

**CARBON MONOXIDE (CO)  
AND DIMETHYLSULPHIDE (DMS) CYCLING  
IN A CHANGING ARCTIC OCEAN**



**Dissertation**

zur Erlangung des Doktorgrades  
der Mathematisch-Naturwissenschaftlichen Fakultät  
der Christian-Albrechts-Universität zu Kiel

vorgelegt von

**HANNA I. CAMPEN**

Kiel, 2024



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gez. Prof. Dr. Frank Kempken, Dekan



## **Eidesstattliche Erklärung**

Hiermit erkläre ich, **Hanna Campen**, dass ich diese Doktorarbeit, abgesehen durch die Beratung meines Betreuers, selbstständig verfasst, sowie alle wörtlichen und inhaltlichen Zitate als solche gekennzeichnet habe.

Die Arbeit wurde unter Einhaltung der Regeln guter wissenschaftlicher Praxis der Deutschen Forschungsgemeinschaft verfasst.

Sie hat weder ganz, noch in Teilen, einer anderen Stelle im Rahmen eines Prüfungsverfahrens vorgelegen, ist nicht veröffentlicht und auch nicht zur Veröffentlichung eingereicht.

Kiel, den 26. März 2024

gez. Hanna Campen



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# MANUSCRIPT OVERVIEW

This dissertation is based on the following manuscripts:

1. Campen, H.I., Arévalo-Martínez, D.L., Artioli, Y., Brown I. J., Kitidis V., Lessin G., Rees A.P. and Bange H. W.: The role of a changing Arctic Ocean and climate for the biogeochemical cycling of dimethylsulphide and carbon monoxide. *Ambio* 51, 411–422 (2022). doi: 10.1007/s13280-021-01612-z

**Author contributions:** HIC conducted literature research and constructed the literature review manuscript with contributions from HWB. HIC conducted the fieldwork during the JR18007 cruise, with background support of IB, and carried out the data analysis with HWB. DLAM provided support with data interpretation as well as manuscript structure. HIC wrote the manuscript with contributions from HWB, DLAM, YA, VK, GL, and APR.

2. Campen, H. I., Arévalo-Martínez, D. L., and Bange, H. W.: Carbon monoxide (CO) cycling in the Fram Strait, Arctic Ocean, *Biogeosciences*, 20, 1371–1379, doi: 10.5194/bg-20-1371-2023.

**Author contributions:** The study was conceived by HIC and HWB. HIC conducted the fieldwork during the JR18007 cruise and carried out the data analysis with HWB. DLAM provided support for the data analysis and interpretation as well as the preparation of the plots. HIC wrote the manuscript with contributions from HWB and DLAM.

3. Campen, H.I., Arévalo-Martínez, D. L., and Bange, H. W.: Late summer dimethylsulphide (DMS) cycling in the Fram Strait, Arctic Ocean (in preparation)

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5. Rees, A. P., Bange, H. W., Arévalo-Martínez, D. L., Artioli, Y., Ashby, D. M., Brown, I., Campen, H. I., Clark, D. R., Kitidis, V., Lessin, G., Tarran, G. A. & Turley, C. (2022). Nitrous oxide and methane in a changing Arctic Ocean. *Ambio*, 51, 398-410. doi:10.1007/s13280-021-01633-8

# ABSTRACT

Our world is facing unprecedented changes with global warming progressing at a rapid pace. A detailed understanding of the many underlying processes is essential to facilitate profound mitigation measures for the complex and intertwined consequences. The radiative budget of the atmosphere over the Arctic Ocean is a major driver of global climate dynamics. The climate-relevant gases carbon monoxide (CO) and dimethylsulphide (DMS) have the potential to alter the radiative budget of the Arctic atmosphere. Ongoing changes in the Arctic, such as sea ice retreat, changes in light conditions and microbial communities, and ocean acidification (OA), may in turn affect DMS and CO cycling processes in the Arctic Ocean. As Arctic CO observations are limited and the details and interactions of DMS-producing processes with environmental factors are not fully understood, future CO and DMS production pathways and emissions in this region are uncertain.

The overall objective of this work was to provide insight into the cycling of CO and DMS in the surface waters of the Arctic Ocean in response to ocean acidification, changing light conditions and interactions with various abiotic factors. To this end, ship-based incubation experiments with ambient seawater were conducted for 48 h at three (for DMS) and four different locations (for CO) in the Fram Strait in August and September 2019. The experimental sites were located close to the two main hydrographic regimes, the West Spitsbergen Current (WSC) and the East Greenland Current (EGC), to cover typical hydrographic conditions in the region. Seawater samples were incubated in dark and light and at ambient pH, and pH adjusted according to two projected ocean acidification scenarios. Samples for CO and DMS concentration measurements were taken after 12, 24 and 48 hours. In addition, concentrations of several environmental factors were measured at the beginning of each

experiment to characterise the initial environment. Overall, the seasonal timing of late summer revealed oligotrophic and probably post-bloom conditions. The experimental stations showed distinct salinity and temperature due to their hydrographic origin and proximity to ice. Both influenced CO and DMS cycling derived from the incubation experiments.

**CO.** No relationship was found between ocean acidification and surface CO concentrations, as pH reduction did not affect CO production ( $GP_{CO}$ ) and consumption ( $k_{CO}$ ) rates. However, increased  $GP_{CO}$  and  $k_{CO}$  were positively correlated with concentrations of coloured dissolved organic matter (CDOM) and dissolved nitrate, respectively, suggesting that photochemical CO production via CDOM is a dominant production pathway, from which CO is subsequently and rapidly consumed by microbes. Thus, CDOM and nitrate ( $NO_3^-$ ) as well as subsequent microbial uptake are identified as key drivers of surface CO concentration variability, with the latter possibly acting as a 'filter' for ultimate CO emissions from the Fram Strait. Consequently, both future CO production and consumption in the Arctic could increase with projected changes in CDOM and dissolved  $NO_3^-$  input. It is not yet clear whether the two processes will balance each other, and more research is needed to determine whether one process will dominate. Since anthropogenic CO sources are declining, the oceanic source might become even more pronounced in the future.

**DMS.** Relatively low DMS as well as Dimethylsulphoniumpropionate (DMSP) and Dimethylsulphoxide (DMSO) concentrations reflected generally oligotrophic post-bloom conditions, explained by the timing of sampling in the late summer-autumn transition. However, an average net DMS production of  $0.005 \pm 0.001 \text{ nmol L}^{-1} \text{ hr}^{-1}$  was found across all stations. No effect of pH or light on DMS/P/O concentrations was found, indicating that the producing community was OA resilient.  $DMSP_p$  was the dominant precursor for DMS production, and production rates of both increased with temperature and salinity, being higher at stations transporting Atlantic water. The association of  $DMSP_p$  release and DMS production with particulate organic nitrogen (PON) and particulate organic carbon (POC) concentrations suggests that a senescent bloom led to  $DMSP_p$  release and subsequent

cleavage to DMS. Given the complexity and interconnectedness of the underlying production and consumption processes, it is difficult to predict how future DMS emissions will ultimately behave. Therefore, more comprehensive, and multidisciplinary research approaches are required, including the analysis of microbial community composition, omics, in situ rate measurements, in interaction with other environmental factors, depending on location and season.

The results indicate that strong spatial gradients in salinity, temperature, and nutrients, which occur suddenly and transiently in the Arctic Ocean, seem to play an important role in both CO and DMS production. These findings may add a piece to the puzzle of seasonal and location diversity in Arctic data sets that could improve CO and DMS parameterisation for predicting future CO and DMS cycling and the effect on the radiative budget and oxidative capacity of the Arctic atmosphere and globally.



# ZUSAMMENFASSUNG

Unsere Welt steht vor noch nie dagewesenen Veränderungen, denn die globale Erwärmung schreitet in rasantem Tempo voran. Ein detailliertes Verständnis der vielen zugrundeliegenden Prozesse ist unerlässlich, um fundierte Maßnahmen zur Eindämmung der komplexen und miteinander verflochtenen Folgen zu ermöglichen. Der Strahlungshaushalt der Atmosphäre über dem Arktischen Ozean ist eine wichtige Einflussgröße für die globale Klimadynamik. Die klimarelevanten Gase Kohlenmonoxid (CO) und Dimethylsulfid (DMS) haben das Potenzial, den Strahlungshaushalt der arktischen Atmosphäre zu verändern. Fortschreitende Veränderungen in der Arktis, wie z.B. der Rückgang des Meereises, Veränderungen der Lichtverhältnisse und der mikrobiellen Gemeinschaften sowie die Versauerung der Ozeane, können wiederum die DMS- und CO-Kreislaufprozesse im Arktischen Ozean beeinflussen. Da die CO-Beobachtungen in der Arktis sehr begrenzt sind und die Details und Wechselwirkungen der DMS-produzierenden Prozesse mit den Umweltbedingungen nicht vollständig aufgeklärt sind, sind die zukünftigen CO- und DMS-Produktionswege und Emissionen in dieser Region ungewiss. Das übergeordnete Ziel dieser Arbeit war es, Aufschluss über die Produktions- und Abbauprozesse von CO und DMS in den Oberflächengewässern des Arktischen Ozeans in Abhängigkeit von der Versauerung der Ozeane, veränderten Lichtverhältnissen und Wechselwirkungen mit verschiedenen abiotischen Faktoren zu gewinnen. Dafür wurden im August und September 2019 an drei verschiedenen Standorten in der Framstraße schiffsgestützte Inkubationsexperimente mit Seewasser für 48 Stunden durchgeführt. Die Versuchsstandorte befanden sich in der Nähe der beiden wichtigsten Strömungsregime, dem Westspitzbergenstrom (WSC) und dem Ostgrönlandstrom (EGC), um die typischen hydrographischen Bedingungen in der Region

abzudecken. Die Proben wurden bei Licht und Dunkelheit und bei normalem pH-Wert inkubiert, sowie pH-Werten die entsprechend zweier prognostizierter Ozeanversauerungs-Szenarien angepasst wurden. Nach 12, 24 und 48 Stunden wurden Proben für CO- und DMS-Konzentrationsmessungen entnommen. Darüber hinaus wurden zu Beginn jedes Experiments die Konzentrationen verschiedener Umweltparameter erfasst, um die Ausgangsbedingungen zu charakterisieren. Insgesamt herrschten entsprechend der Jahreszeit des Spätsommers oligotrophe Bedingungen und vermutlich war die Phytoplanktonblüte bereits vorüber. Das Wasser an den Versuchsstandorten wies durch seine Strömungsherkunft und unterschiedlichen Nähe zum Eis variierende Salinitäten und Temperaturen auf. Beides beeinflusste die in den Inkubationsversuchen ermittelten CO- und DMS-Konzentrationen.

**CO.** Es wurde kein Zusammenhang zwischen Ozeanversauerung und CO-Konzentrationen gefunden, da die Reduzierung des pH-Werts keinen Einfluss auf die CO-Produktions- ( $GP_{CO}$ ) und Abbauraten ( $k_{CO}$ ) hatte. Erhöhte  $GP_{CO}$ - und  $k_{CO}$ -Werte waren jedoch positiv mit den Konzentrationen von farbigem gelösten organischen Material (CDOM) bzw. gelöstem Nitrat korreliert, was darauf hindeutet, dass die photochemische CO-Produktion über CDOM ein dominanter Produktionsweg ist, aus dem CO v.a. unter oligotrophen Bedingungen anschließend und rasch von Mikroorganismen konsumiert wird. CDOM und  $NO_3^-$  sowie die anschließende mikrobielle Aufnahme werden somit als Hauptfaktoren für die Variabilität der CO-Konzentration an der Oberfläche ausgemacht, so dass letztere möglicherweise wie ein "Filter" für die endgültigen CO-Emissionen aus der Framstraße wirken. Folglich könnten sowohl die künftige Produktion als auch der Verbrauch von CO in der Arktis mit den voraussichtlichen Änderungen der CDOM- und Nitrateinträge zunehmen. Es ist noch unklar, ob sich die beiden Prozesse gegenseitig ausgleichen werden, und es bedarf weiterer Forschung, um zu ermitteln, ob ein Prozess dominieren wird. Da anthropogene CO-Quellen abnehmen, könnte der Einfluss der ozeanischen Quelle in Zukunft umso mehr ins Gewicht fallen.

**DMS.** Relativ niedrige DMS-, Dimethylsulfoniumpropionat (DMSP)- und Dimethylsulfoxid (DMSO)-Konzentrationen spiegeln die allgemein oligotrophen Bedingungen nach der

Phytoplanktonblüte wider, was sich durch den Zeitpunkt der Probenahme im Spätsommer-Herbst-Übergang erklärt. Dennoch wurde über alle Stationen hinweg eine durchschnittliche Netto-DMS-Produktion von  $0.005 \pm 0.001 \text{ nmol L}^{-1} \text{ h}^{-1}$  ermittelt. Weder der pH-Wert noch Licht hatten Auswirkung auf die DMS/P/O-Konzentrationen, was darauf hindeutet, dass die produzierende mikrobielle Gemeinschaft gegenüber Ozeanversauerung resistent war. Partikuläres DMSP ( $\text{DMSP}_p$ ) war das wichtigste Vorläufermolekül für die DMS-Produktion, und die Produktionsraten von DMS und  $\text{DMSP}_p$  stiegen mit der Temperatur und dem Salzgehalt, und waren entsprechend höher an Stationen, die Atlantikwasser transportierten. Der Zusammenhang zwischen der Freisetzung von  $\text{DMSP}_p$  und der DMS-Produktion mit den Konzentrationen von partikulärem organischen Stickstoff (PON) und Kohlenstoff (POC) deutet darauf hin, dass eine seneszente, zerfallende Blüte zur Freisetzung von  $\text{DMSP}_p$  und nachfolgender Spaltung zu DMS führte. Angesichts der Komplexität und Verflechtung der zugrundeliegenden Produktions- und Abbauprozesse ist es schwierig vorherzusagen, wie sich künftige DMS-Emissionen entwickeln und verhalten werden. Daher sind umfassendere und multidisziplinäre Forschungsansätze erforderlich, einschließlich der Analyse der Zusammensetzung der mikrobiellen Gemeinschaft, Omics- und In-situ-Ratenmessungen, in Wechselwirkung mit anderen in Abhängigkeit von Standort und Jahreszeit auftretenden Umweltfaktoren.

Die Ergebnisse deuten darauf hin, dass starke räumliche Gradienten in Bezug auf Salzgehalt, Temperatur und Nährstoffe, die im Arktischen Ozean plötzlich und vorübergehend auftreten, eine wichtige Rolle sowohl bei der CO- als auch bei der DMS-Produktion spielen. Diese Ergebnisse tragen zur jahreszeitlichen und regionalen Vielfalt in arktischen Datensätzen bei. Somit könnten sie die CO- und DMS-Parametrisierung und die Genauigkeit in der Vorhersage zukünftiger CO- und DMS-Zirkulation und deren Auswirkung auf den Strahlungshaushalt und die Oxidationskapazität der arktischen Atmosphäre und somit weltweit verbessern.



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# 1 INTRODUCTION

## **The Role of a Changing Arctic Ocean and Climate for the Biogeochemical Cycling of Dimethylsulphide (DMS) and Carbon Monoxide (CO)**

Campan, H.I., Arévalo-Martínez, D.L., Artioli, Y., Brown I. J., Kitidis V., Lessin G., Rees A.P. and Bange H. W.: The role of a changing Arctic Ocean and climate for the biogeochemical cycling of dimethylsulphide and carbon monoxide. *Ambio* 51, 411–422 (2022). <https://doi.org/10.1007/s13280-021-01612-z>

*The Arctic Ocean (AO) plays a central role in global climate dynamics.* Its ice cover substantially contributes to the planetary albedo (IPCC 2019; Thackeray and Hall 2019). Ongoing global warming is predicted to lower the snow and sea ice coverage (IPCC 2019) thereby decreasing albedo and further accelerating warming as part of a process called Arctic amplification (Serreze and Barry 2011). A recent study reveals that the Arctic region will face increasingly frequent and intense heatwave events, which will aggravate the effects of climate change in the Arctic, and accelerate Arctic sea ice retreat, especially if greenhouse gas emissions are continued to increase (Barkhordarian et al., 2024). Consequently, heat fluxes at the surface ocean alter, potentially slowing the Atlantic meridional overturning circulation, which just recently was suggested to approach a tipping point (van Westen et al., 2023), with substantial consequences for global atmospheric processes and climate (Sévellec et al. 2017).

### ***Changes in the Arctic Ocean***

The rapid sea ice loss and permafrost thawing manifests climate change in the Arctic Ocean. It indicates an overarching transition of the Arctic environment since it initiates the modification of numerous biogeochemical processes with far-reaching consequences. Sea ice plays a key role in global biogeochemical cycles by providing suitable habitats for a variety of microorganisms responsible for the cycling of climate-relevant compounds and regulating the exchange of gases across the ocean and the atmosphere (Vancoppenolle et al. 2013).

***Sea ice decrease*** is largest in summer with the strongest loss observed in September:  $12.8 \pm 2.3$  % ice cover has been lost per decade relative to the 1981 – 2010 mean, which equals to  $83\,000\text{ km}^2\text{ yr}^{-1}$  sea ice loss in September (Onarheim et al. 2018). Enhanced erosion (Overeem et al. 2011; IPCC 2019), increased rainfall and greater riverine inputs due to permafrost thawing will flush more and different terrestrial material into the Arctic Ocean (Stedmon et al. 2011). First-year ice will dominate over multi-year ice and the number of melting ponds, ice-edges and open-ocean like areas will increase (Slagstad et al. 2015; Lannuzel et al. 2020). Ice melting increases the freshwater inputs, which leads to increasing stratification, possibly limiting nutrient remineralisation depending on the region (Slagstad et al. 2015), and affecting nutrient and trace metal input (e.g. Hopwood et al. 2018). Furthermore, with expanding first-year ice extent and continuing greenhouse gas emissions, Arctic marine heatwaves of moderate intensity are expected to become a persistent event (Barkhordarian et al., 2024), which hence indicates a further amplification of warming.

***Light availability and penetration*** at the ocean surface will increase due to ice loss and the overall decreasing albedo (Pistone et al. 2014). This potentially increases primary productivity of ice-algae and overall pelagic Arctic primary production (Arrigo and van Dijken 2015). It stimulates an earlier onset of spring phytoplankton blooms and likely regular autumn phytoplankton blooms due to later freeze-up, particularly at the periphery of the Arctic Ocean (Ardyna et al. 2014).

That, in turn, has multiple consequences for *phytoplankton community structure and production* (Horvat et al. 2017). As a consequence of more open-ocean like areas phytoplankton and bacterial communities are likely to shift (e.g. Coupel et al. 2015). With shrinking multiyear ice the overwintering habitat of sympagic algae will be lost (Hardge et al. 2017; Van Leeuwe et al. 2018), which will decrease microalgal diversity favouring pelagic or cryo-pelagic species, such as *Phaeocystis sp.* (Assmy et al. 2017; Lannuzel et al. 2020) and flagellates. The increase of melt pond coverage might support the development of dense algal colonies, e.g. formed by the under-ice pelagic diatom *Melosira arctica* (Fernández-Méndez et al. 2014) (Arrigo and van Dijken 2011). With regional and seasonal heterogeneity, primary productivity is predicted to generally increase in both sea ice and seawater in the Arctic, being possibly constrained by nutrient availability (Vancoppenolle et al. 2013; Tedesco et al. 2019). However, between 2012 – 2018 chlorophyll a concentration in Arctic Ocean surface waters increased 16 times faster than before, suggesting an increased primary production sustained by an additional input of nutrients due to sea ice melt, mixing at shelf breaks or advection from lower latitudes (Ardyna and Arrigo 2020; Lewis et al. 2020).

*Changes in bacterial communities* are also likely, and closely linked to seasonal ice melting and changes in primary productivity. Thus, heterotrophic activity is likely to increase as it is mostly driven by primary productivity (Bowman 2015). The SAR11 clade (Pelagibacterales) is the most abundant and ubiquitous clade of the bacterial communities worldwide (Morris et al. 2002), yet its variation differs among habitats in the Arctic Ocean (Han et al. 2014). In the Chukchi Sea, for example, a few bacterial groups, including species belonging to *Roseobacter* (Malmstrom et al. 2007), dominate community composition and biomass production. For the abundance, production, species composition and activity of under-ice bacterioplankton and bacteria in general, dissolved organic matter (DOM) – often released by pulses of seasonal melting first year ice – is probably a dominant factor (Underwood et al. 2019). Indeed, Jackowski et al. (2020) found that dissolved organic carbon (DOC) was the dominant factor whereas the temperature effect was negligible for bacterial production. Moreover,

phytoplankton community composition also affects availability and characteristics of DOM and semi-labile dissolved organic carbon (DOC), favouring certain bacterial strains (Tisserand et al. 2020). However, DOM and DOC bioavailability decreases strongly from summer to autumn (Jackowski et al. 2020) making it sensitive to climate change-related impacts on Arctic seasonality.

***Ocean acidification*** significantly affects high latitude and Arctic waters. These regions are sensitive to ocean acidification having naturally high concentrations of dissolved inorganic carbon and low alkalinity concentrations (Orr et al. 2005). That has far reaching consequences on phytoplankton and bacterial communities (Hopkins et al. 2020). Sea ice melting and permafrost thawing could even enhance ocean acidification by increasing river and glacial runoff and enhancing terrestrial organic carbon loading (Steinacher et al. 2009; Semiletov et al. 2016). Model results suggest that the pH in the surface waters of the Arctic Ocean could decrease by about 0.45 by the end of this century (Steinacher et al. 2009 Terhaar et al. 2020), although the decrease in pH might show a high regional heterogeneity.

***Gas fluxes between ocean and atmosphere*** may be altered and enhanced by sea ice loss. In particular, less ice implies a stronger transfer of energy from wind to the ocean, with more waves, turbulence and mixing, and increased sea ice mobility, which, in turn, will enhance the air-sea gas exchange (Rainville et al. 2011; Davis et al. 2014; Meneghello et al. 2018).

A recent attribution science study revealed that with the absence of greenhouse gases the very intense heatwave event in 2020 in the Arctic would have been unlikely to happen both in such intensity and duration (Barkhordarian et al., 2024). That demonstrates the tight interaction and feedback between climate relevant gases, Arctic atmospheric processes and global climate regulation, and, hence, emphasizes the need to correctly identify and quantify the forcing by climate relevant gases, such as CO and DMS.

***Carbon monoxide (CO) and Dimethylsulphide (DMS) play important roles in atmospheric chemistry and climate.***

Figure 1 shows schematically their key processes and fluxes in the Arctic Ocean.

**CO** is an indirect greenhouse gas with a radiative forcing nearly twice that of carbon dioxide (CO<sub>2</sub>) on a molecular basis (IPCC 2013). Its presence in the atmosphere triggers a series of reactions increasing other greenhouse gases such as CO<sub>2</sub>, methane and ozone (O<sub>3</sub>): it reacts with hydroxyl radicals (OH·) to form CO<sub>2</sub> and it outcompetes methane in the reaction with tropospheric OH· (Thompson and Cicerone 1986), prolonging its atmospheric lifetime (Forster et al. 2007). Moreover, CO affects the ozone concentrations in the troposphere, where O<sub>3</sub> acts as a strong greenhouse gas (Dignon and Hameed 1985). The lifetime of tropospheric CO of 1-4 months is comparably short (Crutzen 1994; Prather 1996, Szopa et al., 2021).

Both biological and abiotic processes produce CO in the surface ocean, whereas microbial uptake, mixing to subsurface layers and exchange to the atmosphere represent its loss terms (Swinnerton et al. 1970; Conrad and Seiler 1980; King and Weber 2007; Gros et al. 2009; Kitidis et al. 2011; Conte et al. 2019). CO is produced photochemically through the reaction of ultraviolet (UV) or blue light with either coloured dissolved organic matter (CDOM) (Swinnerton et al. 1970; Conrad et al. 1982; Gammon and Kelly 1990; Zafiriou et al. 2008) or, to a lesser extent, particulate organic matter (POM) (Xie et al. 2009), e.g. from ice algae (Song and Xie 2017). Dark (thermal) production and biological production by phytoplankton are additional small sources (Zhang et al. 2008; Gros et al. 2009; Tran et al. 2013). Microbial uptake is the major sink of CO in marine waters (Conrad and Seiler 1980; Conrad et al. 1982; Zafiriou et al. 2003), but details of its physiological function and kinetics are still uncertain. Release to the atmosphere via air-sea gas exchange represents a minor loss term (Conte et al. 2019). The photochemical and microbial-driven sources and sinks of CO could be altered by warming, increased light penetration because of sea-ice loss and increase of DOM inputs to the Arctic Ocean.



compared to other ocean basins (Tran et al. 2013). Studies by Xie et al. (2005) and Song et al. (2011) found high CO concentrations in bottom sea ice suggesting a link between CO production and ice algae blooms.

**DMS** has the potential to counteract warming by increasing the regional albedo. The resulting cooling potential roughly equals the warming effect by CO<sub>2</sub> (Fung et al., 2022; Thomas et al., 2010; Mahajan et al., 2015, Etmnan). DMS, as the precursor of sulphate aerosols, affects the concentration of cloud condensation nuclei (CCN), which in turn increases the formation of clouds, thus the Earth's albedo, and potentially cools the atmosphere (Charlson et al. 1987; Korhonen et al. 2008). This DMS-driven ocean-atmosphere interaction could counteract the decreasing albedo induced by sea ice loss in the Arctic, which could be particularly important in summer when the aerosol burden is low (Mungall et al. 2016).

Furthermore, DMS plays a role in the oxidation pathways of climate-relevant gases. These include isoprene, ammonia and organohalogens (Glasow and Crutzen 2004; Johnson and Bell 2008; Chen and Jang 2012), as well as the potent greenhouse gas methane which, like DMS, can be produced from dimethyl-sulphonio-propionate (DMSP) (Florez-Leiva et al. 2013). DMS occurs globally in association with phytoplankton in surface waters, whereby biologically productive waters around the Arctic pack ice represent a strong DMS source (Levasseur 2013). DMS is produced by the enzymatic DMSP breakdown by heterotrophic bacteria and as a metabolic product in algae (both, planktonic microalgae and macroalgae) (Stefels and Dijkhuizen 1996; Steinke et al. 1998; Niki et al. 2000).

In algae, DMSP may be involved in various cellular processes, such as regulation of the algal carbon and sulphur metabolism via an overflow mechanism (e.g. Stefels 2000) and fulfilling physiological functions including osmoregulation (e.g. Van Bergeijk et al. 2003), cryo-protection (Kirst et al. 1991), and protection against oxidative stress (Sunda et al. 2002). Yet, its cellular function is not entirely understood. Intracellular DMSP concentrations can vary strongly between major microalgal groups, and thus the distribution of DMSP and DMS in the ocean depends on microalgae community

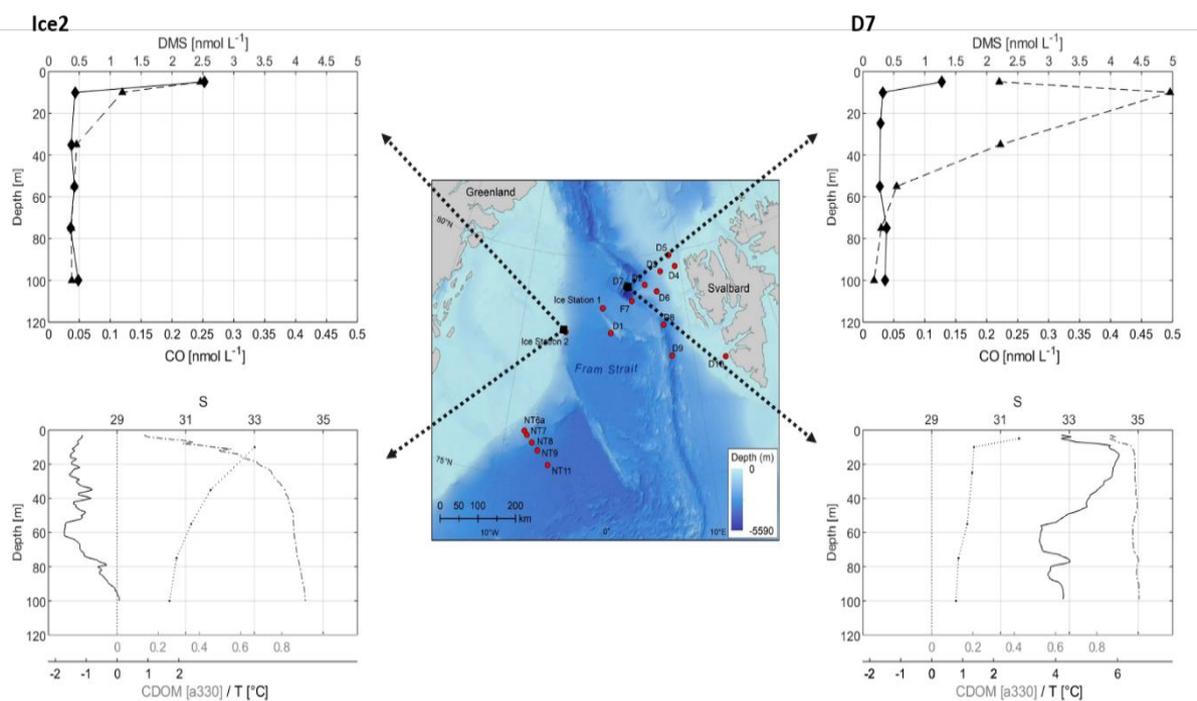
composition. Dinoflagellates and prymnesiophytes are strong DMS producers, and diatoms are weak DMS producers (Keller 1989). DMS production also depends on the physiological status of the algae and environmental stressors such as nutrient limitation and ultraviolet light (Sunda et al. 2002). If DMSP is released into the water column, it is by active exudation, autolysis, viral lysis, and grazing by zooplankton (Stefels et al. 2007). Pelagic bacteria generally either cleave it, generating DMS, or metabolise it to other sulphur compounds by demethylating/demethiolating DMSP to methylmercaptopyruvate, methanethiol or inorganic sulphur (Stefels 2000). Other major loss processes for oceanic DMS are photochemical oxidation to dimethyl sulfoxide (DMSO) and release to the atmosphere via air-sea gas exchange (Vila-Costa et al. 2008; Valle et al. 2009). Given the tight connection between the cycling of marine DMS and microalgae, changes in the Arctic Ocean phytoplankton community structure, further warming and decrease in sea ice coverage can therefore lead to changes in the production and emission of DMS.

Oceanic DMS emissions amount to 15 – 40 Tg sulphur (S) yr<sup>-1</sup>, which represents 80 – 90% of all marine biogenic S emissions, and up to 50% of global biogenic S emissions (Lana et al. 2011, Wang et al., 2020). Emissions from the Arctic Ocean are estimated to be 0.005 – 0.013 Tg S yr<sup>-1</sup> (Galí et al., 2021). Due to high regional and seasonal variabilities in DMS emissions, global estimations reveal high uncertainties (up to  $\pm 10 \text{ W m}^{-2}$ ) (Mahajan et al., 2015; Wang et al., 2020), demonstrating the need for improvement in both, flux estimation methods and measurements (Zhang 2024).

Only ~10% of the DMS produced by plankton finds its way to the atmosphere (Bates et al. 1994). The majority of DMS is oxidized microbially and photochemically in the water (Galí et al. 2015; Uher et al. 2017). Thus, on a global scale, it seems unlikely that oceanic DMS emissions could regulate global climate (Quinn and Bates 2011). However, in regions such as the Arctic oceanic DMS emissions could have a significant influence on climate via CCN formation, because of the low aerosol concentrations in the Arctic atmosphere in summer (Chang et al. 2011; Woodhouse et al. 2013).

*A case study in brief: CO and DMS variability in the Fram Strait related to the proximity of sea ice*

Figure 2 presents the vertical distributions of CO and DMS concentrations with the corresponding salinity, temperature and CDOM profiles at two contrasting locations in the Fram Strait in August 2019 (Campen et al., unpubl.). The salinity and temperature profiles indicate that the surface water (5 m) at the continental shelf break (station Ice2) were of Arctic origin (Salinity, S: 29.02, Temperature, T: -1.05 °C) whereas the waters found in the central open Fram Strait (station D7) originated from the North Atlantic Ocean (S: 34.78, T: 5.68 °C) (Rudels et al. 2005). Ice2 showed a meltwater layer at the surface with a temperature around -1°C, and a generally mixed water column. D7 surface waters, in contrast, were warmer and saltier with a less mixed water column between 10 and 50 m. The surface layer at Ice2 showed higher CO concentrations compared to D7 (0.25 nmol L<sup>-1</sup> vs. 0.13 nmol L<sup>-1</sup>),



**Fig 2** CO and DMS depth profiles at two contrasting stations in the Fram Strait, Arctic Ocean. Station Ice2 (left) is located at the ice edge and D7 (right) is an open ocean station as indicated on the cruise track (center). The top panel shows DMS (triangles, dashed line) and CO concentrations (diamonds, solid line). The bottom panel shows oceanographic parameters: Salinity (dot-dashed line, top axis), CDOM absorption at 300 nm (dotted line, grey bottom axis) and temperature (solid line, black bottom axis).

coinciding with higher CDOM absorbance at Ice2, which could be due to a CDOM originating from meltwater. The opposite was observed for DMS concentrations: D7 reveals a DMS peak of 5.0 nmol L<sup>-1</sup> at 10 m whereas DMS concentrations at Ice2 in 10 m are only 1.2 nmol L<sup>-1</sup> (2.5 nmol L<sup>-1</sup> in 5 m). The DMS maximum at D7 could be explained by the warmer and less mixed conditions, as there seems to be a different water body below 10 m with contrasting hydrographic provenance and therefore likely different algal community composition. Compared to previously published data, the CO surface concentrations in August 2019 are in the lower range possibly reflecting seasonal differences, since the lowest concentration measured in June/July 2011 in the Fram Strait was 0.6 nmol L<sup>-1</sup> (Tran et al. 2013). These data strengthen the view that environmental settings such as the proximity to the ice edge or the open ocean significantly affect the variabilities of DMS and CO surface concentrations.

**Changes of the biogeochemical processes described previously might have substantial consequences on Arctic Ocean CO and DMS concentrations and fluxes.** The production and consumption pathways of DMS and CO depend on light, microalgal and bacterial community structure as well as on CDOM and POM. DMS and CO air-sea gas exchange is regulated by the presence of sea-ice, stratification, wind speed, temperature and salinity. All these processes are directly or indirectly affected by the ongoing environmental changes in the Arctic Ocean such as the loss of sea ice. To this end, we assess here the potential consequences of the ongoing environmental changes for future DMS and CO biogeochemical pathways and emissions in the Arctic Ocean, identify key knowledge gaps and point to potential future research needs.

### **Potential impacts of ongoing environmental changes on DMS and CO cycling in the Arctic Ocean**

In the following section, we discuss the ongoing changes that might play a role for DMS and CO production and consumption processes to be addressed by future studies.

### *Direct impacts of ice melting*

The melting of ice on land and at sea, in addition to permafrost thawing will affect the Arctic Ocean's ecosystems and biogeochemical processes with potential consequences for DMS and CO cycling.

**CO.** Enhanced ice melting could increase CO production in Arctic surface waters. Increasing regions of ice-melt may lead to higher CDOM and POM supply, which – when coupled to greater light availability – may increase photochemical CO production (Osburn et al. 2009). Also progressively thinner sea ice could lead to increased light penetration and CO production within the ice bottom layer. Since ice then will be permeable more frequently (Gosink et al. 1976) it increases the amount of CO that can be released to the atmosphere (Song et al. 2011). Additionally, melting and refreezing of seawater, which could happen more frequently in the future, may lead to higher CO concentrations (Xie and Gosselin 2005), being in line with elevated CO concentrations coinciding with higher CDOM absorbance and more intense stratification due to ice melting (Tran et al. 2013).

Enhanced permafrost thawing and erosion could additionally increase CO photoproduction in the coastal regions of the Arctic Ocean. Especially in the Eurasian basin, it could increase the availability of CDOM and POM via increased riverine input, and potentially alter their spectral characteristics. For instance, in winter, older and more refractory organic material would be exported (Stedmon et al. 2011). Moreover, enhanced erosion of soils potentially increases terrestrial CDOM and POM loads in coastal waters, which could lead to higher CO photoproduction compared to its photoproduction via marine CDOM (Stubbins et al. 2011).

**DMS.** Highly productive ice algae responsible for high DMS concentrations are known to inhabit Arctic sea ice (Levasseur 2013). Thus, the loss of sea ice could lead to a decrease in DMS/P production, or a change in the ratio of ice-associated and open ocean DMS producers promoting the latter (Lannuzel et al. 2020). However, in the phase of increased melting, ice edge effects may stimulate DMS/P production as indicated by elevated DMS/P values in partially ice-covered regions (Jarníková et al. 2018). The results show that DMS production is inextricably linked with the prevailing

phytoplankton and microbial communities in both ice-associated and pelagic habitats. Since the ongoing changes strongly affect phytoplankton and microbial communities, changes therein have to be fully considered for a better understanding of future DMS dynamics.

### ***Increasing light availability***

Ice melting increases the light availability in the Arctic Ocean, possibly resulting in both an increase in biological DMS production (Levasseur et al. 1994; Turner et al. 1995; Levasseur 2013) and in CO photoproduction (Xie and Gosselin 2005; Song et al. 2011). Whether this will also increase emissions, depends however on further production and consumption terms and their reply to ongoing changes.

**CO.** As more light becomes available and penetrates the surface Arctic Ocean when the sea ice retreats, it possibly increases both photochemical and biological CO production over the year. For CO photoproduction, Song and Xie 2017 show that POM dominates over CDOM as a source in the bottom of sea ice. POM content could increase even more in the future as primary productivity increases (e.g. Arrigo and van Dijken 2015), which could promote both photochemical and biological CO production by phytoplankton. However, that depends also on the community composition and possible shifts therein.

**DMS.** Increasing light availability in the Arctic Ocean promotes higher primary productivity due to changes in seasonality (Arrigo and van Dijken 2015). An earlier onset of the bloom increasing the phytoplankton and ice algae biomass could enhance the overall biological production of DMS/P (Lannuzel et al. 2020). However, the fraction of DMSP eventually resulting in DMS emissions depends on the abundance and taxonomy of microalgae, bacterial activity and further environmental conditions (Levasseur 2013), which all underlie large regional variations. Since UVA light is responsible for 60 – 75% of the DMS photooxidation in the sunlit surface (Taalba et al. 2013), increasing UV-A light could increase the photooxidation of DMS to DMSO, thereby decreasing DMS surface concentrations.

### ***Changing phytoplankton community***

Increasing light and open-ocean conditions will probably lead to increased phytoplankton growth and shift towards cryo-pelagic and pelagic species. Shifts in the phytoplankton community will likely influence DMS and CO concentrations in surface Arctic waters, potentially affecting their emissions to the atmosphere.

**CO.** Expected changes in the phytoplankton community distribution could point to an increase in microalgal CO production. During ice algal blooms, large CO accumulations were observed in the lowermost sea ice layer (Xie and Gosselin 2005; Song et al. 2011), which they may produce directly or indirectly, via CDOM input. Laboratory experiments indicated that cyanobacteria and diatoms are large CO emitters (Gros et al. 2009). However, only one field study so far has confirmed biological CO production and observed *Phaeocystis sp.*, dinoflagellates and to lesser extent diatoms to produce CO in the Arctic Ocean (Tran et al. 2013). Given that *Phaeocystis sp.*, flagellates and several diatom species abundances will probably increase in the future (Fernández-Méndez et al. 2014; Arrigo 2017), this could enhance CO production in the Arctic Ocean. Hence, although biological CO production in the Arctic Ocean is of minor importance today, it might become more pronounced in the future.

**DMS.** Expected phytoplankton community shifts will likely lead to an overall increase in DMS production. Its precursor molecule, DMSP, largely depends on the plankton community composition, in particular on the abundance of strong DMSP producers with DMSP-lyase activity (Levasseur 2013). Strong DMSP producers are Dinoflagellates and primnesiophytes such as *Phaeocystis* and *E. huxleyi*, which may increase in abundance in future (Keller 1989; Assmy et al. 2017). Due to their high intracellular concentrations of DMSP it was suggested that their biomass governs DMSP production (Stefels 2000), also in the Arctic Ocean (Park et al. 2018). Weaker DMSP producing species, however, may contribute significantly to DMSP production when being under stress, e.g. nutrient limitation

(Bucciarelli et al. 2013) or high UV light (Levasseur 2013). Both potentially increase in future (Vancoppenolle et al. 2013).

### *Changing bacterial community*

The microbial community may be profoundly altered by changes in seasonality of organic matter supply and algal community structure, which could greatly affect DMS cycling and both CO production and consumption in the water column (Solan et al. 2020). Especially changes in the *Roseobacter* clade may be important, given its role in the biogeochemical cycle of both gases.

**CO.** Changes in the bacterial community could also alter CO concentration in surface waters and ice, with microbial uptake being the major CO sink (Xie et al. 2005; Xie et al. 2009). Diverse communities of marine bacteria are oxidizing CO at environmentally relevant rates (Tolli et al. 2006; King and Weber 2007) with the marine *Roseobacter* group being among those with highest specific rates. However, large uncertainties about dominant CO oxidizers remain (King and Weber 2007). CO oxidation capability is indicated by holding both forms of the gene *coxL* (Cunliffe 2011). *Roseobacter* uses CO mainly as a supplemental energy source, next to DOM (Moran and Miller 2007). Thus, CO oxidation could help heterotrophic bacteria to survive carbon limitation in changeable environments (Cordero et al. 2019), such as the Arctic (Islam et al. 2019). Yet, the physiological details remain unclear. This emphasizes that future research should focus on the relationship between bacterial species composition, their CO oxidation capability and rates, and the resulting CO concentrations as also suggested by Tran et al. (2013). Studies of the microbial CO consumption rates propose that in Arctic waters (Beaufort Sea) the CO microbial consumption depends indeed on bacterial activity which, in turn, mainly follows primary productivity (Xie et al. 2005). This may suggest an increase in CO consumption, which would mean a decrease in CO concentrations in the surface layer and thus in CO emissions. Comparing CO consumption rates in spring and autumn in the Beaufort Sea indicated that bacterial community shifts largely dominate the CO consumption, resulting in much lower rates,

followed by higher CO emissions, in spring than in autumn (Xie et al. 2009). This phenomenon might be intensified in future due to an earlier onset of primary productivity and more ice edges and melt ponds in the Arctic Ocean (Xie and Gosselin 2005).

**DMS.** The composition of the prokaryotic community is as important for DMS production as the phytoplankton community composition (Levasseur 2013). The abundant marine  $\alpha$ -proteobacteria *Roseobacter* catabolize DMSP in high amounts (Kirkwood 2012) by several mechanisms (González et al. 1999; Todd et al. 2012), which field studies confirmed for an Arctic fjord (Kongsfjorden) (Zeng et al. 2016). Sipler et al. (2017) found that some taxa within the *Roseobacter* clade would thrive in a changing Arctic Ocean. Arctic field studies indicate that bacteria use DMSP mostly as a carbon source, with conversion efficiencies of DMSP into DMS of up to 30% (Luce et al. 2011; Motard-Côté et al. 2012). DMS seems to be used as an auxiliary S source by the same clades that consume DMSP (Zubkov et al. 2002; Levasseur 2013). Thus, bioavailability and characteristics of DOM, which determine bacterial community compositions (Jackowski et al. 2020), potentially also govern DMSP to DMS conversion, and thereby, whether DMS is released to the atmosphere.

### ***Ocean acidification***

Ocean acidification is taking place rapidly in polar oceans with consequences especially for DMS and probably also for CO, since their production is linked to phytoplankton and bacterially mediated processes.

**CO.** It is uncertain whether ocean acidification affects CO production. Gao and Zepp (1998) showed that photochemical breakdown of CDOM increased with very low pH (5.5). This could be a hint that ocean acidification may enhance the photochemical formation of CO, particularly in the Arctic Ocean because of increased riverine CDOM inputs (see above). However, this idea needs to be investigated with pH levels characteristic for the Arctic Ocean. Further, it may alter CO production indirectly via

the influence on bacterial and phytoplankton processes affecting also the CDOM and POM pool (Hopkins et al. 2018).

**DMS.** Studies of DMS production under ocean acidification in the Arctic Ocean reveal contradictory results (Archer et al. 2013; Six et al. 2013; Hussherr et al. 2017; Hopkins et al. 2018). Hopkins et al. (2020) provide a comprehensive overview of studies on DMS production under ocean acidification. It shows that future DMS production rates in the Arctic Ocean with lower pH do not show a general increasing or decreasing trend and depend on season, location and experimental approach. Two mesocosm studies showed a decrease of DMS due to decreasing DMSP to DMS conversion by bacteria (Archer et al. 2013; Hussherr et al. 2017). However, several microcosm studies indicated DMS production and emissions to be resilient to ocean acidification in the Arctic (Hopkins et al. 2020). This is in line with the ability of polar bacteria to cope with strong pH fluctuations over the range 7.5–8.3 (Kapsenberg et al. 2015; Hoppe et al. 2018) emphasizing the close link between DMS concentrations and bacterial activity and metabolism under ocean acidification. However, a recently refined modelling study suggests a reduction of DMS concentrations under expected OA ( $R^2 = 0.89$ ) scenarios (socio-economic pathway 5-8.5 scenario) (Zhao et al., 2024). Yet, for the northern hemisphere, probably because of higher human impact, the correlation was less pronounced ( $R^2 = 0.4$ ). Thus, there is still a remaining uncertainty of future DMS production behaviour under OA.

### ***Physical properties***

The melting of sea ice could alter energy transfer between the ocean and the atmosphere, and result in an increased air-sea gas exchange. Although this is likely to happen with high regional variations it will strongly affect DMS and CO fluxes between the ocean and atmosphere. Table 1 summarizes the expected changes and their potential impact on DMS and CO Arctic surface water concentration and their emissions from the Arctic Ocean.

**CO.** Increasing stratification could in future CO emissions from the Arctic Ocean. Higher CO concentrations coincided with intensified stratification (e.g. in the Greenland Sea) compared to other regions (Tran et al. 2013). Moreover, CO surface concentrations within the upper 10 m of the water column were significantly higher when the mixed-layer depth was reduced in combination with an increase of CDOM (Tran et al. 2013). These observations may speak for increasing CO emissions in future, since they can be explained by physical properties such as temperature, salinity, water movement and wind, which are all influenced by the retreat and higher mobility of sea ice (Vancoppenolle et al. 2013; Timmermans and Marshall 2020). However, most important for the overall CO emissions probably is microbial CO consumption, because it determines the time CO resides in the surface (Tran et al. 2013).

**Table 1** Summary of the expected changes discussed in this article, and their potential impact on DMS and CO Arctic surface water concentration and their emissions from the Arctic Ocean. + = probable increase; +/- = might be balanced; ? = uncertain.

	DMS	CO
Ice melting	+/-	+
Increasing light availability	+	+
Changes in phytoplankton community	+	+
Changes in bacterial community	?	?
Ocean acidification	?	?
Air-sea gas exchange	+/-	+/-

**DMS.** Rising temperatures of surface waters and sea ice melting could increase concentrations and sea-air fluxes of DMS (Jarníková et al. 2018). In the open Arctic Ocean, DMS gradients seem to occur with strong surface temperature and salinity gradients, suggesting that oceanographic fronts

could play a role for changes in DMS concentration (Jarníková et al. 2018), and which could occur more often in future with sea ice melting. The annual DMS flux from the Arctic Ocean to the atmosphere was estimated to increase by more than 80% by 2080, and could significantly change summer aerosol concentrations and the radiative balance in the Arctic region (Gabric et al. 2005). However, it is not yet clear to what extent increasing DMS emissions will add to the atmospheric DMS mole fractions (Levasseur 2013). Models that incorporate sea ice DMS production into DMS emission estimates, show that first year ice enhances DMS production by 18 % and DMS release to the atmosphere by 20 – 26 % (Hayashida et al. 2017). This indicates that under-ice DMS production contributes significantly to DMS emissions in the Arctic Ocean when the ice is melting (Elliott et al. 2012) and therefore ice loss might reduce DMS emissions. However, less snow accumulation could promote DMS release to the atmosphere (e.g. Lannuzel et al. 2020), potentially further enhanced by increasing sea ice mobility, whereas increasing rain would promote DMS deposition to the water column (Galindo et al. 2014).

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## 2 THESIS OUTLINE

Dimethylsulphide (DMS) and carbon dioxide (CO) are climate -relevant trace gases which play key roles in the radiative budget of the Arctic atmosphere. As the Arctic plays a central role for global climate dynamics, emissions of CO and DMS are crucial to be understood and correctly estimated in such a sensitive region. Under global warming, Arctic Sea ice retreats at an unprecedented rate, altering light penetration and biological communities, and potentially affect DMS and CO cycling in the Arctic Ocean (AO). Just in this region, CO observations are scarce and DMS cycling is still not fully unravelled, especially the complexity and intertwine of the underlying biochemical processes. Thus, little is known about CO production pathways and emissions in this region and the future development of DMS and CO cycling. Presumably, the production of DMS and CO might increase with progressing ice melt, increasing light availability and shifting bacterial and phytoplankton community. Concretely, knowledge gaps centre on details of the physiological role of DMSP, its interaction with changing physiochemical conditions, for example a reduced pH (ocean acidification) in the AO, the role of bacterial CO and DMS metabolism, the lack of CO measurements and high uncertainties in DMS flux estimates, hindering the improvement of emission projections from the Arctic Ocean. Contributing to that end, we designed ship-based incubation experiments in the Fram Strait, Arctic Ocean, collecting data on the effect of potential Arctic environmental changes on CO and DMS production and consumption processes. Therefore, we asked the following research questions:

1. Does a decrease in pH significantly affect the concentration and production/consumption rates of CO and DMS?

2. Does the presence vs. the absence of light significantly affect the concentration and production/consumption rates of CO and DMS?
3. Which environmental parameters have a significant effect on CO and DMS cycling processes?

To address those questions, we performed incubation experiments at three and four different locations to investigate DMS and CO related processes, respectively, distributed over the eastern, central and western Fram Strait. Ocean acidification scenarios of RCP 4.5 and 8.5 were mimicked by accordingly manipulating the seawater pH. Samples were incubated for 48 hours under dark as well as light conditions to check whether the presence/absence of light e.g. reflecting the presence/absence of an ice cover, has an effect. The experiments took place during August/September 2019, thus in late summer season which adds to the mostly central summer data sets. The Fram Strait is a well-studied and important deep gateway between the northern North Atlantic and central Arctic Ocean harbouring two different hydrographic regimes, the West Spitsbergen Current transporting Atlantic water and the East Greenland Current transporting polar water. Experimental stations touched upon both hydrographic regimes and thereby a variety of environmental conditions to get an idea on how those affect CO and DMS concentrations changes.

Accordingly, this thesis is divided into the following chapters, each one addressing the investigation of one gas:

**Chapter 3:** Carbon monoxide (CO) cycling in the Fram Strait, Arctic Ocean

**Chapter 4:** Late summer dimethylsulphide (DMS) cycling in the Fram Strait, Arctic Ocean

With this work we aim to improve the understanding of the biochemical cycling processes of the two climate active gases CO and DMS in the surface waters of the Arctic Ocean, and to provide observational data that could be incorporated into modelling approaches of the future Arctic radiative budget.

# 3 CARBON MONOXIDE (CO) CYCLING IN THE FRAM STRAIT, ARCTIC OCEAN

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**Abstract.** Carbon monoxide (CO) influences the radiative budget and oxidative capacity of the atmosphere over the Arctic Ocean, which is a source of atmospheric CO. Yet, oceanic CO cycling is understudied in this area, particularly in view of the ongoing rapid environmental changes. We present results from incubation experiments conducted in the Fram Strait in August/September 2019 under different environmental conditions: While lower pH did not affect CO production ( $GP_{CO}$ ) or consumption ( $k_{CO}$ ) rates, enhanced  $GP_{CO}$  and  $k_{CO}$  were positively correlated with coloured dissolved organic matter (CDOM) and dissolved nitrate concentrations, respectively, suggesting microbial CO uptake under oligotrophic conditions to be a driving factor for variability in CO surface concentrations. Both production and consumption of CO will likely increase in the future, but it is unknown which process will dominate. Our results will help to improve models predicting future CO concentrations and emissions and their effects on the radiative budget and the oxidative capacity of the Arctic atmosphere.

## 3.1 INTRODUCTION

Carbon monoxide (CO) is a short-lived atmospheric trace gas which plays an important role for the radiative budget and oxidative capacity of the Earth's atmosphere (Forster et al., 2021). Overall, the surface ocean is a minor source of atmospheric CO contributing about 0.4 to 0.8 % to the natural and anthropogenic sources of CO (Conte et al., 2019; Zheng et al., 2019). However, CO has a comparably short atmospheric lifetime of 1 - 3 months (Zheng et al., 2019) and thus its oceanic emissions can contribute significantly to the atmospheric CO budget in the atmospheric boundary layer of remote areas such as the Arctic Ocean where the influence of other CO sources is marginal (Blomquist et al., 2012; Kort et al., 2012). However, there are only a few studies on dissolved CO in the Arctic Ocean (Tran et al., 2013; Xie et al., 2009; Xie and Gosselin, 2005). In general the variability of dissolved CO concentrations is higher in the Arctic Ocean as compared to other ocean basins (Tran et al., 2013). Particularly high CO concentrations were measured within bottom sea ice colonized by algae (Xie and Gosselin, 2005; Song et al., 2011).

Oceanic CO is mainly produced photochemically via the reaction of UV-light with coloured dissolved organic matter (CDOM) (see e.g., Ossola et al., 2022; Powers and Miller, 2015; Stubbins et al., 2006b; Wilson et al., 1970) and particulate organic matter (POM) (Stubbins et al., 2006; Song and Xie, 2017). There is also evidence for thermal (dark) CO production from dissolved organic matter (DOM) (Zhang et al., 2008) and for biological CO production by phytoplankton (Tran et al., 2013; Gros et al., 2009; Mcleod et al., 2021). Tran et al. (2013) suggested that *Phaeocystis sp.*, dinoflagellates and, to a lesser extent, diatoms are the major biological CO producers in the Fram Strait. However, the CO production by algae lacks research on the physiological mechanisms and their interdependencies with biogeochemical

parameters (Campen et al., 2022). Besides the emissions to the atmosphere, microbial consumption is the major loss process of CO in the ocean (Xie et al., 2005; Conrad et al., 1982; Bates et al., 1995).

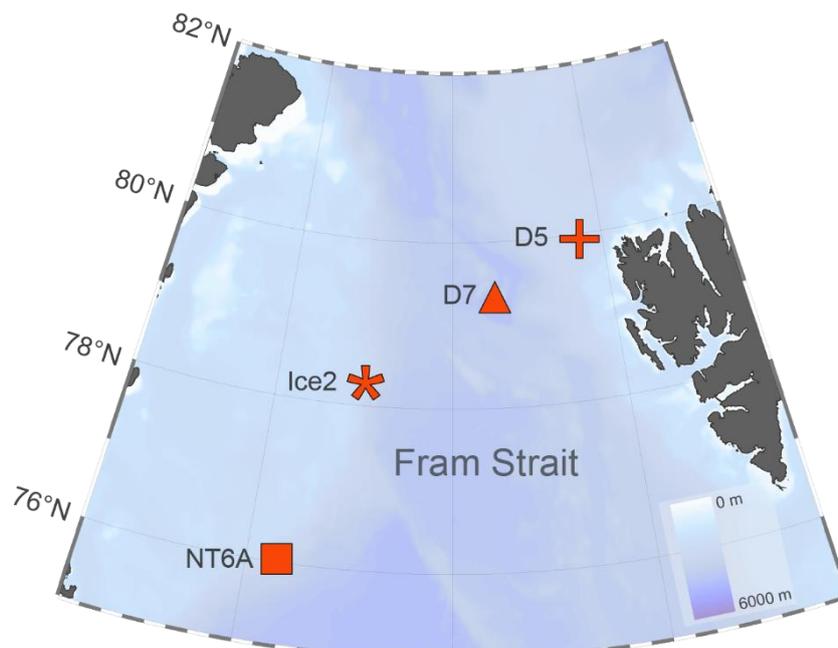
Ongoing environmental changes in the Arctic Ocean such as the loss of sea ice, changing light penetration in the upper ocean, ocean acidification and altered nutrient and organic material supply (e.g. Thackeray and Hall (2019); Stedmon et al. (2011); Hopwood et al. (2018); Terhaar et al. (2020)) might affect CO production and consumption pathways as well as its emissions to the atmosphere from this region (Campen et al., 2022). The distribution and magnitude of coastal nutrient fluxes is predicted to change (e.g. Hopwood et al. (2018)) due to increasing freshwater inputs via ice melting, which could lead to increased stratification and, in turn, limiting nutrient availability in the surface layer (Lannuzel et al., 2020). However, between 2012 and 2018 chlorophyll *a* concentration in Arctic Ocean surface waters increased 16 times faster than before, suggesting an additional input of nutrients that could fuel an increase in primary production (Ardyna and Arrigo, 2020) which in turn might lead to an increase in precursors of CO such as CDOM. Furthermore, light availability and penetration at the ocean surface is projected to increase due to loss of ice and decreasing albedo (Pistone et al., 2014; Castellani et al., 2022), potentially enhancing CO production in open surface waters and under-ice water during the melting season. Due to the increase of atmospheric carbon dioxide (CO<sub>2</sub>), the pH in the surface ocean is decreasing (Canadell et al., 2021) and model projections suggest that pH in Arctic Ocean surface waters could significantly decrease by the end of this century (Terhaar et al., 2020). Decreasing pH (i.e. ocean acidification, OA) is likely to influence the CDOM pool which, in turn, would alter CO production processes (Hopkins et al., 2020). However, to our knowledge, no studies on the effect of OA on CO cycling in the ocean have been published (Hopkins et al. (2020)). How these environmental changes will affect CO production and emissions from the Arctic Ocean is unknown so far due to limited measurements

and knowledge gaps with regards to its sources and sinks. To this end, the major objectives of our study were (i) to identify the main drivers of CO production and consumption in the Fram Strait and (ii) to assess the effect of ocean acidification on CO cycling.

## 3.2 MATERIALS AND METHODS

### 3.2.1 Study area

The study was conducted on board the RSS James Clark Ross during the JR18007 cruise to the Fram Strait from 4 August to 6 September 2019. The Fram Strait, located between the west coast of Svalbard and the east coast of Greenland, is characterized by the inflow of Atlantic water via the West Spitzbergen Current (WSC) in the east and Arctic water outflow via the East Greenland Current (EGC) in the west (Rudels et al., 2015; Rudels et al. (2015)). Four incubation



*Figure 1: Map showing the locations where incubation experiments were performed (stations NT6A, Ice2, D7 and D5).*

experiments were conducted at stations NT6A, Ice2, D7 and D5 (Fig. 1). The stations NT6A, Ice2 and D5 were located at the shelf break, whereas D7 was located in the open ocean region of the Fram Strait. Moreover, Ice 2 and D5 were in proximity to the ice edge. The EGC affected

Ice2 as indicated by its lower salinities and colder water temperatures, whereas D5 and D7 were influenced by warmer and more saline Atlantic waters of the WSC (Table S1 in the Supplement).

### 3.2.2 Experimental setup

For the incubation experiments, seawater from 5 m water depth was drawn from Niskin bottles attached to a 12-bottle CTD/rosette and subsequently incubated in experimental enclosures for up to 48h. In total, eighteen 3.5 L light-transmitting incubation bottles (DURAN®, quartz glass, GL 45, DWK Life Sciences, Germany) were filled with seawater. Lids (GL 45) had Teflon-coated septa to easily press out the bulk water and close the bottles gas tightly. Teflon was chosen to minimize the influence of plastic-derived CO in the experimental setup (Xie et al., 2002). Shading was minimized and natural light exposure was maximized by placing the bottles upside down in t

he incubators, which were fixed on a mostly non-shaded area of the ship's deck. To characterize the setting of the upper water a vertical profile down to 100 m was performed before the start of the incubations. CO concentrations and ancillary measurements (see S2) from 5 m water depth served as sampling time 0 ( $t_0$ ) of the incubations.

Triplicate bubble-free seawater samples for the determination of dissolved CO were taken in 100 mL glass vials (both from Niskin bottles and incubation bottles) by using a Tygon® tubing to avoid contamination by silicone rubber (Xie et al., 2002). The vials were immediately sealed with Teflon-coated stoppers to minimize CO contamination (Xie et al., 2002). The vials were stored between 0 and 6 °C in the dark to suppress further CO photoproduction. CDOM was sampled in brown 500 mL glass vials with a screwed cap. Inorganic nitrate samples were drawn into 10 mL polyethylene tubes, which were pre-rinsed three times with sample water and stored

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at  $-80^{\circ}\text{C}$  until analysis at the Chemical Oceanography Department of GEOMAR. CDOM samples were stored in the dark and below  $5^{\circ}\text{C}$  until filtration (for method details see S2).

The pH in each experiment was manipulated to represent three different atmospheric  $\text{CO}_2$  mole fractions:  $405.43 \pm 0.05$  (Dlugokencky and Thoning, 2021), 670 and 936 ppm  $\text{CO}_2$  for the treatments named ambient, pH1 and pH2, respectively. To this end, the pH in pH1 and pH2 was adjusted by lowering the pH by 0.14 and 0.3, respectively, to approximate the IPCC's representative concentration pathway (RCP) 4.5 (moderate change) and RCP 8.5 (extreme change) relative to the ambient carbonate chemistry of the seawater at the time of the sampling (Table S2). To manipulate the carbonate system,  $\text{NaHCO}_3$  and  $\text{HCl}$  were added (Riebesell et al., 2011) and checked for the resulting total alkalinity (TA) and dissolved inorganic (DIC) concentrations (Table S2). Values of  $p\text{CO}_2$  and  $\text{pH}_T$  (total scale) were calculated with the software CO2sys (Lewis and Wallace, 1998). Immediately after pH manipulation, bottles were gas tightly closed and incubated.

Light incubators had transparent Plexiglas® sidewalls (GS 2458 UV transmitting) and no lid, so that the full natural sunlight spectrum could penetrate the enclosed incubation bottles from the sides and above (self-manufactured according to experimental needs, Fig. S3.1 in the supplements). While these incubators were placed on deck to allow natural sunlight penetration, black and covered water chambers served as dark incubators to exclude any light. The incubation bottles were placed inside the incubators which were filled with ambient seawater pumped through the incubator to keep bottles at ambient seawater temperatures. Light and temperature were monitored continuously in each incubator (HOBO pendant® temperature/light, onset, USA). Oxygen saturation (in %) was monitored to make sure that the incubations did not become anoxic (O2xyDot®, OxySense, USA).  $\text{CO}$  concentrations were determined at the beginning of the incubation ( $t_0$ ), after 12 h ( $t_{12}$ ), 24 h ( $t_{24}$ ) and 48 h ( $t_{48}$ ) of incubation (Fig. S3.1).

### 3.2.3 CO measurements

Dissolved CO concentrations were determined by the headspace method as described by Xie et al. (2002). We established a headspace by injecting 15 mL of CO-free synthetic air (purified via MicroTorr series, 906 media, SAES group, USA). The samples were then equilibrated for eight minutes (Law et al., 2002; Xiaolan et al., 2010). A 5 mL subsample from the equilibrated headspace was injected with a gastight syringe into the sample loop of a CO analyser (ta3000 AMETEK, USA). Every sixth sample injection was followed by the injection of a standard gas mixture with 113.9 ppb CO in synthetic air (DEUSTE Gas Solutions, Germany) which was calibrated against a certified standard gas (250.5 ppb CO, calibrated against the NOAA 2004 scale at the Max Plank Institute for Biogeochemistry, Jena, Germany). This value was chosen as it lies in the expected range of the CO mole fraction equilibrated with open ocean waters. Blank measurements were performed before sample measurements by injecting CO-free synthetic air. No contamination by CO was detectable and, therefore, no blank correction was applied.

Measured CO mole fractions from the headspace were corrected for the drift of the detector with the standard gas measurements and corrected for water vapour (Wiesenburg and Guinasso, 1979). The final dissolved CO concentrations were calculated based on Stubbins et al. (2006) with the solubility coefficients from Wiesenburg and Guinasso (1979). For each of the CO concentration triplicates we calculated the arithmetic mean and estimated the standard error according to (David, 1951). The overall mean error for the measurements of dissolved CO was  $\pm 0.025 \text{ nmol L}^{-1}$  ( $\pm 17.4 \%$ ). The lower detection limit of the CO analyser is 10 ppb CO in air which translates to a detection limit of about  $0.01 \text{ nmol L}^{-1}$  for dissolved CO concentrations at equilibrium at water temperatures of  $-1$  to  $4 \text{ }^\circ\text{C}$  and salinities of 30 to 35.

## 2.4 CO consumption and production rates

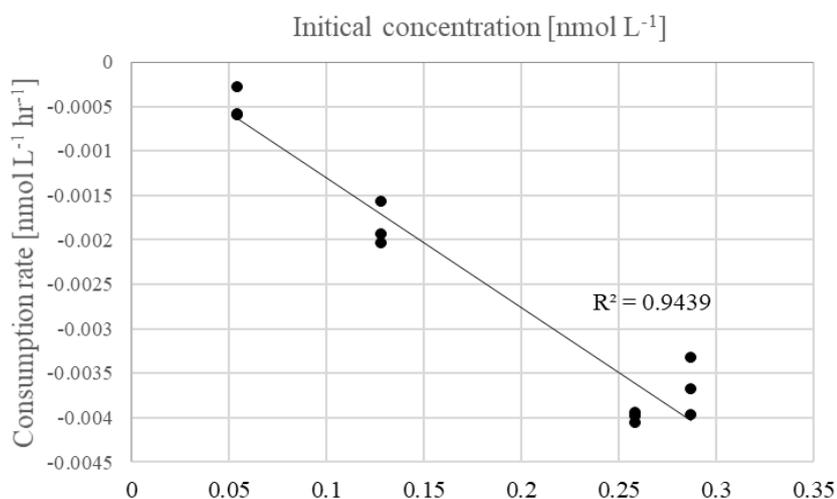
Net CO consumption ( $NC_{CO}$ ) and net production rates ( $NP_{CO}$ ) were calculated as the slope of the linear regression line for CO concentration  $[CO]$  loss and increase over the duration of the experiment (48 hours) and per pH treatment:

$$NC_{CO} = -[CO] * t^{-1} \quad (1)$$

$$NP_{CO} = [CO] * t^{-1} \quad (2)$$

Gross production rates of CO ( $GP_{CO}$ ) were calculated as the sum of  $NP_{CO}$  and the absolute value of  $NC_{CO}$  in order to demask the effect of microbial CO consumption in the light experiments:

$$GP_{CO} = NP_{CO} + NC_{CO} \quad (3)$$



**Fig. 2** Initial CO concentrations plotted against overall consumption rates per experiment. All consumption rates depend on the initial CO concentration (i.e. first order loss;  $R^2 = 0.94$  with  $p < 0.05$ ; see also Fig. S3.2).

To increase data points when possible, single CO gross production rates ( $singleGP_{CO}$ ) were calculated between two sampling times (0 – 12 h, 0 – 24 h, 0 – 48 h) for each treatment and for each experiment, respectively. Since consumption rates followed a first order loss for all

experiments (Fig. 2 and Fig. S3.2), the consumption rate constant ( $k_{CO}$ ) for each experiment was determined as the slope of the respective linear regression.

## 3.3 RESULTS AND DISCUSSION

### 3.3.1 CO concentration development during dark and light incubations

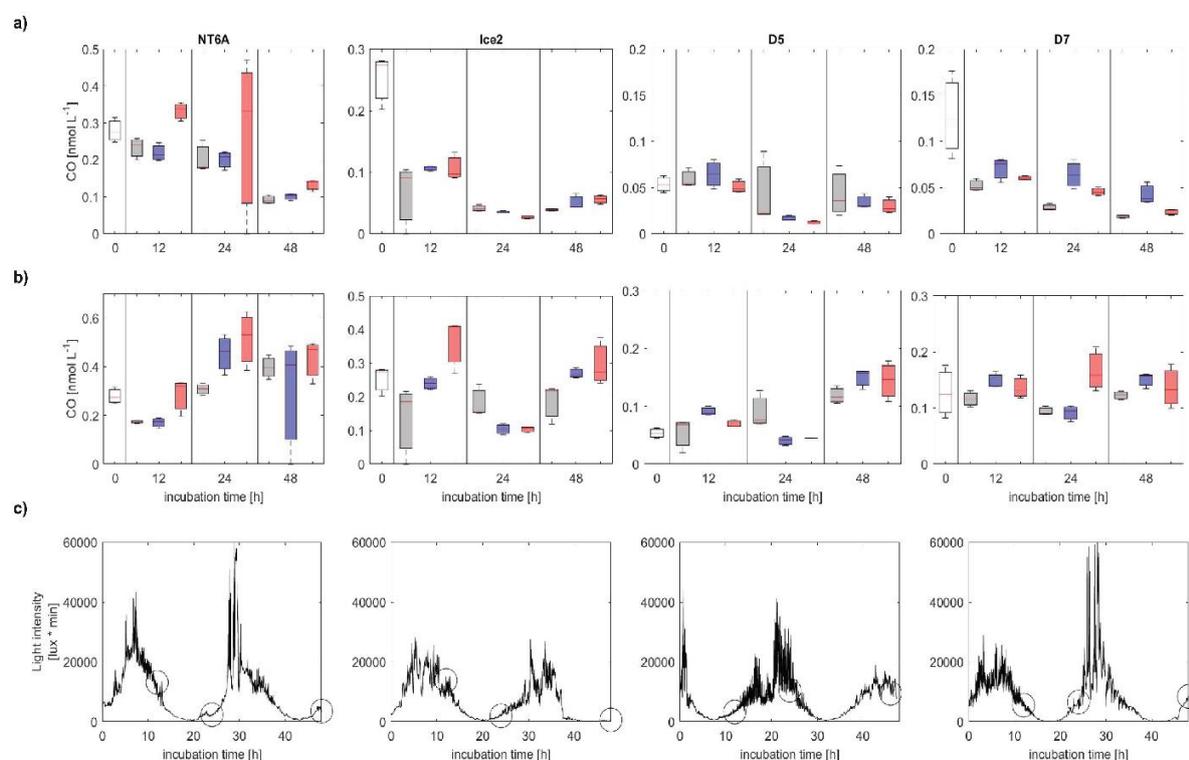
The low initial CO concentrations (Table 2) are in line with the observation that CO in surface waters can show a pronounced seasonal variability in Arctic waters. For example, Xie et al. (2009) reported considerably lower CO concentrations for September/October 2003 (0.17 – 1.34 nmol L<sup>-1</sup>) than for June 2004 (0.98 – 13 nmol L<sup>-1</sup>) in the Amundsen Gulf (Beaufort Sea). Tran et al. (2013) reported a mean CO concentration of 6.5 +/- 3.2 nmol L<sup>-1</sup> in Polar waters of the Fram Strait in July 2010. And only recently Gros et al. (2023) reported mean CO concentrations in the range from 1.5 +/- 1.7 nmol L<sup>-1</sup> (in surface waters at sea-ice stations) to 5.9 +/- 2.9 nmol L<sup>-1</sup> (in Polar waters) from the Fram Strait in May/June 2015.

**Table 2** Initial CO concentrations and CO consumption rate constants ( $k_{CO}$ ) of the four incubation experiments conducted at different pH levels. Data are given as mean  $\pm$  estimate of standard deviation (for the initial CO concentrations) and as the slope of the linear regression  $\pm$  error of the slope (for  $k_{CO}$ ).

Station	Initial CO concentration [nmol L <sup>-1</sup> ]	$k_{CO}$ , amb [hr <sup>-1</sup> ]	$k_{CO}$ , pH1 [hr <sup>-1</sup> ]	$k_{CO}$ , pH2 [hr <sup>-1</sup> ]
NT6A	0.28 $\pm$ 0.035	-0.023 $\pm$ 0.004	-0.021 $\pm$ 0.003	-0.016 $\pm$ 0.012
Ice2	0.25 $\pm$ 0.041	-0.038 $\pm$ 0.015	-0.035 $\pm$ 0.018	-0.034 $\pm$ 0.023
D5	0.05 $\pm$ 0.009	-0.006 $\pm$ 0.003	-0.014 $\pm$ 0.019	-0.016 $\pm$ 0.021
D7	0.13 $\pm$ 0.049	-0.038 $\pm$ 0.0095	-0.021 $\pm$ 0.005	-0.033 $\pm$ 0.005

CO concentrations decreased with time in all dark incubations, with the exception of pH2 at NT6A (Fig. 3 and Fig. S3.2). While the general decrease in CO was most likely driven by microbial consumption which is the major known CO consumption process in Arctic waters (e.g. Xie et al. (2005); Xie et al. (2009)), elevated CO concentrations at NT6A (pH2) could hint

towards ongoing thermal CO production (Zhang et al., 2008). All light treatments showed a diurnal pattern of light intensity, though light was never completely absent because the incubations were performed in the Arctic summer. CO concentrations in the light incubations showed no uniform trend with time. Only during the incubations NT6A and D5 a significant increase of CO concentrations over 48 h was observed. However, this a net production which includes microbial CO consumption. Since there was no obvious relationship between the timing of the sampling, CO concentrations and preceding light intensities (Fig. 3), this indicates that photochemical CO production did not exceed CO consumption. We therefore



**Fig. 3** Development of CO concentrations (nmol L<sup>-1</sup>) over 48 hours of incubations a) in the dark and b) in natural sunlight. c) shows the respective light intensities in the light treatments at each station (light intensities in the dark treatment were zero). Circles indicate the timing of sampling events in dark and light treatments. white = initial concentration, grey = ambient, blue = pH1, red = pH2. The station names are indicated on the top. Please note that the scales of the y axes are varying between stations according to their CO maximum concentrations. The vertical extent of the bars in a) and b) depicts the spread of triplicate samples and the line within each bar indicates the average.

suggest that if there was photochemical CO production, it was directly consumed by bacteria. Alternatively, biological CO production by phytoplankton (Gros et al., 2009; Tran et al., 2013)

or bacterioplankton and/or thermal production might have been dominant at NT6A and D5 (Zhang et al., 2008).

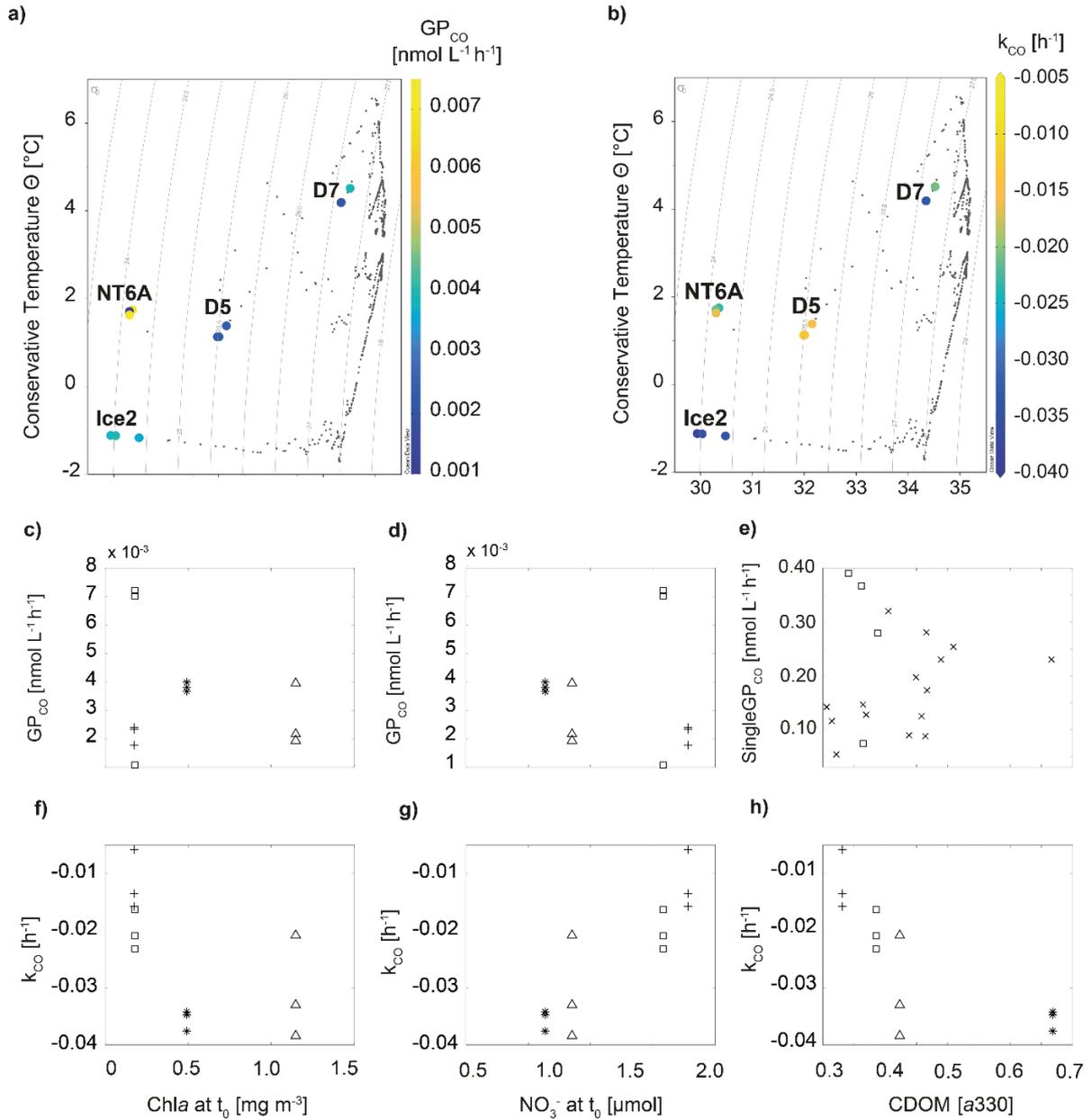
The  $k_{CO}$  computed from our experiments (Table 3) are comparable to previously published findings from Arctic waters: Xie et al. (2005) reported first order consumption rates constants  $k_{CO}$  of  $-0.040 \pm -0.012 \text{ hr}^{-1}$  and  $-0.020 \pm -0.0060 \text{ hr}^{-1}$  in the coastal and offshore Beaufort Sea, respectively. (Please note that  $k_{CO}$  are given as positive values in Xie et al. (2005)).

In general, a lower pH did not affect the CO concentrations neither in the dark incubations nor in the light incubations, since the CO concentrations in the pH manipulated treatments did not differ significantly from the ambient treatments (as indicated by the error bars in Fig. 3). Accordingly, pH affected neither  $k_{CO}$  nor  $GP_{CO}$  significantly during our incubations (see also Fig. S3.3).

### **3.3.2 Effect of environmental variability on CO consumption and production**

We observed contrasting hydrographic settings at the stations selected for the incubation experiments. While Ice2 was located close to the ice edge and had a low water temperature and low salinity at  $t_0$ , D7 was located in the open Fram Strait with a higher water temperature and salinity at  $t_0$  (Fig. 4). Therefore, Ice2 was most probably affected by freshwater input from ice melting and polar waters carried by the EGC (Fig. 4 and Table S1). D5 had a lower salinity compared to D7 and was also (at least partly) affected by freshwater from ice melting. NT6A had a low salinity which was comparable to Ice2 but the water temperature at  $t_0$  was much higher compared to Ice2. Moreover, station NT6A had a steep halocline in about 10 m, whereas Ice2 was well mixed in the upper layer (Fig. S3.4). Therefore, NT6A also being the southernmost station during our study had an apparently different hydrographic setting in comparison to the other three stations. When considering all stations except for NT6A,  $GP_{CO}$  showed a statistically significant correlation ( $R^2 = 0.58$ ,  $p < 0.05$ ) with increasing density. This

suggests that surface waters in the Fram Strait with a higher fraction of freshwater (i.e. lower density), due to e.g. fresh meltwater or polar inflow in the west Fram Strait, potentially lead to higher CO production rates. There was no significant relationship for  $k_{CO}$  with density, which



**Fig. 4** Relationship between  $GP_{CO}$ ,  $k_{CO}$  and selected environmental variables during the study. a) temperature/salinity plot including  $GP_{CO}$ , b) temperature/salinity plot including  $k_{CO}$ , c-d)  $GP_{CO}$  vs.  $Chla$  and  $NO_3^-$  at  $t_0$ , d)  $singleGP_{CO}$  vs.  $CDOM$  absorption (330 nm) at each sampling time, f-h)  $k_{CO}$  vs.  $Chla$ ,  $NO_3^-$  and  $CDOM$  absorption (330 nm) at  $t_0$ . □ = NT6A, \* = Ice2, + = D5, Δ = D7, x =  $CDOM$  values at single sampling times of all stations excl. NT6A. In a) and b) isolines represent density.

indicates that besides meltwater and polar waters additional factors must have influenced CO consumption in the area at the time of sampling.

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Given that CDOM is the major driver for CO photoproduction in the ocean (see e.g. Ossola et al., 2022), a good correlation between both was an underlying assumption during our experiments. We observed that CDOM absorption for all treatments significantly correlated with  $\text{singleGP}_{\text{CO}}$  ( $R^2 = 0.45$ ,  $p < 0.05$ , Fig. 4; data from NT6A excluded). Moreover, CDOM absorption at  $t_0$  was significantly correlated with  $k_{\text{CO}}$  ( $R^2 = 0.57$ ,  $p < 0.05$ ). Given that photochemical production from CDOM is a CO source, this is most likely an indirect correlation: High CDOM absorption induces photochemical CO production which, in turn, results in higher CO consumption (i.e. a lower  $k_{\text{CO}}$ ) because  $k_{\text{CO}}$  depends on the initial CO concentration.

Neither  $\text{GP}_{\text{CO}}$  nor  $k_{\text{CO}}$  was significantly correlated with Chl *a* concentration during our experiments (Fig. 4). This is in contrast to Xie et al. (2005) who reported a negative correlation between Chl *a* and  $k_{\text{CO}}$  (please note again that Xie et al. (2005) reported  $k_{\text{CO}}$  as positive values). This suggests that Chl *a* /  $k_{\text{CO}}$  relationships seems to be variable within the Arctic realm, possibly as a result of the complex interplay between different water masses (Cherkasheva et al., 2014; Rudels et al., 2015). Nitrate ( $\text{NO}_3^-$ ) concentrations at  $t_0$  and  $\text{GP}_{\text{CO}}$  were negatively correlated (albeit statistically not significant at the 95% significance level and after excluding NT6A data; Fig. 4), while  $k_{\text{CO}}$  was positively correlated with  $\text{NO}_3^-$  concentrations at  $t_0$  ( $R^2 = 0.78$ ,  $p < 0.05$ , Fig. 4). The combination of relatively higher Chl *a* concentrations at  $t_0$  with lower  $\text{NO}_3^-$  concentrations at Ice2 and D7 with respect to NTA6 and D5, could explain the higher CO consumption rates at the two stations: On the one hand, CO is known to act as competitive inhibitor for ammonium monooxygenase (*amoA*; the enzyme responsible for ammonium oxidation during nitrification; Zhang et al., 2020), resulting in cell uptake of CO under nutrient-deprived conditions (see Vanzella et al., 1989) as those found at the time of sampling. On the other hand, field and laboratory studies (Moran and Miller, 2007 and references therein; Cordero et al. (2019) have shown the ability of bacterioplankton (e.g. the

*Roseobacter* clade) to oxidize CO during heterotrophic growth (i.e. using it as a supplementary energy source rather than a fixed carbon source for building biomass), in particular under oligotrophic conditions. The fact that we still measured oxidation rates in waters with very low CO concentrations might indicate that the dominant community is rather heterotrophic, which in turn could help explaining the poor correlation with Chl *a*. This finding is important for modelling studies constraining marine CO sources and sinks in the framework of future scenarios where warming-derived stratification reduces NO<sub>3</sub><sup>-</sup> supply to the surface ocean. Under such ‘starvation’ conditions, inorganic compounds such as CO could help sustaining small planktonic communities.

Recent results show that NO<sub>3</sub><sup>-</sup> can enhance the photoproduction of carbonyl sulphide (OCS) (Li et al., 2022). OCS and CO photoproduction have a common intermediate in their photoproduction pathways, but photoproduction of OCS and CO in natural waters is anticorrelated (Pos et al., 1998). Even though based on indirect evidence, we suggest that the trend of decreasing CO photoproduction (GP<sub>co</sub>) with increasing NO<sub>3</sub><sup>-</sup> concentrations might be caused by the mechanism suggested by Pos et al. (1998).

## 3.4 CONCLUSIONS

In order to decipher the cycling of CO in the surface waters of the Fram Strait, we measured CO production and consumption rates in various incubation experiments at four sites in the Fram Strait in summer 2019. We conclude that that ocean acidification may not affect CO gross production ( $GP_{CO}$ ) and consumption ( $k_{CO}$ ) rates. Thus, CO produced in surface waters could be rapidly consumed before being emitted to the atmosphere. In consequence, CO production at these depths does not necessarily result in outgassing towards the atmosphere. We therefore infer that CO consumption mainly drives dissolved CO concentrations and hence could act as a ‘filter’ for the subsequent atmospheric CO emissions from the Fram Strait. High rates of both CO production and CO consumption were favoured by a combination of high CDOM and low  $NO_3^-$  concentrations. This suggests a photochemical production of CO from CDOM which, in turn, is consumed rapidly by microbes preferably under oligotrophic conditions such as those found at the time of sampling. In the Arctic Ocean/Fram Strait, such conditions can be found, at least transiently, both at ice edges as well as in the open ocean where a supply of nutrients via melting and/or mixing is followed by stratification (Cherkasheva et al., 2014). We identified both CDOM and  $NO_3^-$  as key drivers of CO cycling. This has the implication that predicted changes in terrestrial-derived and marine CDOM (e.g. Lannuzel et al., 2020), as well as dissolved  $NO_3^-$  inputs (Tuerena et al., 2022) could affect future CO production and consumption in the region. Both trends might lead to higher CO gross production as well as higher CO consumption. It is yet uncertain whether both terms will balance each other out or whether one process will become dominant. The question if and under which conditions CO consumption rates would stagnate should be addressed in future research, since in that situation CO would actually be emitted. Performing further multifactorial experiments including i.e. UV light

intensity and bacterial community data could help to elucidate the explanatory power of the different environmental factors on both CO production and consumption. This would facilitate a better incorporation of both terms into biogeochemical models and would improve both CO emission estimates for the Arctic realm, and the assessment of how atmospheric CO emissions will affect the radiative budget and oxidative capacity of the Arctic atmosphere.

## **AUTHOR CONTRIBUTIONS**

The study was conceived by HIC and HWB. HIC conducted the field work during the JR18007 cruise and carried out the data analysis with HWB. DLAM supported the data analysis and interpretation as well as the preparation of the plots. HIC wrote the manuscript with contributions from HWB and DLAM.

### **Competing interests**

The authors declare that they have no conflict of interest.

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# SUPPLEMENTS

## S.1 Tables

Table S1: Water mass characterization at the time of sampling in the study area (definitions after Marnela et al. (2016)).

Station	Depth [m]	Density [ $\theta$ , kg m <sup>-3</sup> ]	Salinity	Temperature [°C]	Water mass	Origin	Remarks
NT6A	5	24.12	30.04	1.36	wSW - Warm Surface Water	N Atlantic	Shelf break
Ice2	5	24.83	29.02	-1.05	PSW - Polar Surface Water	Arctic	Ice edge / Shelf break
D5	5	25.61	32.00	1.37	wSW - Warm Surface Water	N Atlantic	Shelf break / Sea ice melting
D7	5	27.22	34.78	5.68	wSW - Warm Surface Water	N Atlantic	Open ocean

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Table S2: Mean initial dissolved inorganic carbon (DIC), total alkalinity (TA) and pH at  $t_1$  ( $= t_0 + 12h$ ) for the various treatments. pH was determined spectrophotometrically on board. We used the TA from the temperature/salinity relationship of Lee et al. (2006) to calculate DIC.

Station	pH			TA [ $\mu\text{mol L}^{-1}$ ]			DIC [ $\mu\text{mol L}^{-1}$ ]		
	Ambient	pH1	pH2	Ambient	pH1	pH2	Ambient	pH1	pH2
NT6A	7.96	7.57	7.29	2317.77	1985.29	1865.94	2078.52	1919.09	1882.26
Ice2	7.90	7.46	7.24	2304.14	1913.66	1843.30	2049.64	1895.55	1887.82
D5	7.68	7.30	7.22	2302.46	1871.91	1852.94	1955.49	1882.90	1888.73
D7	7.75	7.85	7.53	2301.06	2108.34	2064.11	2037.41	2013.11	1968.46

## S.2 Methods

### S.2.1 Ancillary measurements

The spectral absorption coefficient of CDOM at 330 nm ( $a_{330}$ ) was determined for the seawater samples in 5 m from the CTD/rosette cast preceding the incubation experiments ( $= t_0$ ) and from the individual experimental units at each timepoint ( $t_{12}$ ,  $t_{24}$ ,  $t_{48}$ ) during the incubations. Each CDOM sample was filtered through a sterile, sample-washed 0.2  $\mu\text{m}$  membrane (GWSP, Millipore) into pre-combusted, sterile brown glass vials. CDOM absorption was measured according to the procedure as described in Lennartz et al. (2019) and the mean error of the method was 8%. We used purified MilliQ water as the reference. A Seabird SBE9plus sensor

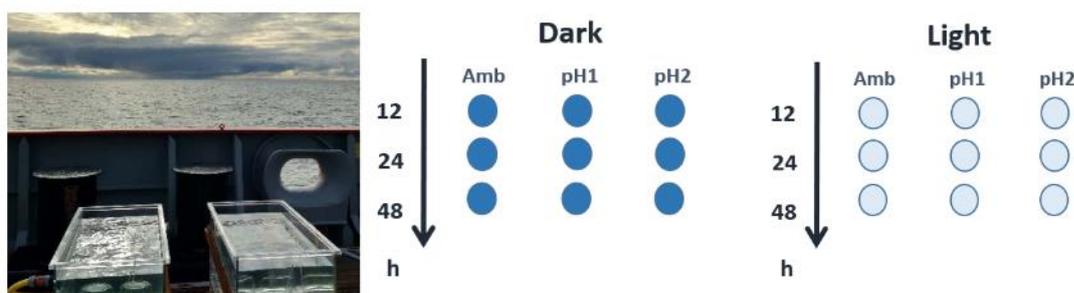
package (<https://www.bodc.ac.uk/data/documents/nodb/pdf/03plusbrochurejan07.pdf>) including an oxygen optode, a fluorescence sensor (Chl a) and a sensor for photosynthetic active radiation (PAR). All sensors were attached to the CTD/rosette. Vertical profiles recorded during lowering the CTD/rosette were considered here only.

Inorganic dissolved nutrients including nitrate were analysed using a Technicon segmented 4-channel flow colorimetric autoanalyser (Bran & Luebbe AAIII, SEAL Analytical). The analytical methods applied are described in Grasshoff et al. (1999). The detection limit was 2 nmol l<sup>-1</sup> during the cruise. The precision of the method was 8%, and of the colorimetric autoanalytical techniques was > 5% (Woodward and Rees, 2001).

### S2.2 Note on statistical analysis

Simple regression test was chosen because multiple regression test had too low explanatory power due to the small number of experimental replicates.

### S.3 Figures



**Fig. S3.1** Experimental set up of incubations. *Left:* The incubator tanks, which were, installed on-deck, supplied with natural seawater and made of natural sunlight-transmitting material, so that natural conditions of the surface ocean were mimicked. *Middle/Right:* Incubations were performed over a total of 48 hours in darkened and light tanks. Each dot represents one experimental unit referring to one treatment and sampling timepoint and was discarded after sampling (gases, CDOM, pH) was done. Samples were taken after 12, 24 and 48 hours. The pH in each experiment was manipulated to two lowered pCO<sub>2</sub> (pH) levels pH1: 670 ppm and pH2: 936 ppm CO<sub>2</sub> in comparison to the ambient pH (amb) as a control.

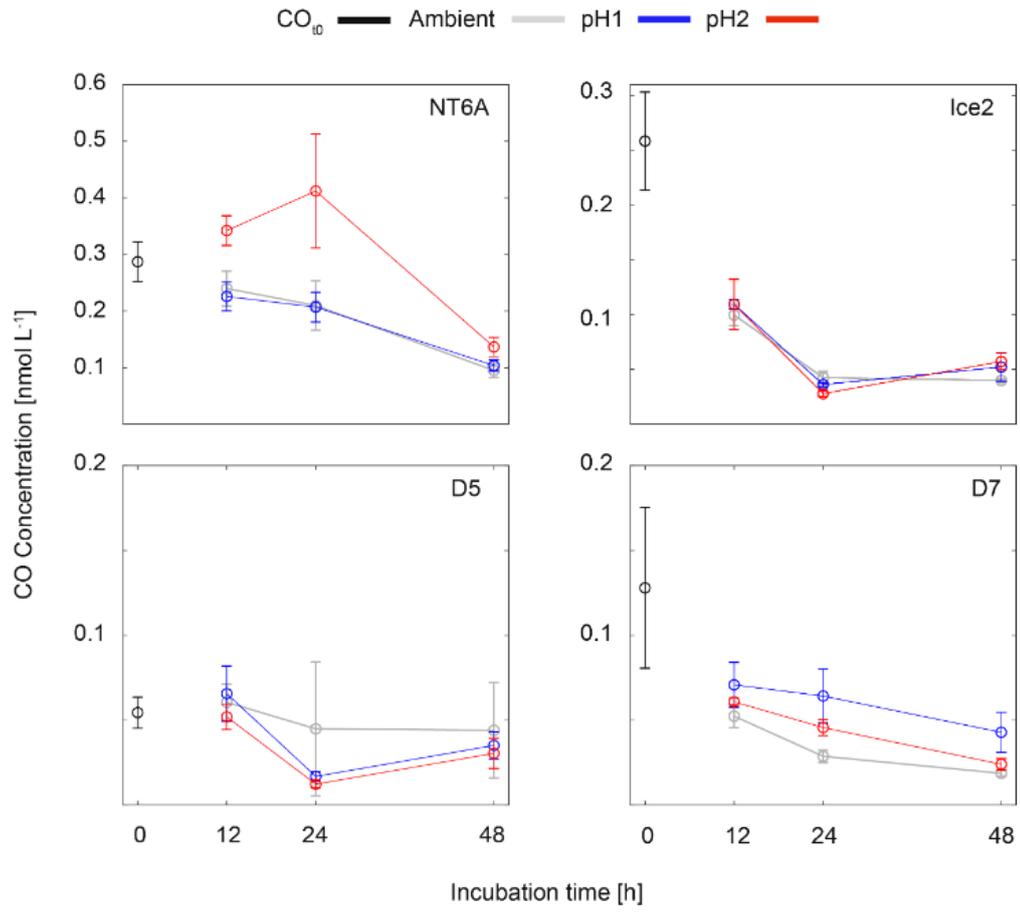


Fig. S3.2 Temporal development of CO concentrations during the dark incubations.  $CO_{t0}$  represents the initial CO concentration for each experiment.

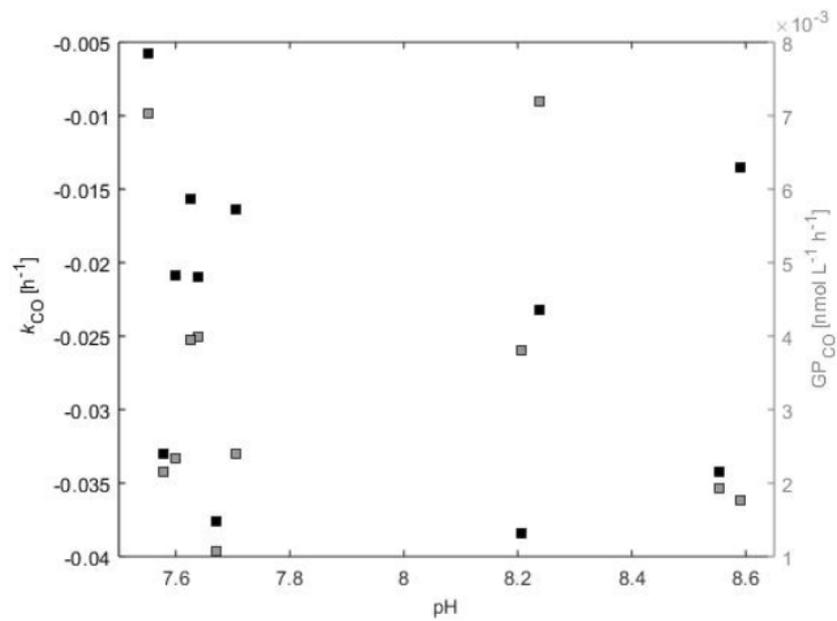
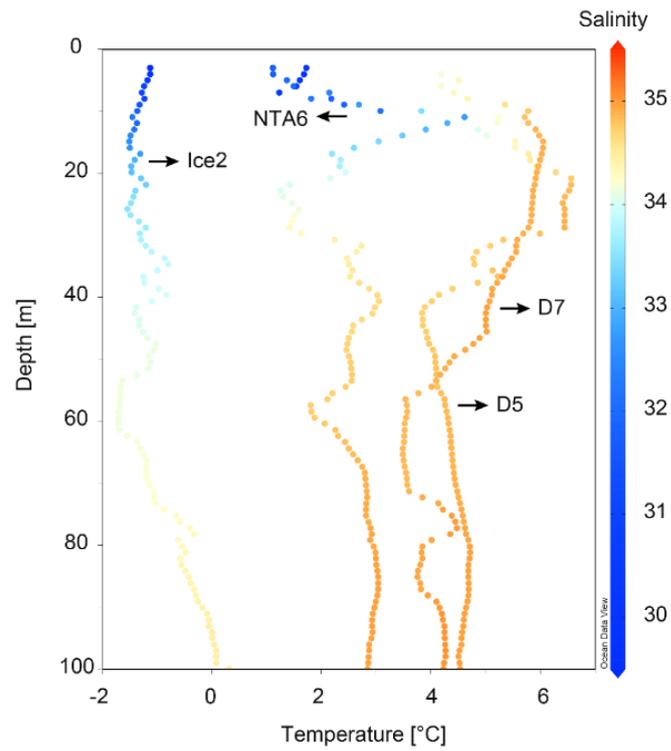


Fig S3.3 pH vs.  $k_{CO}$  and  $GP_{CO}$ .



**Fig. S3.4** Vertical profiles of temperature and salinity at each sampling station in which incubation experiments were conducted.

**S4 Dataset**

**JR18007, RRS James Clark Ross August 2019;  
Vertical profiles**

Station	Date	Lat (N)	Lon East	Depth m	CO [nmol L <sup>-1</sup> ]	nitrate [μmol L <sup>-1</sup> ]	Chl a [mg m <sup>-3</sup> ]	O2 [umol l <sup>-1</sup> ]	Surf PAR [uE*m <sup>-2</sup> *s <sup>-1</sup> ]	Temp [°C]	Sal	density [kg*m <sup>3</sup> ]	Silicate (μmol L <sup>-1</sup> )	Phosphate (μmol L <sup>-1</sup> )
Ice2	16.08.2020	78.30	-4.79	5	<b>0.258</b>	7.8	0.45	418.4	12.95	-1.25	30.89	24.83	2.03	0.49
Ice2	16.08.2020	78.30	-4.79	10	<b>0.044</b>	13.6	0.55	417.2	6.01	-1.37	31.80	25.57	1.97	0.35
Ice2	16.08.2020	78.30	-4.79	35	<b>0.037</b>	17.4	0.37	410.3	0.48	-0.80	33.88	27.24	3.03	0.39
Ice2	16.08.2020	78.30	-4.79	55	<b>0.042</b>	8.4	0.06	340.9	0.13	-1.67	34.14	27.48	4.30	0.85
Ice2	16.08.2020	78.30	-4.79	75	<b>0.036</b>	4.3	0.04	331.4	0.04	-0.87	34.26	27.55	5.61	0.94
Ice2	16.08.2020	78.30	-4.79	100	<b>0.048</b>	8.3	0.03	313.5	0	0.07	34.49	27.69	5.29	1.17
D5	20.08.2020	79.92	8.84	5	<b>0.054</b>	3.9	0.15	351.5	134.65	1.37	32.00	25.61	3.77	0.53
D5	20.08.2020	79.92	8.84	10	<b>0.035</b>	4.6	0.24	341.8	68.7	3.82	33.44	26.56	7.19	0.89
D5	20.08.2020	79.92	8.84	25	<b>0.021</b>	4.6	0.81	323.8	11.01	6.41	34.86	27.39	6.58	0.97
D5	20.08.2020	79.92	8.84	40	<b>0.082</b>	4.9	0.32	335.3	2.76	4.15	34.73	27.56	5.63	0.90
D5	20.08.2020	79.92	8.84	75	<b>0.040</b>	4.3	0.11	312.5	0.26	4.56	34.93	27.67	6.33	1.06
D5	20.08.2020	79.92	8.84	100	<b>0.031</b>	4.4	0.06	308.4	0.05	4.52	34.99	27.72	6.51	1.06
D7	24.08.2020	79.32	2.65	5	<b>0.128</b>	5.3	0.86	347.2	19.54	4.51	34.35	27.22	1.64	0.65
D7	24.08.2020	79.32	2.65	10	<b>0.032</b>	7.1	1.61	340.6	9.15	5.78	34.78	27.41	1.35	0.45

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D7	24.08.2020	79.32	2.65	25	<b>0.029</b>	5.9	0.76	320.5	1.07	5.85	34.91	27.50	2.51	0.57
D7	24.08.2020	79.32	2.65	55	<b>0.027</b>	5.8	0.12	314.9	0.08	4.01	34.88	27.69	3.93	0.87
D7	24.08.2020	79.32	2.65	75	<b>0.038</b>	5.8	0.07	313.9	0.01	4.22	34.97	27.74	5.32	1.64
D7	24.08.2020	79.32	2.65	100	<b>0.036</b>	6.5	0.04	310.1	0	4.24	35.03	27.78		
D10	27.08.2020	77.47	13.49	5	<b>0.009</b>		0.29	341.3	1.6	5.26	33.51	26.47		
D10	27.08.2020	77.47	13.49	10	<b>0.009</b>		0.29	340.5	0.72	5.27	33.51	26.47		
D10	27.08.2020	77.47	13.49	35	<b>0.005</b>		0.8	366.9	0.01	4.43	34.07	27.00		
D10	27.08.2020	77.47	13.49	65	<b>0.004</b>		0.13	331.8	0	3.82	34.48	27.39		
D10	27.08.2020	77.47	13.49	80	<b>0.003</b>		0.08	323.9	0	3.66	34.66	27.55		
D10	27.08.2020	77.47	13.49	100	<b>0.007</b>		0.08	316.9	0	4.04	34.76	27.59		

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**JR18007, RRS James Clark Ross August 2019; Incubations CO**

CO measured in triplicates, CDOM measured in duplicates

treatment: dark=1000/light=2000; pH: amb=-00/pH1=-01/pH2=-02

T0 values for NO<sub>3</sub><sup>-</sup> and CDOM are single values from 5m. Chl *a*, Sal and Temp are avg values calculated from 3 to 7 m

station	date	treatment	sampling time [hrs]	pH	CO [nmol L-1]	CDOM [a330nm]
NT6A		1000	12	8.3	0.21	0.27
NT6A		1000	12	8.3	0.25	0.28
NT6A		1000	12	8.3	0.27	
NT6A		1001	12	7.7	0.25	0.27
NT6A		1001	12	7.7	0.22	0.27
NT6A		1001	12	7.7	0.20	
NT6A		1002	12	7.5	0.37	0.37
NT6A		1002	12	7.5	0.35	0.29
NT6A		1002	12	7.5	0.31	
NT6A		2000	12	8.2	0.18	0.25
NT6A		2000	12	8.2	0.17	0.24
NT6A		2000	12	8.2	0.18	
NT6A		2001	12	7.7	0.18	0.25
NT6A		2001	12	7.7	0.19	0.38
NT6A		2001	12	7.7	0.15	
NT6A		2002	12	7.5	0.34	0.26
NT6A		2002	12	7.5	0.20	0.24
NT6A		2002	12	7.5	0.33	
NT6A		1000	24	8.2	0.19	0.27
NT6A		1000	24	8.2	0.18	0.28
NT6A		1000	24	8.2	0.26	
NT6A		1001	24	7.7	0.21	0.27
NT6A		1001	24	7.7	0.23	0.23
NT6A		1001	24	7.7	0.18	
NT6A		1002	24	7.6	0.34	0.24
NT6A	11.08.- 13.08.2019	1002	24	7.6	0.48	0.26
NT6A		2000	24	8.2	0.29	0.27
NT6A		2000	24	8.2	0.34	0.23
NT6A		2000	24	8.2	0.32	
NT6A		2001	24	7.8	0.55	0.25
NT6A		2001	24	7.8	0.38	0.26
NT6A		2001	24	7.8	0.48	
NT6A		2002	24	7.6	0.55	0.24
NT6A		2002	24	7.6	0.40	0.26
NT6A		2002	24	7.6	0.64	
NT6A		1000	48	8.2	0.11	0.41
NT6A		1000	48	8.2	0.08	0.36
NT6A		1000	48	8.2	0.09	
NT6A		1001	48	7.6	0.11	0.33
NT6A		1001	48	7.6	0.11	0.35
NT6A		1001	48	7.6	0.09	
NT6A		1002	48	7.5	0.15	0.34
NT6A		1002	48	7.5	0.12	0.35
NT6A		1002	48	7.5	0.15	
NT6A		2000	48	8.2	0.41	0.36
NT6A		2000	48	8.2	0.46	0.35
NT6A		2000	48	8.2	0.36	
NT6A		2001	48	7.7	0.50	0.36
NT6A		2001	48	7.7	0.42	0.36
NT6A		2002	48	7.6	0.51	0.34
NT6A		2002	48	7.6	0.34	0.36

NT6A	2002	48	7.6	0.48	
Ice2	1000	12	8.2	0.11	0.46
Ice2	1000	12	8.2	0.09	0.51
Ice2	1001	12	7.7	0.11	0.45
Ice2	1001	12	7.7	0.11	0.48
Ice2	1001	12	7.7	0.10	
Ice2	1002	12	7.6	0.09	0.48
Ice2	1002	12	7.6	0.14	0.47
Ice2	1002	12	7.6	0.10	
Ice2	2000	12	8.2	0.22	0.47
Ice2	2000	12	8.2	0.19	0.47
Ice2	2000	12	8.2	0.24	
Ice2	2001	12	7.7	0.25	0.45
Ice2	2001	12	7.7	0.27	0.46
Ice2	2001	12	7.7	0.23	
Ice2	2002	12	7.3	0.28	0.40
Ice2	2002	12	7.3	0.42	0.42
Ice2	2002	12	7.3	0.42	
Ice2	1000	24	8.2	0.05	0.46
Ice2	1000	24	8.2	0.04	0.47
Ice2	1000	24	8.2	0.04	
Ice2	1001	24	7.6	0.04	0.47
Ice2	1001	24	7.6	0.03	0.50
Ice2	1001	24	7.6	0.04	
Ice2	1002	24	7.4	0.03	0.44
Ice2	1002	24	7.4	0.02	0.46
Ice2	1002	24	7.4	0.03	
Ice2	2000	24	8.2	0.15	0.46
Ice2	2000	24	8.2	0.16	0.45
Ice2	2000	24	8.2	0.12	
Ice2	2001	24	7.6	0.09	0.46
Ice2	2001	24	7.6	0.11	0.45
Ice2	2001	24	7.6	0.12	
Ice2	2002	24	7.5	0.11	0.44
Ice2	2002	24	7.5	0.11	0.42
Ice2	2002	24	7.5	0.10	
Ice2	1000	48	8.2	0.04	0.52
Ice2	1000	48	8.2	0.04	0.54
Ice2	1000	48	8.2	0.04	
Ice2	1001	48	7.7	0.07	0.52
Ice2	1001	48	7.7	0.04	0.51
Ice2	1001	48	7.7	0.04	
Ice2	1002	48	7.5	0.06	0.54
Ice2	1002	48	7.5	0.06	0.52
Ice2	1002	48	7.5	0.05	
Ice2	2000	48	8.2	0.23	0.49
Ice2	2000	48	8.2	0.22	0.49
Ice2	2000	48	8.2	0.30	
Ice2	2001	48	7.7	0.26	0.51
Ice2	2001	48	7.7	0.27	0.54
Ice2	2001	48	7.7	0.29	
Ice2	2002	48	7.5	0.25	0.47
Ice2	2002	48	7.5	0.28	0.47
Ice2	2002	48	7.5	0.38	
D5	1000	12	8.9	0.06	0.20
D5	1000	12	8.9	0.07	0.28
D5	1000	12	8.9	0.05	
D5	1001	12	7.6	0.05	0.18

16.08.  
– 18.08.2019

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D5		1001	12	7.6	0.07	0.16
D5		1001	12	7.6	0.08	
D5		1002	12	7.6	0.05	0.20
D5		1002	12	7.6	0.05	0.19
D5		1002	12	7.6	0.06	
D5		2000	12	8.2	0.07	0.22
D5		2000	12	8.2	0.07	0.17
D5		2000	12	8.2	0.02	
D5		2001	12	7.7	0.10	0.13
D5		2001	12	7.7	0.09	0.17
D5		2001	12	7.7	0.09	
D5		2002	12	7.5	0.08	0.18
D5		2002	12	7.5	0.07	0.18
D5		2002	12	7.5	0.07	
D5		1000	24	8.3	0.02	0.20
D5		1000	24	8.3	0.09	0.21
D5		1000	24	8.3	0.02	
D5	20.08. –	1001	24	7.6	0.02	0.21
D5	22.08.2019	1001	24	7.6	0.02	0.22
D5		1001	24	7.6	0.02	
D5		1002	24	7.8	0.01	0.23
D5		1002	24	7.8	0.01	0.20
D5		1002	24	7.8	0.01	
D5		2000	24	8.3	0.13	0.21
D5		2000	24	8.3	0.08	0.23
D5		2000	24	8.3	0.07	
D5		2001	24	7.6	0.04	0.22
D5		2001	24	7.6	0.05	0.23
D5		2001	24	7.6	0.03	
D5		2002	24	7.5	0.05	0.28
D5		2002	24	7.5	0.05	0.23
D5		2002	24	7.5	0.05	
D5		1000	48	na	0.08	0.30
D5		1000	48	na	0.04	0.37
D5		1000	48	na	0.02	
D5		1001	48	na	0.04	0.32
D5		1001	48	na	0.03	0.38
D5		1001	48	na	0.03	
D5		1002	48	na	0.04	0.32
D5		1002	48	na	0.02	0.32
D5		1002	48	na	0.03	
D5		2000	48	na	0.14	0.31
D5		2000	48	na	0.11	0.51
D5		2000	48	na	0.12	
D5		2001	48	na	0.13	0.36
D5		2001	48	na	0.16	0.34
D5		2001	48	na	0.16	
D5		2002	48	na	0.11	0.31
D5		2002	48	na	0.18	0.30
D5		2002	48	na	0.15	
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D7		1000	12	9.2	0.06	0.27
D7		1000	12	9.2	0.05	0.25
D7		1000	12	9.2	0.05	
D7		1001	12	8.0	0.08	0.25
D7		1001	12	8.0	0.08	0.25
D7		1001	12	8.0	0.06	
D7		2000	12	8.0	0.10	0.25
D7		2000	12	8.0	0.12	0.29
D7		2000	12	8.0	0.13	

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D7		2001	12	8.2	0.14	0.22
D7		2001	12	8.2	0.14	0.23
D7		2001	12	8.2	0.17	
D7		1002	12	na	0.06	0.24
D7		1002	12	na	0.06	0.24
D7		1002	12	na	0.06	
D7		2002	12	na	0.13	0.26
D7		2002	12	na	0.12	
D7		2002	12	na	0.16	
D7		1000	24	8.2	0.03	0.23
D7		1000	24	8.2	0.03	0.23
D7		1000	24	8.2	0.03	
D7	24.08. –	1001	24	7.5	0.05	0.23
D7	26.08.2019	1001	24	7.5	0.06	0.22
D7		1001	24	7.5	0.08	
D7		1002	24	7.4	0.04	0.24
D7		1002	24	7.4	0.05	
D7		1002	24	7.4	0.04	
D7		2000	24	8.3	0.10	0.23
D7		2000	24	8.3	0.09	0.24
D7		2000	24	8.3	0.09	
D7		2001	24	7.5	0.08	0.23
D7		2001	24	7.5	0.10	0.24
D7		2001	24	7.5	0.10	
D7		2002	24	7.1	0.21	0.22
D7		2002	24	7.1	0.16	0.23
D7		2002	24	7.1	0.13	
D7		1000	48	8.2	0.02	0.20
D7		1000	48	8.2	0.02	0.28
D7		1000	48	8.2	0.02	
D7		1001	48	7.4	0.06	0.24
D7		1001	48	7.4	0.04	0.25
D7		1001	48	7.4	0.03	
D7		1002	48	7.3	0.03	0.25
D7		1002	48	7.3	0.03	0.28
D7		1002	48	7.3	0.02	
D7		2000	48	8.3	0.12	0.24
D7		2000	48	8.3	0.13	0.28
D7		2000	48	8.3	0.11	
D7		2001	48	7.5	0.14	0.28
D7		2001	48	7.5	0.16	0.30
D7		2001	48	7.5	0.16	
D7		2002	48	7.2	0.13	0.28
D7		2002	48	7.2	0.10	0.25
D7		2002	48	7.2	0.18	

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# 4 LATE SUMMER DIMETHYLSULPHIDE (DMS) CYCLING IN THE FRAM STRAIT, ARCTIC OCEAN

**Manuscript in preparation:** Campen, H. I. and Bange, H. W.: Late summer dimethylsulphide (DMS) cycling in the Fram Strait, Arctic Ocean

## ABSTRACT

Dimethylsulphide (DMS) is a volatile compound produced in the surface ocean that has an impact on global climate. Especially in remote regions as the Arctic DMS significantly influences climate. Emitted to the atmosphere it has a potential (indirect) cooling effect that is roughly equivalent to the CO<sub>2</sub> warming effect. However, considering the ongoing and projected changes in ocean pH (ocean acidification) and increasing incoming light the consequences for DMS cycling are uncertain. This study investigates the potential effects of a reduced pH according to the Intergovernmental Panel on Climate Change's (IPCC) representative concentration pathway (RCP) 4.5 (moderate change) and RCP 8.5 (extreme change) scenarios under presence and absence of light on the cycling of DMS as well as dimethylsulphoniumpropionate (DMSP) and dimethylsulphoxide (DMSO). Ship-based incubation experiments at three different locations across the Fram Strait were conducted

during an Arctic expedition in late summer 2019. Neither OA nor light were found to have a significant effect. DMS production was tightly coupled to particulate DMSP concentrations. Those in turn correlated significantly with temperature, salinity, POC and PON indicating a regulation by oligotrophic conditions and possibly a senescent bloom. These results add to the seasonal and local diversity in data sets and can therefore contribute to improve DMS modelling estimates to make reliable projections of its behaviour and climate feedback in a future Arctic Ocean.

## 4.1 INTRODUCTION

### 4.1.1 Role of DMS in the Ocean and Atmosphere

Dimethylsulphide (DMS) is a volatile compound that has an important impact on global climate. It is majorly produced in the surface ocean from where it can be emitted to the atmosphere. Oceanic DMS emissions amount to 15 – 40 Tg sulphur (S) yr<sup>-1</sup>, which represents 80 – 90% of all marine biogenic S emissions, and up to 50% of global biogenic S emissions (Lana et al., 2011; Wang et al., 2020). Arctic Ocean DMS emissions are estimated to be 0.005 – 0.013 Tg S yr<sup>-1</sup> (Galí et al., 2021). Due to its sulphur content, it forms sulphate aerosols in the marine atmosphere that can influence the cloud albedo and global radiative forcing (Charlson et al., 1987; Mahajan et al., 2015; Fiddes et al., 2018). Thus, DMS emissions have an indirect cooling effect (-1.7 to -2.3 W m<sup>-2</sup>) (Fung et al., 2022; Thomas et al., 2010; Mahajan et al., 2015) that is roughly equivalent to the warming effect of anthropogenic CO<sub>2</sub> emissions (1.83 ± 0.2 W m<sup>-2</sup>) (Etminan et al., 2016). Though, on a global scale, oceanic DMS emissions do not govern global climate as once hypothesized (Quinn and Bates, 2011). Interdisciplinary research over decades demonstrated that biological DMS production over some regions of the surface ocean substantially affect aerosol distribution, cloud formation and thereby plays a role for the global climate (Carslaw et al., 2013; Fung et al., 2022). Especially in the Arctic summer when aerosol burden is low, oceanic DMS emissions have a significant influence on climate, because it controls the aerosol and cloud condensation in the Arctic atmosphere (Leitch et al., 2013; Woodhouse et al., 2013; Chang et al., 2011). Recent findings of the Atlantic meridional overturning circulation approaching a tipping point (van Westen et al., 2023), emphasized that potentially counteracting processes like DMS emission associated cooling of the Arctic atmosphere become even more important to be estimated correctly. However, due to high regional and seasonal variabilities in DMS emissions, global

estimations reveal high uncertainties (up to  $\pm 10 \text{ W m}^{-2}$ ) (Mahajan et al., 2015; Wang et al., 2020). Those partly rely on observed concentration uncertainties or on the choice of air-sea gas exchange approach which strengthens the need for improvement in both, flux estimation methods and measurements (Zhang 2024) covering a variety of regions and seasons to facilitate accurate modelling projections to yield a better constraint of DMS surface cycling processes. That is especially needed in the Arctic, being a very sensitive region for global climate feedback processes (Arctic amplification) (Serreze and Barry, 2011) and where data coverage is still relatively limited due to seasonal hindrances.

#### **4.1.2 DMS production and consumption**

About 90% of the DMS in the surface ocean is consumed and degraded microbially and photochemically in the water (Galí et al. 2015; Uher et al. 2017). The remaining DMS (<10%) regulates the concentration difference between ocean and atmosphere, hence the sea-to-air flux (Bates et al. 1994).

The ultimate source of DMS in the ocean is dimethylsulphoniopropionate (DMSP). DMSP is predominantly produced in the euphotic zone by photoautotrophs, by bacteria in sediments and in the pelagic (Sun et al., 2016; Moran and Durham, 2019). In several studies the productive waters around Arctic sea-ice and the inhabitant ice algae blooms represent a strong DMS source (Hayashida et al., 2017; Galí et al., 2021; Levasseur et al., 1994) though, they make up a minor contribution globally. DMSP can be either degraded to DMS within algae or it is released and subsequently enzymatically cleaved to DMS by heterotrophs (Fig.1) (Stefels and Dijkhuizen, 1996; Steinke et al., 1998; Niki et al., 2000).

##### ***DMSP production***

So far, DMSP is understood to play a role in many cellular processes, allowing the organism to react and adapt its metabolism to various environmental fluctuations by e.g. regulating the cell's carbon and sulphur content via an overflow mechanism (e.g. Stefels 2000), osmoregulation (van Bergeijk et al.,

2003)), cryo-protection (Kirst et al., 1991), and protection against oxidative stress (Sunda et al., 2002). Thus, pelagic DMSP production is mainly regulated by internal metabolic needs of the producing organisms that is affected by its direct environment: salinity, temperature, nutrient availability, light, oxidants (Kiene et al., 2000; Sunda et al., 2002; Stefels, 2000; Stefels et al., 2012). Since the range and ability of DMSP production varies strongly between phytoplankton taxa, they are grouped into strong and weak producers, where dinoflagellates and prymnesiophytes, e.g. *Phaeocystis* sp. are considered as strong and diatoms as weak DMSP producers (Keller, 1989; Stefels and Dijkhuizen, 1996; Galí et al., 2021). Consequently, DMSP and DMS distribution strongly depends on microbial community composition and their physiological status that in turn is linked to the environmental and hydrographic conditions.

### ***DMSP release and bacterial breakdown***

As said, algal DMSP release followed by bacterial DMSP breakdown are the prerequisites for DMS production. Particulate DMSP (hereafter DMSP<sub>p</sub>) is released into the water column to the dissolved phase (hereafter DMSP<sub>d</sub>) from phytoplankton because of stress, senescence, or active exudation of healthy cells, viral lysis, microbial attack, and grazing by zooplankton (Archer, 2003; Stefels et al., 2007; Stefels, 2000; Bratbak et al., 1995a; Malin et al., 1998; van Boekel et al., 1992).

Once released, the labile DMSP<sub>d</sub> is further metabolised by heterotrophs internally or via extracellular enzymes (Kiene et al., 2000; Yoch et al., 1997), thus represents an important carbon source for bacteria (Azam et al., 1994). As shown in Fig 1 there are two major bacterial degradation pathways (Fig. 1): bacterial demethylation, that degrades ~75% of DMSP<sub>d</sub>, and cleavage, degrading ~10% of the DMSP<sub>d</sub> that is ultimately generating DMS (Moran et al., 2012; Curson et al., 2011; Kiene and Linn, 2000). DMSP demethylation leads to other sulphur compounds like methyl-mercaptopropionate, methanethiol or inorganic sulphur (Stefels 2000).

### *Other pathways for DMS production*

Other, probably minor, pathways for DMS production are direct phytoplanktonic or bacterial reduction of dimethylsulphoxide (DMSO) to DMS (Spiese et al., 2009) or via the intermediate dimethylsulphoxonium propionate (DMSOP) (Fig. 1). DMSOP is produced by algae next to DMSP, released (Andreae, 1980) and then bacterially metabolized to DMS (Dixon et al., 2020). Furthermore, DMS was shown to be produced via the methylation of methanethiol (MeSH) during bacterial DMSP demethylation in soils, and thus is probably a minor important DMS source (Carrión et al., 2015).

DMSO concentrations are generally in similar ranges as DMSP (Simo et al., 1997; Thume et al., 2018). However, in the oxic surface settings, DMSO likely plays a minor role as a source of DMS because most of it was shown to be converted to CO<sub>2</sub> in temperate coastal waters, with any remaining amount possibly undergoing oxidation to form dimethylsulfone (Dixon et al., 2020).

### *DMS loss processes*

Major loss processes for oceanic DMS are photochemical oxidation to DMSO (Brimblecombe and Shooter, 1986; Toole et al., 2006), microbial catabolism for energy supply (Simó et al., 1998; Del Valle et al., 2009) and its release to the atmosphere via air-sea gas exchange (Vila-Costa et al., 2008).

### **4.1.3 The potential effect of ocean acidification on DMS emissions**

In future scenarios a significant amount of 38–70% of CO<sub>2</sub> emissions is absorbed by oceans and land by the end of the 21<sup>st</sup> century. That causes a notable decrease in ocean pH with substantial effects on marine biological processes with potential impact on DMS production. Being especially sensitive to ocean acidification (OA), the Arctic Ocean's pH in the surface waters is expected to decrease by about 0.45 by the end of this century (Orr et al., 2005; Steinacher et al., 2009; Terhaar et al., 2020). Ocean acidification may influence DMS production in the Arctic surface ocean by altering the composition,

abundance of phytoplankton and bacterial communities as well as their internal metabolic processes (Hopkins et al., 2020a). Studies of DMS production under ocean acidification in the Arctic Ocean reveal contradictory results (Archer et al., 2013; Hussherr et al., 2017; Hopkins et al., 2020b; Six et al., 2013). Several mesocosm studies (covering a variety of experimental designs) indicated a decrease in DMS surface concentrations, partly due to lowered bacterial DMSP to DMS conversion, under reduced pH (Hussherr et al., 2017; Archer et al., 2013; Bénard et al., 2021; Zhang et al., 2017). Hence, their implementation into models point toward an amplification of warming in the future (Six et al., 2013; Hopkins et al., 2020b; Schwinger et al., 2017). On the other hand, several microcosm studies indicated DMS production and emissions to be resilient to ocean acidification in the Arctic (Hopkins et al., 2020a). This goes along with polar bacteria found to be able to cope with strong pH fluctuations over the range of 7.5 - 8.3 (Hoppe et al., 2018; Kapsenberg, 2015) which could play a role for DMS concentrations mediated by bacterial degradation under OA. Thus, it is difficult to derive a general trend of future DMS production rates in the Arctic Ocean under lower pH which emphasizes the importance of the season, location and the experimental approach. A recently refined modelling attempt (including so far missing observational data sets to display the complex linkage between biochemical parameters and resulting DMS emissions) revealed overall reduced DMS concentrations under expected OA ( $R^2 = 0.89$ ) scenarios (socio-economic Pathway (SSP) 5-8.5 scenario) (Zhao et al., 2024). Though the correlation for the northern hemisphere was weaker ( $R^2 = 0.4$ ) probably due to a higher human impact. Thus, further unravelling the interplay of DMS production and ocean acidification is essential for accurate projections of DMS emissions, and thus climate comprehensively.

#### **4.1.4 Relevance of this study**

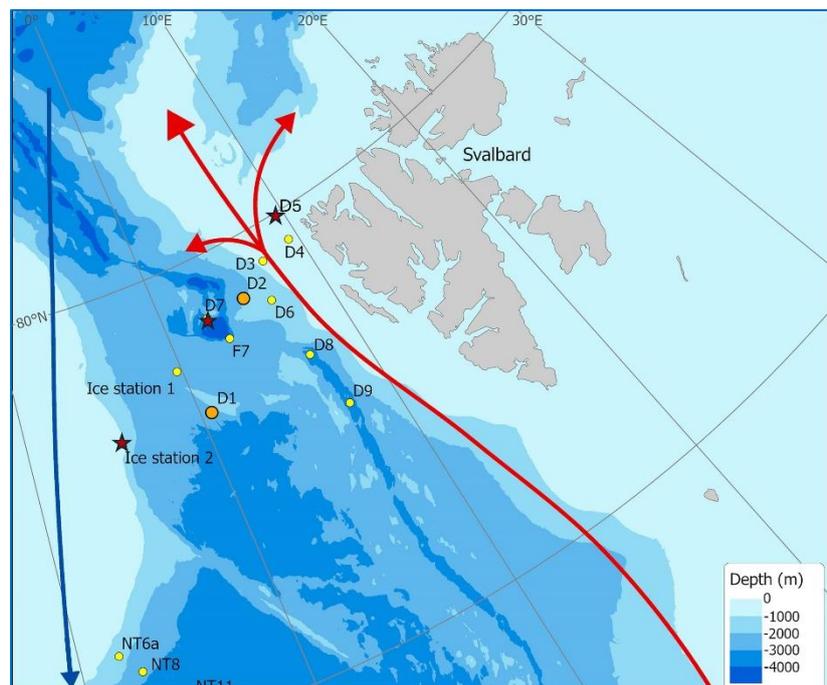
To this end, we performed incubation experiments studying the effects of pH reduction and the presence/absence of light on DMS/P/O concentration and production. The experiments were

conducted at three locations across the Fram Strait, Arctic Ocean: Ice2 (east), D5 (west) and D7 (central), to touch upon the two major hydrographic regimes of the WSC and EGC. Their local environmental conditions are characterized putting DMS/P/O concentrations into context and look for relationships to environmental factors, such as, temperature, salinity, Chl *a* and nutrients. The experimental timing of August/September 2019 adds to the seasonal diversity of the so far available data. By this, the study results add to the available DMS data set from a seasonal and regional perspective, delivering insights to the complex interplay between Arctic environmental conditions and biochemical DMS cycling. Ultimately, these insights can contribute to DMS modelling inputs and thus can help to sharpen the predictions on its future climate impact and feedback in the Arctic and globally.

## 4.2 MATERIAL & METHODS

### 4.2.1 Study area

The incubation experiments were conducted on board the RSS James Clark Ross during the JR18007 cruise to the Fram Strait from 4 August to 6 September 2019. The Fram Strait, located between the west coast of Svalbard and the east coast of Greenland, is characterized by the inflow of Atlantic water via the West Spitzbergen Current



**Figure 2** Locations of incubations experiments (asterix) in the Fram Strait during cruise JR18007 (August 2019): Ice2 (western Fram Strait), D7 (central Fram Strait) and D5 (eastern Fram Strait). (Red – northward flowing Atlantic Water; Blue – southward flowing Polar Surface Water). Figure after Tarling et al., 2022.

(WSC) in the east and Arctic water outflow via the East Greenland Current (EGC) in the west (Rudels et al., 2015). Incubation experiments were performed at three different locations (circles): Ice2 (Western Fram Strait), D7 (Central Fram Strait) and D5 (Eastern Fram Strait) (Fig. 2).

## 4.2.2 Experimental set-up

At each incubation experiment station, seawater from 5 m depth was drawn from Niskin bottles attached to a 24-bottle CTD/rosette and subsequently incubated for 48h. Preceding the incubation sampling, vertical profiles between 5 and 100 m depth were recorded, and water samples taken in 10-20 m intervals to characterize the local environmental setting. DMS/P/O concentrations originating from that CTD cast serve as  $t_0$ -values for the incubation experiment.

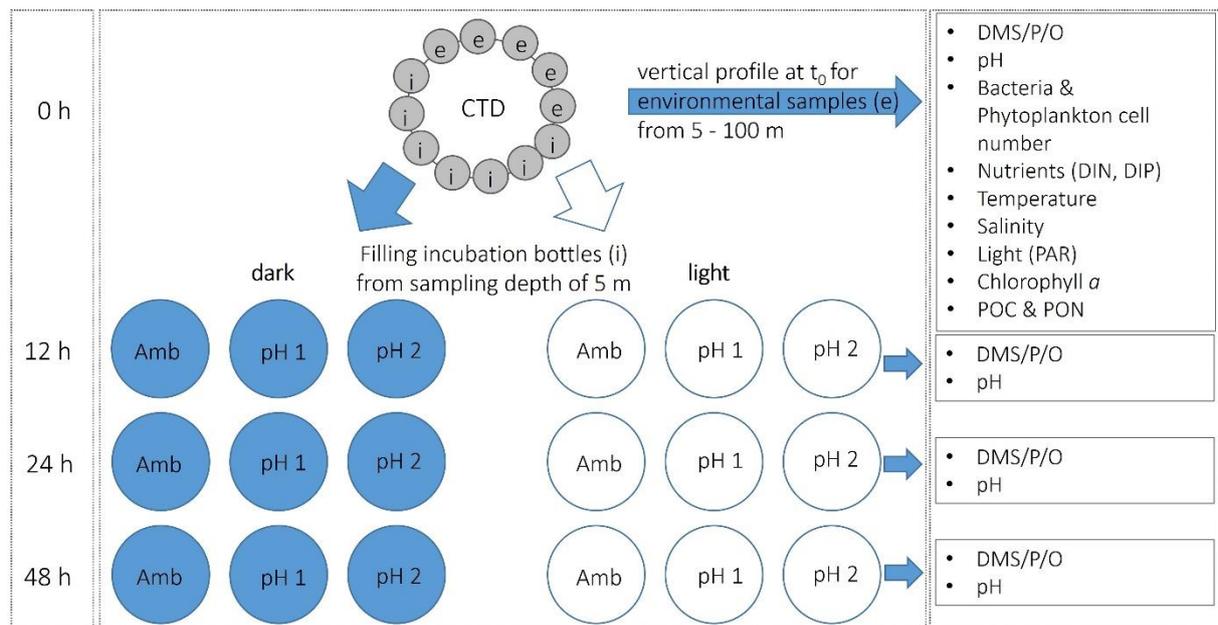
### 4.2.2.1 Sampling of environmental parameters

The analyzed environmental parameters included oxygen and salinity, chlorophyll *a*, PAR, dissolved inorganic nutrients, particulate organic carbon and nitrogen and phytoplankton community composition. Salinity and temperature were recorded by a Seabird SBE9plus sensor package including an oxygen optode, a fluorescence sensor (Chl *a*) and a PAR sensor (photosynthetic active radiation). Inorganic nutrients were analysed using a Technicon segmented 4 channel flow colorimetric autoanalyzer (Bran & Luebbe AAIII, SEAL Analytical). The analytical methods applied were those developed by Brewer and Riley (1965) for nitrate, Grasshoff (1976) for nitrite and Kirkwood (1989) for silicate and phosphate. Particulate organic carbon and nitrogen (POC and PON) measurements followed the standard procedure collecting seawater particles onto glass-fiber filters (i.e., GF/F) and being quantified subsequently with a combustion GC-IR based elemental analyzer (Sharp 1974). Cell numbers of picoeukaryotic phytoplankton and nanophytoplankton as well as heterotrophic bacteria were flow cytometrically (Becton Dickinson FACSort™) determined as described in Tarran et al. (2001).

### 4.2.2.2 Sampling of the incubation bottles

After 12, 24, and 48 hours, triplicate samples for DMS/P/O and pH were taken from each experimental unit (right side). Each unit was discarded afterwards. In total, eighteen 3.5 L

transparent incubation bottles (DURAN®, quartz glass, GL 45, DWK Life Sciences, Germany) served as experimental enclosures. The lids (GL 45) were equipped with Teflon-coated septa to be able to close the bottles gas-tight. After seawater was transferred into the bottles, the pH was manipulated immediately (for details see 2.4) to the targeted RCP scenarios 4.5 (pH1) and 7.6 (pH2) in six bottles each, whereas the remaining six bottles were kept at ambient pH conditions



**Figure 3** Schematic experimental set up. Samples were taken from the CTD rosette from where vertical profiles of certain parameters (given on the right) were analysed per depth.

Immediately after pH manipulation, bottles were closed gas-tight and incubated in dark and light incubators. Light incubators were placed on deck, had transparent Plexiglas® sidewalls (GS 2458 UV transmitting) and no lid (self-manufactured according to experimental needs, Fig. 4). Hence, the full natural sunlight spectrum could penetrate the incubation bottles from the sides and above. Black and covered water chambers served as dark incubators to exclude any light (see Fig. 4 & 5).

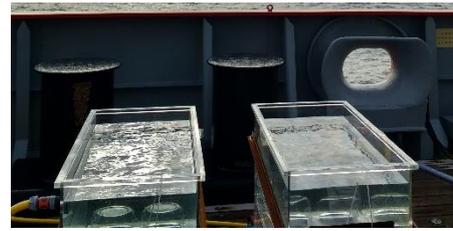
The light measurements showed that light inside the light Incubators was almost identical to ambient conditions, while almost all visible light was blocked in the dark incubators (see Figure S.6). The incubation bottles were placed inside the incubators with a continuous flow of ambient seawater keeping the bottles at ambient seawater temperatures (between -2 and 8 °C, depending on the location). (No circadian rhythm or effects of daytime were tested. For this a design fitted to certain daytimes would have been necessary, but the sampling times differed among experiments and therefore cannot be compared.)

*Unfortunately, we were not able to obtain the  $t_0$ -concentrations for DMSP and DMSO since those 5 m-samples were part of a*

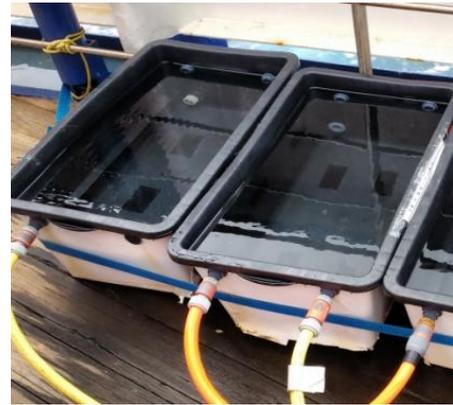
*scientific cooperation and have not been analysed as planned by the cooperation partner up until today. Moreover, severe technical constraints hindered a last-minute analysis in our home lab. For the moment of this thesis, DMSO/P concentrations of the 10 m sample are used as a proxy of the initial concentration in 5 m instead and have thus to be treated with caution.*

#### **4.2.2.3 Sampling from the incubation bottles**

Throughout the 48 h incubations, water samples were taken from the incubation bottles four times at time points 0, 12, 24 and 48. One incubation bottle refers to one experimental unit. Incubation bottles could not be opened and sampled multiple times, because that would have falsified trace gas measurements. Therefore, out of the 18 bottles initially incubated (nine bottles per light treatment), six at a time (amb, pH1, pH2 for dark and light treatment, each) were taken out for DMS sampling at time points  $t_{12}$ ,  $t_{24}$  and  $t_{48}$ . Samples for time point  $t_0$  were taken directly from the CTD cast.



**Figure 4** Picture of the light incubators with incubation bottles inside and a continuous seawater flow through (yellow hose on the left).



**Figure 5** Picture of the dark incubators placed on deck and with continuous seawater flow through installed (yellow hoses). During the experiments they were covered to exclude any light (cover not shown).

All sampling bottles were rinsed before sampling. Samples for the determination of pH as well as for dissolved and particulate DMS/P/O were taken in 500 mL glass vials, both from Niskin bottles at  $t_0$  and incubation bottles at  $t_{12}$ ,  $t_{24}$  and  $t_{48}$ , gas tightly closed and stored in the darkness up until analysis 1 to 2 hours after sampling. Due to limited space, time and (wo)menpower no technical replicates for the single experimental units were incubated. However, triplicate subsamples were taken from the incubation bottles (thus, per treatment and timepoint) to check for analytical errors. Light and temperature were monitored continuously in each incubator (HOBO pendant® temperature/light, onset, USA). Oxygen saturation (in %) was monitored (O2xyDot®, OxySense, USA) inside the incubation bottles to make sure that the water within did not become anoxic, because oxygen stress induced reactions would have falsified the experimental results.

#### **4.2.4 Analysis of pH**

Ocean acidification was mimicked by reducing the pH through addition of  $\text{NaHCO}_3$  and  $\text{HCl}$ . Three different atmospheric  $\text{CO}_2$  mole fractions were targeted (ambient:  $405.43 \pm 0.05$  (Dlugokencky and Thoning, 2021), pH 1: 670 and pH 2: 936 ppm  $\text{CO}_2$ ) to approximate the IPCC's representative concentration pathway (RCP) 4.5 (moderate change) and RCP 8.5 (extreme change) relative to the ambient carbonate chemistry of the seawater at the time of the sampling (as described in Campen et al., 2023). The carbonate system was manipulated through addition of  $\text{NaHCO}_3$  and  $\text{HCl}$  (Riebesell et al., 2011) and the resulting total alkalinity (TA) and dissolved inorganic (DIC) concentrations were checked (Table S2). The calculation of  $p\text{CO}_2$  and  $\text{pH}_T$  (total scale) values were performed by the software  $\text{CO}_2\text{sys}$  (Lewis and Wallace, 1998).

## 4.2.5 Sulphur system measurements and calculations

### 4.2.5.1 Onboard measurements

Dissolved DMS (DMS) was extracted from water samples and its concentration measured onboard using a purge and trap method coupled with a gas chromatograph-flame photometric detector (Varian 3800, GC-FPD) as described by Archer et al. (2013). For DMS measurements triplicate subsamples (of the 500 ml DMS sample taken per incubation bottle) were taken using a 10 ml gas-tight glass syringe. The samples were filtered through a swinnex inline GF/F filter (25 mm diameter, 0.7  $\mu\text{m}$ ) and 5 ml were injected into the purge and trap system and their DMS content determined. DMS calibrations were performed using alkaline cold-hydrolysis (1 M NaOH) of DMSP sequentially diluted three times in MilliQ water to give working standards in the range 0.03 – 3.3 ng S mL<sup>-1</sup>. Five-point calibrations were performed every 2 – 4 days throughout the JR18007 cruise. Preparing dissolved and particulate DMSP samples for later analysis to both, the analyzed samples (filtered and purged to exclude particulate material) and an unanalyzed sample (not filtered, not purged to include particulate material) NaOH was added to hydrolyze DMSP to DMS. Those samples were stored and transported to the home lab in the dark, where their total, dissolved, and particulate DMSP and DMSO contents were analyzed.

### 4.2.5.2 Home lab measurements

Dissolved and particulate DMSP and DMSO concentrations were analysed in the home laboratory using a similar gas chromatograph-flame photometric detector (Agilent 7890, GC-FPD) following Zindler et al. (2012).

Particulate DMSP (DMSP<sub>p</sub>) was calculated by subtracting DMSP<sub>d</sub> and DMS from DMSP<sub>t</sub>. Subsequently, DMSO dissolved (DMSO<sub>d</sub>) and DMSO particulate (DMSO<sub>p</sub>) were analysed using the same samples as for DMSP<sub>d</sub> and DMSP<sub>p</sub>, respectively. By addition of cobalt dosed sodium borohydride (NaBH<sub>4</sub>), DMSO was converted into DMS, which was measured

immediately. By subtraction of  $\text{DMSO}_d$  from the total DMSO concentration,  $\text{DMSO}_p$  values were obtained.

Calibrations were conducted during every measurement day in the lab. DMS standards were prepared with liquid DMS diluted in ethylene glycol as described in Kiene and Service (1993). Standards and samples were measured in triplicates and their standard deviations were calculated. The mean analytical errors throughout the whole experiment were  $\pm 0.06 \text{ nmol L}^{-1}$  ( $\pm 20 \%$ ) for DMS,  $\pm 0.4 \text{ nmol L}^{-1}$  ( $\pm 13 \%$ ) for  $\text{DMSP}_d$  and  $\pm 4 \text{ nmol L}^{-1}$  ( $\pm 17 \%$ ) for  $\text{DMSP}_p$ . For  $\text{DMSO}_d$  and  $\text{DMSO}_p$  a mean analytical error of  $\pm 1.4 \text{ nmol L}^{-1}$  ( $\pm 17 \%$ ) and  $\pm 3.83 \text{ nmol L}^{-1}$  ( $\pm 156 \%$ ) was determined, respectively. The very high mean analytical error for  $\text{DMSO}_p$  concentrations results from similar  $\text{DMSO}_d$  and  $\text{DMSO}_t$  values, some being close to the detection limit. For 94% of the calculated  $\text{DMSO}_p$  concentrations (62 out of 66 samples)  $\text{DMSO}_d$  was almost equal to  $\text{DMSO}_t$ . Hence,  $\text{DMSO}_p$  could not be determined reliably, and its concentrations were negligible (see supplementary material).

#### 4.2.5.3 DMS/P/O production rates

The production rates of DMS, dissolved and particulate DMSP and dissolved DMSO were estimated for all incubation experiments by calculating concentration differences between sampling time points. The average ( $\text{PR}_{\text{DMS/P/O}}$ ) of the single production rates ( ${}_s\text{PR}_{\text{DMS/P/O}}$ ) between the timepoints 0-12 ( $t_{12}$ ), 0-24 ( $t_{24}$ ), 0-48 ( $t_{48}$ ) was determined.

$${}_s\text{PR}_{\text{DMS/P/O}} = [\text{C}_{t_x} - \text{C}_{t_0}] * [t_x - t_0]^{-1} \quad (1)$$

$$\text{PR}_{\text{DMS/P/O}} = \sum {}_s\text{PR}_{\text{DMS/P/O}} * n^{-1} \quad (2)$$

C = concentration of dissolved/particulate DMS/P/O

x = incubation time at timepoint of sampling (12, 24, or 48 hours)

n = number of single production rates  ${}_s\text{PR}$  (3)

Accordingly, an overall negative rate represents the loss (release, cleavage, or consumption), and an overall positive rate represents the production of the respective compound.

#### ***4.2.5.4 Data analysis***

To test for significant pH and light effects on DMS/O/P production rates, ANOVAs followed by post-hoc two-sample t-tests were performed. Therefore, equal variances at a 95%-confidence interval were assumed. When the test revealed unequal variances between samples, an according t-test was performed subsequently. As there were no replicate measurements per time point, outliers cannot be identified as such and therefore the data are mainly descriptively analyzed. Our analysis revealed that neither light nor pH had a significant effect on DMS/O/P concentrations and production rates. Therefore, production rates of the sulphur compounds per pH as well as light treatment were subsequently treated as replicate measurements. To investigate the relationships between DMS/P/O production rates and several abiotic and biotic variables, linear regression analyses were performed. For that, a total of 18 measured response variables (3 experimental stations x 6 replicates each) were assigned to three independent variables (initial concentration at experimental location), that were repeatedly used for the 6 replicates.

## 4.3 RESULTS & DISCUSSION

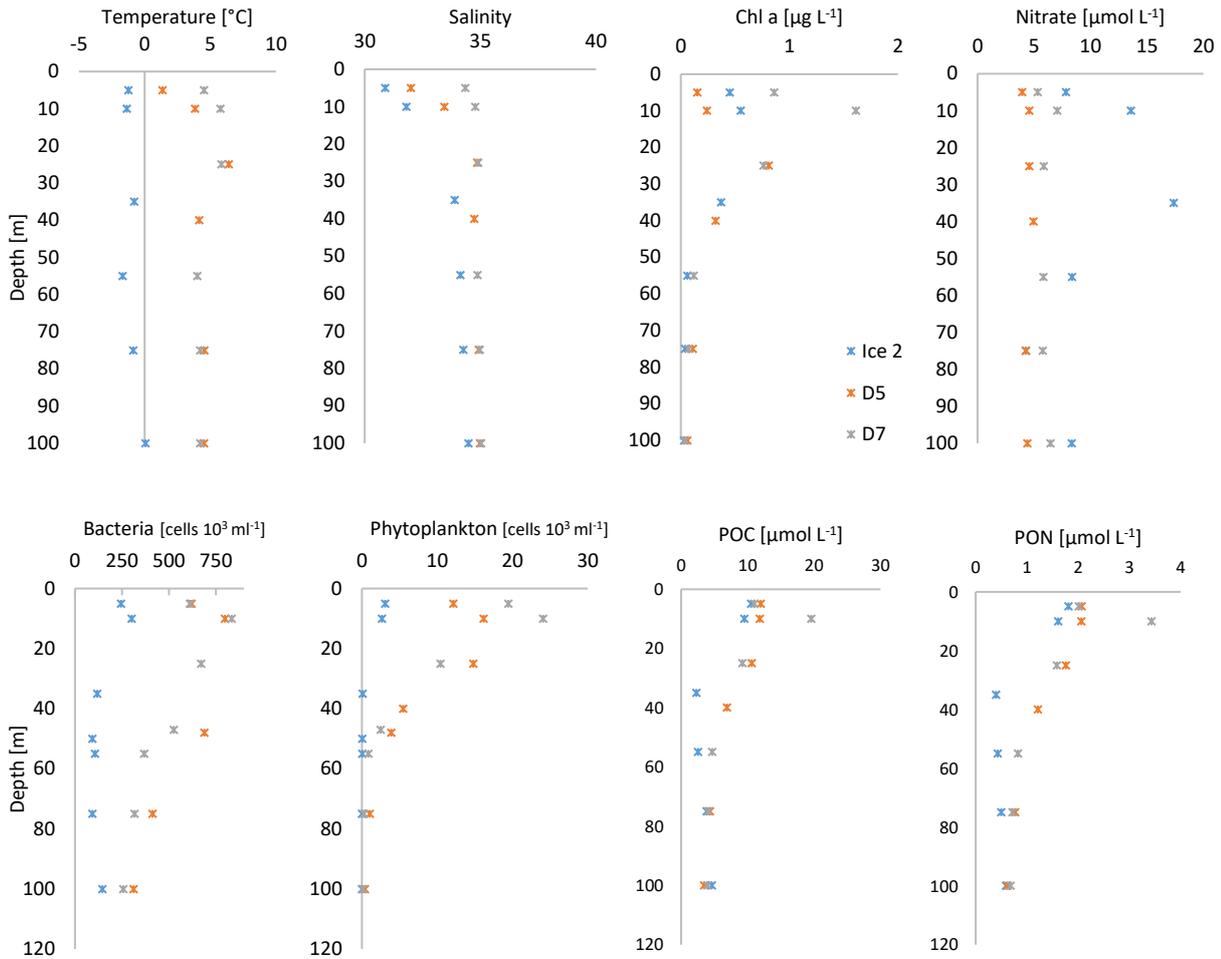
Surface water from three different stations in the Fram Strait was incubated over 48 hours and treated with different pH and light conditions to learn about their potential influence on the sulphur system in the Arctic Ocean. The results are presented in the following.

### 4.3.1 Characterization of season and location

The incubation experiments took place at three locations distributed over western (D5), central (D7) and eastern (Ice2) Fram Strait, in August and September 2019. Consequently, the hydrographic settings were contrasting.

To get an idea of the initial conditions figure 6 shows the vertical profiles of some characterizing environmental parameters: salinity, temperature, Chlorophyll *a* (Chl *a*), particulate organic carbon and nitrogen (POC, PON) concentrations as well as phytoplankton and bacterial cell numbers. Because the incubations were performed with water originating from the euphotic zone, the following characterization focusses on surface waters of the upper 40 m, where light was still available.

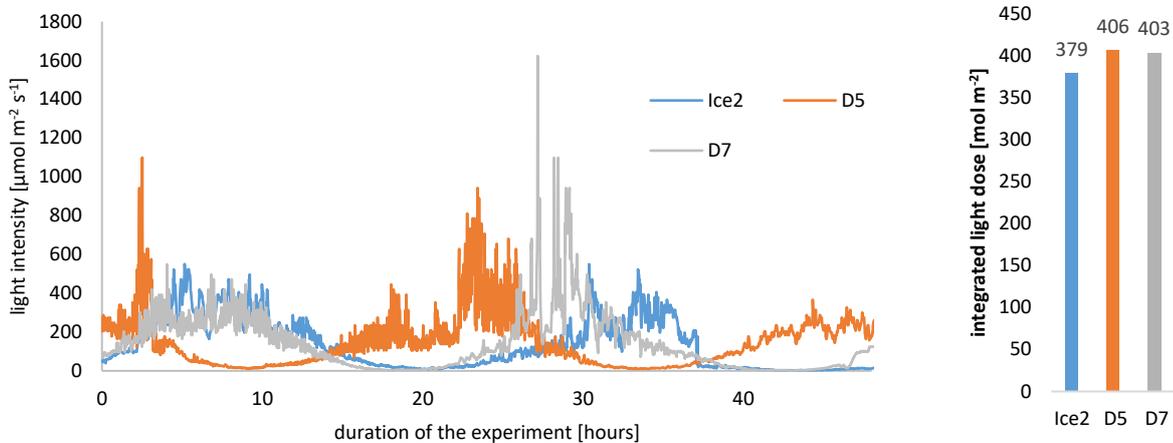
The stations Ice2 and D5 were located at the shelf break, whereas D7 was in the open ocean region of the Fram Strait. Moreover, Ice2 was in proximity to the ice edge. The East Greenland Current, that transports polar water, affected Ice2 as indicated by its lower salinities (30.6) and colder water temperatures ( $-1.2^{\circ}\text{C}$  at 5m). D5 and D7 were influenced by warmer ( $1.4^{\circ}\text{C}$ ,  $4.5^{\circ}\text{C}$  at 5m, respectively) and more saline (32, 34 at 5m, respectively) Atlantic waters of the West Spitsbergen Current (as described in chapter 1, Campen et al., 2022). Therefore, Ice2 was most probably affected by freshwater input from ice melting. D5 had a lower salinity compared to D7 and was also (at least partly) affected by freshwater from ice melting.



**Figure 6** Vertical profiles of selected environmental parameters at each experimental station at  $t_0$  (from top left to bottom right): Temperature, Salinity, Chl  $a$ , Nitrate (DIN), Bacterial & Phytoplankton cell numbers, particulate organic carbon & nitrogen (POC & PON). (blue – Ice2; orange – D5; grey – D7)

Ice2 having a well-mixed upper layer, reveals the highest dissolved nutrient concentration with  $7.8 \mu\text{mol L}^{-1}$  at 5 m and  $17.4 \mu\text{mol L}^{-1}$  at 35 m. These unused, probably recently flushed-in nutrients indicate low productivity, which is also reflected by the lowest cell numbers for phytoplankton ( $3102 \text{ cell mL}^{-1}$ ) and bacteria ( $244345 \text{ cells mL}^{-1}$ ). Chl  $a$  values were between  $0.45 (5\text{m})$ ,  $0.55 (10 \text{ m})$  and  $0.37 (35 \text{ m}) \mu\text{g L}^{-1}$  at the surface. Low salinity (31) and low temperature ( $-1.2 \text{ }^\circ\text{C}$ ) indicate that these settings (well-mixed surface, relatively high DIN, and low in biomass) were probably caused by recent freshwater inflow through ice melting. Moreover, at Ice2 we measured the lowest light dose over time of  $379 \text{ mol m}^{-2}$ .

D5 on the other hand, revealed three times higher cell numbers (D5: 12144) whereas D7 revealed six times higher cell numbers (19442 cells ml<sup>-1</sup>) for phytoplankton. Both stations revealed about twice as



**Figure 7** Left: Light intensity over the course of each experiment. Right: Integrated light dose (cumulated light intensities) the samples were exposed to over the full experimental duration.

(blue – Ice2; orange – D5; grey – D7)

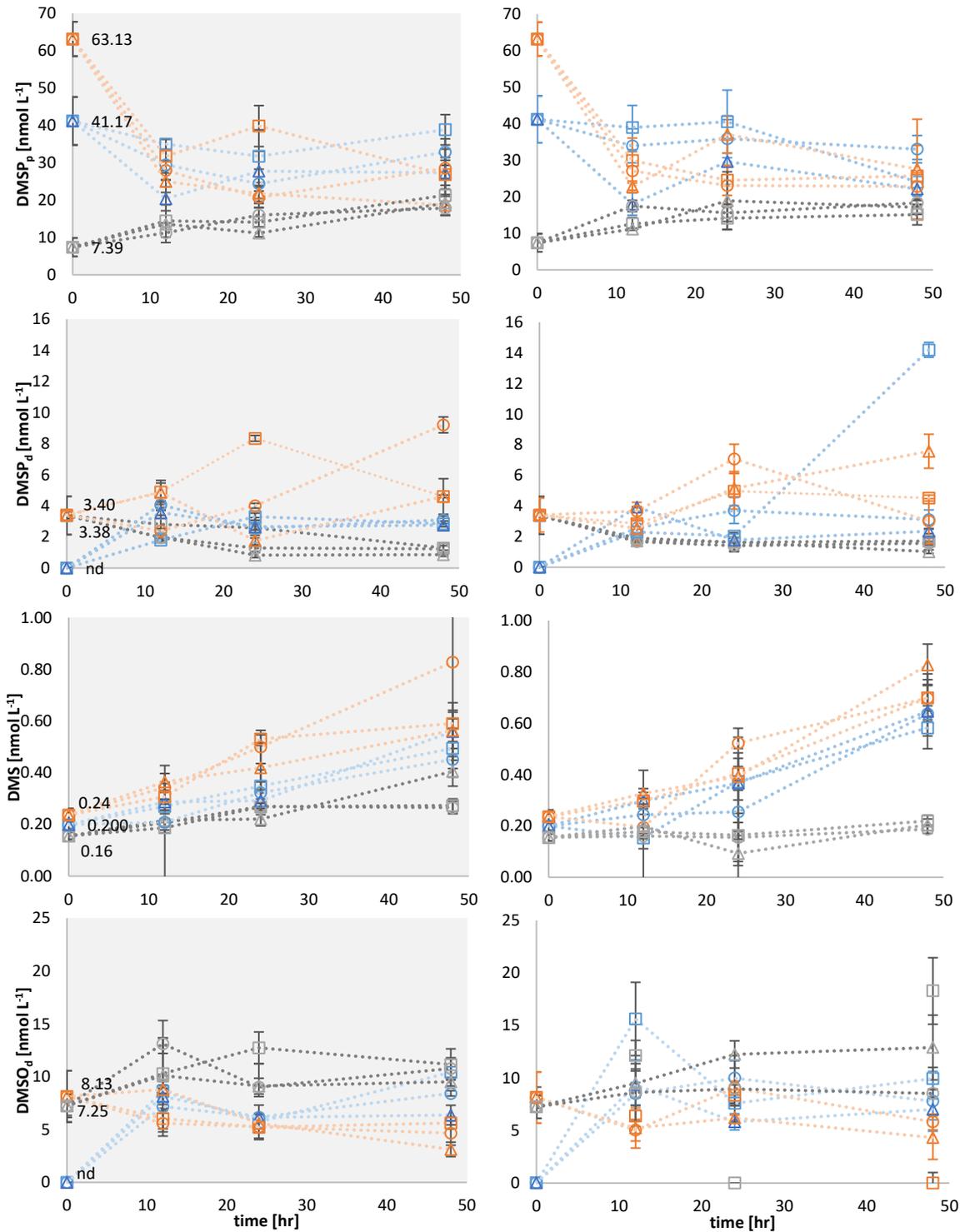
many bacterial cells (D5: 620860, D7: 611529 cells mL<sup>-1</sup>) at 5 m compared to Ice2. POC and PON values were similar at 5 m for all stations (ranging from 10.6 to 12  $\mu\text{mol L}^{-1}$  for POC; 1.8 to 2.1  $\mu\text{mol L}^{-1}$  for PON) but varied between stations at 10 m between 9.6  $\mu\text{mol L}^{-1}$  (Ice2) and 19.6  $\mu\text{mol L}^{-1}$  (D7) and between 1.6  $\mu\text{mol L}^{-1}$  (Ice2) and 3.4  $\mu\text{mol L}^{-1}$  (D7), respectively. At both stations dissolved nitrate (DIN) concentrations were lower compared to Ice2 (D5: 3,98  $\mu\text{mol L}^{-1}$ , D7: 5,38  $\mu\text{mol L}^{-1}$ ). Compared to representative summer DIN concentrations of 0.5 (EGC) to 0.9 (WSC) determined by Tuerena et al. (2021) within the mixed layer, our concentrations were relatively high and thus may have been remineralized by heterotrophs, indicating post bloom conditions.

D5 was relatively mixed showing no clear Chl max, with values ranging from 0.15 to 0.81  $\mu\text{g L}^{-1}$  between 5 and 40 m. D7 showed a Chl max in 10 m of 1.61  $\mu\text{g L}^{-1}$ . These chl *a* values fall into the range of summer ( $1.11 \pm 1.02 \mu\text{g L}^{-1}$ ) and autumn ( $0.36 \pm 0.29 \mu\text{g L}^{-1}$ ) values obtained in the Fram Strait in 2018 (Jackowski et al., 2020) and in 2019 (Wietz et al., 2024). Low Chl *a* values and comparably high dissolved nitrate concentrations indicate a community that is at this time of the year dominated by heterotrophs and mixotrophs (Jackowski et al., 2022) in this region. Figure 7 shows the

circadian light cycle at the three locations with peaks around noon and lows during night. Maximum values for Ice2, D5 and D7 were 549, 1099 and 1623  $\mu\text{mol m}^{-2} \text{s}^{-1}$ , respectively. This results in a slightly lower integrated light dose at Ice2 (379  $\text{mol m}^{-2}$ ) compared to D5 (406  $\text{mol m}^{-2}$ ) and D7 (403  $\text{mol m}^{-2}$ ) calculated over the full experimental duration (Fig 3.1.2 b). According to van de Poll et al. (2021) our experimental timeslot falls into the last weeks of late summer to autumn transition where declining Chl *a* and light intensities can be expected and phytoplankton blooms collapsed (Jackowski et al., 2022). Moreover, overall C:N ratios during JR18007 were at the lower end of range expected ( $5.4 \pm 1.1$ , Redfield = 6.6; see comparable regions in Frigstad et al. (2014), data not shown).

Thus, the seasonal timing of our experiments can be assigned to late summer to autumn transition, with oligotrophic and lower light conditions that result in overall decreasing productivity and possibly a community in which mixotrophs and heterotrophs become more pronounced.

### 4.3.1 DMS Cycling



**Figure 8** Concentration of DMS, DMSP<sub>p</sub>, DMSP<sub>a</sub> and DMSO<sub>a</sub> over the course of the experiment (48 hours) in the dark (left plot) and light (right plot). Stations are represented by colour: grey (Ice2), blue (D5), orange (D7), and pH treatments are represented by symbols: amb (square), pH 1 (circle) and pH2 (triangle). Initial concentrations, given in the left plot, are the same for the right plot.

### 4.3.2.1 General dynamics over time

Figure 8 gives an overview of how the concentration of each sulphur compound developed over the experimental duration of 48 hours per station and treatment.

In general, the oligotrophic conditions and lower productivity were also reflected in relatively low initial DMS/P/O concentrations (Table 4) as well as their behavior over time. Please note again, that for DMSP/O initial concentrations values from 10 m are given as a proxy for the missing  $t_0$ -sample values from 5 m and must be treated with caution.

**Table 4** Initial concentration of DMS/P/O at Ice2, D5 and D7, given in  $\text{nmol L}^{-1}$ . Concentrations that were below the detection limit are indicated with “nd”.

	DMS	DMSP <sub>d</sub>	DMSP <sub>p</sub>	DMSO <sub>d</sub>
Ice2	0.16 ± 0.01	3.4 ± 1.2	7.4 ± 2.5	7.3 ± 1.1
D5	0.22 ± 0.01	nd	41.3 ± 6.4	nd
D7	0.24 ± 0.02	3.4 ± 0.2	63.1 ± 4,6	8.1 ± 2.4

Initial DMS/P/O concentrations at the three experimental locations are given in table 4 (see also Fig. 8). DMS surface concentrations are comparable to those found in March/April (unpublished DMS data from NOAA/PMEL DMS data server, for research details see S.2 in supplementary material). Furthermore, they are much lower than those measured in this area during early summer 2015 ( $31.2 \pm 9.3 \text{ nmol L}^{-1}$ ) (Gros et al., 2023) and 2016 (DMS: 6.3 and DMSP<sub>t</sub>: 70  $\text{nmol L}^{-1}$ ) (Galí et al., 2021). This difference is probably due to the seasonal timing and with that overall lower productivity. Ice2 overall revealed the lowest concentrations and production over time for all compounds (due to mixing and polar water influence) followed by D5 and then D7 being the most productive station (for averaged production rates see table 5).

One should note that between  $t_0$  and  $t_{12}$  dissolved parameters (DMSP<sub>d</sub> and DMSO<sub>d</sub>) increased, while particulate DMSP dropped which at least partly could also be due to the DMSP/O release when cells were put under stress because of the experimental manipulation (Kiene and Slezak, 2006; Luce et al., 2011).

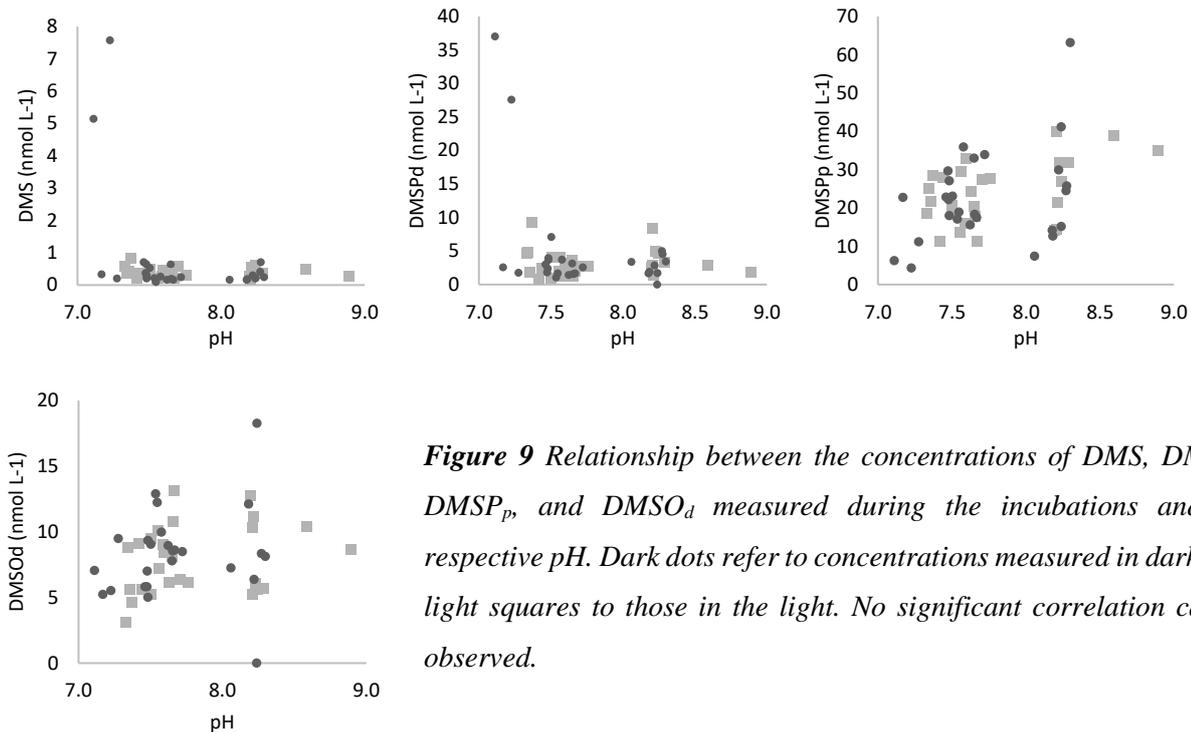
Further details of the concentration behavior DMS and  $\text{DMSP}_{\text{p/d}}$  will be elucidated alongside the analysis of interconnections between sulphur compound concentrations, pH, light and further environmental factors. However, as  $\text{DMSO}_{\text{p}}$  concentrations were negligible, it is concluded that DMSO predominantly occurred in the dissolved phase.  $\text{DMSO}_{\text{d}}$  concentrations were overall in a similar range, revealing no significant differences between stations and treatments, respectively.

**Table 5** Average production rates (PR) of DMS,  $\text{DMSP}_{\text{p}}$ ,  $\text{DMSP}_{\text{d}}$  and  $\text{DMSO}_{\text{d}}$  calculated over 48 hours and from three pH and two light treatments. Values are given in  $\text{nmol L}^{-1} \text{hr}^{-1}$  and with the respective averaged std deviation of the underlying *single*PR.

	$PR_{\text{DMS}}$	$PR_{\text{DMSP}_{\text{d}}}$	$PR_{\text{DMSP}_{\text{p}}}$	$PR_{\text{DMSO}_{\text{d}}}$
<i>Ice2</i>	+ 0.002 ± 35 %	+ 3.8 ± 5 %	+ 0.3 ± 18 %	+ 0.2 ± 47 %
<i>D5</i>	+ 0.005 ± 31 %	+ 4.1 ± 10 %	- 0.5 ± 61 %	+ 0.4 ± 15 %
<i>D7</i>	+ 0.008 ± 16 %	+ 4.0 ± 35 %	- 1.7 ± 9 %	- 0.1 ± 41 %

#### 4.3.2.1 Effect of Ocean Acidification

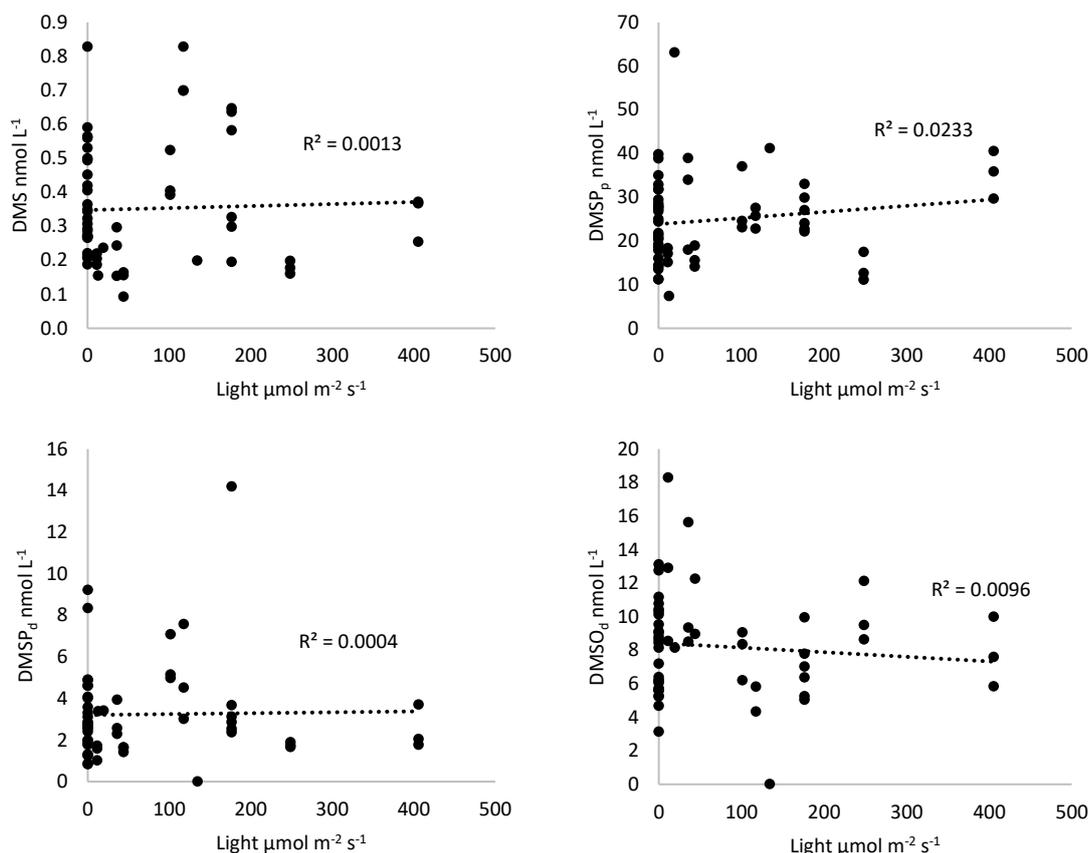
From visual inspection there is no pattern in DMS/P/O concentration associated to pH or light (Fig. 8). Figure 9 shows the concentration of DMS,  $\text{DMSP}_{\text{d}}$ ,  $\text{DMSP}_{\text{p}}$  and  $\text{DMSO}_{\text{d}}$ , plotted against the pH of the respective sample (for treatment specific details see fig S. in appendix). Data points are randomly distributed for all tested relationships and statistical tests comparing the concentrations of DMS/P/O among pH treatments showed no significant effect (ANOVA, followed by post-hoc two-sample t-tests with a 95% confidence-interval). Thus, our data suggest that a reduced pH, as it would be the case under an intensified ocean acidification scenario, does not cause significant changes in the concentration of DMS,  $\text{DMSP}_{\text{p}}$ ,  $\text{DMSP}_{\text{d}}$  and  $\text{DMSO}_{\text{d}}$  in this region and season.



Thus, our data go along with other Arctic experiments revealing no significant effects of short-term OA on planktonic DMS which confirms the idea of polar DMS producing communities (and underlying biochemical processes) being resilient to changes in pH (Hopkins et al., 2020a). This ability to adapt may be a consequence of the Arctic environment favoring organisms that reveal a high phenotypic plasticity and flexibility to react to sudden environmental changes, such as melting events (Sackett et al., 2013). However, there are other studies suggesting that a reduced pH does affect DMS concentrations (Archer et al., 2013; Husserr et al., 2017; Bénard et al., 2021). Thus, the underlying processes ultimately driving DMS production may respond differently to OA depending on the region (Hopkins et al., 2020a), so that a more sophisticated study design is needed to unravel their interactions. As recently discussed in Hopkins et al. (2023) the processes leading to the measured sulphur compound concentrations are most likely too complex to be expressed and depicted in one variable such as dissolved concentration over time. Combining field observations with molecular studies of the according cellular DMS(P) producing processes would be one possibility to get a better understanding of what metabolic pathway may be affected by OA and under which (further) environmental conditions. Moreover, especially in the Arctic, seasonal timing associated with variable physiological

stages (e.g. early vs. senescent bloom) could influence the sensitivity in OA response which thus should be considered carefully.

#### 4.3.2.3 Effect of Light/Darkness



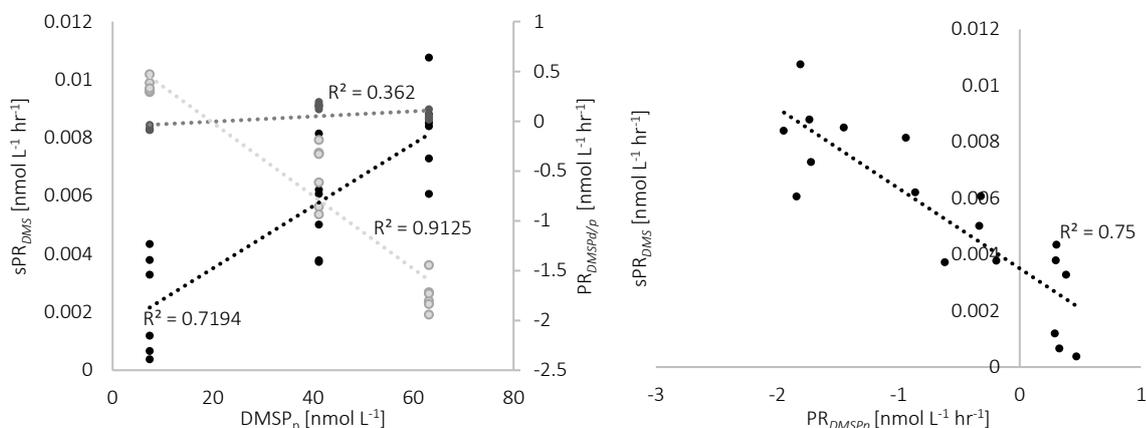
**Figure 10** Relationship between the concentrations of DMS, DMSP<sub>d</sub>, DMSP<sub>p</sub>, and DMSO<sub>d</sub> measured during the incubations of all stations and the respective light intensity at their time of sampling. Data points from different pH treatments were combined, as pH was shown to have no significant effect.

Figure 10 shows the concentration of each sulphur compound with respect to the respective light intensity at the time of sampling ( $t_0$ ,  $t_{12}$ ,  $t_{24}$ ,  $t_{48}$ ). Interestingly, these data reveal no significant relationship between light intensity and sulphur compound concentrations. From visual inspection, this is in line with the concentration development over 48 hours, indicating no pattern associated with the presence or absence of light (Figure 8). The simple effect of presence/absence of light on average production rates was also tested (Figure S.4) and did not result in significantly different production rates. This is statistically confirmed by comparing the concentrations of DMS/P/O among light

treatments revealing no significant effect (ANOVA, followed by post-hoc two-sample t-tests with a 95% confidence-interval). The average light intensities of 132 (Ice2), 138 (D5) and 148  $\mu\text{mol m}^{-2} \text{s}^{-1}$  (D7) are comparably high for this latitude and season, though the estimation of the incoming light in water combined with ice is complex (Castellani et al., 2022). Thus, what is considered “high light” depends on the experimental and estimation approach, and thus varies among studies between 80 and 800  $\mu\text{mol m}^{-2} \text{s}^{-1}$  (Galindo et al., 2016; Castellani et al., 2022; Archer et al., 2010; Sunda et al., 2002). Compared to the study of Galindo et al. (2016) our light intensities would not fall into the range of high light. Moreover, they found that light stress induced DMSP<sub>p</sub> production is species dependent and varies from no to high sensitivity between community composition. Furthermore, speaking of light stress mostly means photoinhibition and that is mostly induced by a sudden (rather than a gradual) increase of light, and which could stimulate DMSP<sub>p</sub> production to counteract the resulting oxidative stress (Sunda et al., 2002). Moreover, conditions in the incubation bottles did not compare to a turbulent mixed layer, where light conditions change more suddenly (Archer et al., 2010), so that the organisms had the chance to acclimatize to the ambient light conditions. Thus, revealing no sudden light changes, and moderate intensities (compared to other study’s high light conditions), our data deliver no hint towards light stress induced DMS/P/O production.

In summary, no light or pH effect on the sulphur cycling was found during this experiment in the Fram Strait in late Arctic summer. This indicates that other environmental parameters affecting the underlying biochemical processes may have been responsible for the differences in concentration and production rate of the sulphur compounds found at this time and in this area.

#### 4.3.2.4 Correlations between sulphur components



**Figure 11** Left plot: Correlation between the  $sPR_{DMS}$  (left x-axis, black;  $R^2 = 0.72$ ,  $p < 0.001$ ),  $sPR_{DMSPd}$  (dark grey,  $R^2 = 0.36$ ,  $p < 0.05$ ), and  $sPR_{DMSPp}$  (right x-axis, light grey;  $R^2 = 0.91$ ,  $p < 0.001$ ) and the initial  $DMSP_p$  concentration. Right plot: Correlation between  $sPR_{DMS}$  and  $sPR_{DMSPp}$  ( $R^2 = 0.75$ ,  $p < 0.05$ ).

Single production rates of DMS ( $sPR_{DMS}$ ) and  $DMSP_d$  ( $sPR_{DMSPd}$ ) both correlated positively with the initial concentration of  $DMSP_p$  (Fig 11). The initial  $DMSP_p$  concentration explained 72 % ( $p < 0.01$ ) of the variation of  $sPR_{DMS}$  and 36 % ( $p < 0.05$ ) of the variation of  $sPR_{DMSPd}$ . Whereas  $sPR_{DMSPd}$  did not correlate significantly with  $sPR_{DMS}$ . Moreover, no significant relationship was found for  $sPR_{DMSOd}$  with any of the other compounds (data not shown).

Looking at the concentration dynamics over time (figure 8), DMS production was following  $DMSP_p$  degradation, being higher when  $DMSP_p$  decreases (D5 and D7) and lower or stagnating when  $DMSP_p$  is increasing in the cells (Ice2) and thus is not further cleaved to DMS. As expected,  $DMSP_p$  concentrations were the highest among all sulphur compounds at all stations. At D5 and D7, where initial  $DMSP_p$  was higher than at Ice2, concentrations at D5 dropped slightly down to  $22 \pm 2 - 38 \pm 4$   $\text{nmol L}^{-1}$  and strongly decreased at D7 to  $19 \pm 3 - 28 \pm 3$   $\text{nmol L}^{-1}$  at  $t_{48}$ , whereas they were increasing to  $15 \pm 3 - 21 \pm 3$   $\text{nmol L}^{-1}$  at Ice2. DMS was produced at all stations during incubation. However, following  $DMSP_p$  decrease, the highest concentration increase was found at D7 with values going from  $0.24 \pm 0.03$   $\text{nmol L}^{-1}$  ( $t_0$ ) to  $0.7 \pm 0.05 - 0.8 \pm 0.08$   $\text{nmol L}^{-1}$  ( $t_{48}$ ), whereas Ice2 revealed significantly

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lower final concentrations of  $0.16 \pm 0.01$  ( $t_0$ ) to  $0.19 \pm 0.02 - 0.41 \pm 0.01$   $\text{nmol L}^{-1}$  ( $t_{48}$ ) (see also production rates in table 5). Similarly,  $\text{DMSP}_d$  tends to increase over time in both D5 and D7 from  $1.8 \pm 0.1$  ( $t_{12}$ ) to  $2.35 \pm 0.2 - 14.2 \pm 0.5$   $\text{nmol L}^{-1}$  ( $t_{48}$ ) and from  $3.4 \pm 0.2$  ( $t_0$ ) to  $3 \pm 1.5 - 9.2 \pm 0.5$   $\text{nmol L}^{-1}$  ( $t_{48}$ ) respectively but decreased from  $3.4 \pm 1.2$   $\text{nmol L}^{-1}$  ( $t_0$ ) to  $0.9 \pm 0.07 - 1.7 \pm 0.16$   $\text{nmol L}^{-1}$  ( $t_{48}$ ) at Ice2. Though concentration differences neither were significant between stations nor between treatments, it shows a tendency of  $\text{DMSP}_d$  at Ice2 behaving similarly to DMS and reversely to  $\text{DMSP}_p$ , which demonstrates the interconnection of the pools. Both,  $\text{DMSP}_d$  and DMS are fed by a release and further cleavage of  $\text{DMSP}_p$ , indicating that  $\text{DMSP}_p$  was driving the concentrations of both in the upper layer (5 - 10 m). DMSO concentration seemed to be of minor importance for ultimate DMS concentrations. This is in line with the many findings of  $\text{DMSP}_p$  being the major and therefore limiting factor for DMS production (e.g. Hopkins et al. (2023) and references therein).

This indicates that both differing hydrographic characteristics of the locations, and initial intracellular concentration of  $\text{DMSP}_p$  could have influenced whether  $\text{DMSP}_p$  was produced or released during incubation. At Ice2, low salinity and temperature as well as mixing may have led to a higher need for internal DMSP in the cells as an osmoregulate (Tison et al., 2010) as rapidly changing conditions in the marginal ice zone may ask for higher metabolic flexibility. High initial  $\text{DMSP}_p$  at D5 and D7 and overall seasonal timing could speak for a release induced due to senescence or microbial attack (grazers were excluded) (Bratbak et al., 1995b; van Boekel et al., 1992) and/or no demand of osmoregulation by the surrounding conditions.

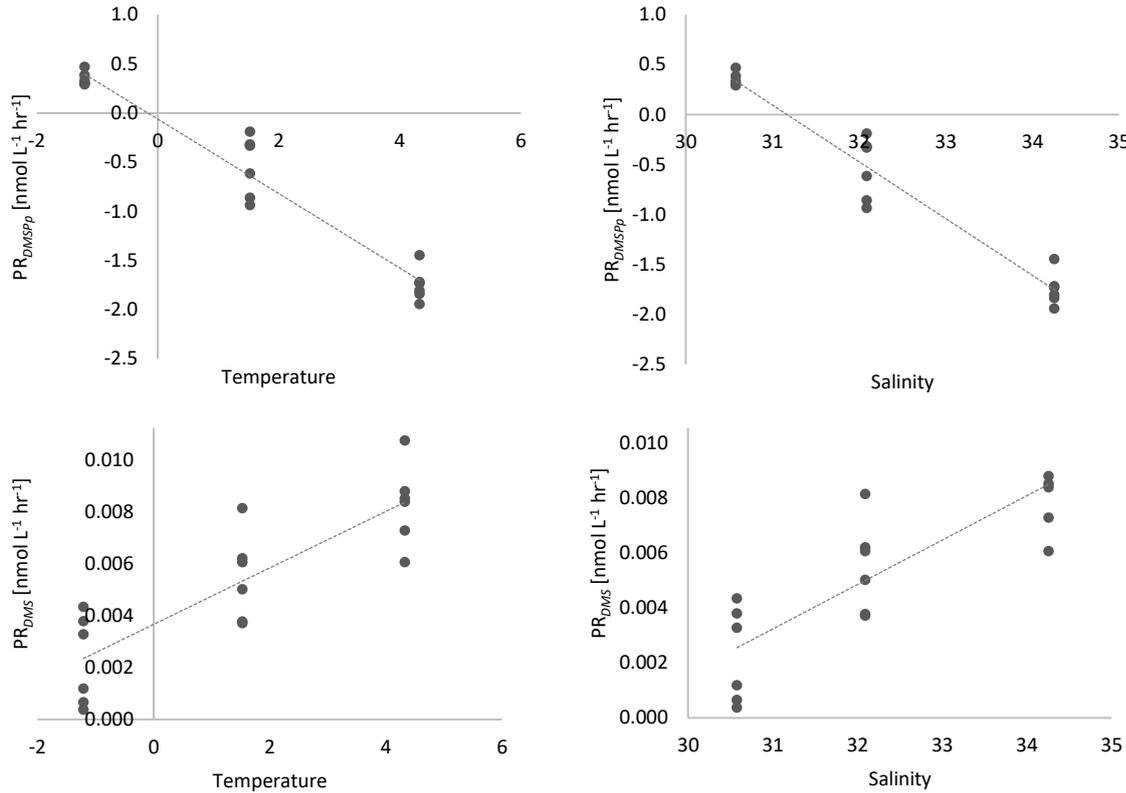
#### ***4.3.2.5 Effect of environmental variability***

This section takes a closer look on which environmental factors predominantly drove and limited  $\text{DMSP}_p$  and DMS production in this region.

### *Temperature and Salinity*

$PR_{DMSP_p}$  correlates significantly with temperature (adjusted  $R^2 = 0.95$ ,  $p < 0.001$ ) and salinity ( $R^2 = 0.95$ ,  $p < 0.001$ ) (Fig. 12). Both correlations are negative, indicating that under warmer temperatures as well as higher salinity more  $DMSP_p$  is released (as  $DMSP_p$  PR become more negative). There is a positive correlation between  $PR_{DMS}$  and temperature explaining 99 % ( $R^2 = 70$ ,  $p < 0.001$ ) of the variation in  $PR_{DMS}$  (Fig 12). The positive correlation with salinity is not significant ( $R^2 = 70$ ,  $p < 0.001$ ). Though,  $PR_{DMS}$  tends to behave the opposite way as  $PR_{DMSP_p}$ , which underlines the tight coupling between  $DMSP_p$  and DMS. Neither  $DMSO_d$  nor  $DMSP_d$  revealed a significant correlation with salinity or temperature (data not shown).

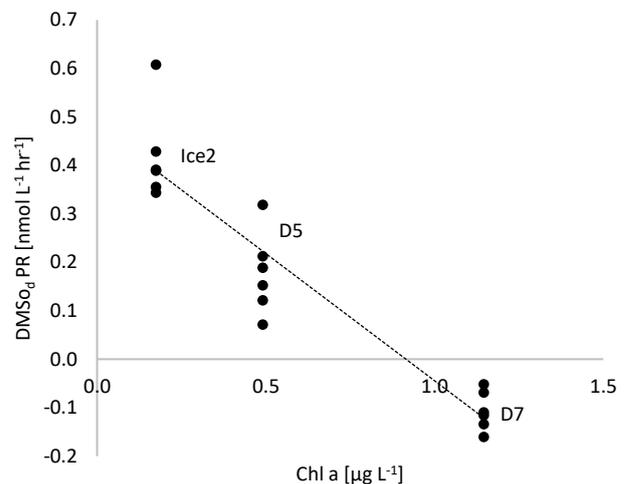
Considering the prevailing conditions at the experimental stations this pattern becomes even more clear: station Ice2 (polar water) being much colder and less saline ( $-1.2^\circ\text{C}$ , 30.8) and revealed, though low, a positive  $PR_{DMSP_p}$ . Whereas D5 ( $1.4^\circ\text{C}$ , 32) and D7 ( $4.5^\circ\text{C}$ , 34), carrying warmer and more saline Atlantic water, showed a moderate and strong  $DMSP_p$  decline, respectively (Fig.8). Thus, probably, the hydrological conditions in the two major water regimes of the Fram Strait result in significantly different  $PR_{DMSP_p}$ , likely because they are harboring differing microbial communities with differing metabolic needs (Jackowski et al., 2022; Wietz et al., 2024; Cherkasheva et al., 2014). Moreover, this relationship emphasizes the role of  $DMSP_p$ , for osmoregulation and cryoprotection under rapidly changing conditions (Yoch, 2002; Kirst et al., 1991; van Bergeijk et al., 2003) as they can be found in the Fram Strait region. Galí et al., 2021 also found a relationship of DMS and  $DMSP_t$  with warmer Atlantic waters, revealing substantially higher concentrations associated with ice-melting and blooms. However, their observations were made during the bloom onset in early summer in the Fram Strait. That indicates that the environmental drivers for DMS/P shift depend on the bloom stage, which was probably senescent, in this case.



**Figure 12** Correlations of  $sPR_{DMSPP}$  (top) and  $sPR_{DMS}$  (bottom) with initial temperature and salinity.

### Chl *a*

$PR_{DMSO_d}$  was negatively correlated with Chl *a* concentration ( $R^2 = 87$ ,  $p < 0.001$ ). That indicates an  $DMSO_d$  decrease the higher the Chl *a* content was, hence, an uptake of  $DMSO_d$  by phytoplankton. It is known that phytoplankton can reduce DMSO to DMS (Spiese et al., 2009) but in that case one would expect a correlation between DMSO and DMS as well. However, that was neither the case for  $PR_{DMS}$  with  $DMSO_d$  nor with

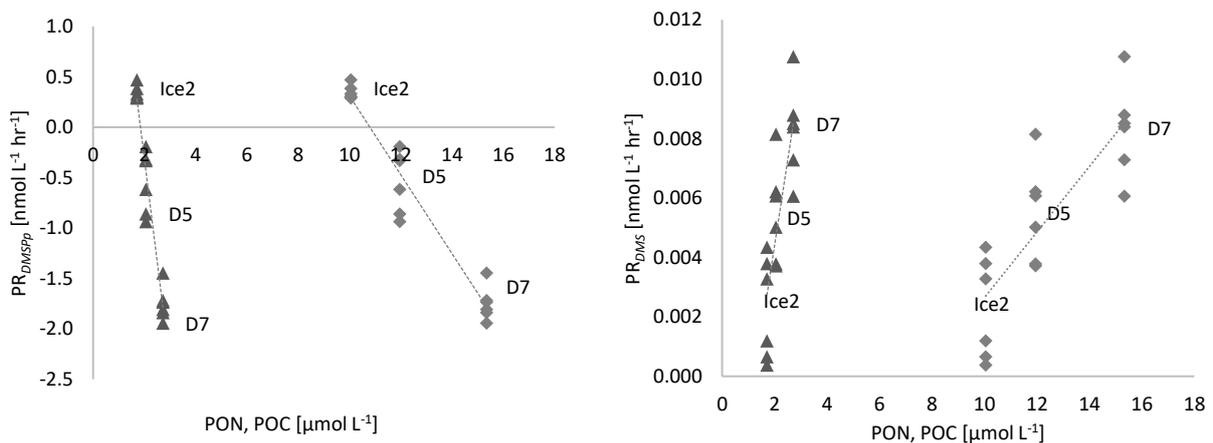


**Figure 13** Correlation of  $PR_{DMSO_d}$  per station and initial Chl *a* concentration.

Chl *a* suggesting that  $DMSO_d$  was not reduced to DMS in a measurable range during our experiments. That paradox could be explained by the finding that  $DMSO_d$  is mostly dissimilated to  $CO_2$  (Dixon et

al., 2020) and is not a major DMS source (Hopkins et al., 2023). Moreover, Chl *a* was neither correlated with  $PR_{DMSP_p}$  nor with  $PR_{DMS}$ . In comparison, there are variable outcomes in other studies, some revealing a correlation between Chl *a* content and DMS/Pp concentration, and some not (Leck and Persson, 2022; Speeckaert et al., 2018). A possible reason is that it depends on the location and the prevailing microbial community whether Chl *a* content is an appropriate proxy for phytoplanktonic  $DMSP_p$  production. As conditions were oligotrophic and presumably after phytoplankton bloom collapse (Jackowski et al., 2022) it is possible that the bacterial, thus heterotrophic or mixotrophic community composition and metabolic needs were a dominating driver of DMS/P cycling – like it was found for CO dynamics, too (Campen et al., 2023). That would be in line with another study where DMS concentrations in the Arctic Ocean were strongly linked to regional water masses, their origin, and microbial communities within (Uhlig et al., 2019). This suggests that DMS production predictability strongly depends on the location with its complex single driving components such as community composition (Hopkins et al., 2023).

### PON and POC



**Figure 14** Left side: Correlation of  $PR_{DMSP_p}$  with PON (left regression line) and POC (right regression line). Right side:  $PR_{DMS}$  with PON (left regression line) and POC (right regression line).

With higher initial PON and POC concentration more  $DMSP_p$  was released (PN:  $R^2 = 94$ ,  $p < 0.001$ ; POC:  $R^2 = 95$ ,  $p < 0.001$ ). Again, for DMS it was contrary: Though relatively low, DMS production

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rate was generally positive and with more initial POC/PON the DMS production rate increased (POC:  $R^2 = 69$ ,  $p < 0.001$ ; PON:  $R^2 = 69$ ,  $p < 0.001$ ). No significant correlations were found for any of the sulphur with DIN (e.g. Fig. S.5). Hence, no relationship of  $PR_{DMSP_p}$  with nutrient limitation was found (data not shown), though this has been demonstrated in other studies (e.g. Archer et al. (2009), Sunda et al. (2007)). However,  $PR_{DMSP_p}$  negatively correlated with the initial PON and POC concentration, indicating that the release of  $DMSP_p$  increased the more organic nitrogen and carbon containing particles were in the water column. Furthermore, as to be expected,  $PR_{DMS}$  was inversely related to the  $DMSP_p$  correlation and was positively correlated with POC and PON (Fig. 14). This could be explained by the fact that the  $DMSP_p$  producing cells (next to detrital material and aggregates, all  $\geq 0.2 \mu\text{m}$  in size) are part of the POC and PON pool (as defined in e.g. Kharbush et al. (2020)), pointing towards a relationship of the cell's need for DMSP not with the outer but the inner cell nitrogen and carbon concentration. On one hand, one could speculate that POC and/or PON saturation favors a release of  $DMSP_p$ , as for example, bacteria use DMSP as a carbon source (Pomeroy, 1993; Azam et al., 1994). On the other hand, and more probably, high POC and PON (at D5 and D7) concentrations together with the rapid decline in  $DMSP_p$  after 12 hours (Fig. 8) indicate the lysis of senescent phytoplankton cells accompanied by  $DMSP_p$  release (Rokitta et al., 2016). However, this idea is speculative and has to be considered with caution because of the limited explanatory power (three values for POC/PON at  $t_0$ ).

## 4.4 CONCLUSIONS

In summary we did not find a significant pH effect, neither was light intensity inducing changes in concentration or production rates of DMS/P/O. However, the relatively low DMS concentrations were tightly coupled to DMSP<sub>p</sub> being the dominant driver for DMS production processes in the surface of the Fram Strait during this time, as DMS production closely followed DMSP<sub>p</sub> concentrations. Though low  $PR_{DMS}$  at all experimental locations was positive, with an average rate of  $0.005 \pm 0.001 \text{ nmol L}^{-1} \text{ hr}^{-1}$ . Ice proximity (lower temperature and salinity) in combination with a rather mixed water column resulted in lower overall productivity and DMSP<sub>p</sub> concentrations. Most of the dynamics seem to be explained by the season of late summer to autumn transition, that is associated with oligotrophic post bloom conditions and possibly a more mixotrophic to heterotrophic microbial community. Environmental conditions such as salinity and temperature, and community composition, were the most important factors for DMSP<sub>p</sub> concentration and, subsequent DMS production. Well-mixed polar waters (lower salinity and temperature) close to ice edges led to lower DMS production and Atlantic water (higher temperature, higher salinity) led to higher DMS production. There was neither a correlation with Chl *a* nor with dissolved nutrients, but a correlation with particulate organic matter (POC, PON). Paired with prevailing overall oligotrophic conditions, this led to the assumption that community may have partly switched to mixotrophy. It was inferred that phytoplankton bloom already collapsed, accompanied by DMSP release and bacterial cleavage to DMS. Since the Arctic, specially the Fram Strait, is a region with rapidly changing environmental conditions, (regarding salinity, temperature, and nutrients availability) the inner cell's role of DMSP<sub>p</sub> as a “molecule of metabolic flexibility” in linkage with the surrounding environmental factors seemed to govern the DSMP and hence DMS dynamics.

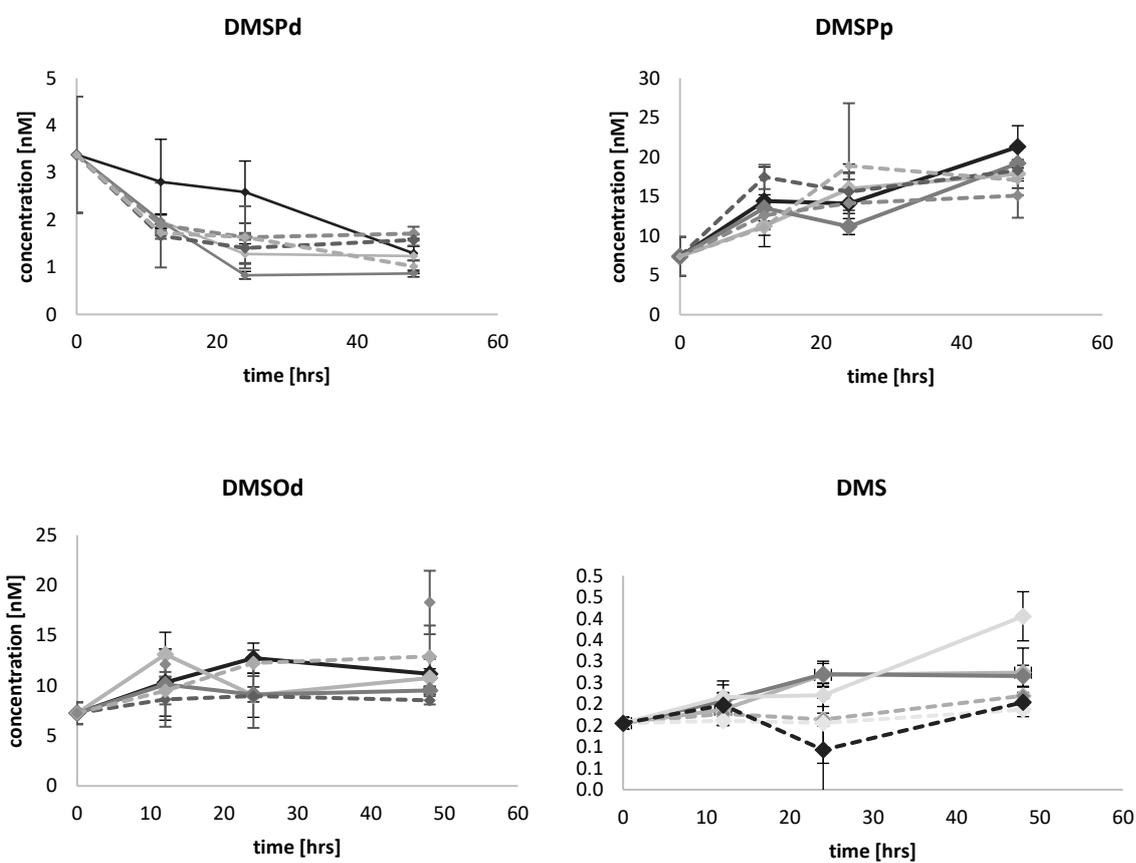
In face of the many and partly ambiguous experimental outcomes, there is still a need for constraining of what controls DMS production in the Arctic Ocean. Although probably challenging, to gain that understanding it requires multidisciplinary co-designed research approaches combining multiple scientific disciplines. For ocean acidification experiments, seasonal and regional variations should be considered by designing multiple forcing factor and longer-term manipulations, including e.g. availability of essential nutrients in- and outside the cell, temperature, salinity and light. Moreover, the community composition should be analysed in detail, combined with omics analysis and in situ rate measurements to study the key DMS(P) producing processes on a molecular level. Probably especially in a highly variable region such as the Arctic Ocean the bacterial processes related to DMS production should be paid more attention to. This could help elucidate the regional and seasonal key processes and hence reduce observational uncertainties. Ultimately that could facilitate improved DMS parameterization in modelling attempts of future DMS concentrations and emission, and its effect on the radiative budget in changing Arctic Ocean.

# SUPPLEMENTS

## S.1 Figures

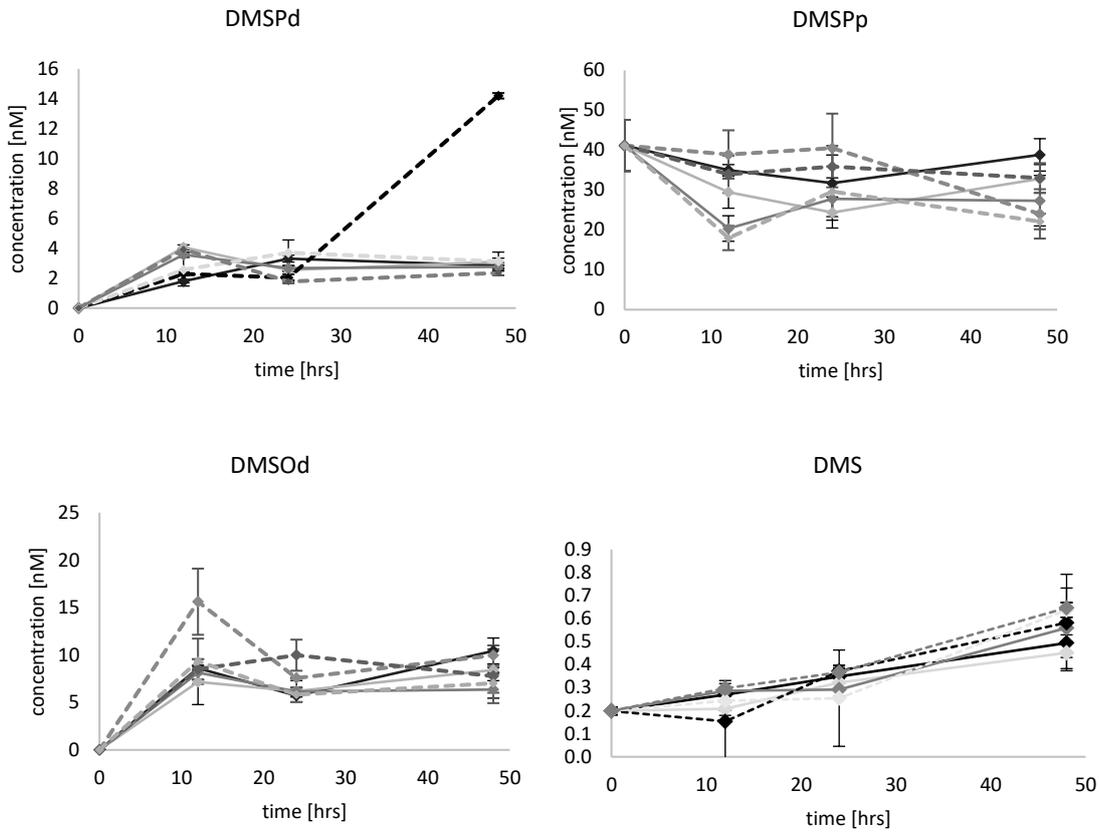
Treatment (pH, light) associated effects in the concentration development over the course of 48hrs of incubation, sorted after station:

Station Ice2:



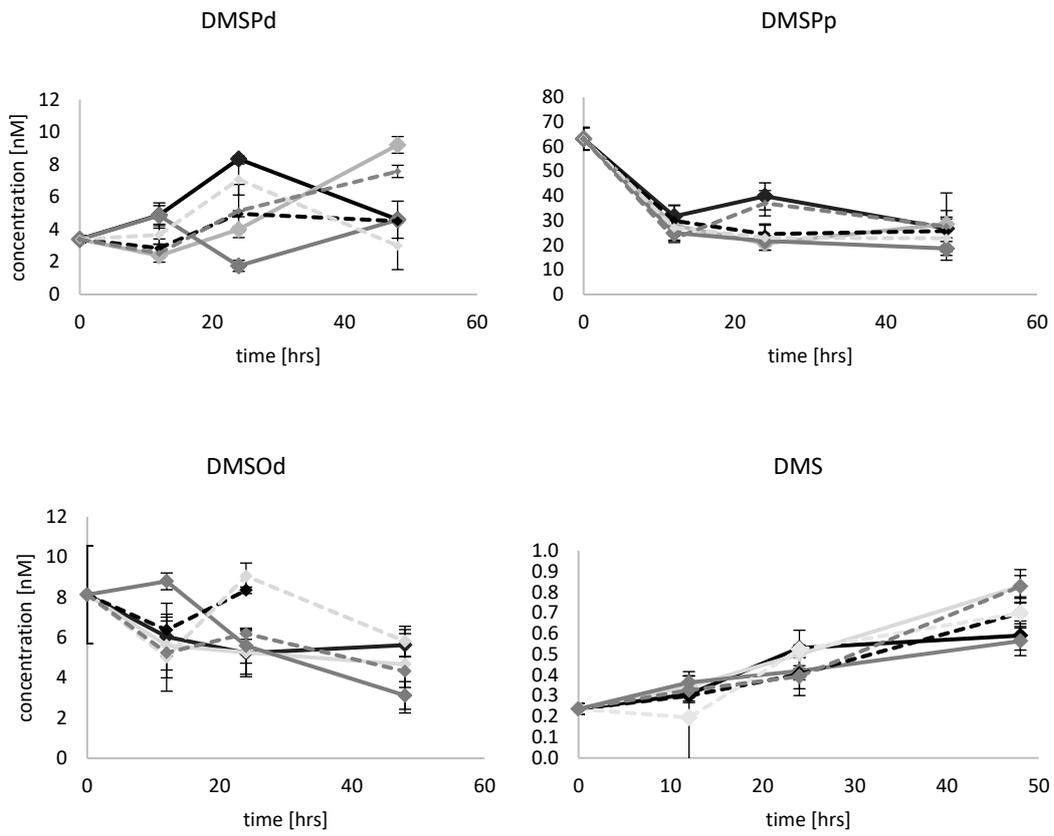
**Figure S.1** Concentration development over the course of 48hours of incubation at station Ice2. Dashed line = light, solid line = dark, amb = black, pH1 = light grey, pH2 = dark grey.

## Station D5:

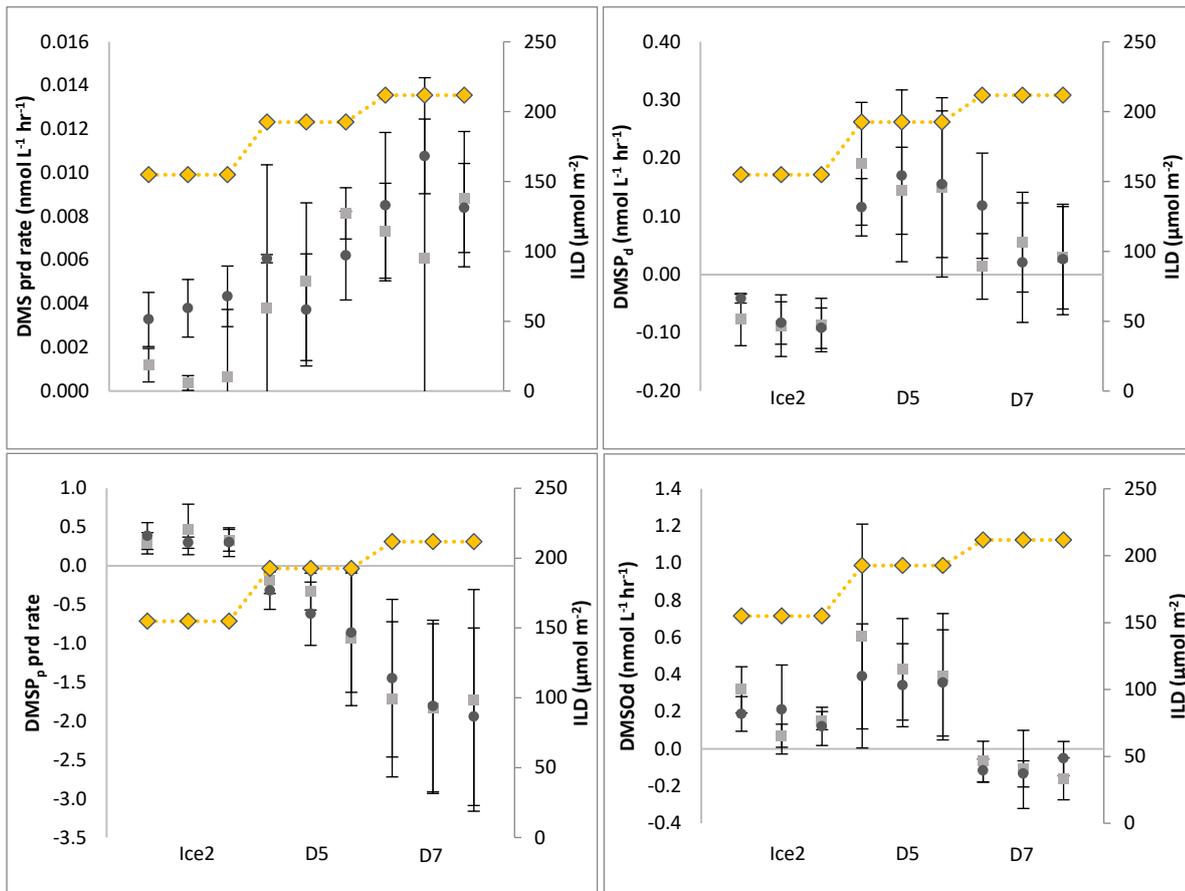


**Figure S.2** Concentration development over the course of 48 hours of incubation at station D5. Dashed line = light, solid line = dark, amb = black, pH1 = light grey, pH2 = dark grey.

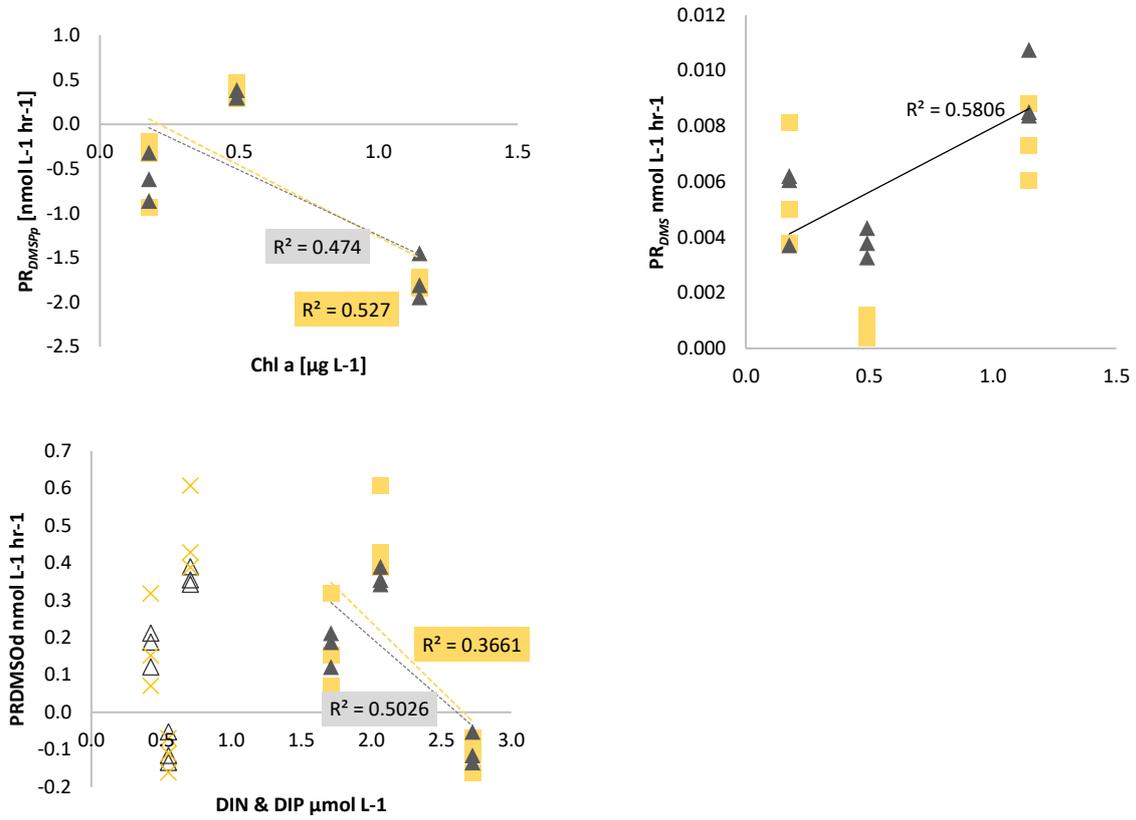
Station D7:



*Figure S.3* Concentration development over the course of 48hours of incubation at station D7. Dashed line = light, solid line = dark, amb = black, pH1 = light grey, pH2 = dark grey.

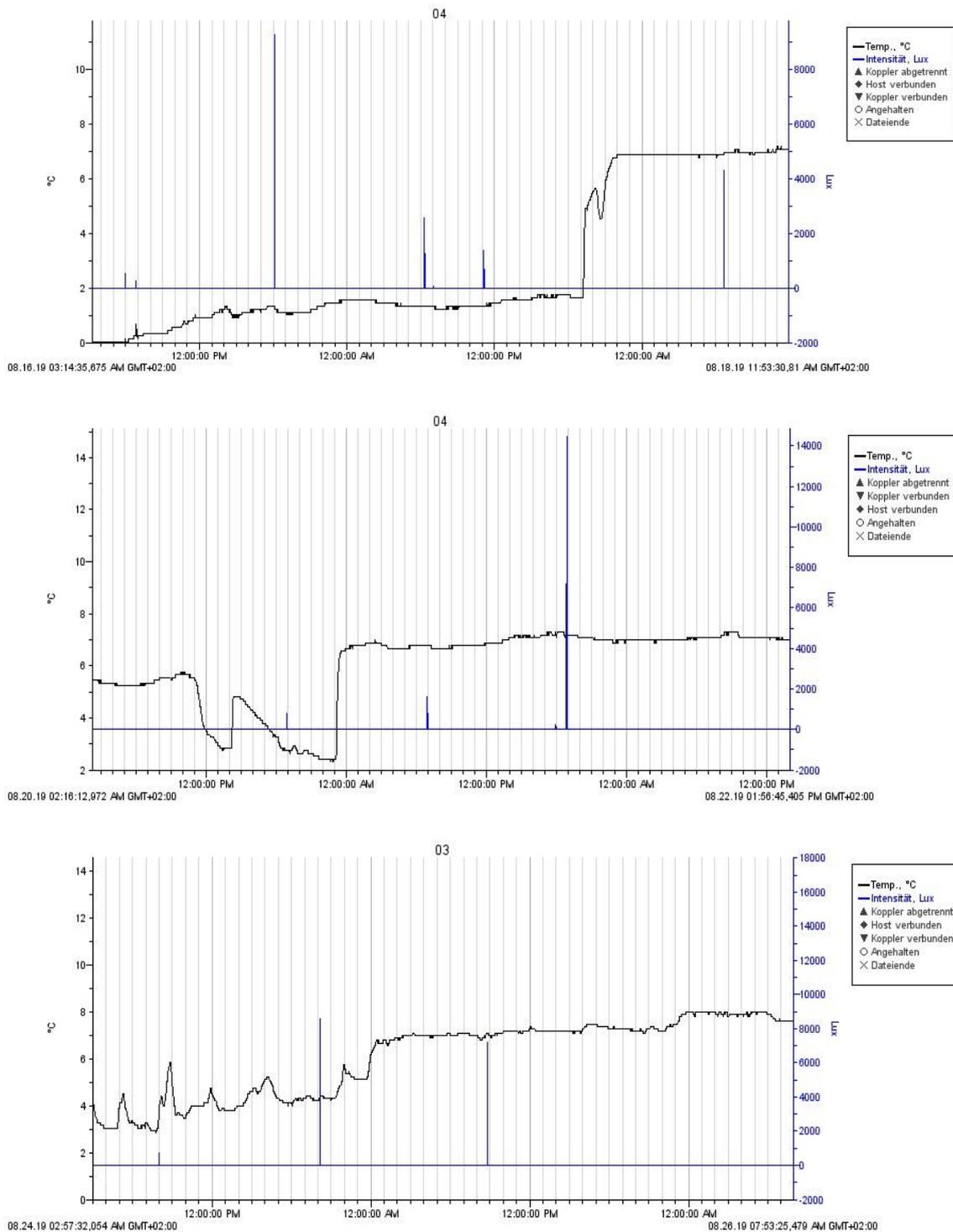
***Light effect:***

**Figure S.4** Average production rates of DMS, DMSP<sub>d</sub>, DMSP<sub>p</sub>, and DMSOd ( $1^{\text{st}}$  y-axis) per station (x-axis) in the light (light grey squares) and dark (dark dots). The  $2^{\text{nd}}$  y-axis represents the respective accumulated light dose (yellow), the samples were exposed to over 48 hours. Overlapping error bars indicate no significant difference between production rates of dark and light treatments.



**Figure S.5** Insignificant correlations of DMSO<sub>d</sub>, DMS and DMSP<sub>p</sub> production rates with environmental parameters. Separated into dark (= dark triangles) & light (= yellow squares).

### ***Light measurements in dark and light incubators***



**Figure S.6** Light (blue) & temperature (black) records in one of the dark incubators during incubation experiment at Ice2 (top), D5 (middle) and D7 (bottom). Spikes refer to moments where cover was lifted for taking or checking samples (less than a minute).

## S.2 Specifications of DMS data bank research

NOAA/PMEL DMS data server -- File Made: 2024-03-06 13:07:32

Latitude Limits: 60 to 90

Longitude Limits: -50 to 50

Date Limits: 2000-03-11 to 2019-04-15

Month(s) : all

## S.3 Dataset

**JR18007, RRS James Clark Ross August  
2019; Vertical profiles DMS/P/O**

Station	Date	Lat (N)	Lon East	Depth m	DMSOd (nM)	DMSPd (nM)	DMSPp (nM)	DMSPt (nM)	DMS (nM)
Ice2	16.08.2020	78.30	-4.79	5					0.16
Ice2	16.08.2020	78.30	-4.79	10	7.25	3.38	7.39	10.77	0.10
Ice2	16.08.2020	78.30	-4.79	35	2.15	0.46	1.67	2.13	0.00
Ice2	16.08.2020	78.30	-4.79	55	0.00	0.25	1.33	1.58	0.00
Ice2	16.08.2020	78.30	-4.79	75	1.48	0.16	0.47	0.62	-0.01
Ice2	16.08.2020	78.30	-4.79	100	0.00	0.00	1.05	1.05	-0.01
D5	20.08.2020	79.92	8.84	5					0.21
D5	20.08.2020	79.92	8.84	10	0.01	0.00	41.17	41.18	0.12
D5	20.08.2020	79.92	8.84	25	0.01	0.00	21.51	21.51	0.10
D5	20.08.2020	79.92	8.84	40	0.00	0.00	1.70	1.70	0.00
D5	20.08.2020	79.92	8.84	75	0.00	0.33	1.31	1.63	0.00
D5	20.08.2020	79.92	8.84	100	0.00	0.00	0.92	0.92	0.00
D7	24.08.2020	79.32	2.65	5					0.24
D7	24.08.2020	79.32	2.65	10	8.13	3.40	63.13	66.54	0.63
D7	24.08.2020	79.32	2.65	25	3.04	1.78	15.74	17.51	0.24
D7	24.08.2020	79.32	2.65	55	1.85	0.48	1.78	2.26	0.00
D7	24.08.2020	79.32	2.65	75	0.00	0.26	0.70	0.96	0.00
D7	24.08.2020	79.32	2.65	100	0.00	0.00	1.37	1.37	0.00

**JR18007. RRS James Clark Ross August 2019;****Vertical profiles  
ancillary data**

SYN	Synechococcus sp. Cyanobacteria		
PEUK	Picoeukaryote phytoplankton (<2µm)	HNAbac	Relatively high nucleic acid-containing bacteria
NEUK	Nanoeukaryote phytoplankton (approx. 2-12µm)	LNAbac	Relatively low nucleic acid-containing bacteria

Station	Date	Lat (N)	Lon East	Depth m	Syn(cells mL <sup>-1</sup> )	Peuk (cells mL <sup>-1</sup> )	Neuk (cells mL <sup>-1</sup> )	HNA bac (cells mL <sup>-1</sup> )	LNA bac (cells mL <sup>-1</sup> )	PON (µmol/L)	POC (µmol/L)
Ice2	16.08.2020	78.30	-4.79	5	0	2910	193	156772	87573	1.8	10.6
Ice2	16.08.2020	78.30	-4.79	10	0	2502	145	191238	110026	1.6	9.6
Ice2	16.08.2020	78.30	-4.79	35	0	76	8	88084	30018	0.4	2.3
Ice2	16.08.2020	78.30	-4.79	55	0	59	5	78925	26612	0.4	2.6
Ice2	16.08.2020	78.30	-4.79	75	0	8	5	71141	21723	0.5	3.9
Ice2	16.08.2020	78.30	-4.79	100	0	0	0	109162	37121	0.6	4.7
D5	20.08.2020	79.92	8.84	5	2409	8542	1193	339272	281588	2.1	12.0
D5	20.08.2020	79.92	8.84	10	4482	10401	1303	441830	355699	2.1	11.9
D5	20.08.2020	79.92	8.84	25	9415	5205	179	580799	462726	1.8	10.7
D5	20.08.2020	79.92	8.84	40	3745	1692	51	541337	365549	1.2	6.9
D5	20.08.2020	79.92	8.84	75	680	341	16	234027	179229	0.8	4.4
D5	20.08.2020	79.92	8.84	100	224	140	14	176145	135969	0.6	3.5
D7	24.08.2020	79.32	2.65	5	5377	12806	1258	347256	264273	2.0	11.1
D7	24.08.2020	79.32	2.65	10	8176	15024	863	450894	383706	3.4	19.6
D7	24.08.2020	79.32	2.65	25	4990	5248	214	367972	304089	1.6	9.2
D7	24.08.2020	79.32	2.65	55	561	288	38	211558	156508	0.8	4.7
D7	24.08.2020	79.32	2.65	75	141	101	30	183823	132591	0.7	4.1
D7	24.08.2020	79.32	2.65	100	87	45	12	149228	108339	0.7	4.0
D10	27.08.2020	77.47	13.49	5	596	10013	1678	503605	330208		
D10	27.08.2020	77.47	13.49	10	880	9991	1609	549172	343614		
D10	27.08.2020	77.47	13.49	35	1484	6644	497	399630	250622		
D10	27.08.2020	77.47	13.49	50	942	1665	81	245252	165550		
D10	27.08.2020	77.47	13.49	65	593	970	65	223580	149144		
D10	27.08.2020	77.47	13.49	80	341	442	35	201341	133661		
D10	27.08.2020	77.47	13.49	100	622	570	41	210446	128710		

**JR18007. RRS James Clark Ross August 2019; Incubations DMS/P/O**

date	treatment	p = depth profile	d = dark	l = light	0 = amb	1 = pH1	2 = pH2	DMSOt [nM]	DMSOd [nM]	DMSOp [nM]	DMS [nM]	pH
		station	depth/timepoint	DMSPt nM	DMSPd [nM]	DMSPp [nM]						
16. - 18.08.19	d0	Ice2	12	17.4	2.8	14.4	13.1	10.3	2.8	0.19	8.21	
	d0	Ice2	24	13.4	2.0	11.3	14.3	12.7	1.6	0.27	8.20	
	d0	Ice2	48	15.7	2.0	13.5	14.0	11.2	2.8	0.27	8.21	
	d1	Ice2	12	14.7	1.9	12.6	13.5	13.1	0.3	0.21	7.67	
	d1	Ice2	24	19.3	1.7	17.5	13.6	9.0	4.6	0.27	7.59	
	d1	Ice2	48	13.0	1.7	11.1	10.0	10.8	-0.8	0.27	7.66	
	d2	Ice2	12	17.0	2.6	14.1	13.7	10.1	3.5	0.22	7.56	
	d2	Ice2	24	17.5	1.3	16.0	13.1	9.1	4.0	0.22	7.42	
	d2	Ice2	48	12.2	0.8	11.2	11.9	9.5	2.4	0.41	7.50	
	l0	Ice2	12	15.9	1.6	14.1	12.1	0.0		0.18	8.18	
	l0	Ice2	24	17.1	1.4	15.6	13.4	0.0		0.16	8.18	
	l0	Ice2	48	20.6	1.6	18.9	18.5	18.3	0.2	0.22	8.24	
	l1	Ice2	12	22.9	1.3	21.3	15.3	8.6	6.6	0.16	7.67	
	l1	Ice2	24	19.4	1.2	17.9	14.9	9.0	6.0	0.16	7.62	
	l1	Ice2	48	20.5	0.9	19.2	16.0	8.5	7.4	0.19	7.66	
	l2	Ice2	12	17.0	1.7	15.1	15.3	9.5	5.8	0.20	7.28	
	l2	Ice2	24	20.1	1.6	18.3	16.2	12.2	4.0	0.09	7.55	
	l2	Ice2	48	18.3	1.0	17.1	16.1	12.9	3.2	0.20	7.54	
20. - 22.08.2019	d0	D5	12	37.1	1.8	35.0	12.9	8.6	4.3	0.27	8.89	
	d0	D5	24	33.7	4.1	29.5	12.3	5.7	6.6	0.35	8.29	
	d0	D5	48	24.2	3.6	20.4	13.0	10.4	2.6	0.49	8.59	
	d1	D5	12	41.4	2.3	38.9	12.5	7.2	5.3	0.21	7.56	
	d1	D5	24	36.7	2.6	33.9	14.8	6.2	8.6	0.32	7.63	
	d1	D5	48	22.2	3.9	18.0	9.5	8.4	1.1	0.45	7.60	
	d2	D5	12	35.4	3.3	31.7	12.6	8.1	4.5	0.29	7.65	
	d2	D5	24	27.3	2.6	24.4	9.2	6.1	3.0	0.29	7.76	
	d2	D5	48	30.7	2.7	27.8	12.4	6.4	6.0	0.56	7.71	
	l0	D5	12	43.0	2.0	40.6	13.1	15.6	0.0	0.15	8.21	
	l0	D5	24	39.9	3.7	35.9	11.7	7.6	4.1	0.37	8.34	
	l0	D5	48	31.8	1.8	29.6	22.3	9.9	12.3	0.58	8.28	
	l1	D5	12	42.2	2.8	38.8	11.0	8.5	2.5	0.24	7.72	
	l1	D5	24	36.4	3.1	32.8	18.5	10.0	8.5	0.25	7.58	
	l1	D5	48	30.7	2.8	27.3	11.1	7.8	3.3	0.64	7.65	
l2	D5	12	38.8	14.2	24.0	11.1	9.3	1.8	0.30	7.48		

	l2	D5	24	36.8	3.1	33.0	10.0	5.8	4.2	0.37	7.48
	l2	D5	48	25.1	2.4	22.1	23.5	7.0	16.5	0.65	7.48
	d0	D7	12	37.0	4.9	31.8	12.2	6.0	6.1	0.31	8.23
	d0	D7	24	30.7	2.4	28.0	11.3	5.2	6.1	0.53	8.21
	d0	D7	48	30.2	4.9	25.0	11.3	5.6	5.7	0.59	8.24
	d1	D7	12	33.0	2.8	29.9	10.5	5.6	4.9	0.34	7.44
	d1	D7	24	25.6	2.5	22.7	9.2	5.3	3.9	0.50	7.50
	d1	D7	48	30.9	3.7	27.0	8.9	4.7	4.2	0.83	7.37
	d2	D7	12	48.7	8.3	39.8	11.1	8.8	2.3	0.36	7.34
	d2	D7	24	25.2	4.0	20.7	7.7	5.6	2.1	0.42	7.36
24. - 26.08.2019	d2	D7	48	23.9	1.8	21.8	7.5	3.1	4.4	0.56	7.33
	l0	D7	12	29.9	5.0	24.5	8.4	6.4	2.0	0.30	8.22
	l0	D7	24	42.6	5.1	37.0	14.2	8.3	5.9	0.40	8.27
	l0	D7	48	30.7	7.1	23.1	12.5	0.0		0.70	8.28
	l1	D7	12	32.0	4.6	26.8	11.0	5.0	5.9	0.20	7.48
	l1	D7	24	38.6	9.2	28.6	10.3	9.1	1.3	0.52	7.50
	l1	D7	48	23.8	4.6	18.7	9.2	5.8	3.4	0.70	7.46
	l2	D7	12	30.9	4.5	25.7	12.8	5.2	7.6	0.33	7.17
	l2	D7	24	36.0	7.6	27.6	13.2	6.2	7.1	5.14	7.11
	l2	D7	48	26.5	3.0	22.8	9.8	4.3	5.5	7.58	7.23

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## 5 CONCLUSIONS AND OUTLOOK

### 5.1 Main outcomes & possible future research directions

The main goal of this work was to increase the understanding of CO and DMS cycling in the Arctic Ocean with regard to expected changes in acidity, light and further environmental parameters. With that we aimed to provide further observational data from the Arctic Ocean realm contributing to decrease the prevailing uncertainties about processes and major drivers controlling CO and DMS distribution (Bange et al., 2024; Song et al., 2011; Song and Xie, 2017).

#### CO.

We found that lower pH did not affect CO production ( $GP_{CO}$ ) or consumption ( $k_{CO}$ ) rates indicating that ocean acidification does not affect CO surface concentrations. Yet, enhanced  $GP_{CO}$  and  $k_{CO}$  significantly increased with coloured dissolved organic matter (CDOM) and dissolved nitrate concentrations, respectively. This suggests a photochemical production of CO from CDOM which, in turn, is consumed rapidly by microbes preferably under oligotrophic conditions such as those found at the time of sampling. Thus, we identified both CDOM and  $NO_3^-$  as well as subsequent microbial uptake as key drivers of CO surface concentration variability. Hence microbial CO consumption could act as a ‘filter’ for the subsequent atmospheric CO emissions from the Fram Strait. In the Arctic Ocean/Fram Strait, oligotrophic conditions can be found, at least transiently, at ice edges or open ocean when nutrient supply via melting and/or mixing is interrupted by stratification. Consequently, projected alterations in terrestrial and marine CDOM as well as dissolved  $NO_3^-$  inputs could affect future CO production and consumption in the Arctic, perhaps leading to an increase in both terms. Yet it

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is unknown which process will dominate. Since anthropogenic CO sources are declining (Szopa et al., 2021), the oceanic source might become even more pronounced in the future. Further research should therefore address the question if and under which conditions CO consumption rates would stagnate, since in that situation CO would be emitted.

For future research attempts the standardization and quality-control of CO measurements would be a necessary step forward, since to date we have no internationally accepted quality standard for CO in seawater as it is the case for CO<sub>2</sub>, nitrous oxide and methane (Wilson et al., 2018). The only available reference is the quality-control threshold for atmospheric CO (Zellweger et al., 2019) to which several groups try to abide by measuring reference gases calibrated against either NOAA (National Oceanic and Atmospheric Administration) or WMO (World Meteorological Organization) standard scales. For high latitudes, models underestimate the simulated CO concentrations compared to in situ measurements, perhaps because they lack the CDOM supply by sea ice and rivers, and their biological consumption term seems not suitable (Conte et al., 2019). Thus, the CDOM-CO relationship should be further assessed regarding seasonal and spatial variations to refine CO parameterizations. Process based models (Kwon et al., 2020) are useful tools to understand such drivers of spatial and temporal variability of CO dynamics and to project the integrated effect of all the changes on CO production. Performing further multifactorial experiments including i.e. UV light intensity and bacterial community data could help to elucidate the explanatory power of the different environmental factors on both CO production and consumption. This would facilitate a better incorporation of both terms into biogeochemical models and would improve both CO emission estimates for the Arctic realm, and the assessment of how atmospheric CO emissions will affect the radiative budget and oxidative capacity of the Arctic atmosphere.

## **DMS.**

Neither the reduction of pH nor light availability had a significant effect on any of the sulphur

compounds. Though, we found that DMS producing communities in our experiments were resilient to OA potentially because of high adaption abilities, this might change when temperate microbial communities further expand poleward due to atlantification (Ahme et al., 2023; Oziel et al., 2020). Relatively lower DMS/P/O concentrations compared to those found in earlier Arctic summer reflected overall oligotrophic post bloom conditions. DMSP<sub>p</sub> was the dominant precursor driving the DMS production rate. Both, DMS and DMSP production rates were linked to temperature and salinity. Though low, PR<sub>DMS</sub> at all experimental locations was positive, with an average rate of  $0,005 \pm 0,001 \text{ nmol L}^{-1} \text{ hr}^{-1}$ . Polar EGC waters with lower temperature and salinity (ice proximity) in combination with a rather mixed water column resulted in lower DMS and DMSP<sub>p</sub> concentrations. Moreover, no correlation between Chl *a* and DMS/P was found. However, the release of DMSP<sub>p</sub> and DMS production increased with increasing PON and POC concentration, indicating a senescent, hence collapsing bloom with consequent DMSP<sub>p</sub> release. We infer, that Arctic DMS cycling depends on a complex intertwine of the physiochemical setting in turn affecting the microbial community composition as well as their physiological stage. Periodical and locational gradients in salinity, temperature as well as nutrients (for example due to melting events, light induced stratification or sudden wind induced vertical mixing) may control which microbial community composition is favored, and through that ultimately influence Arctic DMS production and emissions, especially in the Fram Strait. Thus, mixo- and heterotrophic organisms might play a more pronounced role for DMS dynamics than they might do elsewhere and should be carefully considered in future experimental approaches. The processes involved in DMS cycling will likely change under the ongoing changes of the Arctic environment. Considering the complexity of the underlying production and consumption processes it is hard to predict whether DMS emissions will ultimately increase or decrease in the future.

## CO and DMS.

Overall, our results suggest that both the processes governing CO as well as DMS concentrations are resilient in response to Ocean Acidification, inferring that due to the highly variable Arctic environment microbial communities reveal a phenotypic plasticity that help them to cope with sudden environmental changes (Sackett et al., 2013; Hopkins et al., 2020). However, this resilience could decline under further invasion of temperate microbial communities because of atlantification (Oziel et al., 2020; Ahme et al., 2023). We assume that the prevailing environmental conditions influenced by the two major hydrographic regimes of the Fram Strait, the EGC and WSC, had a large influence on the microbial community (Cherkasheva et al., 2014; Wietz et al., 2024) and resulting concentration dynamics of DMS and CO. The late summer season in transition to fall revealed rather oligotrophic conditions which probably caused bloom senescence favouring mixo- and heterotrophic metabolism (Jackowski et al., 2022) under which rapid microbial CO consumption and senescence-induced DMSP<sub>p</sub> release (Rokitta et al., 2016; Yoch, 2002) become more pronounced. The scenario we observed delivers important insights on CO and DMS cycling during the summer to fall transition, adding to the seasonal coverage of datasets. Incorporating those into models can help to draw a more precise picture of future CO and DMS dynamics over different Arctic seasons and regions and the resulting influence on atmospheric processes that are tightly tangled to global climate.

For both, CO and DMS dynamics understanding and unravelling their relationship with bacterial activity and community structure is an important step forward. Omics analysis of seawater samples combined with in situ trace gas measurements will help to answer open questions: What do microbial CO consumption rates depend on? Which bacterial strains are mainly responsible for DMSP to DMS conversion and CO consumption, and what does their activity depend on? Since the *Roseobacter* clade is known to metabolise both DMSP and CO

(Cunliffe 2011; Kirkwood 2012), changes concerning that clade might be worth investigating further. However, there are other bacterial groups, like non-*Roseobacter* alphaproteobacterial and gammaproteobacteria (King and Weber, 2007; Levasseur, 2013) metabolising one or both gases, and which will have implications, too. Hence, dominant bacterial strains involved in DMS or CO cycling should be identified and further investigated.

Thus, to assess future Arctic CO and DMS production and emissions, sophisticated and multidisciplinary research approaches, e.g. longer-term incubation experiments, are required (Hopkins et al., 2023; Bange et al., 2024). Those should analyse the process details from several perspectives, combining i) community composition analysis – focussing on both phytoplankton as well as bacteria, and maybe even grazers ii) omics analysis, iii) in situ rate measurements in interaction with iv) other environmental parameters, considering spatial and seasonal variability as well as potential shifts due to sea ice loss (Hopkins et al., 2020) and further changes in hydrographic regimes (Tuerena et al., 2021; Cardozo-Mino et al., 2021).

## **5.2 Societal and policy implications**

A resilient and sustainable Arctic environment contributes to global human prosperity. Sustaining its present and future functioning should thus be a main priority of political and societal planning activities. Anthropogenic global warming initiated an overarching transition of the Arctic region, which manifested in the rapid retreat of sea-ice and the thawing of permafrost, which subsequently are affecting numerous natural processes at regional and global level. This thesis discussed how ongoing changes in the Arctic Ocean such as for instance acidification and light availability might alter the biogeochemical cycling of the climate-relevant gases DMS and CO (see Table 1). The production of both gases is likely to increase in the future and yet the direction and magnitude of the emissions to the atmosphere as well as the expected long-term feedback on regional climate remain uncertain. Hence, despite of their major role in climate, elucidating the socio-economic influence of long-term changes in the

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production and emissions of DMS and CO will need extensive multidisciplinary efforts in basic research, as well as adequate transfer of knowledge to stakeholders and policy makers. To this end, we propose to:

1. Increase understanding
  - a. Support international, multidisciplinary studies as well as sustained observations of DMS and CO in the AO. Knowledge transfer between in situ observations and global coupled models should then help establishing more reliable emission projections for DMS and CO, and their effects on the Arctic Ocean.
  - b. Facilitate research co-design by integrating economics, natural and social sciences, and stakeholders to raise awareness across disciplines of the importance and environmental feedbacks caused by the alterations in DMS and CO emissions in the context of ongoing climate change. This approach could provide societal-relevant knowledge and solutions to holistically manage the implications of Arctic change (Alvarez et al. 2020).
2. Think economy long term
  - a. Stick to the Paris agreement and decrease global greenhouse gas emissions because this would reduce warming and ocean acidification as these changes could directly and indirectly affect DMS and CO cycling in the Arctic Ocean (see Table 1).
  - b. Burning of both fossil fuels and biomass (e.g. forest fires) are the major sources of atmospheric CO. To this end CO emissions from these sources must be avoided, e.g. by (i) regulating offshore industrial activities including Arctic ship traffic and oil/gas drilling and (ii) minimizing forest fires in the countries around the Arctic Ocean.
3. Increase general knowledge and acceptance of sustainable political measures
  - a. Support outreach activities aiming to inform the general public on the key role of atmospheric trace gases for the Arctic Ocean and global climate and the complexity and interconnectedness of natural processes.

- b. Promote a societal mind-set shift towards the realization of us being a part of nature, meaning that human wellbeing relies on suitable environmental conditions, to increase the acceptance of sustainable political and economic decisions (see Ives et al. 2018).

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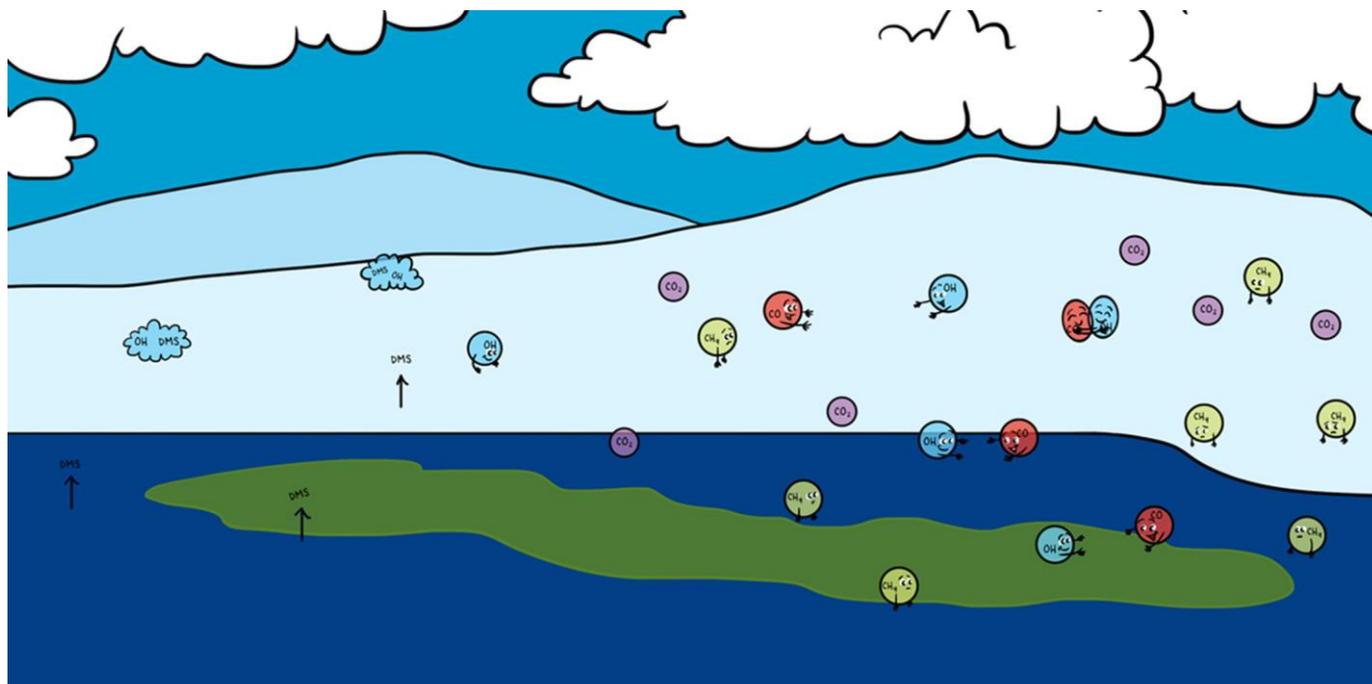
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## SUPPLEMENTS

### **Manuscript 4:**

### **Tiny But Powerful: How Tiny Amounts of Certain Gases Can Make a Big Difference in the Earth's Climate**

Campan H and Bange HW (2021) Tiny But Powerful: How Tiny Amounts of Certain Gases Can Make a Big Difference in the Earth's Climate. *Front. Young Minds.* 9:516417. doi: 10.3389/frym.2021.516417 (see next page)



## TINY BUT POWERFUL: HOW TINY AMOUNTS OF CERTAIN GASES CAN MAKE A BIG DIFFERENCE IN THE EARTH'S CLIMATE

Hanna Campen\* and Hermann W. Bange

GEOMAR Helmholtz Center for Ocean Research Kiel, Kiel, Germany

### YOUNG REVIEWERS:



FINN  
AGE: 11



RUARI  
AGE: 12

Comparable to carbon dioxide, dimethyl sulfide (DMS), and carbon monoxide (CO) are tiny gases that have a great impact on our climate. Though occurring only in very small amounts in the atmosphere they are climate influencers, especially in the Arctic. The Arctic is a unique place on Earth where all life is adapted to the extreme cold. Therefore, global warming is a great threat to the Arctic. DMS and CO are produced in the Arctic Ocean and can go into the atmosphere. There, CO may enhance the warming of the Arctic. On the other hand, DMS possibly cools the atmosphere because it helps forming clouds. The processes CO and DMS are involved in, are complex and will probably alter under a changing climate. It is important to understand these processes to get an idea of the future Arctic Ocean and climate to find ways to save the Arctic.

## TRACE GASES

Gases that make up together <1% of our atmosphere (Figure 1).

## ARCTIC OCEAN

The Arctic Ocean includes the North Pole region and is surrounded by northern parts of Europe and Asia and North America. It is the coldest, smallest and shallowest ocean compared to the Pacific, Atlantic, Indian, and Southern Oceans. Polar bears live in the Arctic region but there are no penguins.

## CARBON MONOXIDE

A less known trace gas that has the potential to enhance global warming.

## DIMETHYL SULFIDE

A gas that possibly cools the atmosphere by helping to form clouds.

## GREENHOUSE EFFECT

The burning of oil and gas releases certain trace gases. Some of those gases are acting as greenhouse gases and accumulate in the atmosphere of the Earth. Like a greenhouse, they keep more warmth of the sunlight in the atmosphere, which leads to global warming.

## TINY GASES MAKE A DIFFERENCE!

That sounds funny at first glance but, looking more closely, this is not only true when we are in an elevator realizing someone had beans for lunch. It is also true for so-called trace gases. Trace gases occur in our atmosphere in very small amounts. But do not be fooled: they influence Earth's climate in a big way, namely through their behaviors and interactions. This is especially true in the Arctic Ocean, one of the most impressive, yet vulnerable, places on Earth. You have probably heard of carbon dioxide since it is one of the key drivers for climate change – the star influencer among trace gases. But have you heard of carbon monoxide and dimethyl sulfide? They are further influencers – trace gases whose forces we should not overlook. Here comes their story. Where do they come from? How powerful are they and will they influence the future of the Arctic? On Instagram, we follow influencers and let them affect our behavior. Why do not we take trace gases as an inspiring example, too? Even though we may feel tiny when facing this overwhelming climate problem, our individual behavior makes a difference!

## WHAT DO WE MEAN BY TINY?

As the name trace gases indicates, these gases only occur in the air in very small (trace) amounts. You may already know that the air we breathe consists mainly of nitrogen and oxygen, so these are not considered trace gases. All trace gases together make up <1% of the atmosphere. Carbon monoxide and dimethyl sulfide are only two of several trace gases, thus they represent an even tinier fraction (Figure 1). We might conclude that a small fraction means a small impact; so we may think that trace gases are not very important. However, this is not true at all! Carbon dioxide (CO<sub>2</sub>) is a trace gas, too. Its properties, in combination with its increasing concentration in the atmosphere, keep the warmth of sunlight trapped close to the Earth longer, so that the Earth warms up. This is similar to the way a greenhouse allows tomatoes to grow, even in wintertime, so we call it the greenhouse effect. The greenhouse effect is so strong that it influences the entire world's climate. But what about carbon monoxide and dimethyl sulfide? In the rest of this article, we will explain the influence of these important trace gases on the Earth's climate.

## WHAT IS CARBON MONOXIDE AND WHERE IS IT FOUND?

**#Climateinfluencer   #Indirectgreenhousegas   #Oceanproduct  
#Interactionlover**

Carbon monoxide (CO) mainly occurs where things are burning. You may have heard that CO is a dangerous gas that can be poisonous at certain levels. Most CO comes from the burning of

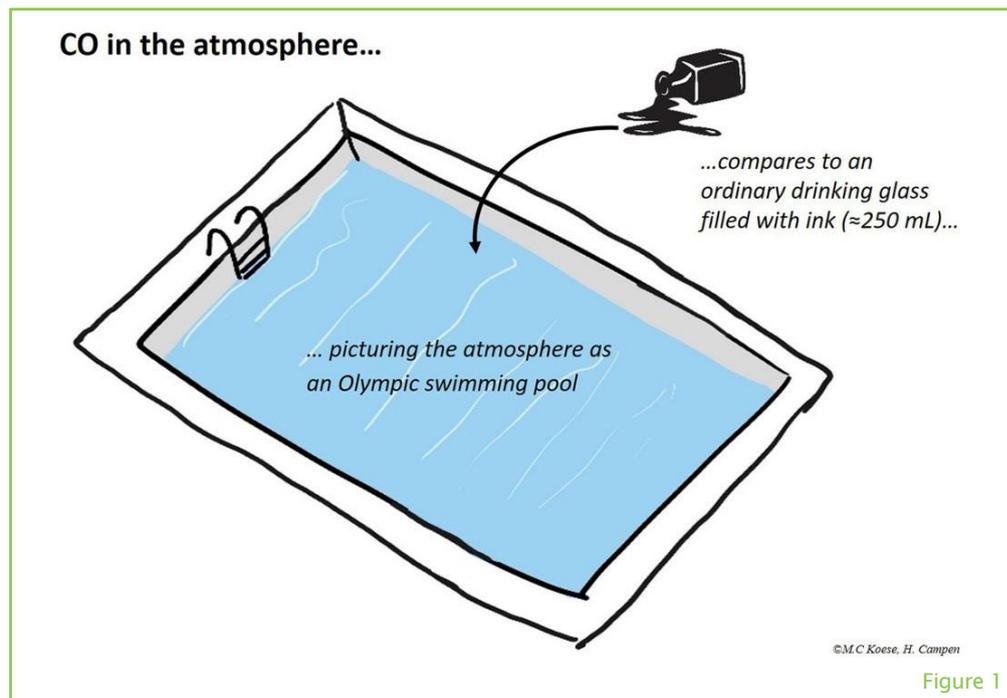
Figure 1

All trace gases together make up <1% of the atmosphere. Carbon monoxide (CO) is one of these trace gases. Picture the atmosphere as an Olympic-size swimming pool. Also picture an ordinary drinking glass filled with ink. Pour this glass of ink into the pool and watch how much it dilutes in the water. That equals approximately the amount of CO in the atmosphere<sup>1</sup>.

<sup>1</sup> Volume of an Olympic-size swimming pool:  $50 \times 25 \times 2 \text{ m} = 2,500 \text{ m}^3 = 2,500,000 \text{ liters}$ . Fraction of CO in the atmosphere:  $10^{-7} = 0.0000001$ . Volume of ink required to obtain the same fraction in the pool:  $0.0000001 \times 2,500,000 \text{ liters} = 0.25 \text{ liters}$ , i.e., an ordinary drinking glass (250 mL) filled with ink.

### PHYTOPLANKTON

Tiny, floating marine algae that are the base of all life in the ocean.



fuels, such as petrol. However, scientists found out that the ocean contains a lot of CO, too. In the ocean, floating dead plant material and tiny marine algae, called phytoplankton, react with sunlight to produce CO [1]. The amounts of CO produced at certain areas of the ocean's surface can become so large that it goes into the atmosphere. That is why scientists call the ocean a source of atmospheric CO - #oceanproduct.

How does CO behave in the atmosphere? As you can see from Figure 2, CO is a simple molecule. It consists only of one carbon and one oxygen atom. However, because of its properties, it likes interacting and reacting with other molecules in the air. That is what characterizes its influence – #interactionlover. Once CO is released into the air, its favorite reaction partners are hydroxyl molecules (OH<sup>•</sup>). This means that OH<sup>•</sup> is CO's best friend and they love to interact with each other. In their interaction, CO rapidly takes up the oxygen atom of OH<sup>•</sup>. Hence, that gives CO + O. Any idea what that forms? Exactly: CO<sub>2</sub> – a greenhouse gas.

OH<sup>•</sup> molecules are often called the cleanser of the atmosphere, because OH<sup>•</sup> can react with and destroy many atmospheric compounds, including some dangerous ones. For example, OH<sup>•</sup> also reacts with methane (CH<sub>4</sub>), another trace gas and a powerful greenhouse gas like CO<sub>2</sub>. When OH<sup>•</sup> reacts with CH<sub>4</sub>, the danger of CH<sub>4</sub> is invalidated. However, OH<sup>•</sup> likes reacting with CO much more. Thus, if CO is present, it takes away OH<sup>•</sup>, the potential reaction partner of CH<sub>4</sub>, and prolongs the time CH<sub>4</sub> stays in the atmosphere [2]. That enhances the harmful warming effect of CH<sub>4</sub> on the atmosphere. So, CO causes a chain reaction that in turn leads to warming. That

Figure 2

(A) Carbon monoxide (CO) and (B) dimethyl sulfide (DMS). CO consists of one carbon (pink) and one oxygen (blue) atom bonded to each other. DMS consists of two methyl groups (pink and green) connected by a sulfur atom (yellow) in its center. A methyl group is one carbon atom binding three hydrogen atoms.

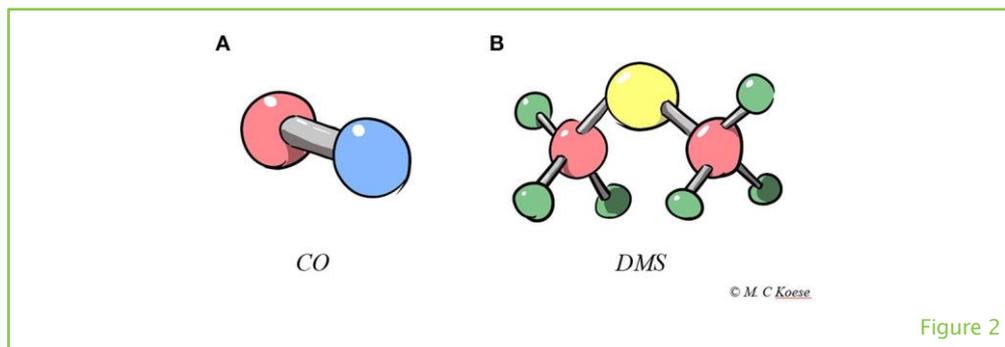


Figure 2

is why CO is called an #indirect greenhouse gas – an influencer of the climate.

At this point, it may be clearer to you why we care how much CO is produced in remote oceanic areas, such as the Arctic Ocean. The Arctic Ocean is less influenced by land-produced CO than many other areas of the world, simply because the surrounding land is not so densely populated. The release of CO from the Arctic Ocean into the atmosphere could make a difference for the Arctic climate. Does this mean there is no good news for the Arctic Ocean? The question is, are there other influencer molecules that might counteract the effect of the CO that is released from the ocean? Now DMS comes into play.

## WHAT IS DIMETHYL SULFIDE AND WHERE IS IT FOUND?

#climateinfluencer  
#biologicalproduct

#sulfurcontainer

#cloudcreator

Dimethyl sulfide (DMS) is a simple molecule, too. It consists of two methyl groups at its ends and one sulfur atom in its center – #sulfurcontainer. A methyl group is a carbon atom binding three hydrogen atoms. However, the sulfur atom makes the molecule special: sulfur is needed for all living organisms to build proteins and other key components of their cells. In the ocean, DMS is produced by phytoplankton and bacteria [3] – #biologicalproduct. Hence, through DMS production, sulfur becomes available to other organisms. However, like CO, DMS can be released from the ocean into the atmosphere. And there, its sulfur plays another central role!

When released into the atmosphere, DMS can help to create clouds. Once DMS is in the air, it also reacts with OH<sup>•</sup> and makes cloud-forming particles called cloud condensation nuclei. You can picture a cloud condensation nucleus (CCN) as a very small particle that acts like a seed – a seed for a cloud that will grow around it – #cloudcreator. You have probably noticed that the more clouds there are in the sky, the less sunlight reaches us on the ground. The clouds reflect the sunlight back to space, and less sunlight at

## CLOUD CONDENSATION NUCLEUS

A particle in the air that acts like a seed for cloud formation. Around it a cloud can grow.

Figure 3

All trace gases together make up <1% of the atmosphere. CO and DMS are two of these trace gases. DMS can help to create clouds, which could potentially lead to a cooling of the atmosphere. CO could further warm the atmosphere because it promotes the formation of further greenhouse gases, such as CO<sub>2</sub>, and prolongs the lifetime of CH<sub>4</sub> in the atmosphere. So, it is difficult to predict what the overall influence of trace gases on the Arctic climate will be in the future.

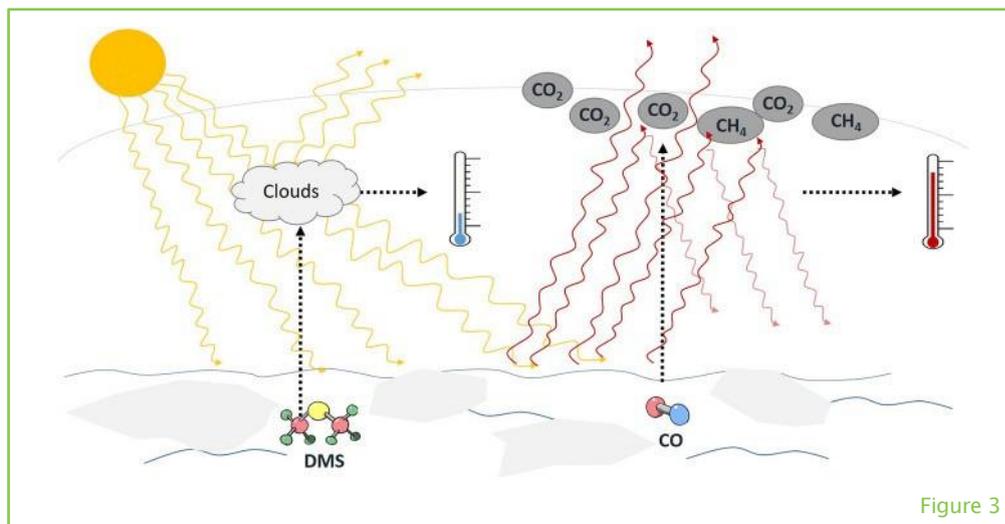


Figure 3

the Earth's surface means the surface gets cooler. Scientists call this cloud formation theory the CLAW hypothesis, which is summarized as follows: marine phytoplankton can cool the Earth by producing DMS, and consequently, clouds [4] – #climateinfluencer. It is crucial that we find out if the CLAW theory is true for remote areas, like the Arctic Ocean, which are especially threatened by warming. That is why we want to study DMS production and all related processes very carefully in the Arctic Ocean.

### WHY IS THE ARCTIC OCEAN SO IMPORTANT?

Cooler areas of the Earth can warm faster than areas that are already relatively warm. Scientists have seen that the Arctic region, therefore, is warming much faster than other regions of the world. This is important because the Arctic region plays an important role in global weather and climate. The Gulf Stream is a good example of the Arctic's influence. The Gulf Stream is an ocean current that brings warmth from the tropics to Europe and is thus responsible for the mild climate in Europe. The Gulf Stream's main driving force is seawater from the Arctic, which is very cold and salty. Cold, salty seawater is so heavy and dense that it sinks down to the ocean bottom, resulting in major water movement, kind of like a pump. Now imagine that the Arctic Ocean's temperature and salt content change. The melting of Arctic ice due to the ongoing warming of the Arctic will add loads of fresh water, which contains less salt than seawater. This warmer, fresher water will not sink like cold, salty water, and this change could weaken the Gulf Stream. Changes to the Gulf Stream would not only affect the Arctic itself but could have consequences for other places in the world too, such as Europe.

So, you can see that it makes sense to investigate the many consequences of climate change in the Arctic, to learn from them, and to determine how these changes might affect other areas of Earth. Moreover, we need this information to predict how weather and

climate will behave in the future – how our world will look when you are 90. By predicting the future climate, we can hopefully find ways to adapt to the changes or even find solutions to stop them.

## HOW WILL CO AND DMS INFLUENCE THE FUTURE OF THE ARCTIC OCEAN AND OUR CLIMATE?

We all know that the Earth is getting warmer, especially the Arctic Ocean. Thinking of the interactions we have just discussed, the picture becomes clear: environmental changes like climate warming and melting ice can affect the production and release of CO and DMS in the Arctic Ocean [5, 6]. However, we also saw how complex the production and release processes of DMS and CO are. That is why we are uncertain whether CO and DMS in the Arctic Ocean will become more or less abundant and, in turn, whether that would cool or further warm the Arctic atmosphere (Figure 3).

Finally, we explained that what happens in the Arctic Ocean does not necessarily stay in the Arctic Ocean, but these changes can affect the rest of the world's climate. Therefore, it is extremely important to continue to investigate the behavior of climate-relevant trace gases like CO and DMS in the Arctic, under different future scenarios. Even though trace gases occur in tiny amounts, they still make a big difference.

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CONFLICT OF INTEREST: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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## YOUNG REVIEWERS



FINN, AGE: 11

My name is Finn and I am 11 years old. My hobbies are running, reading (including this paper!), drawing, football, cooking, and sleeping! I also love swimming, which is really fun, especially butterfly. We go on many holidays together as a family and my favorite ones so far were going to Japan and hiking from hut to hut in the Pyrenees. At school, I like maths the most and in my opinion, it is the easiest subject.



RUARI, AGE: 12

Ruari loves science, particularly anything related to space! He hopes to be an astronaut 1 day and really wants to travel to Mars. He loves reading adventure books, doing back-flips on his trampoline and playing the pipes, when not at school.

## AUTHORS



HANNA CAMPEN

Hanna Campen looks on how certain gases occurring only in tiny amounts in the atmosphere influence climate. She investigates how that will evolve in a future changing Arctic Ocean. She studied biology and biological oceanography in Kiel, Germany. Now she is doing her Ph.D. at the GEOMAR Helmholtz Centre for Ocean Research Kiel. She is passionate about seeing nature as our home and therefore protecting it. She thinks that talking about climate change and its consequences

with as many people as possible eventually helps to change how we treat our only planet. \*hcampen@geomar.de



#### HERMANN W. BANGE

Hermann Bange studied chemistry in Göttingen and Freiburg. He is now working as a marine biogeochemist at the GEOMAR Helmholtz Centre for Ocean Research in Kiel, Germany. He is an expert for measuring climate-relevant gases, such as nitrous oxide, methane, carbon monoxide, and dimethyl sulfide. Since the time of his Ph.D. he is fascinated by the fact that tiny gases with very low abundances in both the oceans and the atmosphere can make a huge impact on the Earth's climate.