentrations of DIN and dissolved phosphate stayed high until February 2015. Subsequently, DIN concentrations decreased from 8.0 µmol L^{-1} in the mixed layer on 23 February to 0.1 µmol L^{-1} on 17 March, with dissolved phosphate decreasing from 0.7 to 0.1 µmol L^{-1} in the same case. Depleted nutrients in March suggested the spring bloom peak between the sampling date in February and in March 2015 was apparently not captured by our monthly measurements and underlines the necessity of frequent sampling. As a minor algae group at BE, prymnesiophytes tend to occur to accumulate towards the end of spring diatom blooms in oligotrophic conditions (Veldhuis et al., 1986), and this was confirmed by the decreasing concentration of silicate from 12.5 µmol L^{-1} in the mixed layer in February 2015 to 2.2 µmol L^{-1} in March, which is the limiting growth factor of diatoms. Therefore, we conclude that the accumulation of nutrients had been consumed by diatoms between February and March before prymnesiophytes formed the bloom. However, the much-higher-than-usual relative abundance of prymnesiophytes in March and April 2015 (see Figure. 3.5a) might have been transported to BE by the saline water from the North Sea, where prymnesiophytes are abundant (Speeckaert et al., 2018).

Another relatively weak MBI occurred in late autumn 2010 (Mohrholz et al., 2015), and we measured elevated salinity concentrations in November 2010 at BE (see Fig. 3.2c). Subsequently, above-average concentrations for DMS (1.9–3.7 nmol L^{-1}), $DMSP_p$ (50.9–84.5 nmol L^{-1}) and $DMSO_p$ (32.2–40.6 nmol L^{-1}) were measured in spring bloom during February – April 2011, coincided with the exceptionally higher relative abundance of chrysophytes in the mixed layer (see Fig. 3.4). We assume that this chrysophyte was rather new and uncommon only occurred in Kiel Bight and Mecklenburg (Wasmund et al., 2012). Therefore, it is possible that this uncommon chrysophyte was brought into the western Baltic Sea via saline waters in autumn 2010 and bloomed in spring 2011, resulting in high concentrations of DMSP and thus DMS(O) at BE.

Overall, enhanced $DMSP_p$ concentrations (> 50 nmol L^{-1}) measured during the spring bloom in 2011 and 2015, both followed after the MBI events in winter and comprised new-forming phytoplankton groups not common at BE. Therefore, we hypothesize that MBI was likely to influence sulfur compounds concentrations by introducing new phytoplankton species which are good DMSP producers.

3.4.3.2 Low-oxygen events

Hypoxia in this study is defined as dissolved O_2 concentrations were being below 62.5 µmol L^{-1} (i.e. 2 mg L^{-1}), according to Vaquer-Sunyer and Duarte (2008). Low-oxygen events (hypoxia/anoxia) are usually observed in the bottom layer at BE, as a result of long-lasting stratification and enhanced remineralisation of organic matter (Lennartz et al., 2014). During seasonal hypoxic/anoxic conditions (see Fig. 3.3e), elevated concentrations of DMS (up to 4.19 nmol L^{-1}) were measured in the bottom layer in August 2009, August–October 2010, September 2016 and September 2018 (see Fig. 3.3g). These elevated DMS concentrations (2.3 ± 1.4 nmol L^{-1}) in the bottom layer (20–25 m) were generally comparable to or lower than those found in the mixed layer (0-5 m; 3.4 ± 2.2 nmol L^{-1}), but higher than those in the overlying water layers (15–20 m; 1.2 ± 1.2 nmol L^{-1}). Shenoy et al. (2012) reported extremely high concentrations of DMS (up to 442 nmol L^{-1}) as well as enhanced $DMSP_t$, $DMSO_t$ and methanethiol concentrations in the bottom layer during an anoxic event at Candolim Time-Series Station (CaTS) off Goa, West India, in September 2009 and suggested that this unusually high DMS concentration might result from a combination of sources such as DMSP cleavage, DMSO reduction, methylation of methanethiol and hydrogen sulfide under anoxic conditions. Later on, Bepari et al. (2020) observed high concentrations of DMS (233 nmol L^{-1}) in the bottom layer during an anoxic event at CaTS in September 2013 and assumed that sediments might also be an important source of DMS, in addition to the breakdown of simultaneously high concentrations of $DMSP_t$ (206–252 nmol L^{-1}) in the water column. However, in the case of BE, concentrations of $DMSP_t$ (4.7 ± 4.9 nmol L^{-1}) or $DMSO_t$ (4.1 ± 2.2 nmol L^{-1}) measured in the bottom layer during hypoxia/anoxia events were lower than those in the mixed layer ($DMSP_t$: 20.6 ± 8.1nmol L^{-1}; $DMSO_t$: 32.4 ± 17.0 nmol L^{-1}) or the overlying water layer ($DMSP_t$: 11.9 ± 4.1nmol L^{-1}; $DMSO_t$: 17.7 ± 11.6 nmol L^{-1}), which indicates that DMSP cleavage or DMSO reduction processes are unlikely to account for the main fraction of DMS production. Therefore, it is reasonable to assume that these elevated concentrations of DMS in the bottom layer might have been at least in part released from the sediments and might originate from the methylation of methanethiol and/or hydrogen sulfide (Nedwell et al., 1994; Song et al., 2020). This assumption is in agreement with Bertics et al. (2013), who reported increased sulfate reduction activities between August and November 2010 in the surface sediment at BE, which would favour the production of hydrogen sulfide and further methanethiol. Additionally, groundwater discharge in Eckernförde Bay may also have an indirect impact on DMS production by increasing sulfate reduction activities (Bussmann et al., 1999). However, elevated DMS concentrations in the bottom layer were not always measured simultaneously with low oxygen-events. In only 5 out of 18 sampling months, we observed elevated DMS concentrations together with low-oxygen events (see Fig. 3.3g and 3.3e). Therefore, we speculate that there is a switch between DMS generation and removal processes in the sediments (Kiene, 1988; Nedwell et al., 1994), which needs to be further investigated at BE.

3.4.4 Relationships between the sulfur compounds and phytoplankton groups

In general, phytoplankton composition and succession (Fig. 3.5a) at BE were similar to previous studies from the Baltic Sea with a recurrent pattern of diatoms dominating the bloom in spring (February–April) and summer (June–August) followed by dinoflagellates in autumn (September–November) (Smetacek, 1985; Wasmund et al., 2008). Diatoms were the most dominant phytoplankton group at the Boknis Eck station, especially during the spring bloom and reached their maximum in March. The fraction of diatoms gradually decreased in April and May whereas the fractions of prymnesiophytes, cryptophytes and chlorophytes increased, accompanied by the development of cyanobacteria. Minor summer blooms most commonly occurred in August below the surface water (e.g., in 15 m or 20 m) at BE, as a result of stratification which restricted the bottom nutrients supply to the surface layer (Fig. 3.5b). The autumn/winter bloom period (September–December) was mainly composed of a mixture of dinoflagellates and diatoms or a succession of these two algae groups. Overall, diatoms and dinoflagellates were the most common phytoplankton groups at BE.

3.4.4.1 Relationship between sulfur compounds and phytoplankton groups

Positive correlations were found between chrysophytes and $DMSP_P$ as well as prymnesiophytes and $DMSP_P$ in the mixed layer (Table 3.1). Enhanced concentrations of $DMSP_P$ (> 50 nmol L^{-1}) were associated with the high relative abundance of chrysophytes (25–62 % between February and April 2011) and prymnesiophytes (29–56 % in March and April 2015, respectively) in the mixed layer. Reports from Wasmund et al. (2012) and Wasmund et al. (2016) confirmed that these two algae groups were higher in their abundances in the years 2011 and 2015 in the western Baltic Sea. Our results suggest that these two algae groups might be the main producers of DMSP in the mixed layer at BE and this is in agreement with the results of the previous studies of Keller et al. (1989) and Belviso et al. (2001) who found that chrysophytes and prymnesiophytes can be significant DMSP producers in general. No correlation was found between dinoflagellates and $DMSP_P$ in the mixed layer (Table 3.1).

In previous studies, massive dinoflagellate blooms were reported to be closely coupled with high concentrations of DMSP. For example, the highest DMSP concentration (4240 nmol L^{-1}) reported so far was found tightly linked to elevated abundance of *A. sanguinea* (Kiene et al., 2019). This could be attributed to that the ability to produce DMSP is considerably variable among different genus and species (Keller et al., 1989). Hence, low or high DMSP concentrations during dinoflagellate blooms are dependent on the dominant species or composition. Typically, *Ceratium* spp was one of the most common genera during dinoflagellate-dominant autumn blooms in the western Baltic (Wasmund et al., 2015). However, the ability of *Ceratium* spp to produce DMSP is rather weak compared to other species or genus belonging to dinoflagellates (Keller et al., 2012). The discrepancy between maximum Chl *a* concentration (12.4 μg L^{-1}) dominated by dinoflagellates and the $DMSP_p$ concentrations (25.2 nmol L^{-1}) at 1 m depth in October 2017, might be attributed to that *Ceratium tripos* being the dominative species during dinoflagellate blooms (Wasmund et al., 2018), which might be of minor importance for the DMSP pool at BE. Positive correlations were found between prymnesiophytes and $DMSO_p$ (Table 3.1) in the mixed layer. Similar to $DMSP_p$, enhanced concentrations of $DMSO_p$ (> 80 nmol L^{-1}) were measured with high proportions of prymnesiophytes in March and April 2015, suggesting prymnesiophytes might also be important producers of DMSO at BE. Overall, despite prymnesiophytes and chrysophytes were good producers of DMSP(O) at BE, the seasonal distributions of $DMSP(O)_p$ in the mixed layer followed that of Chl *a* instead of specific algae groups in terms of their large interannual/seasonal variabilities (Fig. 3.6a).

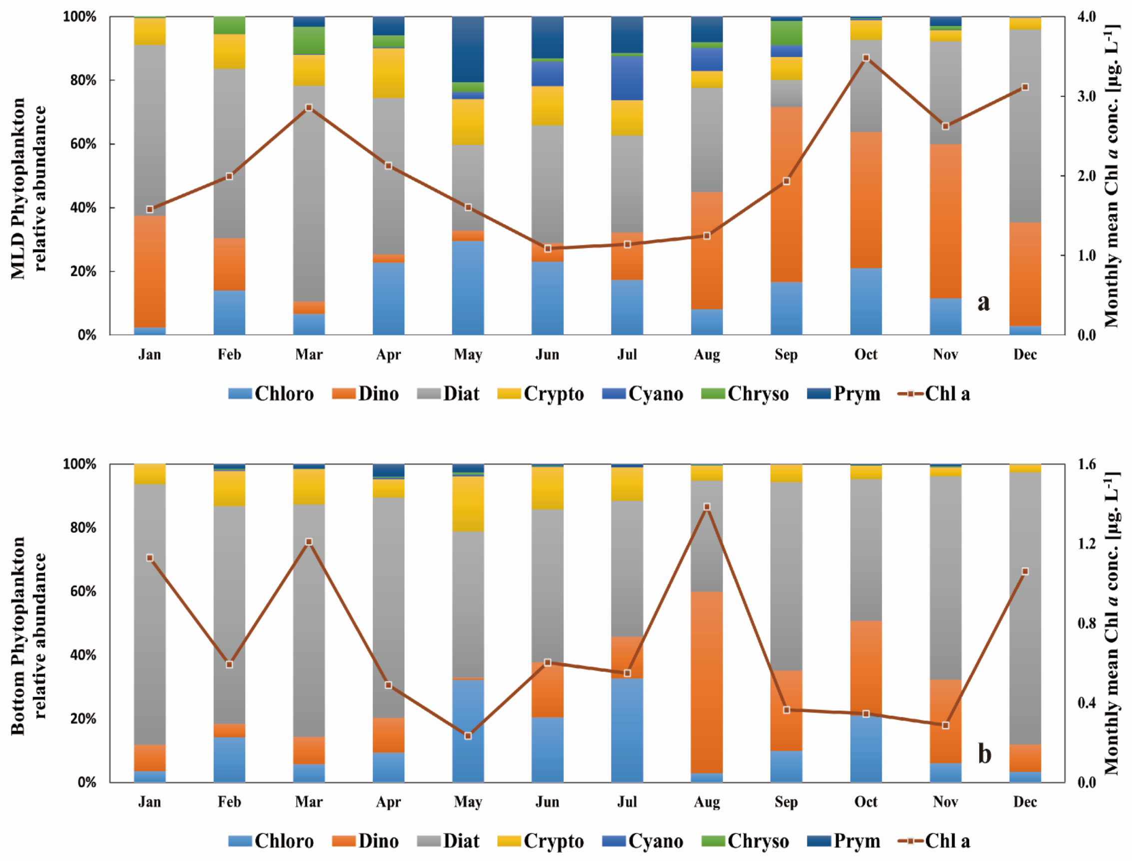

Figure 3.5. Monthly mean phytoplankton composition at the Boknis Eck station from 2009 to 2018 based on the result of CHEMTAX. The same months of each year were averaged. Please note that pigmen samples are available from April 2009 until December 2018. The values are averaged for the mixed layer (a) and bottom layer (b), respectively. Chloro stands for chlorophytes, dino stands for dinoflagellates, diat stands for diatoms, crypto stands for cryptophytes, cyano stands for cyanobacteria, chryso stands for chrysophytes and prym stands for prymnesiophytes. The red lines indicate monthly mean Chl *a* concentrations for the mixed layer and bottom layer.

$DMSP_p$ and $DMSO_p$ concentrations in the bottom layer (25 m) were generally low throughout the year except for August. We observed a higher relative abundance of dinoflagellates at 25 m in August (Fig. 3.6b), which were probably more adapted to seawater stratification (Estrada et al., 1985). The ability of dinoflagellates to migrate vertically helps them to cross the pycnocline to get access to the nutrients which accumulate below the mixed layer during the periods of the pronounced summer stratification. Better nutrient access can promote the metabolic activity and thus the DMSP production within dinoflagellates. Also, as mentioned above, the ability to produce DMSP among dinoflagellates varies substantially. For instance, the elevated concentrations of $DMSP_p$ at 25 m in August 2011, 2012 and 2014 might result from the observed high biomass of *Alexandrium* spp in the phytoplankton community in the Bay of Kiel (Wasmund et al., 2012; Wasmund et al., 2013, 2015), which is generally considered as a good DMSP producer in dinoflagellates (Caruana and Malin, 2014). Therefore, the relationship between dinoflagellates and DMSP at BE may not be well represented at the class levels (Griffiths et al., 2020).

DMS concentrations were negatively correlated with Chl *a* concentrations and poorly correlated with any phytoplankton groups (Table 3.1) in the mixed layer at BE. Similar cases for these correlations have been reported in many studies (Townsend and Keller, 1996; Toole and Siegel, 2004) due to the complex production and removal processes of DMS.

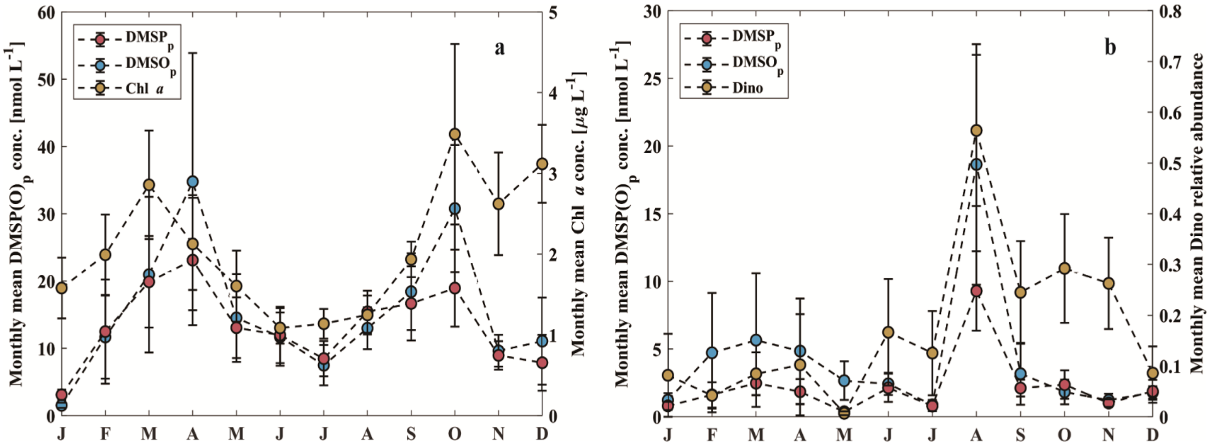

Figure 3.6. (a): Monthly mean DMSP$_p$, DMSO$_p$ and Chl *a* concentrations in the mixed layer during 2009–2018 at BE. (b): Monthly mean DMSP$_p$, DMSO$_p$ concentrations and relative abundance of dinoflagellates at 25 m during 2009–2018 at BE. Error bars represent standard errors of the mean of the samples.

3.4.4.2 Predictive algorithms

An algorithm which is able to predict DMS concentrations and thus its emission to the atmosphere could potentially help to improve climate models (Simó and Dachs, 2002; Wang et al., 2020). To reproduce and predict DMS(P) concentrations, parameters such as Chl *a*, temperature, solar radiation or nutrients are often used. To this end, we tested three predictive algorithms suggested by Simó and Dachs (2002) (S02) and Watanabe et al. (2007) (W07) as well as Nagao et al. (2018) (N18) to predict DMS concentrations and the $DMSP_p$:Chl *a* ratios in the surface layer (5 m) at BE, respectively. The algorithm proposed by Simó and Dachs (2002) makes use of the MLD and the MLD:Chl *a* ratio to predict DMS concentrations in the mixed layer. Watanabe et al. (2007) proposed an empirical equation for the prediction of sea surface DMS concentrations by combining sea surface temperatures, nitrate and latitude. No significant correlations were found between the measured DMS concentrations from this study and the predicted DMS concentrations by applying the S02 and W07 algorithms. Possible reasons might be that S02 was derived from a global dataset from coastal and open-ocean regions and that W07 was based on a dataset from the open North Pacific Ocean, which is in contrast to our coastal dataset.

The Fp ratio was first proposed by Claustre (1994) and was defined as a trophic status ratio. Then, inspired by Aumont et al. (2002), Nagao et al. (2018) proposed new Fp ratios representing the fractions of major and minor DMSP producers in the phytoplankton community to predict the $DMSP_p$:Chl *a* ratios by using phytoplankton pigments:

$$\text{Fp (high)} = (19'\text{-hex} + 19'\text{-but} + \text{peridinin}) / \sum \text{pigments}, \qquad (3.2)$$

$$\text{Fp (low)} = (\text{fucoxanthin} + \text{zeaxanthin} + \text{alloxanthin} + \text{Chl b}) / \sum \text{pigments}, \qquad (3.3)$$

where $\sum$ pigments stands for the sum of fucoxanthin, peridinin, 19′-hex, 19′-but, zeaxanthin, alloxanthin and Chl b. However, results from equations (1) and (2) did not work well with the $DMSP_p$:Chl a ratios from our study (Fig. 3.7a); neither the Fp (high) nor the Fp (low) ratios correlated well with the $DMSP_p$:Chl *a* ratios at 5 m. As discussed above, the ability to produce DMSP for dinoflagellates was generally low at BE in the mixed layer. Therefore, we modified equations (3.2) and (3.3) by moving peridinin from Fp (high) to Fp (low) as follows:

$$\text{New Fp (low)} = (\text{fucoxanthin} + \text{zeaxanthin} + \text{alloxanthin} + \text{Chl b} + \text{peridinin}) / \sum \text{pigments}, \qquad (3.5)$$

$$\text{New Fp (high)} = (19'\text{-hex} + 19'\text{-but}) / \sum \text{pigments}, \qquad (3.6)$$

Significantly negative and positive correlations were found between the DMSP$_p$:Chl *a* ratios and the new Fp (high) and new Fp (low) ratios at 5 m, respectively (Fig. 3.7b). The newly defined Fp (high) and Fp (low) represent the measured DMSP$_p$:Chl *a* ratios accurately, additionally showing that DMSP$_p$ is mainly driven by the phytoplankton community. Then annual mean DMSP$_p$ concentrations at 5 m were simulated by annual mean 19′-hex, 19′-but and Chl a concentrations, and they were compared to the measured concentrations (Fig. 3.7c). Our simulated DMSP$_p$ is in good agreement with our measured DMSP$_P$ except for the year 2017 (the red dot in Fig. 7c). In 2017, we measured the most pronounced spring (Chl *a*: 9.0 µg L^{-1}) and autumn blooms (Chl *a*: 12.4 µg L^{-1}) of the entire observation period. The blooms were dominated by diatoms and dinoflagellates, which led to maximum annual mean Chl *a* but low DMSP$_p$ concentrations.

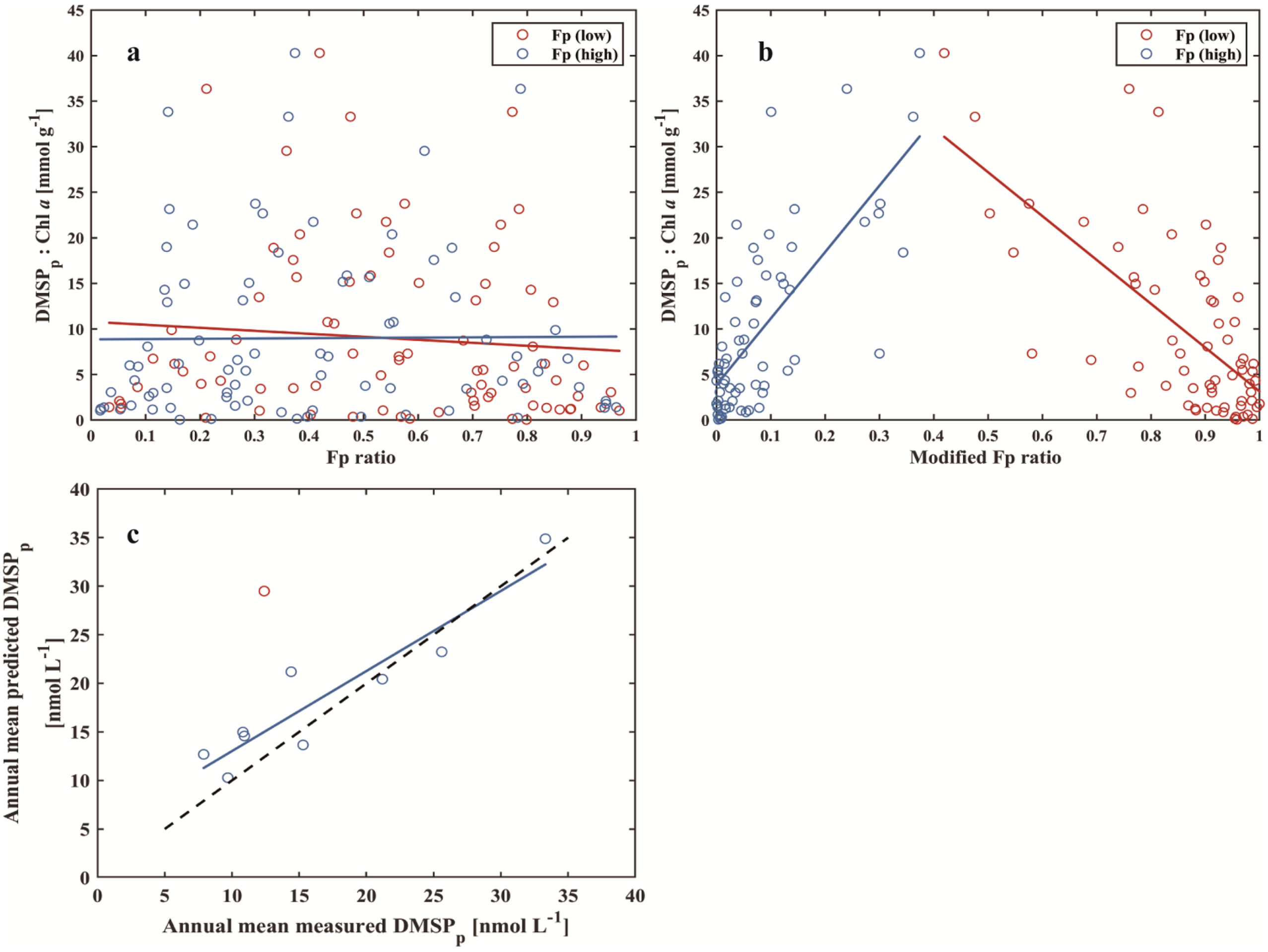

Figure 3.7. (a): DMSP$_P$:Chl *a* vs. Fp ratio (from Nagao et al. (2018)) at 5 m for the period 2009-2018. (b): DMSP$_P$:Chl *a* vs. modified Fp ratio (new Fp ratio) at 5 m for the period 2009–2018: blue open circles depict Fp (high) ($y = 72.90x + 3.78$, $R^2 = 0.54$, $p < 0.01$, $n = 65$) and red open circles depict Fp (low) ($y = -48.33x + 51.35$, $R^2 = 0.46$, $p < 0.01$, $n = 65$). (c): Annual mean measured DMSP$_P$ vs. annual mean predicted DMSP$_P$

concentrations at 5 m for each year during 2009–2018: y = 0.82x + 4.78, $R^2 = 0.86$, $p < 0.01$, n = 9. Note that the red open circle was not included in the linear regression line (blue), and the dash line indicates the identity (1:1) line.

3.5 Conclusions

We present a unique and comprehensive time-series study of sulfur compounds (DMS, DMSP and DMSO) at the Boknis Eck Times Series Station, located in the Eckernförde Bay (SW Baltic Sea), from 2009 to 2018. Distinct interannual and seasonal variabilities of sulfur compounds were tightly linked to the phytoplankton composition at BE. $DMSP_p$ and $DMSO_p$ concentrations were generally enhanced in spring and autumn in the mixed layer, following the pattern of Chl *a*. Mixed-layer $DMSP_t$ and DMS did not follow the increasing trends of the mixed-layer temperature and Chl *a* during the ten-year observation period. The main DMSP and DMS producers, namely, prymnesiophytes and chrysophytes (represented by their marker pigments 19′-hex and 19′-but, respectively) decreased in their total abundances over the ten years.

MBI events, which occurred in November 2010 and December 2014 at BE, might have influenced sulfur compounds concentrations by introducing uncommon but important DMSP producers. Enhanced DMS concentrations in the bottom layer were measured during seasonal hypoxic/anoxic events, suggesting that sediment might be an important source of DMS for the overlying seawater. In contrast to the mixed layer, elevated concentrations of $DMSP_p$ and $DMSO_p$ that usually occurred in the bottom layer in August at BE are due to specific dinoflagellate occurrence and stratification of the water column. Migrating dinoflagellates increased in their abundances due to nutrient-rich conditions in the deep layer and elevated light conditions in the surface layer at BE. A modified algorithm, based on the phytoplankton pigments, shows an improvement to predicting surface (5m) annual mean $DMSP_p$ concentrations at BE when compared with the original approach proposed by Nagao et al. (2018), highlighting the main drivers of DMSP dynamics at BE.

Overall, the variabilities of sulfur compounds at BE were closely linked to a complex interplay of biotic and abiotic factors at BE. Continuous observations at BE, with an emphasis on algae and bacteria group identification together with their activities determination, is of great importance (1) to capture the dynamics of DMS(P/O) and plankton community interactions and (2) to decipher the production pathways for sulfur compounds in the future, especially in view of the ongoing environmental changes such as ocean warming and acidification. Sediment samples from BE are also suggested to be collected in the future, as they are likely to contain high concentrations of sulfur compounds as previously reported (Williams et al., 2019). Moreover, an increasing frequency in sampling during seasonal phytoplankton blooms and low-oxygen events will help to capture the dynamic of sulfur compounds. The decadal observation at BE shows how important long-term observations are to understanding the local impacts and changes due to global warming and climate changes. We recommend establishing more time-series stations and keeping existing stations running to observe and understand the impact of global changes worldwide on marine ecosystems.

3.6 Data availability

Data from Boknis Eck are available from www.bokniseck.de/database-access.

3.7 Acknowledgments

We thank the captain and crew of the RV *Littorina* and *Polarfuchs* as well as many colleagues and students (namely S. Marcks and J.P.M. Heyda) involved in the sampling and measurements of the Boknis Eck Time Series Station. We especially thank Kerstin Nachtigall for the phytoplankton pigments measurements and Frank Malien for the nutrient and dissolved oxygen measurements. The time-series station at BE was supported by DWK Meeresforschung (1957–1975), HELCOM (1979–1995), BMBF (1995–1999), the Institut für Meereskunde (1999–2003), IfM-GEOMAR (2004–2011) and GEOMAR (2012–present). The Boknis Eck Time Series Station (www.bokniseck.de) is run by the Chemical Oceanography Research Unit of GEOMAR, Helmholtz Centre for Ocean Research Kiel. Yanan Zhao is grateful to the China Scholarship Council (CSC) for providing financial support (file no. 201606330066).

3.8 Supplemental material

Table S3.1. Input and output ratios of marker pigments to Chl *a* for the selected phytoplankton groups. Peri, 19′-but, Fuco, 19’-hex, Ddx, Allo, Zea and Chl *b* represent peridinin, 19’-butanoyloxyfucoxanthin, fucoxanthin, 19’-hexanoyloxy fucoxanthin, diadinoxanthin, alloxanthin, zeaxanthin and chlorophyll *b*, respectively. Definition of phytoplankton groups abbreviations is shown in Fig. 3.5.

	Peri	19′-but	Fuco	19’-hex	Ddx	Allo	Zea	Chl *b*	Chl *a*
Input ratios									
Chloro	0	0	0	0	0	0	0.031	0.283	1
Dino	0.547	0	0	0	0.247	0	0	0	1
Diat	0	0	0.81	0	0.318	0	0	0	1
Crypto	0	0	0	0	0	0.354	0	0	1
Cyano	0	0	0	0	0	0	1.337	0	1
Chryso	0	1.563	0.974	0	0.857	0	0	0	1
Prym	0	0.023	0.304	0.27	0.113	0	0	0	1
Output ratios									
Chloro	0	0	0	0	0	0	0.031	0.283	1
Dino	0.852	0	0	0	0.043	0	0	0	1
Diat	0	0	0.81	0	0.044	0	0	0	1
Crypto	0	0	0	0	0	0.354	0	0	1
Cyano	0	0	0	0	0	0	1.337	0	1
Chryso	0	1.563	0.974	0	0.857	0	0	0	1
Prym	0	0.023	0.304	0.27	0.113	0	0	0	1

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4 Dimethylated sulfur compounds in the Peruvian upwelling system

submitted as: Zhao, Y., Booge, D., Marandino, C. A., Schlundt, C., Bracher, A., Atlas, E. L., Williams, J., and Bange, H. W.: Dimethylated sulfur compounds in the Peruvian upwelling system, Biogeosciences Discuss. [preprint], https://doi.org/10.5194/bg-2021-174, in review, 2021.

Abstract. Our understanding of the biogeochemical cycling of the climate-relevant trace gas dimethyl sulfide (DMS) in the Peruvian upwelling system is still limited. Here we present oceanic and atmospheric DMS measurements which were made during two shipborne cruises in December 2012 (M91) and October 2015 (SO243) in the Peruvian upwelling region. Dimethylsulfoniopropionate (DMSP) and dimethyl sulfoxide (DMSO) were also measured during M91. DMS concentrations were 1.9 ± 0.9 nmol L^{-1} and 2.5 ± 1.9 nmol L^{-1} in surface waters in October 2015 and December 2012, respectively. Nutrient availability appeared to be the main driver of the observed variability in the surface DMS distributions in the coastal areas. DMS, DMSP and DMSO showed maxima in the surface layer and no elevated concentrations associated with the oxygen minimum zone off Peru were measured. The possible role of DMS, DMSP and DMSO as radical scavengers (stimulated by nitrogen limitation) is supported by their negative correlations with N:P (sum of nitrate and nitrite: dissolved phosphate) ratios. Large variations in atmospheric DMS mole fractions were measured during M91 (144.6 ± 95.0 ppt) and SO243 (91.4 ± 55.8 ppt); however, the atmospheric mole fractions were generally low, and the sea-to-air flux was primarily driven by seawater DMS. The Peruvian upwelling region was identified as a source of atmospheric DMS in December 2012 and October 2015, however, in comparison to the previous measurements in the adjacent regions, the Peru upwelling was a moderate of DMS emissions at either time (M91: 5.9 ± 5.3 µmol m^{-2} d^{-1}; SO243: 3.8 ± 2.7 µmol m^{-2} d^{-1}).

4.1 Introduction

The trace gas dimethyl sulfide (DMS) is mainly produced in the marine environment and serves as one of the most abundant biogenic atmospheric sulfur sources, transferring approximately 28.1 Tg sulfur from the oceans into the atmosphere annually as estimated by Lana et al. (Lana et al., 2011). DMS can be oxidised to form sulfate aerosols in the atmosphere which, in turn, play an important role in regulating Earth's climate via altering cloud properties and modulating cloud albedo (Stefels et al., 2007). However, the global significance of this DMS-climate link is still under debate (Quinn and Bates, 2011).

Oceanic DMS is mainly produced from its precursor dimethylsulfoniopropionate (DMSP) which is synthesised in phytoplankton cells and then released into the seawater by senescence, virus attacks, and grazing (Stefels et al., 2007). Cellular DMSP concentrations vary in different phytoplankton groups: dinoflagellates and prymnesiophytes are major DMSP producers, whereas diatoms produce less DMSP (Keller, 1989). DMSP can be degraded to methanethiol via demethylation (Howard et al., 2006) or to DMS and acrylate via lyase-mediated cleavage (Curson et al., 2011). The conversion of DMSP to DMS (i.e., cleavage pathway) is only of minor importance for DMSP loss, as up to 75 % of DMSP is metabolised by marine bacterioplankton through the demethylation pathway (Moran et al., 2012).

The formation and consumption processes of dimethyl sulfoxide (DMSO) remain less clear, but DMSO is known to be a photochemical and biological oxidation product of DMS (Hatton et al., 2012). Some studies showed that it could be directly synthesised in marine phytoplankton cells (Simó et al., 1998; Lee et al., 1999). A recent study suggested that dissimilation of dissolved DMSO ($DMSO_d$) to carbon dioxide can be a significant loss pathway in coastal waters (Dixon et al., 2020). Both DMSP and DMSO exert similar intracellular functions (e.g., cryoprotection and antioxidation) in phytoplankton cells (Simó et al., 1998; Sunda et al., 2002) and can support bacterial carbon and sulfur demand (Simó et al., 2002; Dixon et al., 2020).

Biologically productive regions of the ocean can be a significant source of DMS to the atmosphere (Lana et al., 2011). The eastern tropical South Pacific Ocean (ETSP) features one of the four major Eastern Boundary Upwelling Ecosystems (EBUS): year-round coastal upwelling off Peru and northern Chile is driven by offshore Ekman transport resulting from alongshore trade winds, which leads to abundant nutrients in surface waters and enhanced biological production (Chavez and Messié, 2009). The Peru upwelling system is significantly influenced by El Niño-Southern Oscillation (ENSO) events at decadal scales (Espinoza-Morriberón et al., 2017). ENSO is a natural climate event that affects the oceanic and atmospheric conditions worldwide and occurs in intervals between two and ten years (Santoso et al., 2017; Timmermann et al., 2018). ENSO is divided into three phases: El Niño (the warm phase), La Niña (the cold phase), and the neutral phase. El Niño/La Niña events are characterised by warming/cooling of sea surface temperature (SST) in the equatorial Pacific Ocean and result in the deepening/shoaling of thermocline off Peru (Dewitte et al., 2012). During El Niño, the thermocline is pushed away from the surface layer (i.e., reduced coastal upwelling), resulting in limited nutrient supply and leading to a decline in primary production in the ecosystem (Barber and Chavez, 1983). Although upwelling of cold and nutrient-rich waters can be observed along the coast of Peru year-round (Tarazona and Arntz, 2001), surface chlorophyll concentration peaks in austral summer and decreases in austral winter, which is out of phase with the upwelling intensity (Chavez and Messié, 2009). This paradoxical seasonal cycle may arise from both light limitation and dilution due to the deepening of the mixed layer in winter (Echevin et al., 2008).

The Peru upwelling system has been reported to be a source of biogenic halocarbons (e.g., bromoform and methyl iodide) both in surface seawater and atmosphere (Hepach et al., 2016); however, the measurements of biogenic sulfur compounds (DMS, DMSP and DMSO) are relatively sparse in this area (Andreae, 1985; Riseman and DiTullio, 2004; Yang et al., 2011). As a result, abiotic and biotic factors affecting DMS/P/O cycling and distributions are not fully understood. We measured DMS concentrations in the water column in the Peru upwelling region as well as atmospheric DMS mole fractions during two research campaigns in December 2012 (M91) and October 2015 (SO243). In addition to DMS, particulate and dissolved DMSP and DMSO concentrations were measured during M91. This study is intended to focus on (i) deciphering the distributions of DMS, DMSP, and DMSO in the Peru upwelling, (ii) identifying their main drivers and (iii) quantifying the DMS emissions to the atmosphere in order to re-assess the role of DMS emissions from the Peru upwelling region.

4.2 Material and Methods

4.2.1 Sampling sites

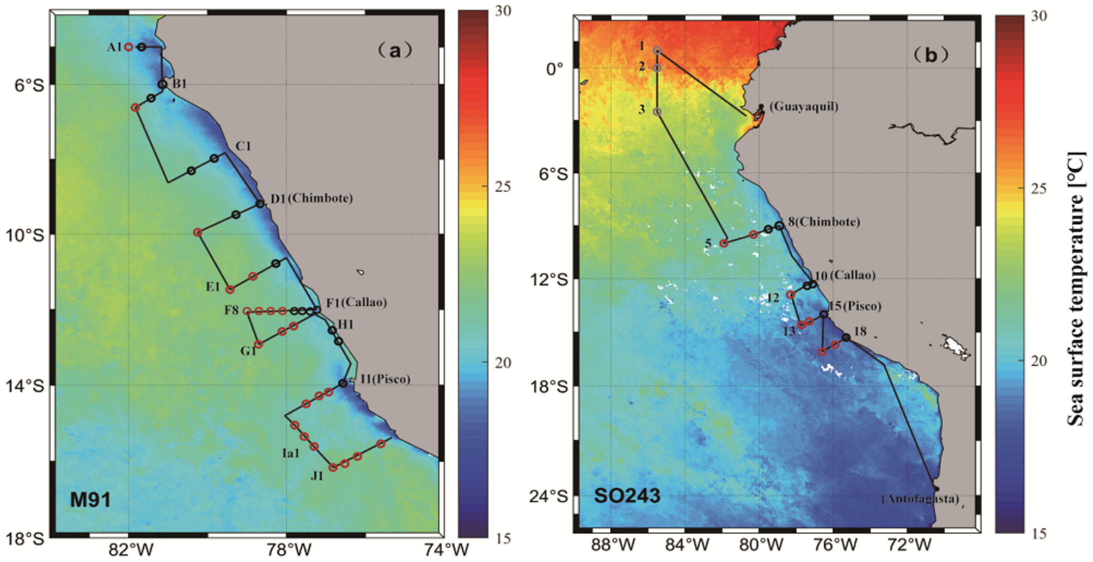


Figure 4.1. Cruise tracks of M91 (a) and SO243 (b) plotted on top of monthly mean SST detected by the Moderate Resolution Imaging Spectroradiometer (MODIS) instrument on board the Aqua satellite. Red circles indicate offshore stations, and black circles indicate coastal stations in both panels. Grey circles in panel b indicate equatorial stations. Note that no CTD cast was performed at stations 4 and 9 during cruise SO243.

The cruise M91 (Fig. 4.1a) was conducted on board the R/V Meteor between 1 and 26 December 2012. The cruise started from the northernmost location at 5 °S and moved to the southernmost position at 16.2 °S with several transects perpendicular to the coastline of Peru. Underway samples were taken from a continuously operating pump in the ship's hydrographic shaft (at ~ 7 m water depth), and profiles were made between 3 and 2000 m water depth from a 24 × 12 L Niskin bottle rosette equipped with a probe for conductivity, temperature, and water depth (CTD). An overview of the methods used for determining oceanographic parameters such as oxygen and nutrients can be found in Czeschel et al. (2015). The cruise SO243 (Fig. 4.1b) took place on board the R/V Sonne between 5 and 22 October 2015, from Guayaquil, Ecuador to Antofagasta, Chile, with perpendicular transects to the shelf between ~ 9–16 °S (Fig. 4.1b). Underway samples were taken from a continuously operating pump in the ship's hydrographic shaft (at ~ 5 m water depth), and profile samples were made between 5 and 150 m from 24 × 10 L Niskin bottle rosette equipped with a CTD. Measurements of oceanographic parameters such as oxygen and nutrients are described in Stramma et al. (2016). Generally, both cruises alternated between offshore and onshore transects (Fig. 4.1) in the Peru upwelling region (4–16 ºS). Therefore, the sampling stations of M91 and SO243 can be categorised into offshore and coastal stations according to their respective depths: stations shallower than 300 m are defined as coastal stations and those deeper than 1000 m are defined as offshore stations. In addition to underway samples, seawater column-integrated (1–10 m) samples from the CTD casts are defined as surface samples for M91.

The Ocean Niño index (ONI; http://origin.cpc.ncep.noaa.gov/products/analysis_monitoring/ensostuff/ONI_v5.php), which quantifies the progress and strength of EI Niño, suggests that M91 (ONI < 0.5 °C from August 2012 to March 2013) took place in a neutral phase while SO243 occurred during a strong El Niño event (ONI ≥ 0.5 °C from November 2014 to May 2016) (Santoso et al., 2017). However, the El Niño during SO243 was still developing with an ONI of 2.2 °C for Aug–Oct 2015.

4.2.2 Sulfur compounds measurements

Sulfur compounds (DMS/P/O) on M91 were analysed by purge and trap coupled to a gas chromatograph-flame photometric detector (GC-FPD) as described in Zindler et al. (2012, 2013). Briefly, DMS samples were analysed immediately after sampling and filtering (GF/F; Whatman; 0.7 µm) during the cruise, while DMSP and DMSO samples were analysed after returning to the lab. Dissolved DMSP ($DMSP_d$) samples were measured after adding sodium hydroxide (NaOH; Carl Roth) to the DMS samples, and total DMSP ($DMSP_t$) was measured from the unfiltered alkaline samples. Particulate DMSP ($DMSP_p$) concentrations were calculated by subtracting measured DMS and $DMSP_d$ concentrations from measured $DMSP_t$ concentrations. Dissolved DMSO ($DMSO_d$) and total DMSO ($DMSO_t$) samples were measured from the same samples of $DMSP_d$ and $DMSP_t$ measurements by adding cobalt-dosed sodium borohydride (NaBH4; Sigma-Aldrich) after DMSP measurements. Particulate DMSO ($DMSO_p$) concentrations were calculated by subtracting measured $DMSO_d$ concentrations from measured $DMSO_t$ concentrations. The mean precision of all sulfur compound measurements using GC-FPD was ± 18 %. Seawater DMS on SO243 was measured using a purge and trap system attached to a gas chromatograph-mass spectrometer (GC-MS), as described in Zavarsky et al. (2018). The mean precision of the DMS measurements using GC-MS was ± 11 %. Dissolved DMS data measured simultaneously using GC-FPD and GC-MS at the GEOMAR time-series stations Boknis Eck (BE; www.bokniseck.de) are used to quality control the comparison of the M91 and SO243 datasets. The BE measurements are performed at 6 different depths on a monthly schedule and an assessment of a year-long dataset shows good agreement (Fig. S1). The BE relationship was used to adjust the dissolved DMS data from M91, which resulted in an increased uncertainty of ± 30.6 %. DMS atmospheric mole fractions during both cruises were measured from whole air samples collected in 2.3 L electropolished stainless steel canisters. Sample analysis was performed on a multi-channel GC/MS/FID/ECD system (Agilent 7890 GC, 5973 MS), which used a Markes Unity system for sample concentration (Andrews et al., 2016). Samples were collected approximately every 3 hours (in parallel with seawater DMS samples). In addition, measurements of DMS atmospheric mole fraction (parts per trillion) during M91 were performed using a commercial proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS) from Ionicon Analytik GmbH (Innsbruck, Austria). The PTR-ToF-MS was operated under standard conditions, pressure 2.2 mb, E/N 137, and mass resolution of between 3700-4000. The PTR-ToF-MS was calibrated at the beginning, during, and at the end of the cruise. The DMS was measured at mass 63.026 and calibrated to a gravimetrically prepared pressurized standard (Apel Riemer Environ. Inc, USA). The mean precision of the atmospheric DMS measurements using PTR-ToF-MS was ± 18 %. The comparison between atmospheric DMS data using two methods during M91 shows a good correlation, but not 1:1 agreement, with PTR-ToF-MS measurements exhibiting higher concentrations (Fig. S1). For more details about this comparison, please see the supplemental material. It is not possible to determine which dataset is more accurate. In this study, we used the atmospheric DMS PTR-ToF-MS data which were adjusted to the discrete canister samples because of the higher temporal resolution of the continuous PTR-ToF-MS measurements, which resulted in an increased uncertainty of ± 24 %.

4.2.3 Calculation of sea-to-air fluxes

Sea-to-air fluxes, F (μmol m^{-2} day^{-1}), of DMS were calculated according to Eq. (4.1):

$$F = k_w(C_w - x'P/H), \tag{4.1}$$

where C_w and x' are the dissolved DMS surface concentrations and the DMS atmospheric dry mole fractions, respectively. P is the ambient pressure (set to 1 atm) and H is Henry's law solubility coefficient (Dacey et al., 1984), k_w is the gas transfer velocity calculated with the in-situ wind speed

(U) of the shipboard observations and a Schmidt number (Sc) normalised to 600 (which was chosen to allow a direct comparison to the Lana et al. (2011)
climatology), according to Nightingale et al. (2000); thus k_w was calculated according to Eq. (4.2):

$$k_w = (0.222U^2 + 0.33U)\,(Sc/600)^{-0.5}, \tag{4.2}$$

where Sc was calculated using SST according to Saltzman et al. (1993) and the wind speed measurements were corrected to a height of 10 m above the sea level following the method of Hsu et al. (1994).

4.2.4 Phytoplankton pigments and Chlorophyll *a* concentration of major groups

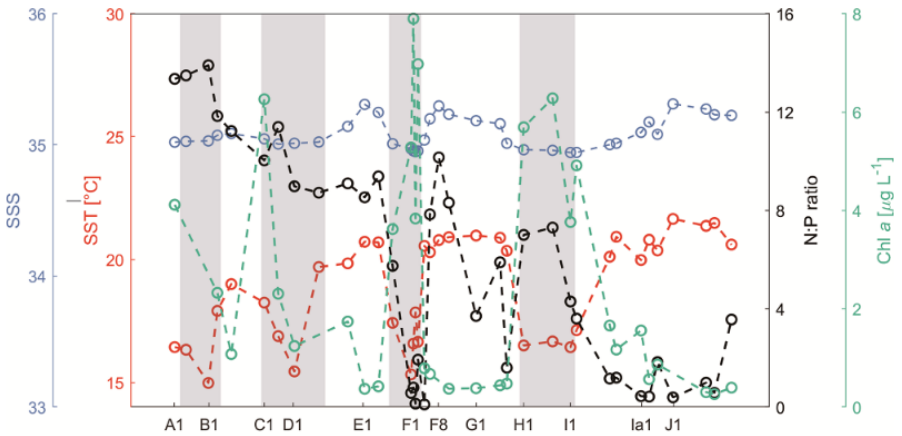
Phytoplankton pigment samples were generally taken in parallel with DMS samples in depths between ~ 3–200 m during both cruises. The process for measuring phytoplankton pigments and further converting them into phytoplankton groups are identical for the cruises M91 and SO243. Pigment samples were filtered through Whatman GF/F filters at the stations where DMS was sampled and then stored at -80 °C until analysis. Pigment concentrations, as described in Booge et al. (2018), were determined using high-pressure liquid chromatography (HPLC) according to the method of Barlow et al. (1997), which was adjusted to our temperature-controlled instruments as detailed in Taylor et al. (2011). Pigments, as listed in Table 2 of Taylor et al. (2011), were quality controlled according to Aiken et al. (2009), and were published in Hepach et al. (2016) and Bracher (2019). Phytoplankton composition was derived, as in Booge et al. (2018) already for SO243 also for M91 data: Using the diagnostic pigment analysis developed by Vidussi et al. (2001) and subsequently refined by Uitz et al. (2006), seven marker (diagnostic) pigments as proxies for specific phytoplankton groups (diatoms, dinoflagellates, haptophytes, chrysophytes, cryptophytes, cyanobacteria (excluding prochlorophytes), and chlorophytes) are used to relate their weighted sum of concentrations to the sum of monovinyl-Chl *a*. By applying then the specific weights determined by Uitz et al. (2006) the specific Chl a for each group is determined. The Chl *a* of prochlorophytes was directly derived from the divinyl-Chl *a* (the marker pigment for this group). The eight identified phytoplankton groups are assumed to represent the entire phytoplankton community and the sum of their Chl *a* represents the total Chl *a*.

4.3 Results and Discussion

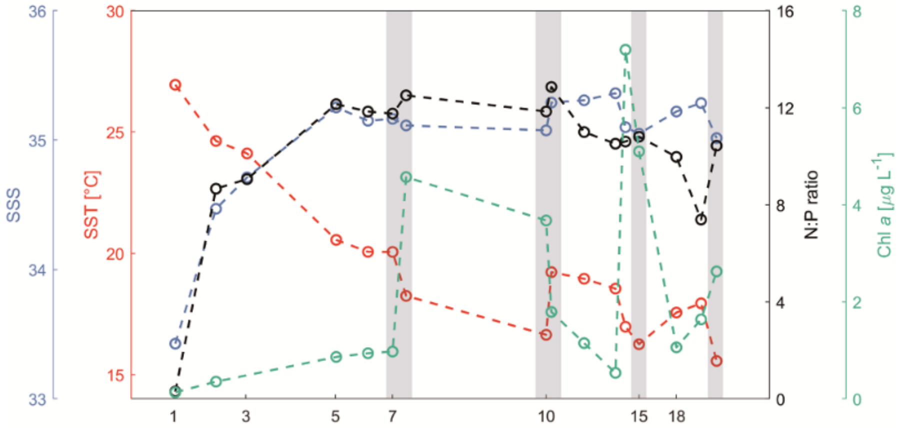
4.3.1 Cruise settings

M91 took place in the coastal, wind-driven Peruvian upwelling system with southeasterly winds at 6.6 ± 2.1 m s^{-1}. The mean ± std (min–max) SST and sea surface salinity (SSS) during M91 were 18.9 ± 2.1 (15.0–22.4) °C and 35.1 ± 0.1 (34.9–35.3), respectively. Generally, SSTs below 18.0 ºC were measured at the coastal stations (Fig. 2a), where upwelled water was found. The mean Chlorophyll *a* (Chl *a*) concentration was 2.5 ± 2.3 (0.3–7.9) µg L^{-1}, displaying a decreasing trend in the offshore direction (Fig. 4.2a). Diatoms were the most dominant algae group and were observed at all stations in surface waters with the mean relative abundance of 41 %, followed by haptophytes (24 %) and chlorophytes (10 %) in the phytoplankton community (Hepach et al., 2016). The N:P ratio, defined as the ratio of the sum of nitrate (NO_3^-) and nitrite (NO_2^-) to dissolved phosphate (PO_4^{3-}) for both cruises, is a good indicator of nutritional status: the constant 12.6, which is the empirically determined N:P ratio of organic matter produced in these waters, is used as the threshold for nitrogen repletion/limitation (Codispoti and Packard, 1980). N:P ratios ranged between 0.1 and 13.9 during M91, with a general decreasing trend southward and nitrogen-deficient conditions at coastal stations near Callao (F1–F4; Fig. 4.2a), which may suggest different phytoplankton bloom stages (e.g., a fully developed bloom at station F1 and F2 as indicated by higher Chl *a* and lower N:P values).

SO243 started with a section passing the Equator at around 85.5 °W with a mean (± std) SST and SSS of 25.2 ± 1.5 °C and 34.2 ± 0.7 as well as low Chl *a* values 0.4 ± 0.2 µg L^{-1} (Fig. 4.2b). Afterwards, SST, SSS, and Chl *a* values between stations 5 and 18 were 18.8 ± 1.6 (15.6–20.5) °C, 35.2 ± 0.1 (35–35.4), and 2.5 ± 2.1 (0.5–7.2; Fig. 4.2b) µg L^{-1}, respectively, with constant southeasterly winds of 8.2 ± 2.5 m s^{-1}, comparable to those measured during M91. The phytoplankton composition during SO243 is similar to M91, with the most abundant phytoplankton groups being diatoms (45 %), haptophytes (24 %), and chlorophytes (18 %) (Booge et al., 2018). N:P ratios were generally between 8–13 in the Peru upwelling region during SO243, indicating non/slightly limiting nitrogen conditions (Fig. 4.2b). Although the cruise SO243 took place during the strong EI Niño event in 2015/2016, typical EI Niño signals of warmer, saline, and oxygen-depleted upwelled waters were only apparent at the shelf stations at ~ 9 °S off Peru. The EI Niño signals were still weak at ~ 12, 14, and 16 °S transects as regularly cold and nutrient-rich upwelled waters were still present at the easternmost stations of these transects (Stramma et al., 2016). Overall, this indicates that at the time of our measurements in October 2015, the El Niño signal was not fully developed.



(a): Station numbers during M91 in December 2012



(b): Station numbers during SO243 in October 2015

Figure 4.2. Sea surface temperature (SST; red), Sea surface salinity (SSS; blue), N:P ratio (black; N stands for the sum of dissolved nitrate and nitrite, and P stands for phosphate) and Chl a (green) at each station during M91 (a) and SO243 (b). Grey rectangles indicate coastal CTD stations. All values from both cruises are integrated between 1–10 m.

4.3.2 Seawater DMSP and DMSO

During M91, the mean concentrations of DMSP$_p$, DMSP$_d$, DMSO$_p$, and DMSO$_d$ in surface waters were 85.0 ± 68.9 (10.3–288.9) nmol L^{-1}, 16.8 ± 16.5 (0.8–61.9) nmol L^{-1}, 40.1 ± 45.4 (2.8–167.9) nmol L^{-1} and 14.0 ± 9.5 (1.3–28.9) nmol L^{-1}, with DMSP$_p$ and DMSO$_p$ displaying a decreasing trend in an offshore direction along the F transect parallel to Callao (Fig. 4.3, a–d). Vertical profiles at station F4 exhibited typical patterns of these sulfur compounds and Chl *a* during M91 (Supporting Information; Fig. S4.2): higher concentrations were measured in surface waters than those in bottom waters, with no enhanced signals in the oxygen minimum zone (OMZ).

The significant correlation between $DMSP_p$ and $DMSO_p$ ($DMSO_p = 0.62 * DMSP_p - 0.91$, $r^2 = 0.8$; see also Table 1) in this study is in good agreement with a correlation reported previously ($[DMSO_p] = 0.73 \times [DMSP_p] - 0.66$, $r^2 = 0.9$) off the Peruvian coast in September 2000 (Riseman and DiTullio, 2004). The strong correlation and remarkable similarity of the ratio between the two particulate sulfur compounds from these two studies spanning a decade interval may indicate that they share a similar biogenic source and/or have related physiological functions in phytoplankton cells (Stefels et al., 2007). However, the concentrations of $DMSP_p$ (1–45.7 nmol L^{-1}) and $DMSO_p$ (0.1–30.8 nmol L^{-1}) reported by Riseman & DiTullio (2004) are generally lower than those measured in our study. Considering phytoplankton community composition (dominated by diatoms) and biomass (represented by Chl *a*) are comparable between the two studies, and no significant relationship was observed between individual phytoplankton groups and $DMSP(O)_p$ during M91 (Table 4.1), phytoplankton does not seem to be the main driver for the difference of $DMSP(O)_p$ between the two studies. In contrast, nutrient availability (indicated by N:P ratios) might be the reason. Sunda *et al.* (2007) reported a substantial increase in intracellular DMSP concentrations in coastal diatoms under nitrogen limitation, which is assumed to be in response to oxidative stress within phytoplankton cells. Recently, Theseira et al. (2020) observed the accumulation of DMSP in diatoms (*Thalassiosira weissflogii*), which can reduce intracellular reactive oxygen species. N:P ratios were generally low (< 10) during M91 while they were > 10 (NO_x > 17 µmol L^{-1}, PO_4^{3-} > 1.2 µmol L^{-1}) in September 2000 (Riseman and DiTullio, 2004). Therefore, higher $DMSP_p$ and $DMSO_p$ concentrations during M91 were potentially up-regulated in response to increased oxidative stress induced by nutrient limitation, and this is in line with negative correlations between N:P ratios and $DMSP(O)_p$ (Table 4.1). Moreover, negative correlations (Table 4.1) between ß-carotene (a known antioxidant) and $DMSP(O)_p$ concentrations in both studies further support this speculation. Additionally, Riseman & DiTullio (2004) reported enhanced concentrations of $DMSP(O)_p$ under low-iron conditions, which exemplifies that either macro-, micronutrients or co-limitation conditions might elevate $DMSP(O)_p$ concentrations against oxidative stress.

In contrast to our observations, Zindler et al. (2012) reported a general decreasing trend of $DMSP_t$ concentrations with decreasing N:P ratios (1–12) in the Mauritanian upwelling region, which was dominated by diatoms. This may be because the response to nitrogen limitation differs among specific algae groups. For instance, Gaul (2004) reported decreasing DMSP production rates with decreasing nitrogen concentration among nine strains within the groups of dinoflagellates, diatoms, prymnesiophytes and cryptophytes. Therefore, despite the fact that diatoms were the dominant algae group off Peru and off Mauritania, variability at the species or genus level might result in different responses under nitrogen limitation (Keller and Korjeff-Bellows, 1996; Keller et al., 1999a, b).

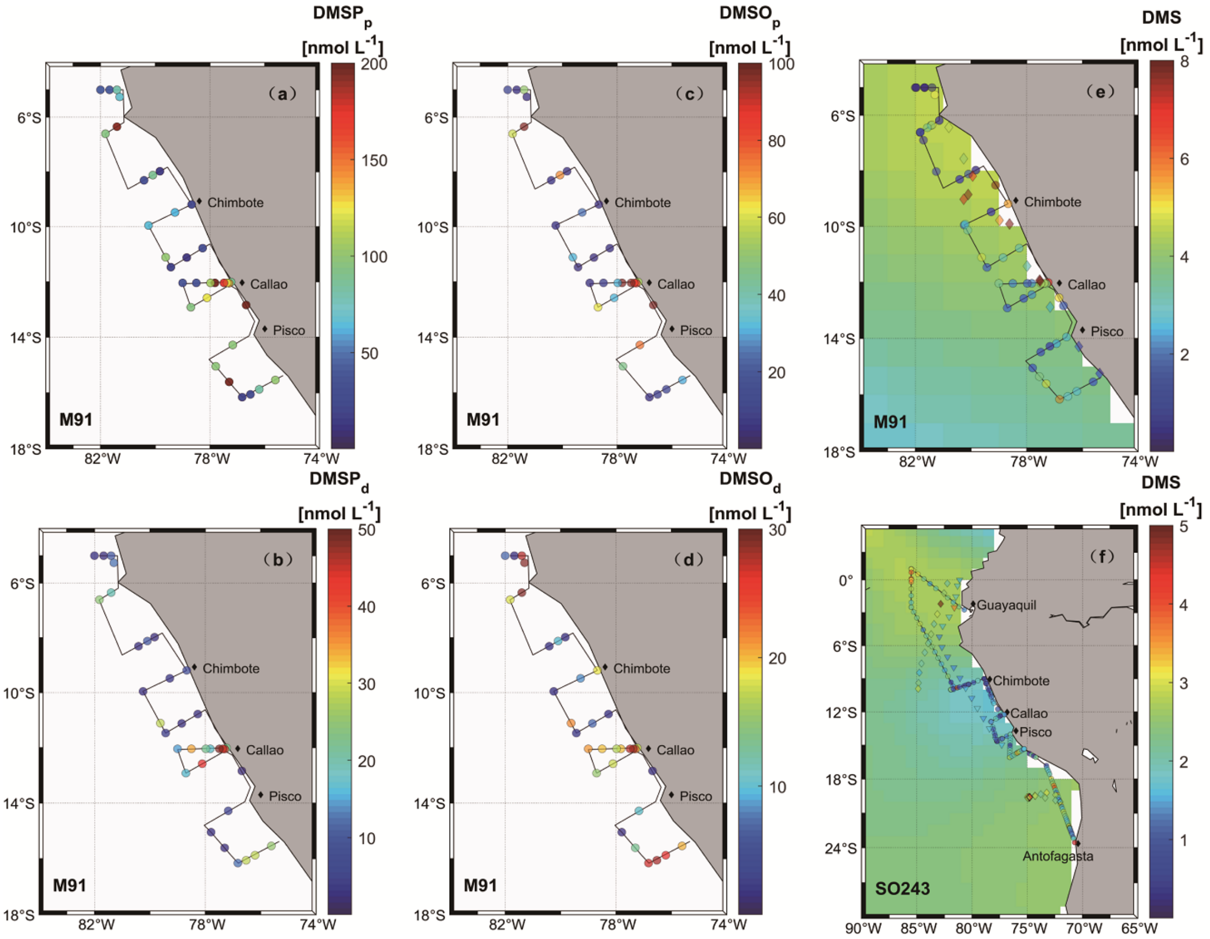


Figure 4.3. Surface seawater measurements of sulfur compounds are shown in panels a–f (circles) for $\mathrm{DMSP_p}$ (M91), $\mathrm{DMSP_d}$ (M91), $\mathrm{DMSO_p}$ (M91), $\mathrm{DMSO_d}$ (M91), DMS (M91) and DMS (SO243), respectively. Monthly (December and October) surface DMS concentrations from the Lana et al. (2011) climatology are colour-coded in the background in e and f, respectively. Diamonds in panel e, as well as diamonds and triangles in panel f, are recorded DMS concentrations in adjacent waters retrieved from the PMEL database for June–July 1982 (Andreae, 1985), October–November 2007 (unpublished DMS data) and October–November 2008 (Hind et al., 2011), respectively. Note that to ensure readability of the plots, the scale in panel e is capped at 8 nmol $L^{-1}$with a few values exceeding the upper threshold, and DMS data retrieved from the PMEL database were averaged every ten samples.

4.3.3 Seawater DMS

Surface DMS concentrations were variable during M91, with a mean concentration of 2.5 ± 1.9 (0.2–8.2) nmol L^{-1} (Fig. 4.3e). Elevated concentrations were observed at the major upwelling centres (e.g., Chimbote and Callao), with the highest value measured north of Chimbote. The cross-shelf section starting from Callao during M91 displayed decreasing trends of DMS towards an offshore direction. DMS concentrations of 1.9 ± 0.9 (0.5–4.5) nmol L^{-1} (Fig. 4.3f) in surface waters during SO243 could be grouped into three sections: the equatorial section (Guayaquil–station 5), the Peruvian upwelling section (stations 6–18) and the Chilean waters section, with mean concentrations of 2.4 ± 0.8 nmol L^{-1}, 1.2 ± 0.8 nmol L^{-1} and 2.1 ± 0.7 nmol L^{-1}, respectively. DMS values were generally low in the Peru upwelling section, regardless of coastal or offshore areas. Similar to DMSP and DMSO, vertical profiles of DMS for both cruises presented decreasing trends with increasing depths (Fig. S4.2) and again, no elevated concentrations were measured associated with OMZ in the water column, which is in agreement with Andreae (1985).

Except for the positive correlation between DMS and $DMSO_d$ during M91 (Table 4.1), which serves as a hint that DMS photo-degradation was an important source of $DMSO_d$ in surface waters (Xu et al., 2021), DMS was significantly correlated only with N:P ratios for both cruises (Table 4.1). Nutrient availability is essential to plankton (phytoplankton and bacterioplankton) communities and therefore, N:P ratios, as well as fixed nitrogen deficit (Ndef), were used as indirect indicators to investigate the nutrient status on the coastal DMS distributions for both cruises. Ndef was calculated using the following equation (Graco et al., 2017):

$$\mathrm{Ndef} = 12.6 \times [PO_4^{3-}] - [NO_3^-] - [NO_2^-], \quad (4.3)$$

where the constant 12.6 is adopted from Codispoti and Packard (1980), and positive Ndef indicates nitrogen-depleted conditions. Generally, both N:P ratios and Ndef significantly correlated with coastal DMS values in the surface waters (Fig. 4.4). Enhanced DMS concentrations associated with nitrogen limitation could be linked to an increase in the activity of the DMSP lyase enzyme, probably in response to increased oxidative stress (Sunda et al., 2007). This might also explain the discrepancy in coastal DMS values between the two cruises: higher DMS values from M91 might be up-regulated in a more nitrogen-limited environment, as compared to SO243. Our observation of nutrient availability and DMS concentrations are in line with other field studies (Leck et al., 1990; Zindler et al., 2012).

Table 4.1. Spearman's rank coefficients of correlations of all sulfur compounds surface data with selected abiotic and biological parameters. Bold numbers indicate correlations that are significant ($p < 0.05$) with a sample size of 27 for M91, 36 (environmental and biological parameters) and 13 (nutrients) for SO243 between 9–16 °S. ß-caro represents ß-carotene, diat represents diatoms, hapto represents haptophytes, and chloro represents chlorophytes. NA represents not available.

M91	SST	SSS	N:P	Chl *a*	ß-caro	Diat	Hapto	Chloro	DMSO$_d$	DMSO$_p$	DMSP$_d$	DMSP$_p$
DMS	0.05	-0.08	**-0.51**	0.11	0.12	0.29	-0.20	0.37	**0.68**	0.28	0.34	0.09
DMSP$_p$	-0.15	**-0.43**	**-0.40**	0.28	**0.39**	0.25	-0.14	-0.18	**0.56**	**0.92**	**0.71**	
DMSP$_d$	0.25	-0.05	**-0.46**	-0.13	-0.01	0	-0.08	-0.01	**0.90**	**0.50**		
DMSO$_p$	-0.11	**-0.49**	**-0.63**	**0.39**	**0.46**	0.35	0.10	-0.17	0.31			
DMSO$_d$	0.36	0.14	**-0.52**	-0.23	-0.14	-0.07	0.04	0.03				
SO243												
DMS	-0.07	-0.09	**-0.61**	0.01	NA	0.21	-0.03	-0.26				

4.3.4 Seawater DMS comparison

DMS is heavily undersampled in the ETSP, especially for the coastal areas (defined as bathymetry < 300 m in this study), with only one other published DMS data set from June–July 1982 (Andreae, 1985). Coastal DMS concentration reported by Andreae (1985) was 6.5 ± 6.2 (1–43.9) nmol L^{-1} (Fig. 4.3e) which is much higher compared to the measurements reported here. However, Andreae (1985) reported comparable mean Chl *a* values (dominated by diatoms) and intermediate N:P ratios (9–11). Therefore, phytoplankton biomass or nitrogen limitation would not explain the extremely high DMS concentrations measured by Andreae (1985). One possible reason could be the seasonality of the upwelling strength, as upwelling is strongest in austral winter (Echevin et al., 2008) and more intense upwelling might be favourable to the biogenic production of DMS. This is in line with the highest DMS concentrations measured at the southern upwelling centres between Chimbote and Callao (> 40 nmol L^{-1}), where the most intense upwelling occurred (Andreae, 1985). A comparison with DMS data from other EBUS and the Arabian Sea illustrates that DMS concentrations off Peru (up to 44 nmol L^{-1}) are higher than those measured off northwest Africa (Mauritania and Morocco) (Belviso et al., 2003;

Franklin et al., 2009; Zindler et al., 2012), Benguela (Andreae et al., 1994), California (Herr et al., 2019) and the west Arabian Sea (Oman) (Hatton et al., 1999). Only DMS concentrations reported from the east Arabian Sea (Shenoy and Kumar, 2007) are comparable or much higher during non-upwelling or upwelling conditions, respectively (Fig. 4.5b). However, compared to global coastal DMS distributions, DMS concentrations in the Peru upwelling are in the average range (see Table 4.2 in Zhao et al., 2021), especially in October and December.

To examine our data in a broader context, DMS data from the global Surface Seawater DMS database (PMEL; http://saga.pmel.noaa.gov/dms) and DMS monthly climatology from Lana et al. (2011) have been extracted. Generally, DMS concentrations reported in our study are comparable to those from the PMEL database (Fig. 4.3f) (Hind et al., 2011) and the Lana climatology (background in Fig. 4.3e and 4.3f) in open ocean ETSP, which is close to those published in the equatorial Pacific (Bates and Quinn, 1997). Only DMS concentration data in October–November 2007 (triangles in Fig. 4.3f) are slighter lower in adjacent waters, which were more likely to be affected by advective processing from the coastal environments, especially considering that the PMEL 2007 cruise took place in a La Niña event indicated by ONI (ONI < -0.5 between July 2007 and July 2008), which likely triggers stronger westward propagation (Hu et al., 2014). Indeed, we measured lower DMS concentrations in the coastal region off Peru during SO243. In addition, to investigate the effects of ENSO events (represented by the ONI) on surface DMS concentrations in the ETSP, more DMS datasets are included, which covers the last four decades (Turner et al., 1996; Hatton et al., 1998; Huebert et al., 2004). The result indicates that no relationship is found between ONI and surface DMS concentrations in the ETSP (Fig. 4.5a), which is in agreement with the finding of a previous study in the equatorial Pacific Ocean (Bates and Quinn, 1997).

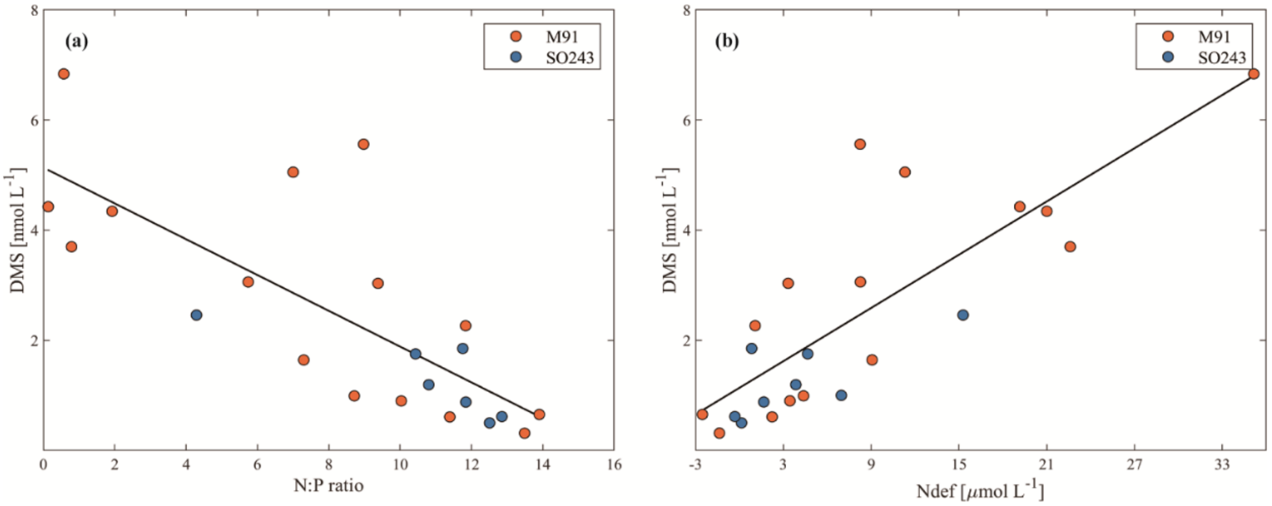


Figure 4.4: (a): N:P ratio vs. surface DMS concentrations in the coastal Peruvian upwelling (y = -0.32x + 5.14, $r^2 = 0.58$, $p = 3.61 \times 10^{-5}$, n = 22). (b): Ndef vs. surface DMS concentrations in the coastal Peruvian upwelling (y = 0.16x + 1.14, $r^2 = 0.67$, $p = 3.62 \times 10^{-6}$, n = 22).

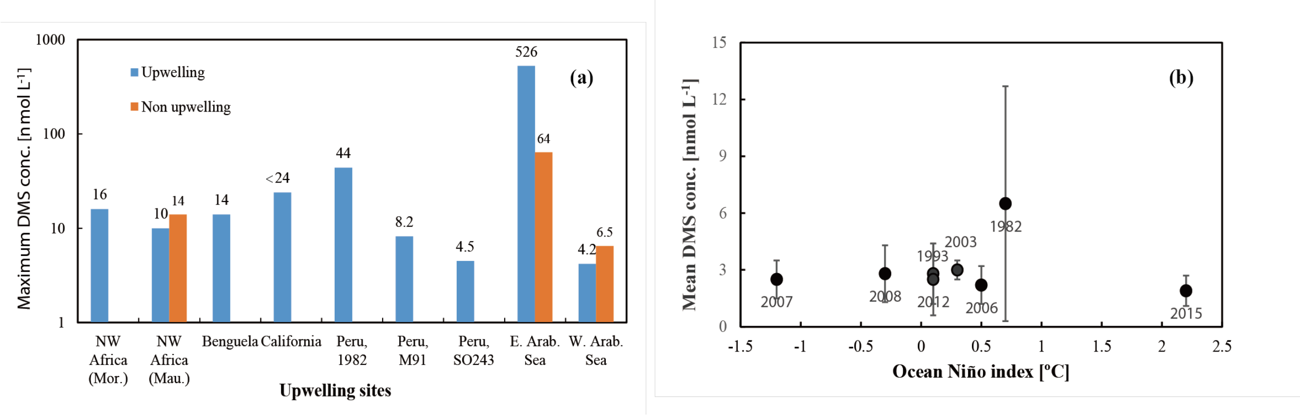


Figure 4.5. (a): Maximum DMS concentrations measured in various upwelling regions worldwide. Mor. stands for Morocco and Mau. stands for Mauritania. (b): Mean and standard deviation of DMS concentrations for each cruise in the ETSP. Note that the value from 2003 only includes the data east of 95 °W.

4.3.5 DMS fluxes

To our knowledge, this is the first report of atmospheric DMS distributions above the coastal Peruvian upwelling. We used the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT;

http://www.arl.noaa.gov/HYSPLIT.php) model to calculate air mass backward trajectories (24 h; starting height: 50 m) based on the DMS sampling sites for both cruises. The trajectories convey that the air masses encountered on both cruises were from the ocean for more than 24 h (Fig. 4.6a and 4.6b) and 48 h (figures not shown) prior to sampling and thus, the air masses sampled during the two campaigns most likely had not been affected by terrestrial DMS sources, which have been reported in South America and other terrestrial regions (see e.g., Crutzen et al., 2000; Meinardi, 2003; Chan et al., 2006; Jardine et al., 2015).

DMS mole fractions ranged from below the detection limit (~ 25 ppt) to 571.3 (mean: 144.6 ± 95.0) ppt during M91 (Fig. 4.7a), with the highest value measured around Pisco. Generally, DMS mole fractions did not follow the pattern of dissolved DMS in surface seawater during M91; however, they were affected by the wind speeds, which could affect the sea-to-air exchange process. This was supported by the positive correlation between atmospheric DMS mole fractions and wind speeds ($r = 0.39$, $p < 0.01$, n = 44). DMS mole fractions varied between 11.6 and 253.3 (mean: 91.4 ± 55.8) ppt during SO243 (Fig. 7b), with the same distribution as dissolved DMS in the surface layer ($r = 0.43$, $p < 0.01$, n = 96;). Generally, atmospheric DMS mole fractions measured in the open ocean ETSP (~ 100 ppt) during SO243 were within the same magnitude as those measured by Huebert et al. (2004) (~ 150 ppt) between 7.5 °N–7.5 °S over the equatorial Pacific Ocean. However, atmospheric DMS mole fractions measured over the coastal Peru upwelling were lower (~ 65 ppt) compared to those measured in similar regions during M91 (~200 ppt), which might be a result of the different seawater DMS concentrations between the two cruises (Fig. 4.7). Overall, the mean atmospheric DMS mole fractions measured during M91 and SO243 were comparable and they fell within the range between 61–340 ppt previously reported over the South Pacific Ocean (Marandino et al., 2009; Lee et al., 2010).

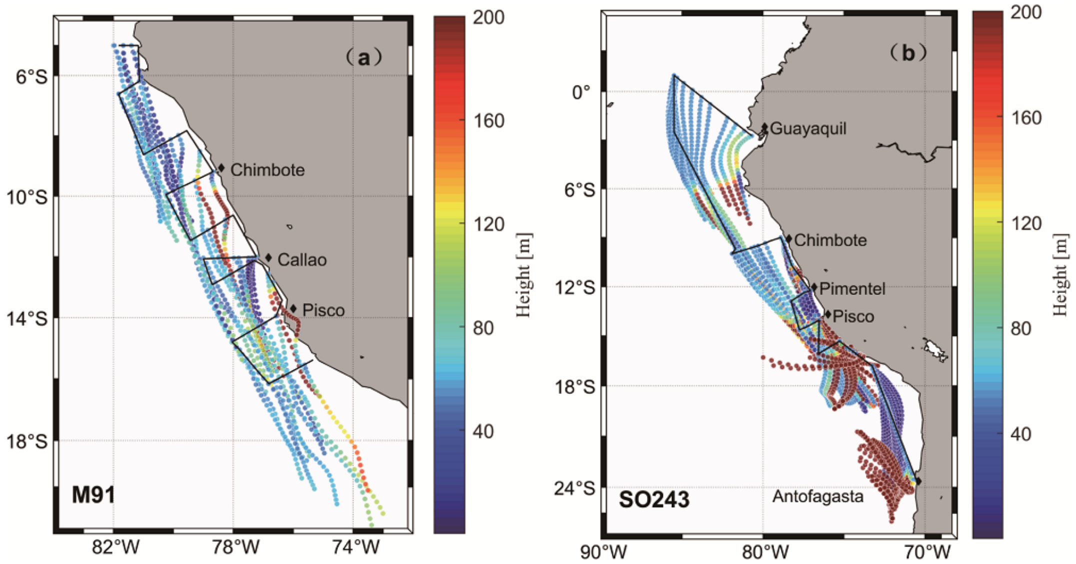


Figure 4.6. Air mass backward trajectories of cruise M91(a) and SO243 (b), with colorbar indicating the height above sea level. Note that both scales are capped at 200 m to ensure readability of the plots, despite that some values exceed the upper threshold.

DMS fluxes ranged from 0.4 to 28.2 (mean: 5.9 ± 5.3) µmol m^{-2} d^{-1} during M91 (Fig. 4.7a), with the highest value at station J1. Although a few coastal sampling sites where low wind speeds were associated with high seawater DMS concentrations (e.g., Callao), DMS fluxes generally showed a similar distribution as the seawater DMS distribution ($r = 0.68$, $p < 0.01$, n = 44) during M91. DMS fluxes during SO243 ranged between 0.3 and 30.5 (mean: 7.4 ± 5.4) µmol m^{-2} d^{-1} (Fig. 4.7b), with the peak DMS flux around the equator. DMS fluxes were mainly driven by seawater DMS concentrations ($r = 0.68$, $p < 0.01$, n = 93) and exhibited similar distributions: 10 ± 5.8 µmol m^{-2} d^{-1} in the equatorial section, 3.8 ± 2.7 µmol m^{-2} d^{-1} in the Peru upwelling section and 6.5 ± 3.7 µmol m^{-2} d^{-1} in the Chilean waters section. Overall, mean DMS fluxes obtained from M91 (5.9 ± 5.3 µmol m^{-2} d^{-1}) and SO243 (3.8 ± 2.7 µmol m^{-2} d^{-1}) over the coastal Peru upwelling are generally comparable to 5.5 µmol m^{-2} d^{-1} reported from Marandino et al. (2009) and 7.2 µmol m^{-2} d^{-1} from Omori et al. (2017) in the Southern Pacific Ocean, and slightly higher/comparable to those reported from Yang et al. (2011) in northern coastal Chile (~ 0–4 µmol m^{-2} d^{-1}). In addition, the difference of DMS flux calculation with and without considering the atmospheric DMS mixing ratios indicates DMS fluxes (calculated only by seawater DMS) were not greatly overestimated (< 10 %) in the Peru upwelling region.

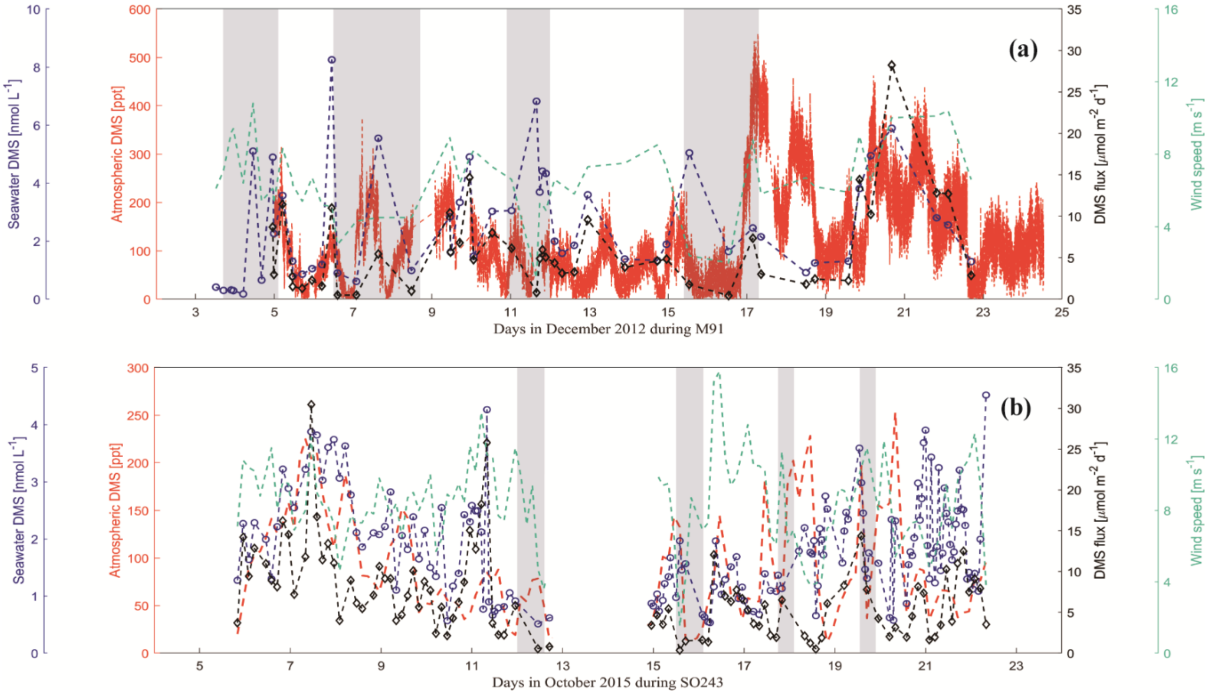


Figure 4.7: Atmospheric DMS mole fractions (red dash line), surface seawater DMS concentrations (blue circles) and DMS fluxes (black diamonds) and wind speeds (green dash line) during the cruise M91 (a) and SO243 (b). Grey rectangles (a and b) indicate coastal CTD stations for both cruises. Note that DMS mole fractions during M91 were averaged for 10 min to calculate fluxes.

4.4 Summary

As one of the world's most productive oceanic regions, the upwelling region off Peru is of great interest for studying biogenic trace gas production and its emissions to the atmosphere. We present here, for the first time, simultaneously measured DMS/P/O seawater concentrations and DMS atmospheric mole fractions from the Peruvian upwelling region during two cruises in December 2012 and October 2015. Large variations were determined in seawater DMS concentrations off Peru upwelling. Anticorrelations were found between nutrient availability (represented by the N:P ratios) and sulphur compounds, which may reinforce their potential roles as antioxidants in response to oxidative stress. We found a significant relationship between DMS concentrations and nitrogen availability related indicators in the coastal region, pointing to the importance of the interaction between environmental parameters and DMS distributions in the Peruvian upwelling, where diatoms dominate the algal assemblages. DMS fluxes, computed with seawater and atmospheric DMS measurements, indicated that the coastal region off Peru upwelling was a moderate source of DMS to the atmosphere in both December 2012 and October 2015. Further attention should be given to the improvement of the understanding of DMS cycling as well as its underlying production and consumption processes (e.g., regular monitoring) since our study reveals highly variable season/interannual DMS concentrations in the Peru upwelling system.

4.5 Data availability.

DMS data for the M91 and SO243 cruises have been submitted to the NOAA PMEL database (http://saga.pmel.noaa.gov/dms). Phytoplankton pigment data for M91 and SO243 are available at PANGAEA at https://doi.pangaea.de/10.1594/PANGAEA.864786 and https://doi.pangaea.de/10.1594/PANGAEA.898920, respectively. For further data, please contact the corresponding author (yzhao@geomar.de).

4.7 Acknowledgements.

We thank the captain and crew of the R/V Meteor during cruise M91 and R/V Sonne during cruise SO243, as well as the co-chief scientist Damian Grundle (SO243). We would like to thank Patrick Veres and Bettina Derstroff for the atmospheric DMS measurements during M91 as well as Luisa Hannig, Jens Radde, Helge Wieck, and Verena Ihnenfeld for measuring the samples of dissolved DMS/P/O from M91. We would like to thank Kerstin Nachtigall for nutrient measurements (M91), Sonja Wiegmann for HPLC pigment analysis (M91, SO243) and Martina Lohmann for nutrient measurements (SO243). We also thank Dr. Philip Froelich for providing data from the cruise the R/V Robert Conrad in 1982. The authors gratefully acknowledge NASA for providing the MODIS-Aqua satellite data as well as NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT model used in this publication. The cruise M91 was part of the German research projects SOPRAN II (grant no. FKZ 03F0611A) and III (grant no. FKZ 03F0662A) funded by the Bundesministerium für Bildung und Forschung (BMBF). The cruise SO243 was financed by the BMBF through grant 03G0243A. Astrid Bracher's contribution was supported by the Helmholtz Infrastructure Initiative

FRAM. Elliot Atlas acknowledges support from the NASA Upper Atmosphere Research Program Grants NNX13AH20G and NNX17AE43G. Yanan Zhao is grateful to the China Scholarship Council (CSC) for providing financial support (File No. 201606330066).

4.8 Supporting Information

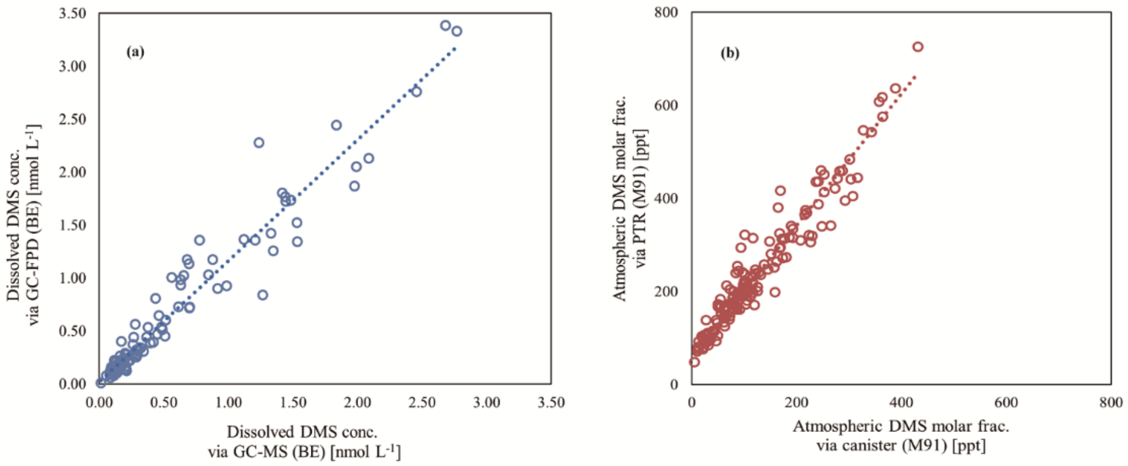


Figure S4.1. (a): Dissolved DMS conc. via GC-MS (BE) vs. dissolved DMS conc. via GC-FPD (BE): y = 1.14x + 0.02, r^2 = 0.94, n = 121. (b): Atmospheric DMS molar fractions via PTR (M91) vs. atmospheric DMS molar fractions via the canister (M91): y = 1.43x + 59.87, r^2 = 0.93, n = 155. Atmospheric DMS data via PTR were averaged over the filling time of those via the canister and included two min prior and two minutes post filling. As stated in the main text, the two atmospheric measurements were well correlated but not exactly on the 1:1 line (Fig. S1b). The PTR measurements were slightly higher than the GC measurements. This was not tested in the laboratory, but there might be some potential reasons for the discrepancy between the two instruments. For instance, the canisters can experience loss during storage, leading to lower values, and the PTR cannot distinguish between compounds at the same mass, leading to potentially higher values. In addition, it is possible that some issues occurred with the calibration and standardization which applied in one or both techniques and, therefore, led to the discrepancy between the two instruments. The latter is the most likely explanation, as the loss/artifact explanation would be unlikely to produce the good correlation between the methods. However, considering the exact reasoning cannot be addressed at this late stage, we proceed as outlined in the main text.

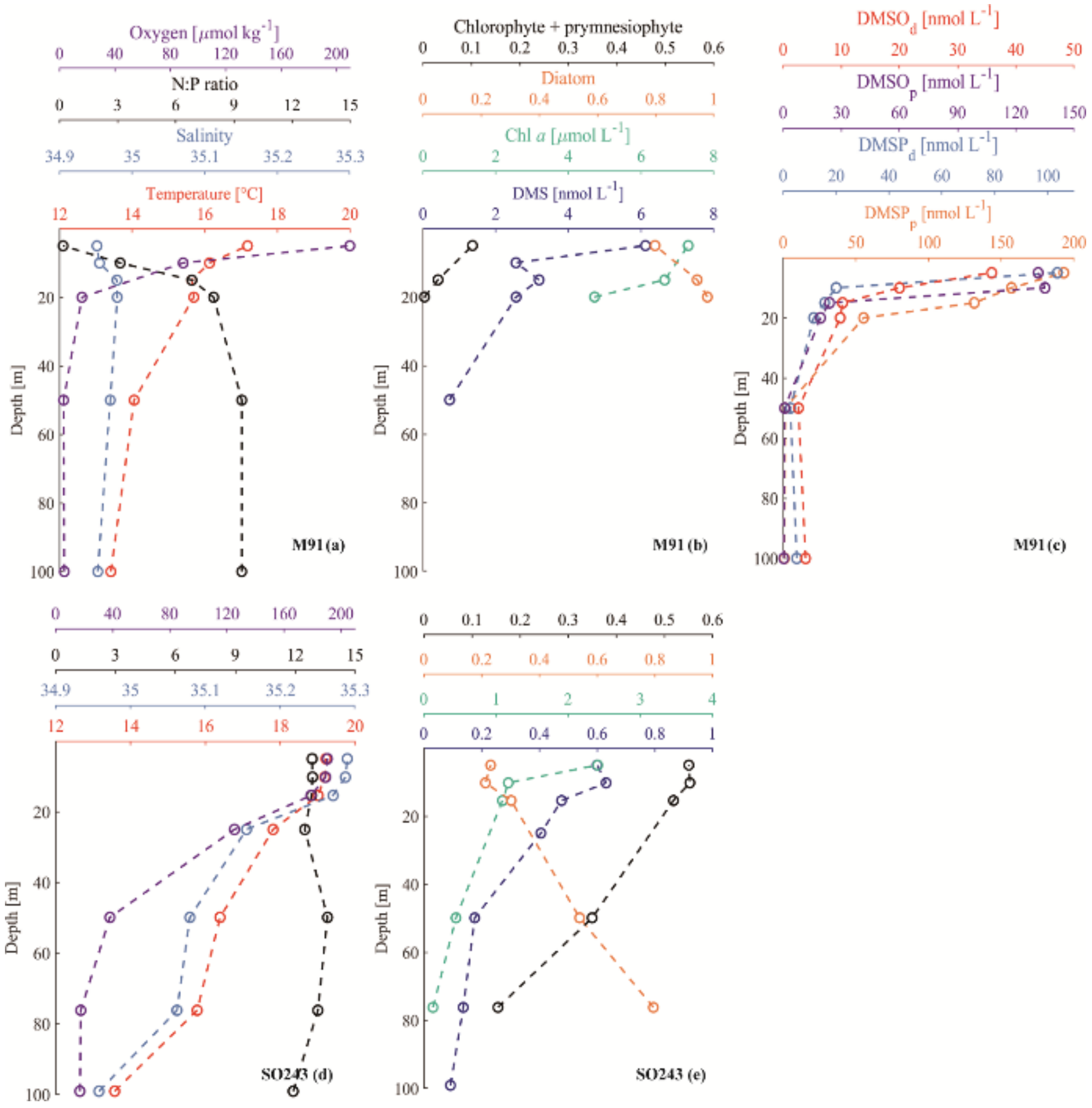


Figure S4.2. Selected depth profiles of temperature, salinity, N:P ratio, oxygen, Chl *a*, relative abundance of phytoplankton groups (diatom, sum of chlorophyte and prymnesiophytes) and DMS, as well as other sulfur compounds (only M91) such as DMSP$_p$, DMSP$_d$, DMSO$_p$ and DMSO$_d$ at the geographically similar shelf stations F4 and 11 in December 2012 (a–c) and October 2015 (d and e), respectively.

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5 Dimethylated sulfur compounds and bromoform in the Southwest Indian Ocean

Manuscript in preparation: Zhao, Y., Booge, D., Marandino, C. A., Schlundt, C., Bracher, A., Quack. B and Bange, H. W.: Dimethylated sulfur compounds and bromoform in the Southwest Indian Ocean.

Abstract. The southwestern Indian Ocean (SWIO) is a globally significant source of the climate-active gas dimethyl sulfide (DMS) to the atmosphere, yet the processes driving oceanic DMS variability in this region are poorly understood. In the present study, DMS and related dimethylated sulfur compounds dimethylsulfoniopropionate (DMSP) and dimethyl sulfoxide (DMSO) were determined simultaneously in the SWIO during two cruises of SO234-2 (8–20 July 2014) and SO235 (23 July–8 August 2014). Significant variation in DMS, total DMSP ($DMSP_t$) and total DMSO ($DMSO_t$) concentrations was observed in surface seawater, with higher concentrations measured during SO235, especially around the Mascarene Plateau, which might be related to the enhanced nutrient concentrations. Vertical profiles of sulfur compounds showed typical oceanic patterns with maxima in the subsurface layer, which paralleled with haptophytes and total bacteria counts. For the first time, we validated the hypothesis that hypobromous acid (HOBr) might be a potential sink for marine DMS by using observational data of DMS, $DMSO_t$ and bromoform ($CHBr_3$).

5.1 Introduction

The biogenic trace gas dimethyl sulfide (DMS) has been hypothesised to affect cloud properties and modulate cloud albedo via forming sulfate aerosols in the atmosphere, thus regulating Earth's radiation budget (Charlson et al., 1987). However, this hypothesis is still under debate (Quinn and Bates, 2011). Oceanic DMS originates from its precursor dimethylsulfoniopropionate (DMSP), which is synthesised in phytoplankton cells, and there are species-specific differences in DMSP production (Keller, 1989), which in turn, are affected by the nutrient status of the cells (Stefels, 2000). However, the process of DMSP conversion to DMS (i.e., cleavage pathway), which depends on complex food web interactions, is only of minor importance for DMSP loss, as up to 75 % of DMSP is metabolised by marine bacterioplankton through the demethylation pathway (Moran et al., 2012). Relative to DMSP and DMS, the production and consumption pathways of dimethyl sulfoxide (DMSO) remain poorly understood. Nonetheless, DMSO is present throughout the surface ocean and is known to be a photochemical and biological oxidation product of DMS (Hatton et al., 2012). Similarly, some studies showed that DMSO could be directly synthesised in marine phytoplankton cells (Simó et al., 1998). Furthermore, it has been suggested that DMSP and DMSO exert similar intracellular functions (e.g., cryoprotection and antioxidation) (Simó et al., 1998; Sunda et al., 2002) and can be an important carbon and sulfur source for marine bacteria (Kiene et al., 2000; Dixon et al., 2020). Overall, DMS, DMSP and DMSO play important physiological and ecological roles for the marine plankton community and are key to understanding sulfur biogeochemical cycling in the oceans (Simó, 2004; Stefels et al., 2007).

Halogenated very short-lived substances (VSLSs) are naturally produced in the ocean originating from chemical and biological sources (e.g., macroalgae and phytoplankton) (Quack and Wallace, 2003). When emitted to the atmosphere, the halogenated VSLSs can be transported to the stratosphere by tropical deep advection and participate in ozone depletion by contributing to the halogen burden, thus impacting the climate (Hossaini et al., 2015). Bromoform ($CHBr_3$) is one of the most important biogenic VSLSs because it is the largest single natural source of atmospheric organic bromine (Hossaini et al., 2012). $CHBr_3$ is produced by the reaction of dissolved organic matter (DOM) with hypobromous acid (HOBr), which can be released from extracellular bromoperoxidase (V-BrPO). In addition to the reaction between HOBr and DOM, recently, Müller et al. (2019) suggested HOBr could react with marine DMS to produce DMSO, representing a potentially neglected DMS sink. Moreover, further experiments carried out by Müller et al. (2021) pointed out that the reaction of HOBr and DMS might lead to the suppression of $CHBr_3$ production. However, these findings have not been examined in marine environments to date.

The Indian Ocean is considered a key region that profoundly impacts climate change on regional and global scales (Schott et al., 2009). The major upper oceanographic regimes of the Indian Ocean are the monsoon-driven tropical and subtropical Northern Hemisphere circulation and the Southern Hemisphere subtropical gyre circulation, which are separated by the South Equatorial Current (Schott et al., 2009). One relevant feature for the Indian Ocean is the occurrence of wind-driven open ocean upwelling (i.e equatorial upwelling) at 5–10 ºS, where Ekman drift transports water southward from the northern edge of the trades (Schott et al., 2009). In addition, the West Indian Ocean experienced more rapid warming than any other tropical ocean over the last century (Roxy et al., 2014), causing a reduction in marine primary production (Roxy et al., 2016), which potentially influences seawater DMS and $CHBr_3$ concentrations (Miles et al., 2012; Hepach et al., 2016).

On a global scale, the southwest Indian Ocean (SWIO) is a hotspot for DMS emissions during July and August (Lana et al., 2011; Zavarsky et al., 2018); however, the processes driving oceanic DMS variability in this region are poorly understood. Most studies conducted so far have been concentrated in the northern Indian Ocean, particularly in the Arabian Sea and the Bay of Bengal (see e.g., Shenoy et al., 2006, 2012). Therefore, to improve our current understanding of dimethylated sulfur compound cycling in the SWIO, we present measurements of DMS/P/O and $CHBr_3$, as well as abiotic and biotic parameters in the SWIO during the two research campaigns SO234-2 (8–20 July 2014) and SO235 (23 July–8 August 2014). The overarching objectives in this study are to (i) decipher horizontal and vertical patterns of DMS/P/O, (ii) identify the main drivers of DMS/P/O cycling in the SWIO, and (iii) explore the potential relationship between DMS/DMSO and $CHBr_3$.

5.2 Methods

The fieldwork was conducted on board the R/V *Sonne* sailing from Durban, South Africa, to Port Louis, Mauritius (SO234-2, 8–20 July 2014) and from Port Louis, Mauritius, to Malé, Maldives (SO235, 23 July to 8 August 2014), with cruise tracks depicted in Fig. 1. The cruises covered the area between 3 °N–30 °S, where the trade wind regime predominantly affects the hydrographic settings in the SWIO.

5.2.1 Sulfur compound and bromoform measurements

During SO234-2 and SO235, underway samples were measured from a constant seawater supply pumped from the ship's moon pool at 5 m water depth (3 h sampling interval). Profiles were made between 5–150 m water depth from 24 × 10 L Niskin bottles mounted on a standard CTD-Rosette. DMS concentrations were measured using a purge and trap system attached to a gas chromatograph-mass spectrometer (GC-MS; Zavarsky et al., 2018). Total DMSP ($DMSP_t$) and total DMSO ($DMSO_t$) concentrations were analysed by purge and trap coupled to a gas chromatograph-flame photometric detector (GC-FPD) as described in Zindler et al. (2012, 2013). Briefly, DMS samples were measured immediately after collection during the cruise, while $DMSP_t$ and $DMSO_t$ samples were measured after returning to the lab. After DMS was measured, sodium hydroxide (NaOH; Carl Roth, Germany) was added to the samples to convert $DMSP_t$ into DMS. $DMSO_t$ was measured from the same $DMSP_t$ samples by adding cobalt-dosed sodium borohydride (NaBH4; Sigma-Aldrich, Germany). The mean precisions of DMS, $DMSP_t$ and $DMSO_t$ measurements are ± 6 %, ± 15 % and ± 18 %, respectively. Calibrations were performed with a liquid standard prepared in ethylene glycol.

$CHBr_3$ samples were generally taken in parallel with DMS samples during both cruises. The samples were then analysed using a purge and trap system attached to a GC-MS, described in more detail in Hepach et al. (2016). An analytical reproducibility of 10 % was determined by measuring duplicate water samples. Calibration was performed with a liquid mixed-compound standard prepared in methanol.

5.2.2 Phytoplankton pigment and bacteria measurements

Phytoplankton pigment and bacteria samples were generally taken in parallel with DMS samples during both cruises. Pigment samples were filtered through Whatman GF/F filters and then were stored at -80 °C until analysis. Phytoplankton pigments, as described in Taylor et al. (2011), were analysed using high-performance liquid chromatography (HPLC), according to Barlow et al. (1997). Phytoplankton composition was derived from marker phytoplankton pigment concentrations and chlorophyll concentrations by analysing the diagnostic pigments developed by Vidussi et al. (2001) and subsequently refined by Uitz et al. (2006). This method uses marker pigments as proxies combined with pigment specific weight coefficients to estimate phytoplankton composition. Identified phytoplankton groups include diatoms, dinoflagellates, cryptophytes, chlorophytes, chrysophytes, haptophytes, cyanobacteria (excluding *Prochlorococcus*), and *Prochlorococcus*, which are assumed to represent the entire phytoplankton community.

For measuring bacterial cell counts, 4 µl of the samples were preserved with 200 µL glutaraldehyde (1 % *v*/*v* final concentration) and stored at -20 °C until analysis. SYBR Green I (Invitrogen) stock solution was prepared by mixing 5 µL of the dye with 245 µL dimethyl sulfoxide (Sigma Aldrich, Germany). Ten microliters of the dye stock solution and 10 µL of Fluoresbrite YG microspheres beads (diameter 0.94 µm, Polysciences) were added to 400 µL of the thawed sample and incubated for 30 min in the dark. The samples were then analysed at a low flow rate using a flow cytometer (FACSCalibur, Becton Dickinson) (Gasol and Giorgio, 2000). Trucount beads (Becton Dickinson) were used for calibration and in combination with Fluoresbrite YG microsphere beads (0.5–1 µm, Polysciences) for absolute volume calculation. Calculations were done using the software program "CellQuest Pro". Measurements of oceanographic parameters such as nutrients are described in Booge et al. (2018).

5.2.3 Mixed-layer depth, euphotic depth, and photosynthetically available radiation

Mixed-layer depth (MLD) was obtained from climatological monthly means (Montégut et al., 2004) and compared to those calculated by in-situ CTD (conductivity, temperature and depth) profiles. MLD was defined as the depth at which the temperature is at least 0.2 °C higher or lower than the temperature at 10 m depth (Montégut et al., 2004). The euphotic depth (Z_{eu}) was calculated from the Chl *a* profile for all stations using the approximation by Morel and Berthon (1989), which was further refined by Morel and Maritorena (2001). Further details can be found in Booge et al. (2018).

Due to the absence of underwater light data during the cruises, global radiation data from the ship's meteorological station as well as the light attenuation coefficients (determined from the Chl *a* concentration profiles) were used to calculate the photosynthetically available radiation (PAR) within the water column during a day. To account for the variation during the day, PAR above the surface layer ($PAR0^+$) derived from the hourly resolved global radiation data was fitted with a sine function. In short, $PAR0^+$ in µmol m^{-2} s^{-1} during the course of a day was calculated via daily global radiation values multiplied by a factor of 2 (Jacovides et al., 2004). PAR at each depth (z) in the water column was calculated employing Beer-Lambert's law:

$$PAR\ (z) = PAR\ (0^{+}) \times e^{-z \times k_d}, \tag{5.1}$$

where K_d (PAR) is the diffuse attenuation coefficient for PAR and calculated as follows:

$$K_d(PAR) = \frac{4.6}{Z_{eu}} \tag{5.2}$$

The comparison between fitted PAR profiles (PAR (z)) and directly measured downwelling PAR (E_dPAR) shows that PAR (z) obtained from the ship's global radiation data and chlorophyll profiles were robust (see Fig. S2 in Booge et al. (2018)).

5.3 Result and discussion

5.3.1 Environmental settings

The oceanographic conditions during SO234-2 and SO235 were described elsewhere (see e.g., Fiehn et al., 2017; Booge et al., 2018; Ma et al., 2018), and therefore, only the main features are briefly described here. The cruises took place during the Asian summer monsoon season and traversed a range of oceanic regimes, including the Agulhas Current, the Indian Ocean Gyre, the South Equatorial Current, the Equatorial Countercurrent, and the North Equatorial Current. Additionally, equatorial overturning cells described in Schott et al. (2009) and the shallow Mascarene Plateau were also traversed. Sea surface temperature (SST; Fig. 5.1a) ranged between 18.8–31.5 °C, and sea surface salinity (SSS; Fig. 5.1b) varied from 34.3 to 35.8. Generally low nutrient concentrations (e.g., DIN (the sum of nitrate and nitrite) < 1 µmol L^{-1} and dissolved phosphate < 0.2 µmol L^{-1}; Fig. 5.1c and 5.1d) were measured within the mixed layer depth (mean: ~60 m), excluding occasionally enhanced nutrient concentrations between 5–10 °S. Prevailing south-easterly winds south of the Equator and south-westerly winds north of the Equator were encountered during the cruises, with the average wind speeds of 10.3 m s^{-1} during SO243-2 and then gradually decreasing until the Maldives, after reaching the maximum (16.4 m s^{-1}) north of Mauritius (Zavarsky et al., 2018).

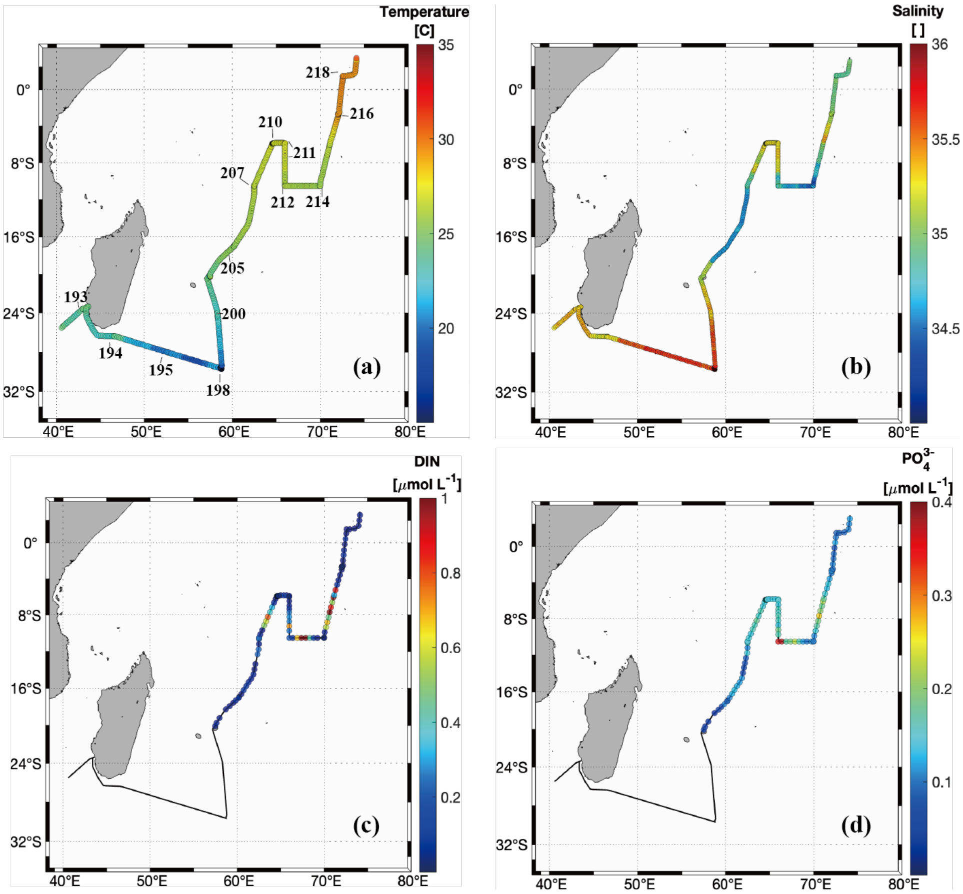

Figure 5.1. Surface distributions of temperature (a), salinity (b), DIN (c) and PO_4^{3-} (d) during SO234-2/SO235. The numbers in (a) indicate the day of the year (DOY) as well as stations where a depth profile was performed. Black solid lines in a–d indicate the cruise tracks of SO234-2/SO235. Note that underway measurements were not performed for nutrients during SO234-2 and only a few cases exceeded 1 µmol L^{-1} DIN concentration.

5.3.2 Surface distributions of Chl *a*, DMS, $DMSP_t$ and $DMSO_t$

Surface Chl a concentration ranged between 0.1–1.4 (mean ± SD: 0.3 ± 0.2) µg L^{-1} (Fig. 5.2a), coinciding with generally low nutrient concentrations. Throughout the cruises, the three dominant phytoplankton groups were Prochlorococcus (relative abundance: 39 ± 10 %), haptophytes (23 ± 9 %) and cyanobacteria (23 ± 8 %), while other phytoplankton groups were minor constituents. The surface distribution of DMS during SO234-2/SO235 was described by Zavarsky et al. (2018). Briefly, DMS concentrations ranged from 0.4 to 5.2 (mean ± SD: 1.2 ± 1.1) nmol L^{-1} (Fig. 5.2b), with elevated concentrations (as well as maxima) in the north of Mauritius between 5–18 °S. Surface DMS concentrations presented in this study are generally lower than those previously reported in July/August in the SWIO (Mihalopoulos et al., 1992; Spencer et al., 2005), primarily due to different sampling locations around the Mascarene Plateau (Spencer et al., 2005).

Surface $DMSP_t$ and $DMSO_t$ concentrations ranged from 2.8 to 26.2 (mean ± SD: 9.2 ± 6.4) nmol L^{-1} and from 1.1 to 12.4 (mean ± SD: 4.3 ± 3.0) nmol L^{-1}, respectively (Fig. 5.2c and 5.2d). The patterns of $DMSP_t$ and $DMSO_t$ were comparable to DMS, with elevated values (as well as maxima) between 5–18 °S. Our $DMSP_t$ concentrations are consistent with previously measured concentrations during the northeast monsoon season in the central Indian Ocean (1.3–35.9 nmol L^{-1}) (Shenoy and Kumar, 2007). DMSO concentrations have been reported in coastal areas (see e.g., Shenoy et al., 2012; Bepari et al., 2020); however, this is the first time that DMSO concentrations have been reported in the open Indian Ocean. $DMSP_t$ and $DMSO_t$ have a significant relationship (Table 1), as reported in many studies (e.g., Zindler et al., 2013; Zhao et al., 2021). The mean ratio of $DMSP_t$: $DMSO_t$ was 2.5 ± 1.6 in surface seawater in this study, which agrees with the widespread finding that DMSP dominates over DMSO in the surface ocean (Simó and Vila-Costa, 2006). Moreover, our data fits to the inverse relationship between $DMSP_p$: $DMSO_p$ ratios and SST first proposed by Simó and Vila-Costa (2006) (see Fig. 5 in Zindler et al. (2013)). Our average values ($DMSP_t$: $DMSO_t$ ratio: 2.5, SST: 24.7 °C) support the hypothesis that increased solar radiation induces oxidative stress within phytoplankton cells and stimulates the production of DMSO via a cascade system (DMSP-DMS-DMSO), which is an efficient scavenger for reactive oxygen species (Sunda et al., 2002).

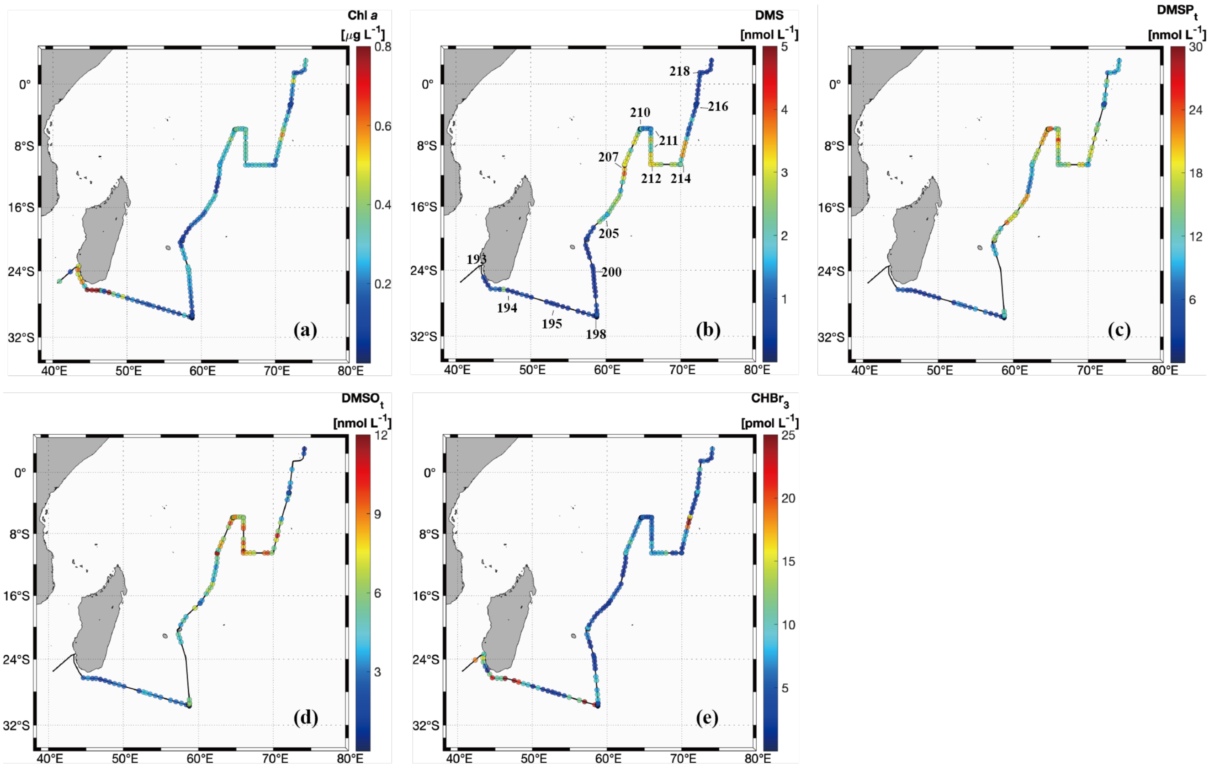

Figure 5.2. Surface distributions of Chl *a* (a), DMS (b), $\mathrm{DMSP_t}$ (c), $\mathrm{DMSO_t}$ (d) and $\mathrm{CHBr_3}$ (e) during SO234-2/SO235. Black solid lines in a–e indicate cruise tracks of SO234-2/SO235, and the numbers in (b) indicate DOY as well as stations where a depth profile was performed. Note that no measurements of $\mathrm{DMSP_t}$ and $\mathrm{DMSO_t}$ were performed between DOY 198–200. Only a few cases exceeded 0.8 µg L^{-1} Chl *a* concentration and 25 pmol L^{-1} ChBr3 concentration.

5.3.3 Controlling factors of surface dimethylated sulfur compounds

A principal component analysis (PCA) of the surface seawater parameters was performed to investigate the abiotic and biotic variables controlling the variability of dimethylated sulfur compounds in the SWIO (Fig. 5.3). Two principal components were extracted from these factors, accounting for 57.7 % and 59.2 % of the total variability for SO234-2 and SO235, respectively. During SO234-2, DMS played an insignificant role in explaining the variation on PC1, while $\mathrm{DMSP_t}$ and $\mathrm{DMSO_t}$ had positive loadings on PC2. Additionally, dimethylated sulfur compounds and biotic variables (e.g., Chl *a* and haptophytes) did not gather in this plot (Fig. 5.3a). During SO235, all dimethylated sulfur compounds had clear positive loadings on PC1 (Fig. 5.3b). In contrast to SO234-

2, significant correlations were observed between dimethylated sulfur compounds and Chl *a*/haptophytes as well as nutrient data (see also Table 5.1). Considering Chl *a* concentration and the relevant abundance of haptophytes were consistent between SO234-2 and SO235 (except for the southern tip of Madagascar), nutrient concentrations might lead to the different patterns of dimethylated sulfur compounds in the two PCA plots. During SO234-2, the near-surface layer is mainly driven by the South Indian Ocean Countercurrent (Siedler et al., 2006), and it is primarily characterised as an oligotrophic oceanic environment. Therefore, oceanic nutrient limitation might decrease $DMSP_t$ and $DMSO_t$ production by limiting phytoplankton growth rates, thus weakening the linkage between sulfur compounds and Chl *a*/certain phytoplankton classes (e.g., haptophytes, which are considered as strong DMSP producers) (Anderson et al., 2018). Given the complex interplay within the DMS production and loss processes, it is reasonable that no variables were grouped with DMS during SO234-2. During SO235, the near-surface layer is mainly dominated by the South Indian Ocean Current (SEC) (Schott et al., 2009), which flows westward crossing the Mascarene Plateau, which is considered as a productive region due to the upwelling of nutrients (New et al., 2005; Spencer et al., 2005). Therefore, the elevated dimethylated sulfur compound concentrations during SO235 were possibly related to the enhanced nutrient (e.g., DIN and PO_4^{3-}) concentrations, which might stimulate the production and synthesis of sulfur compounds within certain phytoplankton classes (e.g., haptophytes). Overall, surface dimethylated sulfur compound distributions were subject to two disparate regimes (oligotrophic and productive regions), and biological factors played a predominant role during SO235.

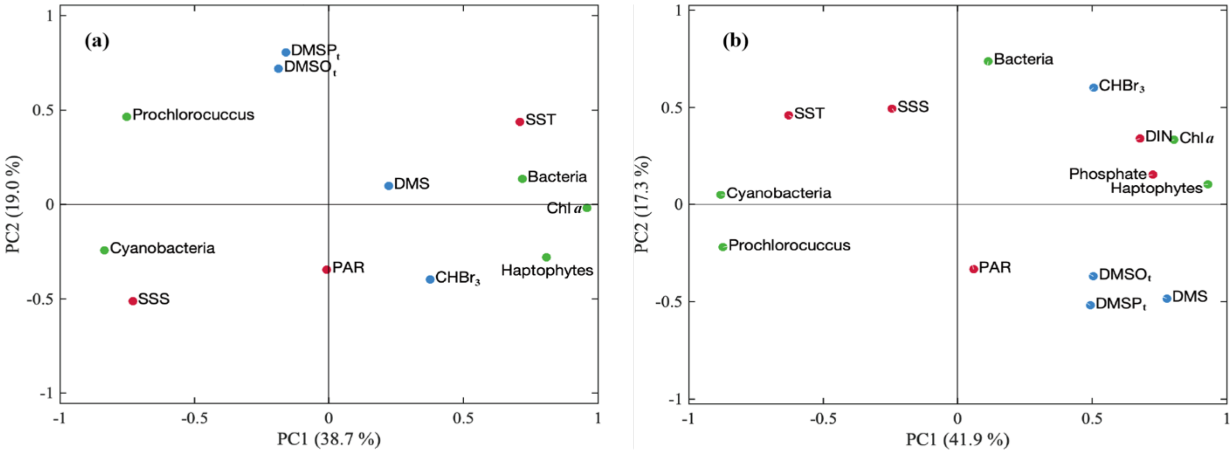

Figure 5.3: Principal component analysis of 12 and 14 variables measured in surface waters of southwest Indian Ocean during SO234-2 (a) and SO235 (b), respectively. The data matrix includes biogenic sulfur compound and bromoform (blue circles; DMSP$_t$, DMS, DMSO$_t$ and CHBr$_3$), biotic variables (green circles; Chl *a*, total bacteria counts, and the relative abundance of selected phytoplankton groups) and abiotic variables (red circles; PAR, SST, SSS, DIN and PO$_4^{3-}$).

5.3.4 Potential relationship between DMS and CHBr$_3$

The surface distribution of CHBr$_3$ during SO234-2/SO235 was described in Fiehn et al. (2017). CHBr$_3$ ranged from 1.3 to 33.4 (7.1 ± 5.8) pmol L^{-1} (Fig. 2e), with elevated concentrations (> 10 pmol L^{-1}) south of Madagascar and the open Indian Ocean between 5–10 ºS and 25–30 ºS, which was generally coincident with the Chl *a* distribution. Similarly, CHBr$_3$ showed positive correlations with haptophytes during SO235 (Table 5.1), suggesting they may contribute to CHBr$_3$ production (Liu et al., 2013). CHBr$_3$ was not directly correlated to the dimethylated sulfur compounds in this study. As suggested by Müller et al. (Müller et al., 2019, 2021), HOBr could react with DOM to produce CHBr$_3$ or react with DMS to produce DMSO in seawater, and the reaction between HOBr and DMS may lead to the suppression of CHBr$_3$ production. Therefore, we used the ratio of CHBr$_3$: DMSO$_t$ (i.e., two end products of the reaction between HOBr and DOM/DMS) to investigate the potential DMS-HOBr-DOM competitive mechanism in seawater. We observed elevated CHBr$_3$:DMSO$_t$ ratios combined with CHBr$_3$ > 10 pmol L^{-1} (marked as triangles in Fig. 5.4a) when DMS concentration was generally low, and the ratios became constantly lower (as well as CHBr$_3$ < 10 pmol L^{-1}) when DMS concentration was increasing (Fig. 5.4a). Moreover, we observed elevated CHBr$_3$:DMSO$_t$ ratios when CHBr$_3$ concentrations increased combined with low DMS concentrations (marked as triangles in Fig. 5.4b).

Both figures imply that the decrease of $CHBr_3$ concentrations was attributed to the higher DMS concentration, which can consume more HOBr and simultaneously produce more DMSO, thus leading to lower $CHBr_3$:$DMSO_t$ ratios (Müller et al., 2021). When DMS concentrations were low, the reaction between HOBr and DMS become less competitive and thereby more CHBr3 could be produced via the reaction between HOBr and DOM. Therefore, it is reasonable to assume that in the SWIO, DMS concentrations may influence the formation of $CHBr_3$ via reactions between HOBr and DOM and accordingly, HOBr could be a sink for marine DMS.

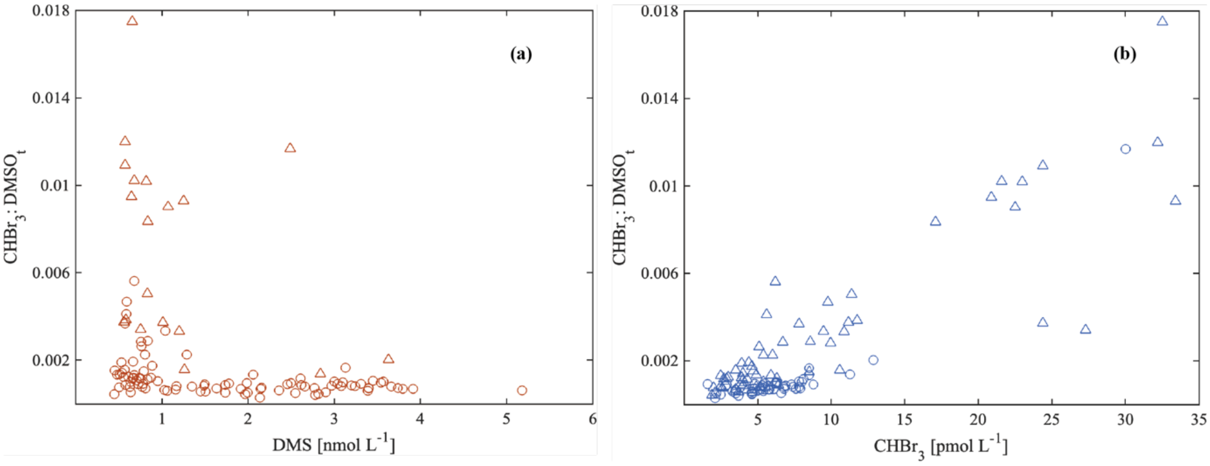

Figure. 5.4: (a): Scatter plot of measured DMS concentration versus $CHBr_3$:$DMSO_t$ ratio during SO234-2/SO235. (b): Scatter plot of measured $CHBr_3$ concentration versus $CHBr_3$:$DMSO_t$ ratios during SO234-2/SO235. Triangles in (a) and (b) represent $CHBr_3$ > 10 pmol L^{-1} and DMS < 1.5 nmol L^{-1}, respectively.

5.3.5 Vertical distributions of dimethylated sulfur compounds and $CHBr_3$

Averaged profiles of various variables are shown in Fig. 5.5. In agreement with previous studies conducted in open ocean environments, dimethylated sulfur compound and $CHBr_3$ concentrations presented in this study were mostly restricted to the MLD and reached their maxima at around 30 m and 55 m, respectively (Wong et al., 2005; Quack et al., 2007; Lee et al., 2010). Below the subsurface maxima, sulfur compound and $CHBr_3$ concentrations decreased as water depth increased. In general, $CHBr_3$ showed a similar vertical distribution of Chl *a*, suggesting a local biological source (Quack et al., 2004). In contrast, sulfur compounds and Chl *a* presented different profile patterns, which had been reported in other studies (see e.g., Simo et al., 1997; Aranami, 2004). In this study, we observed that sulfur compound maxima paralleled those of relative abundance of haptophytes and total bacterial counts within the MLD, with the former being strong DMSP producers (Keller, 1989) and the latter being considered as the major consumers (heterotrophic biological consumption) for sulfur compounds in marine environments (Valle et al., 2009). Therefore, we concluded that sulfur compound profiles are primarily shaped by marine organisms above the MLD in the SWIO.

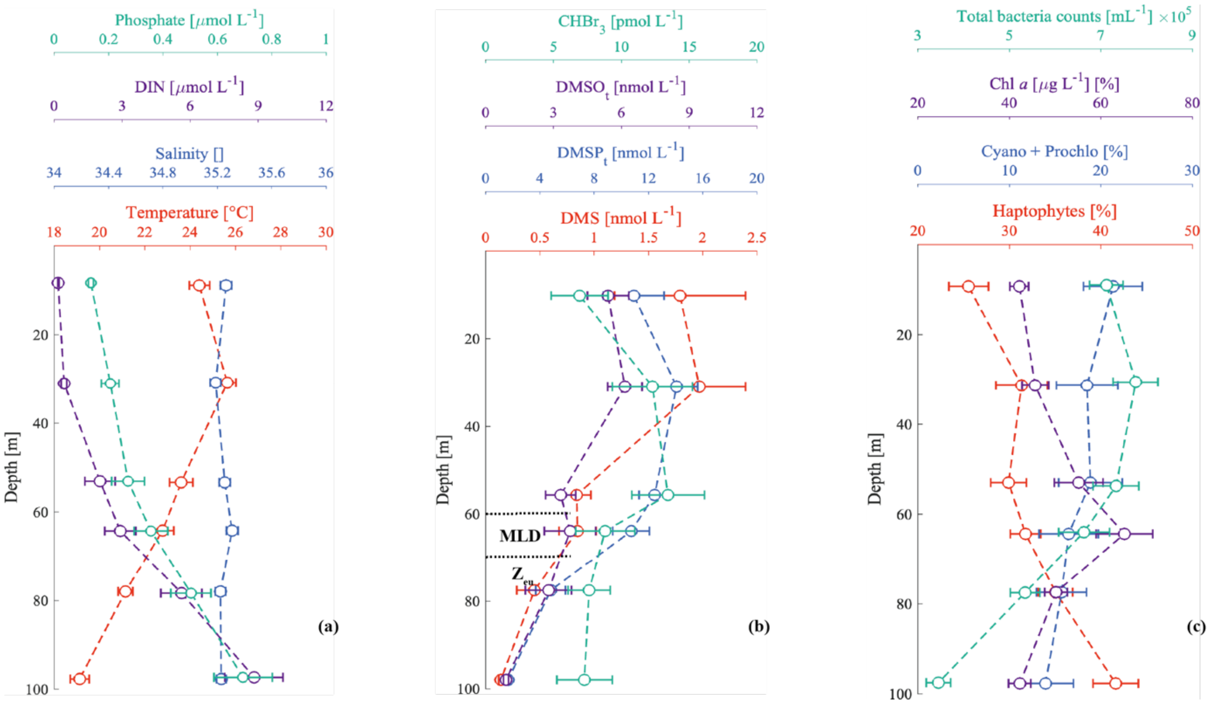

Figure. 5.5. (a): Depth profiles of temperature, salinity, DIN, and phosphate. (b): Depth profiles of DMS, DMSP$_t$, DMSO$_t$ and CHBr$_3$. (c): Depth profiles of relative abundance of haptophytes, the sum of cyanobacteria and *Prochlorococcus* Chl and total bacteria counts. Depth profiles were calculated as mean depth profiles from all available CTD stations during SO234-2/SO235, and error bars represent standard error. Z$_{eu}$ and MLD in (b) are the mean euphotic depth (70.6 ± 10 m) and mixed layer depth (60.2 ± 16.8 m), respectively.

Table 5.1. Correlation analysis (Spearman's *r*) of dimethylated sulfur compounds and bromoform data with selected abiotic and biotic variables during SO234-2/SO235. Spearman's *r* with *p* value < 0.01 are shown in bold. DIN is the sum of nitrate and nitrite, and PO_4^{3-} is dissolved phosphate. Hapto represents haptophytes, Cyano represents cyanobacteria and Prochlo represents *Prochlorococcus*. Only datasets were used for which all environmental variables (SST, SSS; n = 41/85), biotic variables (phytoplankton groups and bacteria; n = 41/71) and other variables (n = 63 for DIN and PO_4^{3-} and n = 13/44 for PAR) were available. NA represents not available.

SO234-2	DMS	$DMSP_t$	$DMSO_t$	Chl·*a*	SST	SSS	DIN	PO_4^{3-}	Bacteria	PAR	Hapto	Cyano	Prochlo
$CHBr_3$	0.30	-0.12	-0.19	0.16	-0.04	-0.06	NA	NA	**0.39**	-0.23	0.26	-0.14	**-0.42**
DMS	1	0.12	0.11	-0.11	-0.29	0.20	NA	NA	0.18	-0.33	0.09	0.10	**-0.37**
$DMSP_t$		1	**0.87**	0.13	-0.08	-0.15	NA	NA	0.15	-0.13	-0.24	-0.09	0.29
$DMSO_t$			1	0.12	0.07	-0.43	NA	NA	-0.03	-0.07	-0.23	-0.02	0.24
SO235	DMS	$DMSP_t$	$DMSO_t$	Chl·*a*	SST	SSS	DIN	PO_4^{3-}	Bacteria	PAR	Hapto	Cyano	Prochlo
$CHBr_3$	0.03	0.11	0.09	**0.42**	-0.01	0.16	**0.47**	**0.65**	0.16	0.09	**0.41**	**-0.37**	**-0.53**
DMS	1	**0.34**	**0.61**	**035**	**-0.59**	**-0.41**	**0.51**	**0.49**	-0.23	0.12	**0.48**	**-0.55**	**-0.40**
$DMSP_t$		1	**0.57**	**0.57**	-0.29	-0.14	**0.21**	**0.36**	-0.16	0.02	**0.63**	**-0.52**	**-0.59**
$DMSO_t$			1	**0.43**	-0.23	0.05	**0.29**	**0.61**	-0.13	0.08	**0.65**	**-0.60**	**-0.59**

5.4 Summary

We conducted a comprehensive study of dimethylated sulfur compounds (DMS, $DMSP_t$ and $DMSO_t$) and $CHBr_3$ in the southwest Indian Ocean in July/August 2014, and for the first time, DMSO concentrations were present in the open Indian Ocean. Surface sulfur compound distributions were coherent with underlying patterns of oceanographic variability, with generally lower concentrations in oligotrophic marine environments and higher concentrations in nutrient-rich marine environments. Vertical distributions of sulfur compounds showed subsurface maxima and were generally within the mixed layer depth. Haptophytes appeared to play the main role in the distribution of $DMSP_t$ and, thus, possibly DMS and $DMSO_t$, at both horizontal and vertical scales. $DMSO_t$ and $CHBr_3$ are the two end products via HOBr reacting with DMS and DOM, respectively. Using $CHBr_3$: $DMSO_t$ ratios, we observed higher ratios when DMS concentrations were below 1.5 nmol L^{-1} and lower ratios when DMS concentration was above 1.5 nmol L^{-1}. This general switch point suggests that the accumulation of DMS may indirectly lead to the suppression of $CHBr_3$ production by reacting with HOBr, and accordingly, HOBr might also be a previously neglected sink for marine DMS. However, owing to the high reactivity of HOBr, its concentration in marine waters cannot be measured; this needs to be further examined in future studies which is helpful to validate this hypothesis in the remote ocean.

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6 Conclusions and Outlook

This thesis provides new perspectives which can improve our understanding of temporal and spatial distributions of the climate-relevant trace gas DMS and related sulfur compounds DMSP and DMSO. Accurately capturing their variabilities and the controlling factors in the water column is key to quantifying DMS emissions and estimating the impact of DMS on the climate and, in turn, how changing environmental conditions can impact DMS cycling and exchange in the future. In this thesis, from a coastal site to the productive shelf areas, then to the open ocean regions, each academic chapter addresses one research question, which was presented in the outline of this thesis. The answers to these questions and the corresponding suggestions on these studies will be given in the following:

1) What are the long-term trends/seasonal cycles and controlling factors of dimethylated sulfur compounds in the water column?

Chapter 3: The longest time-series data set of DMS, DMSP and DMSO, is presented in coastal waters in the southwestern Baltic Sea, which was strongly influenced by anthropogenic input. During the research period, DMS, DMSP and DMSO exhibited large interannual and seasonal variabilities. Overall decreasing long-term trends of DMS and $DMSP_t$ in the mixed layer were identified and linked to the sum of the marker pigments of prymnesiophytes and chrysophytes, which are good producers of DMSP and/or DMS. The seasonal distribution $DMSP_t$ and $DMSO_t$ followed the patterns of Chl *a* and dinoflagellates in the mixed layer and bottom layer, respectively. In addition to the biotic factors, MBI events and sediments are also considered to influence sulfur compound distribution occasionally in the mixed layer and bottom layer, respectively. Since DMSP is mainly produced by the phytoplankton, we proposed a modified algorithm to predict annual $DMSP_t$ concentrations at 5 m depth based on the phytoplankton pigment structure, which would be beneficial to modelling approaches in other coastal ecosystems.

Overall, sulfur compounds in the water column at this coastal ecosystem resulted from the complex interplay of abiotic and biotic factors. As one of the most rapid increased temperature regions in large marine ecosystems (Belkin, 2009), the Baltic Sea is ideal for investigating the variabilities of sulfur compounds in response to global warming. Our study deals with a to-date under-investigated topic and presents the first decadal observation data set between temperature and DMS in the water column. However, our study is limited by the identification of the marine phytoplankton groups, which were taxonomized by their marker pigments. Also, considering the quick turnover times of sulfur compounds (Dixon et al., 2020), their concentrations are hypothesized to vary rapidly in seawater. Therefore, an emphasis on improving different phytoplankton groups identification (e.g., by microscopy) and increasing frequency in sampling, especially during phytoplankton blooms (e.g., weekly), is recommended in future studies.

2) What is the main controlling factor of dissolved DMS in the highly productive region (Peruvian upwelling system), and is it a significant source of seawater DMS and, thus, its emissions?

Chapter 4: The first comprehensive data set of oceanic DMS, DMSP, and DMSO in the Peruvian upwelling system and the first measurement of atmospheric DMS over the Peruvian coastal regions are reported in this study. All sulfur compounds ($DMSP_t$, DMS and $DMSO_t$) negatively correlated with N:P (sum of nitrate and nitrite: dissolved phosphate) ratios, implying their potential role as radical scavengers. A significant correlation was observed between DMS concentration and N:P ratios/Ndef based on two cruises data in the coastal regions, suggesting nutrient availability might be the main driver of DMS distributions in the surface layer. Although large variations in atmospheric DMS mole fractions were measured, the atmospheric mole fractions were generally low, and the sea-to-air fluxes calculated by transfer models were primarily driven by seawater DMS. In comparison to previous measurements made in adjacent regions, the Peru upwelling was identified as a moderate source of DMS emissions during either of our cruises.

As one of the world's most productive regions, the upwelling region off Peru is expected to be a significant source of seawater DMS in the upper mixed layer. However, our results showed significantly lower concentrations compared to those previously measured in June–July 1982 (Andreae, 1985), and the reason for this difference is still elusive. Additionally, the influence of ENSO variability on the DMS concentrations off Peru upwelling is still unclear, and this is attributed to the absence of representative data collected during fully developed El Niño/ La Niña events. Therefore, in order to get a comprehensive picture (seasonal and interannual) of seawater DMS in this region and to better explore what the influence of ENSO events on DMS concentrations is, more observational

DMS data is needed, especially those that could represent extremes in ENSO cycles. This would also be helpful for modelers to predict future DMS variabilities with more frequent ENSO events. Moreover, we recommend including sulfur compound sampling into the currently running time-series stations off Peru and Chile (Graco et al., 2017; Farías et al., 2021), which would allow the investigation of the environmental parameters affecting their distributions.

3) Is there a potential relationship between DMS and $CHBr_3$ in the surface waters?

Chapter 5: The relationship between DMS and $CHBr_3$ has not been examined in the marine environment yet. We presented a unique data set of sulfur compounds and $CHBr_3$ in the water column in the southwest Indian Ocean, and for the first time, DMSO concentrations were measured in the open Indian Ocean. In the surface layer, sulfur compound distributions were coherent with underlying patterns of oceanographic variability, with generally higher/lower concentrations in nutrient-rich/oligotrophic marine environments, while the distributions of $CHBr_3$ generally followed those of Chl *a*. Sulfur compounds and $CHBr_3$ showed subsurface maxima within the mixed layer in their vertical profiles; however, the maxima of sulfur compounds generally paralleled with those of haptophytes and bacterial, while maxima $CHBr_3$ followed that of Chl *a*, indicating that they were affected by different biotic factors. Additionally, an indirect relationship was observed between sea surface DMS and $CHBr_3$ by using $CHBr_3$: $DMSO_t$ ratios, with $CHBr_3$ and $DMSO_t$ being the two end products produced via HOBr reacting with DOM and DMS, respectively (Müller et al., 2019). This scenario suggests that the accumulation of DMS may indirectly lead to the suppression of $CHBr_3$ production by reacting with HOBr, and accordingly, HOBr might also be a previously neglected sink for marine DMS. However, due to the high reactivity of HOBr, its concentration in marine waters cannot be measured currently; this needs to be further investigated in future studies. Also, DMS and $CHBr_3$ measurements are suggested to be made simultaneously during future research campaigns and at existing time-series stations, which would favour the investigation of their interaction on broader scales.