



# **Assessing climate-driven variability in phytoplankton functional groups and dimethyl sulfur compounds from space in the northern Benguela upwelling system**

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## Declaration

I, Tebatso Martin Moloto, hereby declare that this thesis, entitled "Assessing climate-driven variability in phytoplankton functional groups and dimethyl sulfur compounds from space in the northern Benguela upwelling system", is my own original work and has not been submitted for any degree or examination at any other institution. All sources used have been properly acknowledged, and all research was conducted in accordance with ethical guidelines.

Signed : .

Date : 05 November 2025

## **Dedication**

To my family, for their unconditional love, encouragement, and belief in my dreams.

In the hopes that this work may contribute in some way towards the monitoring and exploration of the Namibian productive marine ecosystem, I also dedicate this work to the scientists and crew of the RV Mirabilis.

## Acknowledgements

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## Abstract

Marine phytoplankton form the base of oceanic ecosystems influencing food webs, biogeochemical cycling and climate dynamics. Different phytoplankton functional groups (PFGs) play distinct roles, contributing to varying climate and ecosystem functioning. For example, planktonic dimethyl sulfur compounds (DMSc), such as dimethyl sulfide (DMS) and its precursor dimethyl sulfoniopropionate (DMSP), play a key role in sulfur cycling, which influences cloud formation and albedo with significant climate feedback. The northern Benguela upwelling system (nBUS) is considered one of the most productive Eastern Boundary Upwelling Systems, with intense and regular phytoplankton blooms that sustain rich fisheries. It also features a semi-permanent stratocumulus cloud deck that strongly impacts radiative forcing and global climate. However, large-scale seasonal and multidecadal trends in phytoplankton biomass, functional composition and their role in DMSc production in response to climate change remains poorly studied. This knowledge gap is primarily due to limited data coverage from ship-based environmental monitoring efforts.

This study develops and validates remote sensing algorithms for the nBUS and applies them to two decades (2003–2022) of daily satellite observations to examine the spatial and temporal variability in PFGs and DMSc in the context of environmental adjustments in sea surface temperature (SST) and equatorward winds ( $W_{EQ}$ ) that are associated with climate change. A multispectral remote sensing approach to detect the PFGs commonly observed in the nBUS, namely diatoms, dinoflagellates, flagellates, and coccolithophores, is presented. This is achieved using a large, microscopic phytoplankton dataset and coincident satellite matchups from the Moderate Resolution Imaging Spectroradiometer of aqua (MODIS-Aqua) to generate relationships between the spectral characteristics of in water constituents and community dominance of a specific PFG. The algorithm, validated with an independent dataset, is applied to two decades of daily satellite observations to reveal regional and seasonal characteristics and trends in the *Spatial Extent* and *Frequency* of dominant PFGs, with evidence of niche conditions favoring particular PFGs. PFG trends show distinct regional and seasonal variability. Diatoms exhibit positive trends in their *Frequency* and *Spatial Extent* in autumn, indicating prolonged dominance over time and an expansion of their spatial occupation. However, their *Spatial Extent* declines in summer. In contrast, dinoflagellates display increasing trends in *Spatial Extent* and *Frequency* in summer and, together with flagellates, shrink in *Spatial Extent* in autumn. Diatoms, as key carbon exporters, show the strongest trends, emphasizing their sensitivity to climate change with implications for carbon drawdown and energy transfer to higher trophic levels. The nBUS is impacted by general warming trends, whereas  $W_{EQ}$  shows coherent offshore increasing trends and contrasting trends in alongshore patterns. Positive alongshore trends are observed off the Kunene and Central cells while negative trends are observed off the Northern and Lüderitz upwelling cells. The link between alongshore  $W_{EQ}$  and diatom trends relative to upwelling cells strongly suggests an altered nutrient

supply-driven response. That is, increasing alongshore  $W_{EQ}$  trends aligned with increasing diatom trends (Kunene and Central cells) and vice versa for regions of decreasing  $W_{EQ}$  (Northern and Lüderitz cells). Warming trends, which characterize the nBUS, are also likely to increase phytoplankton's ability to exploit events of enhanced nutrient availability. Declines in coccolithophores was evident offshore and linked to offshore accelerating  $W_{EQ}$ .

Subsequently, a satellite-based DMSc detection algorithm using chlorophyll-a (Chl) and SST as predictors was developed (using *in situ* observations) and validated (using independent satellite matchups). This regional algorithm was applied to the same 20-year daily satellite datasets and facilitated the first spatially and temporally comprehensive assessment of the regional, seasonal and multidecadal trends in DMSc. The DMSc seasonal cycle in the nBUS displays a classical “summer DMS paradox”, in which the DMSc peak in summer coincides with minimum Chl concentrations. Our results suggest that the seasonal cycle of DMSc is driven by phytoplankton community succession, with coccolithophores associated with the summer DMSc peak while the winter minimum in DMSc is associated with a maximum in Chl that is instead dominated by diatoms and flagellates. Annual trends in DMSc show a coherent increase offshore which contrasts with the heterogeneous alongshore trends. The increasing trend in DMSc offshore tends to be associated with warming and an expansion in the *Spatial Extent* of dinoflagellates whereas alongshore regions of declining DMSc are more aligned with declining Chl and diatoms relative to the Northern and Lüderitz cells.

Overall, this study advances our understanding of seasonal and long term PFG dynamics and their role in dimethyl sulfur cycling in the nBUS through the development, application and interpretation of novel satellite remote sensing algorithms. The results and insights gained from this study have the potential to advance environmental monitoring capabilities (through novel region-specific satellite algorithms) and enhance our understanding of large-scale phytoplankton community and dimethyl sulfur dynamics in the nBUS, one of the world's most productive and climatically sensitive marine ecosystems. The observed multidecadal trends in PFG and DMSc suggest potential shifts in ecosystem structure under a warming climate with altered winds and nutrient supply, with key implications for regional productivity, trophic interactions and climate regulation.

**Keywords:** ocean colour, satellite, remote sensing, algorithm development, phytoplankton functional group, dimethyl sulfide, dimethylsulfoniopropionate, climate change, northern Benguela, long-term trends

## Thesis outline

The introductory chapter provides a brief summary of the general background information regarding environmental monitoring of PFGs and dimethyl sulfur compounds in the nBUS, highlighting research gaps and key research questions associated with the scientific and practical relevance of the thesis. **Chapter 2** provides an in-depth literature review on the nBUS, focusing on its physical characteristics and phytoplankton dynamics across event-scale, seasonal and multidecadal variability. It further focuses on key PFGs and their key ecological roles, emphasizing DMSP production by phytoplankton. The review covers DMSP sources, abundance, distribution, variability controls, and catabolism, as well as its role as a precursor to DMS. Finally, it explores DMSP research in the nBUS, identifying gaps to be addressed in this study. **Chapter 3** addresses the need for an ocean colour satellite remote sensing algorithm that allows detection of multiple PFGs in the nBUS, which would allow their determination on unprecedented spatio-temporal scales with an overarching potential of advancing environmental monitoring efforts in this region. In **Chapter 4**, the ocean colour remote sensing algorithm from Moloto *et al.* (2023) (i.e., **Chapter 3**) and the modified method of Smith *et al.* (2023) are applied to 20 years (2003–2022) of daily Moderate Resolution Imaging Spectroradiometer of aqua (MODIS-Aqua) satellite observations of 4-km spatial resolution to elucidate the seasonal characteristics and multidecadal trends of specific PFGs (i.e., diatoms, dinoflagellates, flagellates and coccolithophores) in relation to the key climate drivers of SST and  $W_{EQ}$ . **Chapter 5** embarks on developing a satellite remote sensing algorithm tailored for the detection of DMS and its precursor DMSP as a collective within the nBUS utilizing SST and Chl as predictors. In **Chapter 6**, the resulting algorithm from **Chapter 5** is applied to 21 years (2003–2023) of daily MODIS-Aqua data of 4-km spatial resolution to elucidate the previously unobserved seasonal cycle and multi-decadal DMSP-DMS trends in relation to phytoplankton community composition and other environmental variables (i.e., SST and  $W_{EQ}$ ). **Chapter 7** concludes the thesis by discussing key findings and insights gained from previous chapters in relation to the overall research aim and objectives. This is followed by an outline of the study limitations and avenues for future research.

## Publications

The research presented in this thesis is the culmination of my work undertaken solely during my graduate studies at North-West University. A portion of this research has already been published in peer-reviewed journals, while other findings are currently undergoing or awaiting peer review, or are in the final stages of preparation for submission to peer-reviewed journals as the following articles:

Paper 1 (published, Chapter 3)

1. Moloto, T.M., Thomalla, S.J., Smith, M.E., Martin, B., Louw, D.C. and Koppelman, R. 2023. Remote sensing of phytoplankton community composition in the northern Benguela upwelling system. *Frontiers in Marine Sciences*. 10:1118226. Doi: 10.3389/fmars.2023.1118226

Paper 2 (published, Chapter 4)

2. Moloto, T.M., Smith, M.E., Bell, T.G., Piketh, S.J., Thomalla, S.J., 2025. Seasonal patterns and multidecadal trends in phytoplankton functional groups in the Benguela upwelling system off Namibia. *Sci. Total Environ.* 999, 180217. Doi: <https://doi.org/10.1016/j.scitotenv.2025.180217>

Paper 3 (in preparation, Chapters 5 and 6)

3. Moloto, T.M., Bell, T.G., Booge, D., Marandino, C.A., Thomalla, S.J., Smith, M.E., Piketh, S.J. **YEAR**. Determination of planktonic dimethyl sulfur compounds from space and an analysis of climatological patterns in the northern Benguela upwelling system. *JGR: Oceans (In prep)*.

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### Chapter 2

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**Figure 2.2:** Partial marine food web diagram showing the pelagic aquatic food chain from primary producers (phytoplankton) to apex predators indicated by red arrows as well as the partial biogeochemical cycle involving carbon and sulfur cycles indicated by black arrows. In the biogeochemical cycle, which, together with atmospheric carbon dioxide (CO<sub>2</sub>) and sunlight, fuel photosynthesis and phytoplankton blooms that produce oxygen (O<sub>2</sub>), dimethyl sulfoniopropionate (DMSP) and organic matter (POC). DMSP is cleaved to form DMS that is subsequently ventilated into the atmosphere together with O<sub>2</sub> while some POC sinks to the bottom of the ocean as dead plankton and sinking particles.

**Figure 2.3:** Depiction of wind-driven alterations to physicochemical conditions that result in different upwelling stages: 1) Newly upwelled, 2) matured and 3) aged upwelled waters. Each of which is associated with a succession in dominance of different phytoplankton groups in the nBUS as described by Hansen *et al.* (2014).

### Chapter 3

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## Chapter 6

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## Abbreviations

|                                       |                   |
|---------------------------------------|-------------------|
| Angola Benguela Frontal Zone          | ABFZ              |
| Angola Current                        | AC                |
| Benguela upwelling system             | BUS               |
| Biological carbon pump                | BCP               |
| Calcium carbonate                     | CaCO <sub>3</sub> |
| Carbon dioxide                        | CO <sub>2</sub>   |
| Chlorophyll-a                         | Chl               |
| Chlorophyll-b                         | Chl-b             |
| Chlorophyll-c                         | Chl-c             |
| Cloud condensation nuclei             | CNN               |
| Coastal zone colour scanner           | CZCS              |
| Coccolithophores                      | COC               |
| Coefficient of determination          | R <sup>2</sup>    |
| Coefficient of variation              | CV                |
| Color Index                           | CI                |
| Coloured dissolved organic matter     | CDOM              |
| Conductivity-temperature-depth        | CTD               |
| Diatoms                               | DIA               |
| Dimethyl sulfide                      | DMS               |
| Dimethyl sulfoxide                    | DMSO              |
| Dimethylsulfoniopropionate            | DMSP              |
| Dinoflagellates                       | DIN               |
| dissolved dimethylsulfoniopropionate  | DMSPd             |
| Eastern boundary upwelling systems    | EBUSs             |
| Eastern South Atlantic Central Waters | ESACW             |
| Equatorward winds                     | $W_{EQ}$          |
| Flagellates                           | FLA               |
| Fluorescence line height              | FLH               |
| <i>Frequency</i>                      | $F_{trend}$       |
| Gas chromatography–mass spectrometry  | GC-MS             |
| Global Surface Seawater               | GSS               |
| Harmful algal blooms                  | HABs              |

|                                                       |                  |
|-------------------------------------------------------|------------------|
| High biomass                                          | HB               |
| High-performance liquid chromatography                | HPLC             |
| Hydrogen sulfur                                       | H <sub>2</sub> S |
| interquartile range                                   | IQR              |
| Kernel density estimation                             | KDE              |
| Light penetration depth                               | <i>Zeu</i>       |
| Low biomass                                           | LB               |
| Mann-Kendall                                          | MK               |
| Maximum line height                                   | MLH              |
| Mean absolute percentage error                        | MAPE             |
| Mean relative bias                                    | MRB              |
| Mean relative error                                   | MRE              |
| Median relative difference                            | MedRD            |
| Medium Resolution Imaging Spectrometer                | MERIS            |
| Methanethiol                                          | MeSH             |
| Mixed communities                                     | MIX              |
| Mixed layer depth                                     | MLD              |
| Moderate Resolution Imaging Spectroradiometer of aqua | MODIS-Aqua       |
| National Aeronautics and Space Administration         | NASA             |
| National Marine Information and Research Centre       | NatMIRC          |
| Near infrared                                         | NIR              |
| Net primary production                                | NPP              |
| Normalized fluorescence line height                   | nFLH             |
| Northern Benguela upwelling system                    | nBUS             |
| Ocean and Land Colour Imager                          | OLCI             |
| Oxygen-minimum zones                                  | OMZs             |
| Particulate dimethylsulfoniopropionate                | DMSPp            |
| Particulate inorganic carbon                          | PIC              |
| Particulate Organic matter                            | POC              |
| Phytoplankton functional groups                       | PFGs             |
| Phytoplankton functional types                        | PFTs             |
| Planktonic dimethyl sulfur compounds                  | DMSc             |
| Red-near infrared                                     | RNR              |
| Remote sensing reflectance                            | <i>Rrs</i>       |

|                                       |                                |
|---------------------------------------|--------------------------------|
| Root mean squared error               | RMSE                           |
| Sea surface temperature               | SST                            |
| Sea-viewing Wide Field-of-view Sensor | SeaWiFS                        |
| Sodium hydroxide                      | NaOH                           |
| South Atlantic Central Waters         | SACW                           |
| Southern Benguela upwelling system    | sBUS                           |
| <i>Spatial Extent</i>                 | $SE_{trend}$                   |
| Sulfuric acid                         | H <sub>2</sub> SO <sub>4</sub> |
| Ultraviolet                           | UV                             |
| Volatile organic carbons              | VOCs                           |

## Chapter 1: Introduction

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The Benguela upwelling system (BUS) along the southwestern coast of Africa, divided into its northern and southern subsystems, stands as a testament to the intricate interplay between physical and biological processes in the world's oceans. In this dynamic marine ecosystem, wind-driven coastal upwelling of cold nutrient-rich subsurface waters to the euphotic zone provides the foundation for a thriving ecosystem (Hutchings *et al.*, 2009). Central to this ecosystem are phytoplankton, microscopic photosynthetic organisms at the base of marine food webs that support organisms at higher trophic levels and play a pivotal role in biogeochemical cycles. These organisms, with varying morphological and ecological traits, have the capacity to shape the very essence of ecosystems and the important services (biodiversity, fisheries, aquaculture, climate regulation, recreation, etc.) they provide to humanity (Tweddle *et al.*, 2018).

In the nBUS, decades of environmental monitoring efforts using shipboard measurements has shed light on phytoplankton dynamics, including event scale variability in their response to wind-driven upwelling (Hansen *et al.*, 2014), seasonal dynamics (Louw *et al.*, 2016), bloom phenology (Matlakala, 2019) as well as long-term trends (Louw *et al.*, 2017, 2016). Such studies have advanced our understanding of how environmental (e.g., winds, temperature, light, nutrients, etc.) and biological (e.g., zooplankton grazing, viral attacks, etc.) forcing mechanisms govern phytoplankton dynamics in this region. Changes in phytoplankton communities have ecological implications for energy transfer that impact higher trophic levels and climate regulation through air-sea fluxes of climatically relevant gases (e.g., carbon export, aerosol precursors, etc.). In the context of climate change, understanding multidecadal spatiotemporal trends in phytoplankton dynamics, especially in highly productive ocean regions such as the Benguela upwelling system, is essential for detecting early ecosystem disturbances and predicting the magnitude and direction of ecosystem shifts. This knowledge is necessary for informed decision-making and the implementation of effective conservation and management strategies to ensure sustainable ecosystems and the preservation of their vital services.

Nonetheless, environmental monitoring efforts using shipboard surveys are severely hampered both spatially (limited to distinct geographical locations and monitoring transects) and temporally (sampled quasi-monthly) (Louw *et al.*, 2017, 2016; Matlakala, 2019), thus limiting a synoptic scale account of phytoplankton dynamics. While satellite remote sensing has advanced our ability to observe bulk phytoplankton community (i.e., using Chl as a proxy for abundance) at high spatial and temporal resolution (Lamont *et al.*, 2019; O'Reilly and Werdell, 2019; Weeks and Shillington, 1994), they have not been fully exploited in the nBUS to resolve phytoplankton communities according to PFGs (i.e., diatoms,

dinoflagellates, flagellates, coccolithophores). Given the varying ecological roles of different phytoplankton groups, there is a need for the development and application of advanced approaches that can resolve phytoplankton beyond Chl at high spatial and temporal resolutions, and resolve both seasonal and multidecadal variability for improved environmental monitoring capabilities in this key region.

The Benguela upwelling system, a region of paramount importance for the global marine environment and the communities that depend on it, has been undergoing changes due to various anthropogenic and natural influences. Climate-driven changes such as the reduction in upwelling (Lamont *et al.*, 2018b), ongoing warming (Demarcq *et al.*, 2003; Sweijd and Smit, 2020), and altered wind patterns (Polonsky and Serebrennikov, 2020), raise important questions about how these alterations are affecting phytoplankton communities and the ecosystem services they provide. Through the analysis of extensive oceanographic *in situ* shipboard data integrated with satellite remote sensing techniques, this thesis aims to develop an ocean colour satellite remote sensing algorithm for the detection of various phytoplankton groups from space. By applying the algorithm to 20 years (2003–2022) of high spatial (4 km) and temporal (daily) resolution satellite observations, the goal is to elucidate the previously unobserved seasonal patterns as well as multidecadal trends in PFGs on unprecedented spatiotemporal scales.

A less studied aspect of the nBUS relates to phytoplankton's role in the production of volatile sulfur compounds, namely DMS gas and its precursor DMSP, which influence the Earth's radiation budget through cloud formation and contributes to climate regulation (Bates *et al.*, 1987; Charlson *et al.*, 1987; Kiene *et al.*, 2000). There appears to be a dearth of DMSP and DMS observations in the nBUS as evidenced by the limited number of shipboard observations housed in the global surface seawater DMS database (<https://saga.pmel.noaa.gov/dms/>) (Andreae *et al.*, 1995; Bates *et al.*, 2001; Tanzer and Heumann, 1992). This is of particular concern given the important role that DMS plays in affecting the climate both directly by backscattering solar radiation and indirectly as cloud condensation nuclei (Bates *et al.*, 1987). Satellite remote sensing provides an affordable, near-real time and high spatial and temporal resolution alternative to shipboard environmental monitoring. In this regard, this thesis aims to develop an ocean colour satellite remote sensing algorithm for DMSP and DMS estimation for the nBUS. This would allow a large-scale investigation of the seasonal dynamics of DMSP–DMS and how phytoplankton response to multidecadal climate adjustments in the nBUS may be impacting the trajectory of the production of DMSP and DMS within the BUS.

The relationship between phytoplankton and DMSP-DMS in this context offers an exciting avenue for exploration, potentially yielding insights into the system's responses to environmental changes and its

implications for climate regulation and ecological balance. This study addresses the need for advancements in environmental monitoring efforts through approaches that allow synoptic scale determination of specific PFGs. The ability to regionally and seasonally characterize phytoplankton community structure of the region and evaluate how phytoplankton community structure may be changing with drivers associated with climate change, notably ocean warming and altered wind patterns that may affect the nutrient supply, over longer periods are crucial for understanding long-term effects of climate change. In addition, changes in community composition are important with regard to the role that different PFGs play in DMSP-DMS production. A deeper understanding of phytoplankton and DMSP-DMS dynamics in the Benguela upwelling system carries significant ecological, economic and climatic relevance. Insights gained from this study have the potential to inform sustainable fisheries management in the region, as phytoplankton underpin the entire food web. By exploring this multifaceted system and deciphering the intricacies of phytoplankton-DMSP-DMS interactions, this thesis hopes to shine a light on the potential key drivers of change within the Benguela upwelling system, positioning it at the forefront of marine ecological research and climate science.

## Chapter 2: Literature review

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### 2.1. The Benguela upwelling system

Eastern boundary upwelling systems (EBUSs) are oceanic regions situated along the eastern margins of the world's oceans. The four major EBUSs are the California (situated along the coasts of British Columbia, Canada to Baja and Mexico), the Humboldt (which lies off the coasts of Peru and Chile), the Canary (north-west Africa) in the eastern Atlantic basin and the Benguela (along the coasts of South Africa, Namibia and southern Angola) (Chavez and Messié, 2009). Strong and seasonally variable equatorward alongshore wind jets induce ocean currents that transport surface coastal waters offshore, thereby forcing the deep, cold and nutrient-rich waters to the upper sunlit ocean surface near the coast in a process referred to as upwelling (Kämpf and Chapman, 2016). Once upwelled, the nutrient-enriched surface waters fuel marine primary production, which manifests in the form of phytoplankton blooms (Hansen *et al.*, 2014). Although comprising less than 1% of the total global ocean area, EBUSs are among the most productive marine environments globally, accounting for ~2% ( $1 \text{ Gt C year}^{-1}$  or  $3 \text{ g Cm}^{-2} \text{ day}^{-1}$ ) of global production (Carr and Kearns, 2003) and for approximately 20% of global fisheries yields, thereby offering great socio-economic benefit to communities reliant on these systems (Carr and Kearns, 2003; García-Reyes *et al.*, 2015; Lachkar and Gruber, 2012; Messié *et al.*, 2009; Pauly and Christensen, 1995).

The Benguela Upwelling System (BUS) is situated on the southwestern coast of the African continent, stretching from Cape Agulhas in South Africa along the Namibian coast and northwards into Angola (Figure 2.1). The inner and outer shelves of the BUS are separated by approximately 100 km, while the outer shelf width exceeds 100 km South of  $19^\circ \text{S}$  and extends beyond 200 km between  $28^\circ \text{S}$  and  $32^\circ \text{S}$  (Carr and Kearns, 2003). The BUS is unique to other EBUSs in that it is bound by two warm water masses, the Agulhas current in the south and the Angola current in the north (Figure 2.1) (Hutchings *et al.*, 2009). Of the four EBUSs, the BUS is estimated to be the most productive, with a net primary production rate of  $0.371 \text{ Gt C year}^{-1}$ , which is estimated to be ~0.9% of global ocean production (Carr, 2001). The largest, most intense, and perennial upwelling cell located at  $\sim 26^\circ \text{S}$  near the coastal town of Lüderitz partitions the BUS into its northern and southern subsystems, nearly coinciding with the country borders of Namibia and South Africa (Rae, 2005). The Lüderitz cell is thought to act as a barrier for exchange of some pelagic fish species between the two subsystems (Lett *et al.*, 2007).

The nBUS is influenced by two different water masses: 1) the poleward propagation of South Atlantic Central Waters (SACW) undercurrent from the Angola Gyre (Figure 2.1), which transports nutrient rich but low oxygen waters onto the nBUS shelf by penetrating the Angola-Benguela front to be upwelled. The

Lüderitz upwelling cell prevents further poleward propagation of oxygen-deficit SAWC into the sBUS (Rae, 2005) and 2) the comparatively well aerated Eastern SACW (ESACW) subsurface current (Figure 2.1) originating from the Cape basin off South Africa, which spreads northwards into the nBUS (Mohrholz *et al.*, 2008; Rae, 2005). The SACW are characterized by high salinity relative to potential temperature when compared to the ESAWC, and the SACW dominate the nBUS in summer while the ESACW dominates in winter (Mohrholz *et al.*, 2008; Rae, 2005). The seasonal variability of these water masses in the nBUS impacts the signal of upwelled waters thought to be controlled by variations in trade winds and by remote forcing from the equatorial Atlantic (Lass and Mohrholz, 2008). The dominant surface currents are the poleward flowing Angola Current (AC) and its northward flowing Benguela Current (BC) counterpart, which converge at the Angola Benguela Frontal Zone (ABFZ) with a seasonally and interannually variable geolocation between 15 – 18 °S (Figure 2.1) (Bartholomae and Van Der Plas, 2007; Hutchings *et al.*, 2009; Shannon and Nelson, 1996). The ABFZ separates the oligotrophic tropical ecosystem to the north from the nutrient-rich BUS to the south and unlike the Lüderitz upwelling cell, does not act as a strong barrier between the two regions (John *et al.*, 2001). Cases of extreme warm water intrusion into the nBUS from the Angola Basin occur periodically in a phenomenon known as the Benguela Niño, a small-scale and weaker analogue of the Pacific El Niño event that impacts the nBUS at decadal scales (Imbol Koungue *et al.*, 2021, 2019).

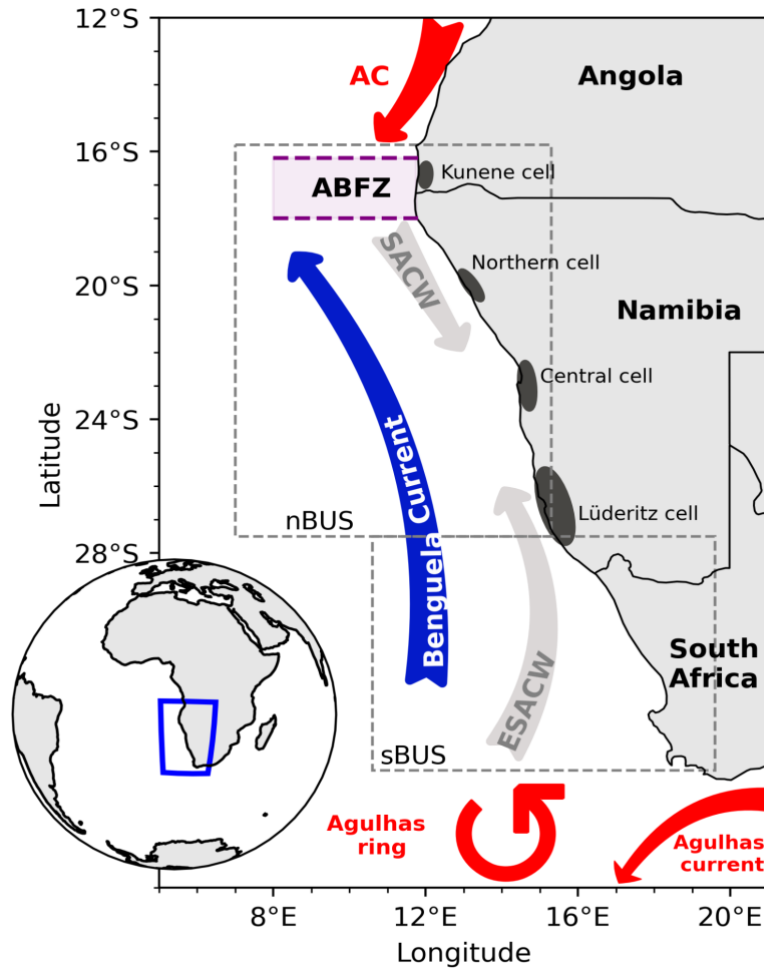


**Figure 2.1:** The Benguela upwelling system along the southwestern tip of the African continent (inset) shared between South Africa, Namibia and Angola (shown in bold) with its northern (nBUS) and southern (sBUS) subsystems indicated by dashed grey boxes. The northward flowing cold and nutrient-rich Benguela current is shown by the blue arrow while the warm nutrient-deficient Angola Current (AC) and Agulhas current are shown in red. The South Atlantic Central Waters (SACW) and Eastern SACW (ESACW) subsurface currents are indicated by grey arrows. Upwelling centers in the nBUS are indicated as grey shaded areas while the Angola-Benguela frontal zone (ABFZ) is indicated by the purple shaded area.

The tropical atmospheric forcing (high pressure system) over the central south Atlantic Ocean gyre induces seasonally variable meridional wind stress patterns. These give rise to seasonally variable (in terms of strength) south-easterly trade winds in the northern and central cells, whereas the central Benguela current near Lüderitz experiences perennial equatorward meridional winds (Shannon and Nelson, 1996). The upwelling-favorable wind jets (i.e., equatorward South-easterly alongshore trade winds) drive coastal upwelling of the cold and nutrient-enriched subsurface SAWC to the euphotic zone as a consequence of

Ekman transportation of coastal surface waters further offshore. The northern BUS is characterized by 4 upwelling cells, namely the Kunene, Northern, Central and Lüderitz cells (Hutchings *et al.*, 2009). The seasonally variable upwelling in the nBUS tends to peak in late winter to early spring (August-September) and in autumn (April-May) in Cape Frio (Northern cell) and Walvis Bay (Central Namibian cell) (Hutchings *et al.*, 2009; Louw *et al.*, 2016) whereas the Lüderitz cell experiences perennial upwelling (Hutchings *et al.*, 2009). Upwelling of nutrient-rich deep waters to the surface drives high net primary production (NPP) levels in the BUS that manifest as sporadic phytoplankton blooms. These blooms, visible even from space, are vital sources of organic matter, supporting higher trophic levels like zooplankton and fish. This rich food web nourishes an array of marine animals, from large mammals such as whales to microscopic copepods, underpinning the extraordinary biodiversity of the nBUS.

## **2.2. Significance of marine phytoplankton**

Marine phytoplankton are single-celled microscopic plants that float in the upper sunlit layer (euphotic zone) of the global ocean. Forming the base of aquatic ecosystems, marine phytoplankton are photosynthetic primary producers of organic carbon and oxygen from greenhouse gas carbon dioxide (CO<sub>2</sub>), solar radiation and nutrients. Phytoplankton in the Benguela system are estimated to have a net primary production rate of 0.371 Gt C year<sup>-1</sup>, which is estimated to be ~0.9% of global ocean production (Carr, 2001). The drawdown of CO<sub>2</sub> in the form of sinking organic matter mediated by marine phytoplankton is referred to as the biological carbon pump. Some of which is consumed by organisms in the mesopelagic zone, while the other fraction is remineralized by bacteria into dissolved inorganic carbon to be reused in primary production. The sinking fraction that isn't remineralized is sequestered into the deep ocean (Zhang *et al.*, 2018). By regulating long-term ocean carbon storage, the biological carbon pump plays a key role in the uptake of atmospheric CO<sub>2</sub> which impacts global climate. Although the nBUS is generally considered a net source of CO<sub>2</sub> to the atmosphere due to upwelling of CO<sub>2</sub>-rich waters (Siddiqui *et al.*, 2023), this outgassing is partially offset by carbon uptake through the biological carbon pump in these highly productive waters (Messié *et al.*, 2009).

In addition, marine phytoplankton act as a direct food and energy source fueling organisms at higher trophic levels such as zooplankton and fish larvae, which in turn, are consumed by larger organisms such as fish, marine mammals and birds, thereby impacting and sustaining higher trophic levels and ecosystem biodiversity (Figure 2.2). Many commercially important marine species rely on phytoplankton as a food source, affecting fisheries and aquaculture activities that promote human economies reliant on seafood (Napp *et al.*, 1996; Richardson, 2000). Indeed, the fisheries industries of the BUS are vital to the economies of Namibia, Angola, and South Africa, contributing significantly to the Gross Domestic Product and

supporting livelihoods through employment and food security. Furthermore, some phytoplankton produce DMS gas from DMSP (Figure 2.2), a volatile sulfur compound that contributes to atmospheric aerosol and cloud condensation nuclei (CCN). This affects cloud formation and radiation budgets through enhanced albedo and provides an additional example of how phytoplankton play a role in global climate regulation (Bates *et al.*, 1987; Charlson *et al.*, 1987). Phytoplankton's role on aerosol air-sea fluxes, is thought to be particularly important in the nBUS where a key feature of the upwelling system is the presence of one of the largest and most persistent stratus marine cloud decks that contributes to the variability and long-term trends of global albedo with impacts on both regional and global climate.

Although most phytoplankton blooms are beneficial, there are instances where phytoplankton blooms may instead negatively impact marine ecosystem functioning or industries like fisheries, aquaculture, and tourism - primarily through so-called harmful algal blooms (HABs). HABs can lead to oxygen depletion (anoxia), clogging of fish gill tissue, while toxin producing HABs may cause paralysis or mortality of marine animals, or result in shellfish poisoning in humans who consume the affected marine organisms (Pitcher and Calder, 2000; Pitcher and Louw, 2021; Wells *et al.*, 2015). HAB's are a frequent and significant phenomenon in the BUS, with severe impacts on fisheries and aquaculture (Pitcher and Louw, 2021). Given the key role that phytoplankton play in supporting critical ecosystem services in the BUS, it is not surprising that changes in phytoplankton populations (biomass, distribution and community composition) can have cascading effects on the entire marine ecosystem, affecting climate regulation and the transfer of carbon, energy, and nutrients through pelagic and benthic food web (Blanchard *et al.*, 2012).

Marine phytoplankton constitute a diverse community with varying morphological and functional traits and can be conceptually classified into functional types based on their distinct biogeochemical and/or ecological roles into nitrogen fixers, silicifiers, calcifiers, and DMS producers (Reynolds *et al.*, 2002). These groupings are not necessarily related to physiological characteristics but are based on functionality (biogeochemical cycling). Alternatively, phytoplankton can be grouped according to other characteristics such as cell size (pico-, nano- and micro-phytoplankton). In this study, PFGs are evaluated based on their morphological characteristics, with a specific focus on four principal contributors to marine productivity in the form of diatoms, flagellates, dinoflagellates, and coccolithophores, all of which are frequently encountered in the nBUS, with each having a specific ecological function.

- Diatoms

Diatoms are chain-forming and fast-growing phytoplankton in nutrient-rich environments that are typically within a cell size range between 2  $\mu\text{m}$  – 200  $\mu\text{m}$ , with a few larger species (Barlow *et al.*, 2018; Hansen

*et al.*, 2014). Diatoms use silica and other organic components to create their cell walls, called frustules, which are thought to provide mechanical protection from ultraviolet (UV) radiation DNA damage, grazing by predators and provide control of light absorption during photosynthesis (Cassaignon *et al.*, 2014). In addition, the silicious cell walls increase the density of diatom cells, which causes them to sink faster thereby enhancing the effectiveness of their role in driving carbon export (Hamm *et al.*, 2003; Raven and Waite, 2004; Tesson and Hildebrand, 2013). Indeed, diatoms contribute ~40% of global ocean primary production and up to 20% of the Earth's primary productivity, and are considered key role players in the biological carbon pump (BCP) (Allen *et al.*, 2005; Brownlee and Taylor, 2002; Field *et al.*, 1998; Smetacek, 1999). Diatoms are a regular blooming phytoplankton group in the nBUS that are typically responsible for the highest biomass (i.e., Chl-*a*) (Louw *et al.*, 2017, 2016), suggesting that they are key role players in the BCP in this region. The toxin-producing and bloom-forming diatoms *Pseudo-nitzschia* also occur regularly in the BUS (Louw *et al.*, 2018). These constitute HABs of diatoms that produce domoic acid, a neurotoxin that causes amnesic shellfish poisoning, which can be harmful or even fatal to humans if contaminated shellfish is consumed (Blanco *et al.*, 2010; Pitcher and Louw, 2021).

- Cocolithophores

Cocolithophores are small-sized (<3  $\mu\text{m}$ ) calcifying phytoplankton that produce small calcium carbonate ( $\text{CaCO}_3$ ) platelet scales, called coccoliths, which form external spherical coatings called coccospheres (McClelland *et al.*, 2016). Precipitation of  $\text{CaCO}_3$  during coccolith formation (calcification) reduces the total alkalinity of seawater and releases carbon dioxide ( $\text{CO}_2$ ) (Brownlee and Taylor, 2002; McClelland *et al.*, 2016; Rost and Riebesell, 2004). However, their calcareous shell also adds density that increases their sinking velocity to the deep ocean by ballasting organic matter, which partially offsets the  $\text{CO}_2$  that is released during their calcification process (Klaas and Archer, 2002; Poulton *et al.*, 2007). As such, cocolithophores are considered efficient exporters of carbon to the deep ocean and are important for ocean carbon cycle processes (Balch, 2018; Krumhardt *et al.*, 2019), especially in regions of dense cocolithophore blooms such as those which occur in the oligotrophic offshore region in the nBUS (Siegel *et al.*, 2007). Furthermore, cocolithophores have been identified as hyper producers of intracellular DMSP (Belviso *et al.*, 1990; Saltzman and Cooper, 1989; Turner *et al.*, 1988), a sulfur substrate in marine environments and a precursor to the climatically active DMS gas. DMS emissions from marine environments are the main source of biogenic sulfur into the atmosphere, with an estimated 28.1 (17.6–34.4) Tg of sulfur fluxed from the oceans into the atmosphere (Lana *et al.*, 2011). Once released to the atmosphere, DMS is a potential precursor of sulfate aerosols that affect the climate directly by backscattering solar radiation and indirectly as cloud condensation nuclei (Bates *et al.*, 1987; Charlson *et al.*, 1987). DMSP is predominantly produced by phytoplankton and bacteria, with a limited number of

species of algae capable of DMSP biosynthesis with considerably varying concentration among different phytoplankton (Saltzman and Cooper, 1989). Coccolithophores were determined as one of the hyper producers of intracellular DMSP (Belviso *et al.*, 1990; Saltzman and Cooper, 1989; Turner *et al.*, 1988). In this regard, coccolithophores also play an important indirect radiative forcing role through the release of aerosol and cloud formation precursors affecting albedo and thus climate regulation.

- Dinoflagellates

These are a sub-type of flagellated phytoplankton bearing two dissimilar flagella and have a similar size range as diatoms, although the vast majority are of a smaller size ( $<20\ \mu\text{m}$ ) as is the case for the nBUS as observed from using light and scanning electron microscope for size fractions (Hansen *et al.*, 2014), with an inverted microscope used for identification and enumeration (Hansen *et al.*, 2014), whereas pigment analyses and CHEMTAX were employed for phytoplankton community determination (Barlow *et al.*, 2018; Hansen *et al.*, 2014). Dinoflagellates are capable of producing light and are responsible for most of the bioluminescence observed in the surface ocean by bloom-forming dinoflagellate species (Valiadi *et al.*, 2012; Valiadi and Iglesias-Rodriguez, 2013). Similarly to coccolithophores, dinoflagellates are among the identified hyper producers of DMSP in the surface ocean (Belviso *et al.*, 1990; Saltzman and Cooper, 1989; Turner *et al.*, 1988) and thus play a key role as a source of sulfur to marine microbial communities, which contributes to atmospheric aerosol precursor molecules (i.e., DMS gas). Relative to diatoms, dinoflagellates generally have slower growth rate (Chan, 1980; Tang, 1996) and, unlike in the southern Benguela, they do not bloom as regularly in the nBUS. Dinoflagellate blooms do, however, occur and are known for their ability to form HABs or red tides. Toxic dinoflagellate blooms are a result of toxin-producing species that cause paralytic or diarrhetic shellfish poisoning (Pitcher and Louw, 2021). Non-toxin producing high biomass blooms of dinoflagellates have also been found to be responsible for anoxic events during die off leading to fish mortalities (Pitcher and Calder, 2000). Dinoflagellate HABs are of particular interest in the BUS since they threaten marine animals, fisheries, aquaculture industries as well as recreational activities provided by this highly productive system.

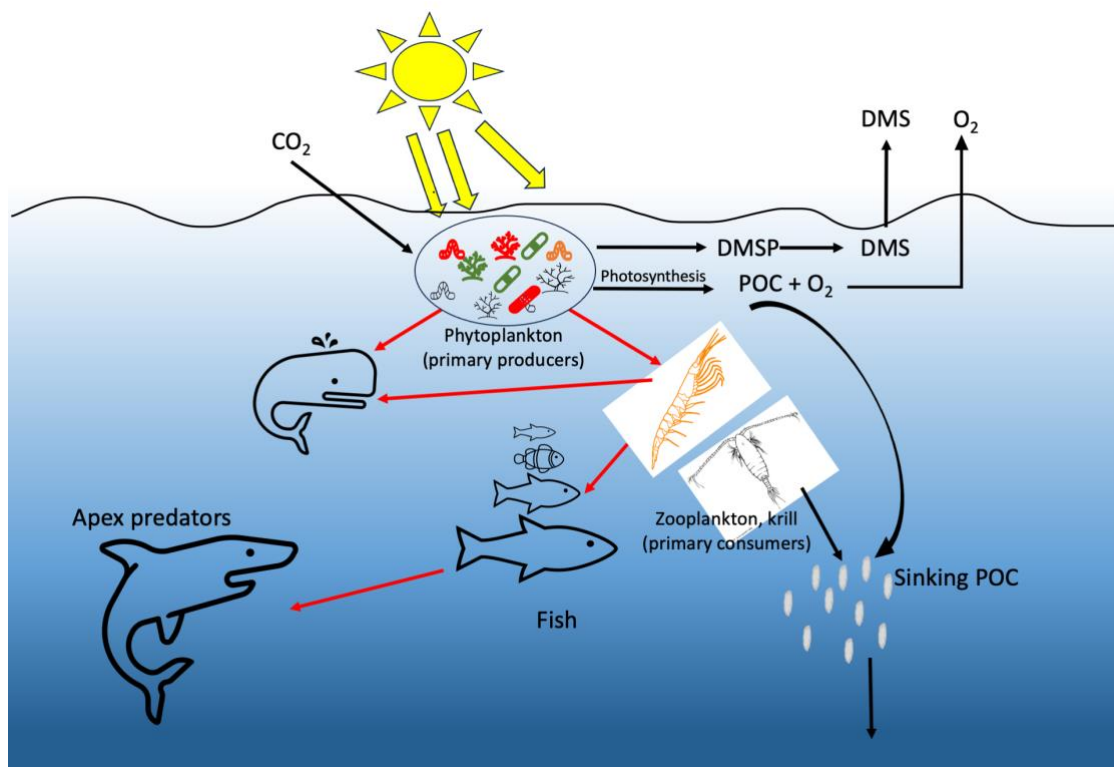


**Figure 2.2:** Partial marine food web diagram showing the pelagic aquatic food chain from primary producers (phytoplankton) to apex predators indicated by red arrows as well as the partial biogeochemical cycle involving carbon and sulfur cycles indicated by black arrows. In the biogeochemical cycle, which, together with atmospheric carbon dioxide ( $\text{CO}_2$ ) and sunlight, fuel photosynthesis and phytoplankton blooms that produce oxygen ( $\text{O}_2$ ), dimethylsulfoniopropionate (DMSP) and organic matter (POC). DMSP is cleaved to form DMS that is subsequently ventilated into the atmosphere together with  $\text{O}_2$  while some POC sinks to the bottom of the ocean as dead plankton and sinking particles.

In summary, PFGs are fundamental to the functioning of ocean ecosystems and have far-reaching implications for the health of the planet. Their role in carbon sequestration, the production of climatically relevant gases (e.g., DMS), in addition to their position at the base of the marine food web highlights their critical importance in maintaining the balance of marine ecosystems (Figure 2.2). In this regard, marine phytoplankton are considered key indicators of ecosystem health and a key consideration for effective environmental management of ocean ecosystems (Tweddle *et al.*, 2018). The nBUS has been the focus of numerous studies investigating phytoplankton dynamics using both *in situ* observations and satellite remote sensing aimed at understanding phytoplankton dynamics. *In situ* methods have traditionally involved ship-based sampling and the analysis of Chl concentration (Louw *et al.*, 2016), a proxy for phytoplankton abundance, and community composition through identifying functional groups and species via microscopy

and pigment analysis (Barlow *et al.*, 2018). These studies have provided valuable insights into upwelling-induced species succession (Hansen *et al.*, 2014), the seasonal cycle of blooms (Louw *et al.*, 2017, 2016; Matlakala, 2019), and the spatial patterns of phytoplankton communities (Barlow *et al.*, 2018) all in the context of environmental forcing mechanisms that drive their spatial and temporal distribution patterns.

### **2.3. Upwelling succession in the nBUS**

Coastal upwelling enriches the sunlit upper layer with nutrients fueling phytoplankton primary production. Investigations have shown upwelling to induce phytoplankton community succession associated with different phases (pseudo-age) of the upwelling event that coincide with alterations in physicochemical conditions (Figure 2.3). Three upwelling stages associated with different physicochemical conditions have been documented in the nBUS according to the pseudo-age (Hansen *et al.*, 2014), namely 1) newly upwelled water (<13 days), associated with high turbulence, low temperatures (~13 °C), high nutrients, relatively less saline waters (~35.17 PSU) and low Chl-*a* (0.7–7 µg l<sup>-1</sup>) (Hansen *et al.*, 2014). Under these inshore conditions, smaller dinoflagellates typically dominate and are associated with a mixed population of coccolithophores and nanoflagellates, 2) matured upwelled water (13–55 days), associated with the relaxation of strong winds, moderate temperatures (~14.5 °C), depleting nutrients, more saline (35.27 PSU) waters and high Chl-*a* (0.7–14 µg l<sup>-1</sup>) concentrations (Hansen *et al.*, 2014). These conditions are generally dominated by diatoms, typically of *Pseudo-nitzschia* spp. (Louw *et al.*, 2017), and lastly 3) aged upwelled water (>55 days) characterized by warmer (>16 °C), more saline (>35.4 PSU), nutrient-depleted waters (Hansen *et al.*, 2014). These waters (that are characteristically found further offshore) are associated with a decline in diatoms and a succession back to dinoflagellate dominance associated with low biomass (<0.9 µg. l<sup>-1</sup>) to mark the end of upwelling-induced phytoplankton community succession (Figure 2.3) (Hansen *et al.*, 2014).

| Upwelling stage                     |                                                         |                        |                     |
|-------------------------------------|---------------------------------------------------------|------------------------|---------------------|
|                                     | 1                                                       | 2                      | 3                   |
|                                     | Newly upwelled water                                    | Matured upwelled water | Aged upwelled water |
| Pseudo-age (days)                   | < 13                                                    | ~ 52                   | > 60                |
| Temperature (°C)                    | ~ 13                                                    | ~ 14                   | > 16                |
| Salinity (psu)                      | 35.17                                                   | 35.27                  | > 35.4              |
| Nutrients                           | high                                                    | declining              | depleted            |
| Chl- <i>a</i> (µg l <sup>-1</sup> ) | < 7 g l <sup>-1</sup>                                   | ~ 14                   | < 0.9               |
| Dominant groups                     | dinoflagellates<br>nano-flagellates<br>coccolithophores | diatoms                | dinoflagellates     |

**Figure 2.3:** Depiction of wind-driven alterations to physicochemical conditions that result in different upwelling stages: 1) Newly upwelled, 2) matured and 3) aged upwelled waters. Each of which is associated with a succession in dominance of different phytoplankton groups in the nBUS as described by (Hansen *et al.*, 2014).

#### 2.4. Seasonal and multidecadal dynamics of phytoplankton in the nBUS

In two extensive multi-year studies based on quasi-monthly sampled *in situ* Chl-*a* and microscopy in the top 30 m, the seasonal development of phytoplankton blooms (Louw *et al.*, 2016) and diatoms of *Pseudo-nitzschia* spp (Louw *et al.*, 2017) were examined in the shelf and open ocean waters off Walvis Bay on a monitoring transect (23 ° S). Annual seasonal blooms (Chl-*a* 10–13 mg m<sup>-3</sup>) usually develop inshore, with peaks in April (autumn), August (winter) and December (summer) while a strong decrease was found in June and July (Louw *et al.*, 2016). In addition – major blooms (Chl-*a* >18 mg m<sup>-3</sup>) occurred in 5 of the 12 years sampled and showed no obvious seasonal patterns. Blooms of diatoms of *Pseudo-nitzschia* spp were shown to initiate in Summer (low biomass blooms, coinciding with a period of high winds during active upwelling) and reach their maximum (high biomass blooms) between May – July, a period coinciding with a relaxation in wind after the main wind peak season (Louw *et al.*, 2017). Seasonal fluctuations in the wind field, which consequently result in seasonality in upwelling and surface-water temperatures, as well as mixing, stratification, thermocline development, and nutrient availability are considered key forcing mechanisms driving these seasonal patterns in biomass as species dominance (Louw *et al.*, 2016).

While ship based *in situ* observations provide detailed snapshots of community composition and their variability between occupations, they are limited in their spatial and temporal coverage, which hinders the assessment of ecosystem-wide seasonal and longer-term dynamics. Ocean colour satellite remote sensing has revolutionized ocean research owed to their large spatial and temporal scale resolutions. Early applications of satellite ocean colour remote sensing focused on estimating phytoplankton biomass using Chl-*a* concentration as a proxy from the coastal zone colour scanner (CZCS) aboard the Nimbus 7 satellite. This approach significantly improved our understanding of ocean primary production at synoptic scales in the BUS region (Weeks and Shillington, 1994). Advancements in satellite remote sensing applications in the BUS has seen the development of ocean colour satellite remote sensing algorithms capable of computing size-fractionated Chl-*a* for the detection of the presence of different phytoplankton size classes (microphytoplankton [ $>20\ \mu\text{m}$ ], nanophytoplankton [ $2\text{--}20\ \mu\text{m}$ ], and picophytoplankton [ $<2\ \mu\text{m}$ ]), contributing to a more comprehensive understanding of the seasonal (Lamont *et al.*, 2019, 2018a) and long-term annual trends (Lamont *et al.*, 2019) in phytoplankton community dynamics. In a 20-year analysis of phytoplankton trends, Lamont *et al.* (2019) reported an increase in annual Chl-*a* and microphytoplankton size fraction and decreasing trends in pico- and nanophytoplankton in the nBUS shelf ( $<1000\ \text{m}$ ) and open ocean region. Long-term decreases in upwelling were suggested as a strong forcing mechanism of the observed trends.

Despite these advancements, several research gaps remain regarding seasonal and long-term dynamics of different PFGs (i.e., diatoms, dinoflagellates, flagellates and coccolithophores) within the nBUS, thus limiting our comprehension of phytoplankton dynamics in the region. Further research exploring the seasonal variability and succession of multiple PFGs as well as shifts in community structure over longer temporal and spatial scales is crucial for a more comprehensive account of phytoplankton dynamics in the nBUS ecosystem. This understanding is necessary as phytoplankton community structure dynamics play a vital role in sustaining fisheries, biodiversity and climate regulation (Tweddle *et al.*, 2018). While recognizing the diverse PFGs and the varying ecological roles they play in shaping ecosystem functioning and services they elicit, this PhD thesis focuses on the links between phytoplankton community composition and climate regulation through the release of aerosol and cloud precursors in dimethyl sulfur compounds (Bates *et al.*, 1987).

## **2.5. The role of phytoplankton in driving the production of dimethyl sulfur compounds**

It is recognized that not all phytoplankton groups contribute equally to the production of DMS. Understanding the dynamics of phytoplankton communities in the nBUS becomes critical as specific groups (i.e., coccolithophores, dinoflagellates) are known to be key producers of DMSP and DMS (Yoch, 2002).

Additionally, shifts in phytoplankton community composition due to climate change may alter DMSP and DMS production, potentially impacting the nBUS' contribution to seawater DMSP and ultimately to atmospheric sulfur cycling and climate regulation.

### **2.5.1. Dimethylsulfoniopropionate**

Oceanic DMSP is a tertiary sulfonium metabolite produced intracellularly by marine phytoplankton, bacteria, macro- and microalgae (Li *et al.*, 2010; Raina *et al.*, 2017; Yoch, 2002). Intracellular DMSP, also referred as particulate DMSP (DMSPp), plays a role in countering various stressors such as oxidative stress (acts as an antioxidant), regulating osmotic imbalance and acting as a cryoprotectant against ultraviolet (UV) light for marine algae (Stefels, 2000; Sunda *et al.*, 2002; Van Alstyne and Puglisi, 2007). DMSP is released into the ocean environment [making up the dissolved pool of DMSP in the ocean (DMSPd)] through different mechanisms. This can be by cell disruption during death, ageing (senescence), grazing by zooplankton, and by viral lysis of cells (Brussaard *et al.*, 2005; Dacey and Wakeham, 1986; Wolfe *et al.*, 1994). Once released into the ocean environment, DMSP can undergo either degradation or oxidation pathways into major volatile compounds. DMSP degradation involves either reduction to DMS gas and acrylate through cleavage by algal or bacterial lyase enzymes and/or demethylation to the bacterial substrate methanethiol (MeSH) and other non-volatile degradation products. DMSP can further be oxidized to dimethyl sulfoxide (DMSO) and in other instances assimilated by phytoplankton or by bacteria incapable of producing their own DMSP (Kiene and Linn, 2000; Kloster *et al.*, 2006; Lizotte *et al.*, 2017; Zeyer *et al.*, 1987). Assimilated DMSPd serves as an intracellular osmolyte in bacteria and phytoplankton, while sulfur from MeSH is used as a substrate for amino acid synthesis in bacteria. DMSP appears to support between 5 to 15% of the bacterial carbon demand in surface waters, making it one of the most significant substrates for bacteria so far identified (Kiene *et al.*, 2000). These findings, coupled with the fact that the small fraction of DMSP converted to DMS may influence atmospheric chemistry, draws attention to DMSP as a molecule of fundamental importance to marine biogeochemical and environmental processes (Kiene *et al.*, 2000; Kiene and Taylor, 1988). The dynamics surrounding the competing DMSP pathways are not yet fully understood. As such, the conversion of DMSP to either DMS, DMSO, MeSH or its consumption by bacteria can range anywhere between 2–90 % of the total DMSP as the DMSP pathways compete for its utilization (Kiene *et al.*, 2000). Accordingly, further research aimed at disentangling oceanic DMSP utilization in the upper ocean is a necessary scientific endeavor for enhanced understanding of biological and environmental controls of DMSP degradation pathways.

### 2.5.2. Dimethyl sulfide

Dimethyl sulfide is a volatile semi-soluble compound omnipresent in the upper ocean surface and is the most abundant source of sulfur in aquatic and tropospheric environments. It is produced in the surface ocean primarily from the breakdown of the phytoplankton osmolyte DMSP by lyase enzymes (Li *et al.*, 2014). DMS is produced intracellularly from DMSPp by phytoplankton with DMSP lysis capability, while DMSPd is catabolized to DMS by bacterial lyases (Kiene and Linn, 2000). Once produced in the marine environment, DMS can be ventilated from the surface ocean to the marine atmospheric boundary layer where it can get oxidized by hydroxy (-OH) molecules to form sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) (Boucher *et al.*, 2003). Atmospheric H<sub>2</sub>SO<sub>4</sub> acts as a precursor to non-sea-salt sulfate aerosol formation and these can grow rapidly to form cloud condensation nuclei (CCN) or cloud seeds (Charlson *et al.*, 1987). These aerosols and CCN are capable of absorption and reflectance of incoming solar radiation, and can alter cloud properties by increasing their solar reflective properties (thus increasing their albedo effect), and thereby directly and indirectly influence incoming solar radiation budgets reaching the Earth's surface (Korhonen *et al.*, 2008).

### 2.5.3. Controls of DMSP and DMS variability

Seawater DMSP and DMS levels vary across spatial and temporal gradients in the global ocean (see global DMS database available at <https://saga.pmel.noaa.gov/dms/>). Both biological (phytoplankton species composition, bacterial DMSP-lyase activity, zooplankton) and non-biological factors (temperature, nutrients, oxygen, radiation, salinity, wind) of the upper ocean ecosystem strongly affect DMSP cycling, and their interactions are not fully understood (Stefels *et al.*, 2007). Intracellular DMSP is influenced by phytoplankton species diversity and abundance (Masotti *et al.*, 2010; McParland and Levine, 2019; Zhou *et al.*, 2009), which is in turn determined by seasonal drivers that dictate temperature and level of nutrients in the water column and other dynamics (e.g., mesoscale eddies, upwelling, land inputs from rivers and dust deposits) (Spilling *et al.*, 2015; Stefels *et al.*, 2007). Different marine environments have been shown to produce different ratios of DMS to methanethiol depending on the levels of dissolved DMSP, salinity (Salgado *et al.*, 2014; Speeckaert *et al.*, 2019; Thariath *et al.*, 2019; Zhuang *et al.*, 2011), solar radiation (Vallina and Simó, 2007), temperature (Baumann *et al.*, 1994; Huertas *et al.*, 2011; Kiene and Service, 1991) and localized sulfur demand by marine bacteria (Howard *et al.*, 2006). Efforts to identify factors which govern the oceanic DMS dynamics (production and removal) have shown no simple relationships with phytoplankton biomass, but suggest that the concentration of DMS in the upper ocean is regulated by a complicated interplay between phytoplankton species diversity, environmental conditions and other marine microorganisms (Andreae, 1990).

There is still a substantial knowledge gap in our understanding of the underlying processes of DMS cycling in the upper ocean. Largely, enzymatic cleavage of DMSP is the main pathway for production of DMS. This process is mediated by phytoplankton that possess intracellular DMSP lyase activity, although some phytoplankton don't have this ability. However, the major contributors of DMS production are bacterial DMSP lyase enzymes that act on dissolved DMSP (Daly and DiTullio, 1996). Consumption of DMS by bacteria (Brock *et al.*, 2013; Motard-Côté *et al.*, 2012), biotic photo-oxidation of DMS to DMSO (Zeyer *et al.*, 1987), consumption and reconstitution of DMSP in fecal pellets by zooplankton (Kasamatsu *et al.*, 2004), and demethylation of DMSP to methanethiol (MeSH) (Howard *et al.*, 2006) are processes that serve as sinks for DMS, the magnitude of which remains elusive.

Given the indirect role of phytoplankton in mediating climate dynamics through DMS production (Bates *et al.*, 1987), a hypothesis was proposed that links marine phytoplankton to long-term climate regulation. This proposed climate feedback mechanism by oceanic phytoplankton was termed the CLAW hypothesis after the first initials of the authors Charlson, Lovelock, Andreae and Warren (Charlson *et al.*, 1987). The CLAW hypothesis proposes that an increase in SST would have either a positive or negative effect on the production of DMS by marine phytoplankton. This would in turn have either a negative or positive climate feedback as a result of enhanced or diminished nss-sulfur-aerosols and CCN, which would regulate the temperature of the earth (Charlson *et al.*, 1987). The CLAW hypothesis has since sparked an interest in research that evaluated DMS and its relationships with marine biological and environmental variables.

## 2.6. Problem statement

Environmental monitoring programs are paramount to our ability to detect shifts in marine ecosystems and hold practical relevance for environmental management efforts in support of policy formulations and establishing marine protected areas for climate-resilient conservation strategies. Given how phytoplankton diversity shapes ecosystem functioning through varying ecological roles, it's not surprising that they form a key part of environmental monitoring programs in the nBUS (Louw *et al.*, 2017, 2016). Such efforts have classically relied on shipboard observations however these are spatially and temporally limited, prompting the need for remote sensing technologies that advance these efforts. Current ocean colour satellite remote sensing algorithms are limited to Chl and its size fractions (Lamont *et al.*, 2019; O'Reilly and Werdell, 2019; Weeks and Shillington, 1994) with no resolve of phytoplankton by functional groups (i.e., diatoms, dinoflagellates, flagellates, coccolithophores). This PhD thesis addresses this limitation through the development of an ocean colour satellite remote sensing algorithm for detection of multiple PFGs from space with far-reaching potential for mapping phytoplankton groups on at unprecedented spatial and temporal scales towards advanced ecosystem understanding and environmental monitoring in the nBUS.

A fundamental question regarding climate change is how the diversity of phytoplankton might change in response to modifications to the environmental conditions, and how this will impact the various ecosystem services that the various key functional groups elicit (e.g., food security and carbon sequestration). Of note (and relevant to this thesis) is how variations in phytoplankton community composition may impact DMSP and DMS production, with subsequent feedback on climate. Although efforts have been made to map the global spatial and temporal distribution of DMS and its precursor DMSP in the upper ocean (see the Global Surface Seawater DMS database at <https://saga.pmel.noaa.gov/dms/>), there is a dearth of DMSP and DMS observations in the nBUS, despite it being recognized as a hotspot for DMS emissions due to its high productivity. Although a few DMS studies have focused on its spatial variability (Andreae *et al.*, 1995; Bates *et al.*, 2001; Tanzer and Heumann, 1992), less effort has been put into assessing DMS, its precursor DMSP and the biological and environmental drivers of regional and temporal variability, which is critical when considering the prominent role of the seasonal cycle and event scale community succession in the region. As such, the seasonality and long-term variability of surface water DMSP and DMS remains an important and poorly studied aspect in the BUS. Phytoplankton biomass and community composition respond to seasonal variations in environmental conditions, namely temperature, stratification, wind strength, upwelling intensity, and nutrient supply. Evaluating the response of DMSP and DMS emissions on a seasonal scale is therefore essential for understanding their role in biogeochemical cycles and for assessing their contribution to cloud formations and climate regulation. This seasonal understanding is

crucial for predicting how sulfur emissions may shift in response to climate change, which is expected to drive similar physicochemical changes in environmental conditions.

Understanding how phytoplankton and associated DMSP and DMS production is responding to a changing environment is necessary for early detection and forecasting of ecosystem disturbances and potential drawbacks, which allows for implementation of measures aimed at environmental protection and conservation. There is a critical need for innovative approaches that can overcome the limitations of traditional *in situ* methods that can provide a more comprehensive account of phytoplankton and the dynamics of associated dimethyl sulfur compounds (DMSP and DMS, abbreviated DMSc for both) in the nBUS. Satellite ocean colour remote sensing offers a promising solution, as it allows for continuous monitoring of large marine areas at high spatial and temporal resolution. However, current global remote sensing algorithms (Gali *et al.*, 2018, 2015) are not yet optimized for accurate DMSP and DMS detection in the complex and dynamic coastal environments such as that of the BUS. This highlights the need for further research towards the development and validation of regionally specific algorithms that can effectively identify and quantify DMSP and DMS concentrations from satellite data specific to the Benguela coastal region.

Since the BUS is associated with one of the largest and most persistent stratus cloud systems, any advances in constraining DMSP and DMS dynamics in the region will significantly enhance our understanding of the system's contribution to global biogeochemical cycles and climate regulation. In particular, when incorporated into climate models for improved seasonal prediction of stratus cloud formulation and thus their impact on albedo and climate regulation.

## 2.7. Aim and objectives

### Aim

This study aims to elucidate the following on large spatial and temporal scales:

1. Regional and seasonal characteristics of PFGs in the nBUS.
2. Long-term trends in Key PFGs in the context of key drivers of variability (SST and  $W_{EQ}$ ).
3. Seasonal cycle and long-term trends of DMS and its precursor DMSP in relation to phytoplankton community dynamics.

### Objectives:

1. Development of a novel ocean colour satellite remote sensing algorithm for the detection of key PFGs (diatoms, dinoflagellates, flagellates) specific to the nBUS. This objective addresses the need for advancements in environmental monitoring efforts through technologies that allow synoptic scale determination of specific PFGs.
2. Application of the validated ocean colour satellite algorithm for PFGs to 20 years of daily satellite observations to assess the previously unexplored seasonal and long-term dynamics on unprecedented spatial and temporal scales in the nBUS.
3. Evaluate trends in PFG's in the context of changing environmental conditions associated with changing temperatures (notably warming) and  $W_{EQ}$  that drive upwelling and influence nutrient supply of primary production.
4. Development of a regionally specific satellite remote sensing algorithm for estimating DMSP and DMS concentrations as a collective, followed by
5. Application of the validated algorithms to 20 years of daily satellite data to assess the regional and seasonal characteristics and long-term trends of DMSP and DMS in relation to phytoplankton communities with an overarching goal of understanding the large-scale patterns of these important marine components.

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## Chapter 3: Ocean colour satellite remote sensing of PFGs

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### 3.1. Abstract

Marine phytoplankton in the nBUS serve as a food and energy source fueling marine food webs at higher trophic levels and thereby support a lucrative fisheries industry that sustain local economies in Namibia. Microscopic and chemotaxonomic analyses are among the most commonly used techniques for routine phytoplankton community analysis and monitoring. However, traditional *in situ* sampling methods have limited spatiotemporal coverage. Satellite observations far surpass traditional discrete ocean sampling methods in their ability to provide data at broad spatial scales over a range of temporal resolution over decadal time periods. Recognition of phytoplankton ecological and functional differences has compelled advancements in satellite observations over the past decades to go beyond Chl as a proxy for phytoplankton biomass to distinguish phytoplankton taxa from space. In this study, a multispectral remote sensing approach is presented for detection of dominant phytoplankton groups frequently observed in the nBUS. Here, a large, microscopic dataset of phytoplankton community structure and the MODIS satellite matchups are used to relate spectral characteristics of in water constituents to dominance of specific phytoplankton groups. The normalized fluorescence line height, red-near infrared as well as the *green/green* spectral band-ratios were assigned to the dominant phytoplankton groups using statistical thresholds. The ocean colour remote sensing algorithm presented here is the first to identify phytoplankton functional types in the nBUS with far-reaching potential for mapping the phenology of phytoplankton groups on large spatial and temporal scales towards advanced ecosystem understanding and environmental monitoring.

### 3.2. Introduction

The BUS, situated on the south western coast of Africa in the South Eastern Atlantic ocean (Figure 3.1a), is estimated to be the most productive Eastern Boundary Upwelling System (Carr, 2002; Carr and Kearns, 2003; Chavez and Messié, 2009). It stretches from Cape Agulhas in South Africa along the Namibian coast to Cape Frio and northwards into Angolan waters (Hutchings *et al.*, 2009; Kampf and Chapman, 2016). The central perennial Lüderitz upwelling cell positioned at 27.5 °S in Namibia (Figure 3.1a) partitions the BUS into the southern and northern BUS (Duncombe Rae, 2005; Lett *et al.*, 2007; Hutchings *et al.*, 2009). The perennial upwelling in the nBUS is driven by strong equatorward south easterly alongshore winds with a strong seasonality, tending to peak in late winter to early spring (August-September) and in autumn (April-May) (Hutchings *et al.*, 2009; Louw *et al.*, 2016). These winds induce an Ekman transport of coastal surface waters offshore, forcing the deep, cold and nutrient-enriched waters to upwell into the euphotic zone where they fuel the high productivity characteristic of the region in the form of marine phytoplankton blooms (Shillington *et al.*, 2006; Lass and Mohrholz, 2008; Lachkar and Gruber, 2012). This increase of productivity in the food web supports a diverse ecosystem and a very lucrative commercial fisheries industry contributing to both economic growth and food security (Allison *et al.*, 2009; Stock *et al.*, 2017).

Marine phytoplankton contribute nearly half of the global primary production and serve as a direct food and energy source fuelling marine food webs at higher trophic levels (Field *et al.*, 1998; Kwak and Park, 2020). In addition, phytoplankton blooms play an important role in global climate regulation through their contribution to the net annual uptake of atmospheric CO<sub>2</sub> (Arrigo *et al.*, 1999; Caldeira and Duffy, 2000; Tortell *et al.*, 2008; Pollard *et al.*, 2009) and the production and release of aerosol particle precursors (e.g., DMS gas and volatile organic carbons (VOCs)) that modulate cloud formation (Charlson *et al.*, 1987; Stefels, 2000; Lizotte *et al.*, 2017). This is of particular relevance in the nBUS, which is characterised by the presence of one of the largest and most persistent stratiform marine cloud decks that contribute to the variability and long-term trends of global albedo with impacts on both regional and global climate.

Marine phytoplankton encompass a diverse community of organisms, whose dominance varies in response to physicochemical variability in environmental conditions, that subsequently determines their ecological and biogeochemical function. For instance, diatoms are typically large cells that grow fast, reaching high concentrations and due to their silica ballast and increased density, tend to sink fast and are considered very effective exporters of organic carbon to the deep ocean and important role players in the biological carbon pump (Smetacek, 1999; Brownlee and Taylor, 2002). Coccolithophores on the other hand are calcifiers that reduce seawater alkalinity and the carbonate concentration of surface waters in the process that forms their coccoliths (external calcium carbonate platelets), which impacts the ocean-atmosphere exchange of CO<sub>2</sub>

(Brownlee and Taylor, 2002; Riebesell and Rost, 2004; McClelland *et al.*, 2016). Together with dinoflagellates (Keller, 1989), coccolithophores have the highest intracellular DMSP content and are considered prominent climate-active DMS gas producers (Archer *et al.*, 2001; Lizotte *et al.*, 2017) that may impact cloud formation and the radiation budget. Some species of cyanobacteria (e.g., *Trichodesmium*), on the other hand, fix atmospheric nitrogen ( $N_2$ ) in a process that contributes to  $N_2$  input into the ocean to compensate for  $N_2$  loss from denitrification (Agawin *et al.*, 2007). Moreover, there are some bloom-forming and toxin-producing phytoplankton species (e.g., diatoms of *Pseudo-nitzschia* spp.), commonly referred to as harmful algal blooms (HABs) that are detrimental to both humans and aquatic life and have devastating consequences for the fisheries industry with important economic ramifications (Hoagland *et al.*, 2002; Dermastia *et al.*, 2022). As such, phytoplankton community structure and diversity is considered a key component of marine ecosystems as they have a direct impact on food web energy supply, fisheries and food security, ecosystem health and climate (Otero *et al.*, 2020; Bestion *et al.*, 2021). It is therefore crucial to study and understand phytoplankton community composition and its variability, especially in the face of global warming and the changing climate. The knowledge of the phytoplankton community composition and its sensitivity to climate forcing can provide a valuable understanding of ecological balance in marine ecosystems (Kruk *et al.*, 2011), which can aid in informed policy drafting decisions for improved implementation of sustainable fisheries and environmental management for the protection and conservation of ecosystems.

Phytoplankton communities are highly dynamic and susceptible to seasonal (and intra-seasonal), interannual and long term variability in environmental drivers such as wind driven mixing (Louw *et al.*, 2016), upwelling (Hansen *et al.*, 2014) and radiative forcing. The nBUS is reported to have been progressively impacted by longer-term variability associated with climate change and other human-induced activities that have resulted in drastic changes to the ecosystem over the last decades. For example, fish catches and populations (sardines and anchovy most notably) have dramatically declined over the past five decades as a result of overfishing and possible environmental events such as hypoxia and Benguela Niños, that negatively affect organisms at both lower and higher trophic levels (Cury and Shannon, 2004). Moreover, upwelling indices indicate a decline in the frequency of upwelling events in recent years (2009 and 2014) in the nBUS (Lamont *et al.*, 2018; Polonsky and Serebrennikov, 2020), with major implications for ocean productivity in support of marine food webs and the biological carbon pump. Consequently, there is a necessity for routine monitoring of phytoplankton as key role-players in this unique marine ecosystem for effective management as a scientific priority towards a better understanding and predictive ability of their role in maintaining ecosystem balance and climate feedback. Efforts to acquire long-term datasets towards adequately monitoring the nBUS for assessment of ecosystem changes have been made by the

National Marine Information and Research Centre (NatMIRC, Namibia). The monitoring programme involves discrete *in situ* field observations collected quasi-monthly along two longitudinal transects off the coast of Namibia. These data have been used to assess trends in phytoplankton biomass (Louw *et al.*, 2016), bloom-forming and toxin-producing diatoms of the genus *Pseudo-nitzschia* (Louw *et al.*, 2017) and other environmental variables for nearly two decades. Field observations, although very useful in studying and monitoring marine ecosystems, are nonetheless severely limited in their regional and temporal coverage. Furthermore, they are labour intensive, costly and unable to provide near real-time monitoring observations.

Satellite ocean colour remote sensing observations have the ability to surpass traditional ocean sampling methods, that involve discrete samples collected on-board research vessels, owed to their large spatial and temporal scale resolution and ability to provide near real time information. Early studies of ocean colour remote sensing focused on the computation of global phytoplankton biomass using chlorophyll-*a* concentration ([Chl-*a*]) as a proxy, which improved our understanding of synoptic scale ocean primary production and biogeochemistry (O'Reilly *et al.*, 1998). However, recognition of the importance of different phytoplankton taxonomic groups and their varying biogeochemical functions has compelled the need for the development of satellite products with the ability to resolve complex phytoplankton dynamics from space. At the forefront of this endeavour is the ability to provide information on the composition of the phytoplankton community (phytoplankton functional types – PFTs) in which each PFT represents a group of species aggregated according to distinct functional characteristics (e.g., size structure or taxonomic composition). More recent advancements in ocean colour remote sensing have seen the development of indirect techniques to derive phytoplankton functional types and size distribution such as the abundance-based algorithms that are based on [Chl-*a*] (Vidussi *et al.*, 2001; Uitz *et al.*, 2006; Hirata *et al.*, 2011; Brewin *et al.*, 2015). Spectral-based approaches, on the other hand, are more direct and rely primarily on the unique characteristics of light absorption and backscattering of different phytoplankton taxa, which can be retrieved from water-leaving reflectance (Bracher *et al.*, 2017; IOCCG, 2014; Moore *et al.*, 2012). Variations in photosynthetic pigment composition, morphology, size, shape, and inner structure of different phytoplankton species is what drives the characteristics of inherent optical properties of surface waters that can subsequently be used to differentiate phytoplankton groups or species from satellite ocean colour remote sensing (Aguirre-Gomez *et al.*, 2001; Vaillancourt *et al.*, 2004; Soja-Wozniak *et al.*, 2018). One example of this type of approach is the dual ratio approach, which utilises the ratio between 2 spectral bands to identify specific phytoplankton functional types. For instance, Bernard *et al.* (2005) used the 665 nm and 709 nm *red/red* band-ratio of the Medium Resolution Imaging Spectrometer (MERIS) sensor to identify HABs in the sBUS. Another approach uses spectral band differences to derive phytoplankton

optical fingerprints. Typically, these algorithms are used to identify algal blooms of a particular taxa using three adjacent spectral bands in the red and near infrared or blue-green spectral regions that quantify the amplitude of a specific peak of absorption. One particularly useful example of this approach utilises the [Chl-*a*] fluorescence peak signal between 678 and 683 nm. Quantification of this signal, known as the fluorescence line height (FLH) (Letelier and Abbott, 1996; Kritten *et al.*, 2020), is based on the height of the reflectance peak above a baseline formed between the two adjacent wavebands. This approach has previously been applied to identify HABs in the coastal waters of SW Florida (Hu *et al.*, 2005) and the sBUS (Smith and Bernard, 2020). Past and current ocean colour satellite sensors with appropriate wavebands in the red and near infrared (NIR) spectral regions, that are able to use these approaches, include the Moderate Resolution Imaging Spectroradiometer of aqua (MODIS-Aqua) [2002-present], the Ocean and Land Colour Imager (OLCI) [2016-present], and the MERIS sensors [2002-2012] (Letelier and Abbott, 1996).

Although there exist a limited number of satellite ocean colour remote sensing algorithms for aiding in the detection of multiple phytoplankton functional types (Aiken *et al.*, 2007) and HABs in the sBUS (Bernard *et al.*, 2005; Smith and Bernard, 2020), there is, to our knowledge, no satellite ocean colour remote sensing algorithm for detection of PFGs in the nBUS counterpart. While the regional abundance-based phytoplankton size class model of Lamont *et al.* (2019) for the BUS provides useful information on the variability of phytoplankton size classes (picophytoplankton, nanophytoplankton and microphytoplankton), it is not able to approximate functional phytoplankton group composition (needed for the assessment of their various key ecological functions). The optical based algorithms derived by Aiken *et al.* (2007) and Smith and Bernard (2020) on the other hand are geared at providing information on the functional composition of phytoplankton for the sBUS (specifically diatoms, *Pseudo-nitzschia*, dinoflagellates, flagellates and mixed communities) and it cannot be assumed that they are applicable to the nBUS (or to different satellite products).

This study addresses the need for an ocean colour remote sensing algorithm for the detection of phytoplankton groups in the nBUS. It does so by first selecting the most suitable satellite sensor for the nBUS based on matchups between *in situ* and satellite (MODIS-Aqua, MERIS/OLCI) derived Chl-*a*. It subsequently follows a similar methodological approach to the algorithm developed for the sBUS by Smith and Bernard (2020) by identifying the spectral reflectance characteristics unique to stations dominated by particular PFGs. A combination of these unique optical characteristics is then used to derive an algorithm that can be applied to ocean colour data from the nBUS to elicit broad scale high resolution information on the likely distribution of the dominant functional types. Such an algorithm will allow observations of the

spatio-temporal distribution and variability of key phytoplankton groups on an unprecedented scale in the nBUS, which is a scientific priority for understanding the marine food web and detecting its response to a changing climate in this globally important upwelling region.

### 3.3. Materials and Methods

#### 3.3.1. *In situ* data

##### 3.3.1.1 Expeditions

This study focused on the nBUS off the coast of Namibia (Figure 3.1a) within the latitudes and longitudes of 20–26 °S and 9–15 °E, which included the Cape Frio, Central and the Lüderitz upwelling cells. Two expeditions were carried out on-board the RV Meteor (M153) and Mirabilis (RGNO2019) for data collection (Figure 3.1b). Cruise M153 took place from 15 February to 15 March 2019 covering both the northern and southern Benguela upwelling systems whereas cruise RGNO2019 took place from 9 to 10 of May 2019 covering 2 longitudinal transects (23 and 20 °S). The stations sampled during the two expeditions (41 in total) are presented in Figure 3.1b. Seawater samples were collected in surface waters (0-5 m) using Niskin bottles attached to a conductivity-temperature-depth (CTD) carousel setup on-board the RV Meteor and Mirabilis. The author personally participated in both research cruises and was responsible for collecting the seawater samples used in this study. These data were supplemented with additional data from previous cruises in the region covering the period between 2001 and 2020 (Figure 3.1b, Table 3.1).

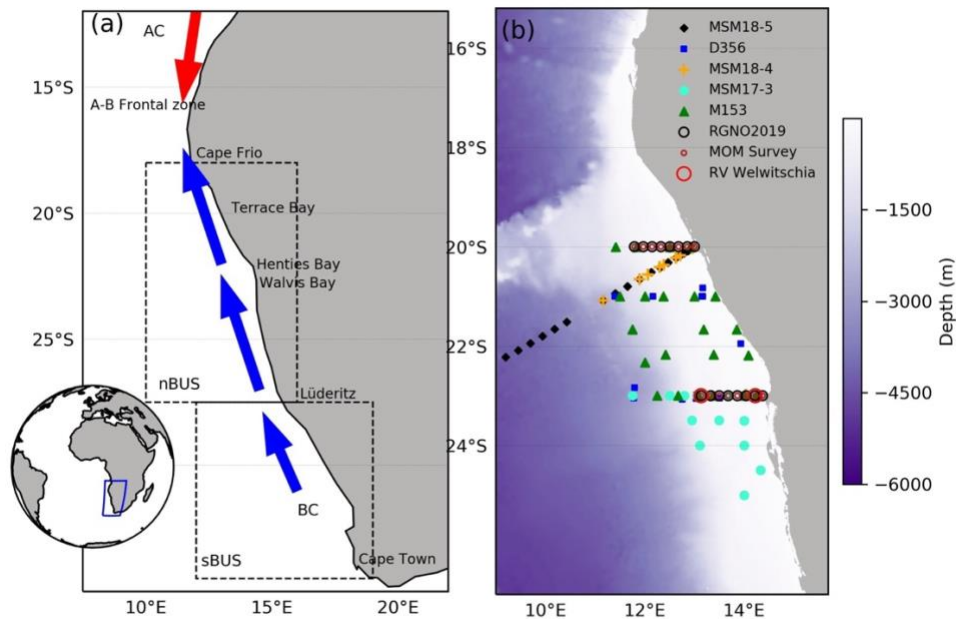


**Figure 3.1:** Map of western Africa showing the location of the Benguela Upwelling System (blue rectangle, inset). The BUS is partitioned into the northern (nBUS) and southern (sBUS) region separated by the Lüderitz upwelling cell at 27 °S (a). The nBUS is bound by the cold water from the Benguela current (BC)

and the warm water from the Angola current (AC) that converge at the Angola-Benguela frontal zone (A-B frontal zone). The right panel (b) shows bathymetry and the geolocations of stations sampled in the nBUS for Chl-*a* and phytoplankton community structure on the RV Meteor (M153) (green triangles) and Mirabilis RGNO2019 (black open circles). The geolocations of all additional cruise data (Table 3.1) are similarly identified with unique symbols as per the figure legend.

#### 3.3.1.2 *Chlorophyll-a*

For the M153 and RGNO2019 cruises total [Chl-*a*], 200 ml of seawater was filtered through glass microfiber filters (Whatman GF/F, 25 mm diameter, 0.7  $\mu$ m pore size) and stored immediately in the freezer (-20 °C) for later analysis. Total [Chl-*a*] was determined following the method of (Welschmeyer, 1994). [Chl-*a*] was extracted from the GF/F filters by addition of 9 mL of 90% acetone for 24 hr in the dark at -20 °C. These were then transferred into glass tubes and fluorescence was measured using a Turner (Model 10AU) fluorometer. The [Chl-*a*] was determined from a seven-point [Chl-*a*] calibration curve and represented as equivalents of chlorophyll-*a* ( $\mu$ g l<sup>-1</sup>).

#### 3.3.1.3 *Phytoplankton cell counts*

For the M153 and RGNO2019 cruises phytoplankton cell enumeration and taxonomic identification, water from the Niskin bottles was transferred to 200 mL glass amber bottles and immediately preserved with either acidic (M153) or neutral (RGNO2019) Lugol's iodine solution, shaken gently and stored in the dark at room temperature for later analysis in the land-based laboratory. The lugol-preserved phytoplankton cells were settled in a 25 ml glass/plastic chamber for 24 hours prior to analysis. The phytoplankton cells were identified and counted using a Zeiss Axiovert 200 inverted light microscope following the Utermöhl (1958) method. Cells were counted and identified to genus and to species level where possible. Approximately 400 cells were counted to achieve an estimation of cell concentration with  $\pm 10\%$  precision, whereas at least 50-200 cells were counted when cells occurred in smaller concentrations with a precision of approximately 15–30% (Anderson and Throndsen, 2004). Although microscopic taxonomic identification of phytoplankton provides a resolution to genus and species levels, counted cells in this study were only grouped into diatoms, flagellates, dinoflagellates, cyanobacteria, coccolithophores, and others/unknown.

#### 3.3.1.4 *Additional in situ data sources*

The M153 and RGNO2019 cruise datasets (detailed above) were supplemented with additional [Chl-*a*] and phytoplankton cell count data from multiple expeditions from publicly available, published and unpublished sources that were conducted in the nBUS covering the period between 2001 and 2020 (Table 3.1). A total of 25 surface water samples were collected during the RV Meteor (M153) cruise and 16

samples during the RV Mirabilis (RGNO2019) cruise, resulting in a combined dataset to make a total pool of 252 stations for analysis. Data from the additional sources were similarly obtained from samples collected in the top 5 m and were similarly assessed for [Chl-*a*] using a fluorometer according to the principle of Welschmeyer (1994) and phytoplankton cell counts according to the method of Utermöhl (1958). The geolocations of the additional stations sampled are shown in Figure 3.1b with the respective sampling dates and data sources summarised in Table 3.1 below.

**Table 3.1:** Research expeditions in the nBUS off Namibia where concurrent [Chl-*a*] and phytoplankton cell count samples were collected between 2001 and 2019. Detailed spatial locations of the various studies appear in Figure 3.1b.

| Cruise expedition         | Date                           | No. of stations  | Source                                            |
|---------------------------|--------------------------------|------------------|---------------------------------------------------|
| RV Meteor 153 (M153)      | 15 February – 15 March 2019    | 25               | This study <sup>ab</sup>                          |
| RV Mirabilis (RGNO2019)   | 9 – 10 May 2019                | 16               | This study <sup>ab</sup>                          |
| Maria S. Merian (MSM18-5) | 27 August – 15 September 2011  | 26               | Wasmund <i>et al.</i> , 2014 <sup>ab</sup>        |
| Discovery 356 (D356)      | 11 September – 07 October 2010 | 14               | Wasmund, 2011a, 2011b <sup>ab</sup>               |
| Maria S. Merian (MSM18-4) | 16 – 19 August 2011            | 09               | Wasmund, 2015a, 2015b <sup>ab</sup>               |
| Maria S. Merian (MSM17/3) | 30 January – 02 February 2011  | 13               | Wasmund, 2012, 2015a <sup>ab</sup>                |
| RV Mirabilis (MOM survey) | January 2004 – February 2020   | 149 <sup>+</sup> | NatMIRC unpublished monitoring data <sup>ab</sup> |
| RV Mirabilis (MOM survey) | February 2001 – December 2012  | 149 <sup>+</sup> | Louw <i>et al.</i> , 2016 <sup>a</sup>            |
| RV Welwitschia            | February 2001 – December 2012  | 149 <sup>+</sup> | Matlakala 2019 <sup>ab</sup>                      |

<sup>a</sup> = [Chl-*a*] data; <sup>b</sup> = phytoplankton cell counts data; <sup>+</sup>denotes expeditions with overlapping datasets and stations, the total stations were consolidated.

### 3.3.2 Satellite data

#### 3.3.2.1. Data acquisition and processing

Daily Level-2 (L2) 1 km resolution ocean colour satellite data from the Moderate Resolution Imaging Spectroradiometer on board the Aqua satellite (MODIS-Aqua), the Medium Resolution Imaging Spectrometer (MERIS) on board Envisat, and the Ocean and Land Colour Instrument (OLCI) on board Sentinel-3 were obtained from the National Aeronautics and Space Administration (NASA) Ocean Colour Web (<https://oceancolor.gsfc.nasa.gov/>), MERIS catalogue and inventory (MERCI, <http://meris-ds.eo.esa.int/oads/access/>) and the Copernicus online data access website (CODA, <https://codat.eumetsat.int/>), respectively. The OLCI [Chl-*a*] data were derived from OLCI reflectance bands using the blended switching algorithm of Smith *et al.* (2018), which was developed specifically for the high biomass waters of the southern Benguela. The standard MODIS-Aqua [Chl-*a*] product is based on an empirical relationship derived from remote sensing reflectance (*R<sub>rs</sub>*) between 440 and 670 nm and *in situ* Chl-*a*. This product is a combination of the standard OC3 algorithm (O'Reilly *et al.*, 2000) and the colour index (CI) algorithm (Hu *et al.*, 2012), where the OC3 algorithm is applied at [Chl-*a*] > 0.2 mg m<sup>-3</sup>, whereas the CI algorithm is applied at [Chl-*a*] < 0.15 mg m<sup>-3</sup>, and a weighted blending approach is applied between 0.15 and 0.2 mg m<sup>-3</sup>. Other products obtained from MODIS L2 include the L2 flags, the nFLH and the remote sensing reflectance (*R<sub>rs</sub>*) at 412, 443, 469, 488, 531, 547, 555, 645, 667 and 678 nm wavebands of the visible spectrum. The normalized fluorescence line height (nFLH, W m<sup>-2</sup> μm<sup>-1</sup> sr<sup>-1</sup>) (Letelier and Abbott, 1996) is a standard product provided with the MODIS L2 Ocean colour data derived as follows:

$$nFLH = L_w678 - L_w667 - \left[ (L_w748 - L_w667) \times \left( \frac{678-667}{748-667} \right) \right] \quad (1)$$

where  $L_w$  is the normalized water-leaving radiance.

#### 3.3.2.2. Matchups with *in situ* data

The L2 data from MODIS-Aqua, MERIS and OLCI were matched to field observation stations and extracted using a 5 x 5 pixel box centred around the *in situ* measurements as satellite navigation may not be accurate to a single pixel. The multi-pixel box increases the number of pixels of satellite retrievals and the possibility of a valid *in situ* matchup. A time window of ≤12 hrs between the satellite overpass and *in situ* observations was given preference as a temporal threshold for coincidence. However, when coincident satellite and *in situ* observations weren't available within a 12 hr window, this criteria was relaxed to allow matchups to be considered within a ≤24 hr time window. The mean was then calculated for valid pixels within the 5 x 5 pixel box for [Chl-*a*], nFLH and *R<sub>rs</sub>* at spectral bands in the visible range as outlined above, together with their respective statistical error metrics (e.g., standard deviations).

### 3.3.3 Data quality control

A set of quality control measures were adopted to minimize the inclusion and effect of bad/erroneous data from the L2 satellite data using a set of corrective measures as outlined in Figure S3.2 of Annexure I. The *L2flags* product contains science and quality “flags”, with set atmospheric correction thresholds that were used to eliminate invalid pixels. Briefly, pixels were masked and excluded when flagged as “land” (pixel is over land), “clouds” (cloud contamination), “chlfail” (satellite ocean colour [Chl-*a*] algorithm failure), “higlnt” (sunglint detected via reflectance exceeds threshold), “hisatzen” (sensor view zenith angle exceeds 60 °), “lowlw” (very low water-leaving radiance), and “hilt” (observed radiance very high or saturated). In an effort to remove invalid averaged matchup retrievals, further exclusion criteria were applied following Bailey and Werdell (2006), which removes matchups where fewer than 13 pixels were valid (i.e., where <50% of the 25 pixels within a 5 x 5 pixel box were valid). Furthermore, mean values whose standard deviations were >50% of the mean (indicative of large variability within the 5 x 5 pixel box) were removed to ensure spatial stability or homogeneity. Quality control measures applied to *in situ* [Chl-*a*] measurements included removal of measurements that were below the minimum detection threshold of the Turner fluorometer (<0.02  $\mu\text{g l}^{-1}$ ). Finally, *in situ* stations were excluded that were too close to one another and overlapped with a 5 x 5 pixel box (a flow diagram detailing the data quality control steps can be found in Figure S3.2 in Annexure I).

### 3.3.4 Evaluation of MODIS-Aqua and MERIS/OLCI [Chl-*a*] algorithms

Statistical uncertainties between matchups of satellite ocean colour derived [Chl-*a*] and *in situ* fluorometric derived [Chl-*a*] were used to determine the most appropriate satellite sensor for algorithm development. The MERIS mission covered the period between 2002 and 2012, whereas OLCI and MODIS-Aqua were launched in 2016 and 2002, respectively, and both are still operational (at the time of writing). OLCI was developed on MERIS heritage with a similar spectral setup in order to provide continuity in algorithms and derived data; for this reason the match-ups from these two sensors were combined to create a single dataset. However, only the datasets covering the period between 2002-2012 and 2016-present were used for MODIS-Aqua so as to facilitate a fair comparison with MERIS/OLCI in this evaluation. Statistical metrics were used to quantify the agreement between *in situ* Chl-*a* and satellite-derived observations. Prior to the analysis, both the *in situ* and satellite retrievals were log-transformed. The statistics used for comparison were the mean relative error (MRE), mean absolute relative difference (MARD), median relative difference (MedRD), root mean squared error (RMSE) and relative bias, the exact equations of which can be found in the supplementary material. In addition, a linear regression model was used to assess the degree of

agreement between the *in situ* and satellite-derived Chl-*a*. The intercept, slope and coefficient of determination ( $R^2$ ) were computed.

### 3.3.5 Algorithm development

#### 3.3.5.1. Subdividing the data by phytoplankton group dominance

The quality-controlled *in situ* data were subdivided according to phytoplankton group dominance. Dominance, in the context of this study, was typically achieved when a phytoplankton group contributed more than 50% to the total phytoplankton community abundance. In this study, phytoplankton dominance was determined based on relative cell abundance derived from microscopy counts (cells  $L^{-1}$ ). It is important to note that this approach reflects numerical dominance rather than biomass dominance, as cell size differences among taxa can result in varying biomass contributions even when abundance is low. Biomass-based estimates were not derived due to the absence of corresponding carbon or pigment measurements. It should be noted however that the nBUS is, for the most part, diatom-dominated (See Figure S3.3 in Annexure I) and therefore the majority of the datasets were considered diatom dominated. For diatoms only, dominance was instead defined as a  $\geq 80\%$  contribution to the total phytoplankton community with a cell concentration of  $\geq 10^6$  cells  $L^{-1}$ . The 80% threshold was chosen specifically to distinguish community assemblages that are strongly dominated by diatoms from those where other PFGs make a more notable contribution, thereby improving the sensitivity of the resulting optical characteristics of diatoms. For flagellates and dinoflagellates, dominance was considered when cells were  $>50\%$  of the total cell abundance. No cell count minima were set for these subsets, as these stations typically did not reach high cell concentrations (i.e.,  $>10^6$  cells  $L^{-1}$ ). We acknowledge, however, that a consistent 50% threshold across all groups could provide a more standardised measure of dominance, though it may obscure meaningful ecological variability in regions where diatoms naturally dominate most of the time.

Further analysis of the data showed dominance for dinoflagellates in both low [Chl-*a*] and high [Chl-*a*] ( $> 4 \mu g L^{-1}$ ) waters. Dinoflagellate dominance was thus subdivided into either low biomass or high biomass dominance (LB and HB, respectively). For HB dinoflagellate-dominated waters, dominance was considered when contributing  $>50\%$  to the total cell abundance with cell counts of  $\geq 10^6$  cells  $L^{-1}$ . Unfortunately, there were no *in situ* stations where either coccolithophores or cyanobacteria met the criteria for dominance. As such, this study focused only on identifying unique spectral characteristics of diatoms, flagellates and dinoflagellates from the satellite spectral matchup data. In addition, unique spectral characteristics were determined for a phytoplankton community that was considered mixed, i.e., when all the identifiable groups (including coccolithophores and cyanobacteria) and unidentifiable groups (i.e., classified as “other” in the

phytoplankton taxonomic datasets) each contributed <50% to the total phytoplankton abundance with no set cell count minima.

### 3.3.5.2. Determining unique optical characteristics

The remote sensing spectral characteristics associated with dominance of the aforementioned phytoplankton groups were assessed using 4 approaches, namely 1)  $Rrs$  at different spectral bands, 2) dual-band  $Rrs$  ratios, 3) spectral band difference approaches and 4) a Chl-*a* abundance-based approach. For these approaches, the magnitude and shape of  $Rrs$  at 10 spectral bands were compared between waters dominated by the different phytoplankton groups. For dual-band spectral ratios, a total of 87 different ratio combinations among the violet, blue, green and red spectral regions were investigated. The spectral band difference or line height (LH) was calculated at eight different adjacent spectral band-triplets between 410 and 678 nm. LH is a measure of the height of the  $Rrs$  at a “signal” band above a baseline formed by any two given spectral bands, and was calculated as follows:

$$LH = Rrs_{signal} - Rrs_{left} - (Rrs_{right} - Rrs_{left}) \times \left( \frac{\lambda_{signal} - \lambda_{left}}{\lambda_{right} - \lambda_{left}} \right) \quad (2)$$

Where  $\lambda$  is the wavelength value at a spectral band of interest,  $Rrs_{signal}$  is the  $Rrs$  value at the signal band centred between two spectral bands,  $Rrs_{left}$  is the  $Rrs$  to the left of  $Rrs_{signal}$ ,  $Rrs_{right}$  is the  $Rrs$  to the right of  $Rrs_{signal}$ ,  $\lambda_{signal}$  is the  $\lambda$  value of  $Rrs_{signal}$  whereas  $\lambda_{right}$  and  $\lambda_{left}$  are the  $\lambda$  values of  $Rrs$  to the right and left of the  $Rrs_{signal}$  respectively. The nFLH, a downloadable L2 MODIS-aqua product as described in the “*data acquisition*” section above, is a well-known example.

Spectral reflectance peaks may occur near 685 nm in low to moderate [Chl-*a*] waters as a consequence of [Chl-*a*] fluorescence emission (Gordon, 1979). However, this [Chl-*a*] fluorescence peak may be masked in high phytoplankton biomass waters (e.g., [Chl-*a*] > 20  $\mu\text{g l}^{-1}$ ) as a result of increased absorption and backscattering by phytoplankton coupled with increased water absorption (Gordon, 1979; Schalles, 2006; Gilerson *et al.*, 2007); this is often observed as a shift in the red reflectance peak towards the NIR region. In this study, this red shift is quantified as the ratio between a red ( $Rrs_{667}$ ) and NIR ( $Rrs_{748}$ ) spectral bands, the red-NIR ratio ( $RNR$ ). The  $Rrs_{748}$  is not provided in the standard L2 MODIS files, and is instead calculated from the available nFLH,  $Rrs_{667}$  and  $Rrs_{678}$ , and solar spectral irradiance values from Thuillier *et al.* (2003) as follows:

$$Rrs_{748} = \left[ \left( \frac{81 \cdot Rrs_{678} \cdot 1481.93}{11} \right) - \left( \frac{81 \cdot nFLH}{11} \right) - \left( \frac{70 \cdot Rrs_{667} \cdot 1517.73}{11} \right) \right] \div 1288.25 \quad (3)$$

The *RNR* was then calculated as:

$$RNR = \frac{Rrs748}{Rrs667} \quad (4)$$

[Chl-*a*] was used as a proxy for phytoplankton abundance for the development of the abundance-based algorithm, based primarily on the understanding that at high biomass the phytoplankton community was dominated by either diatoms or dinoflagellates.

### 3.3.6 Statistical analysis

Box and whisker plots were used to graphically display the distribution and statistical parameters of the data which included the median (Q2), lower (Q1 or 25<sup>th</sup> percentile) and upper (Q3 or 75<sup>th</sup> percentile) quartiles as well as the lower (Q0 or minimum) and upper (Q4 or maximum) extremes of the datasets. The box represents the interquartile interval where 50% of the data is distributed. The whiskers display the lower (minimum) and upper (maximum) extremes of the datasets. Outliers were defined as data points that are 1.5 times higher than the interquartile range (IQR) calculated from both the lower (Q1) and upper (Q3) quartiles and indicated as circles in the box and whisker plots. The 25<sup>th</sup> and 75<sup>th</sup> percentiles were used to define optical signature thresholds associated with dominance of the phytoplankton groups under investigation. The Matplotlib, Scipy.stats, Numpy and Sklearn.metrics Python (version 3.7.3) packages were used for statistical data analysis.

### 3.4. Results

#### 3.4.1. Evaluation of MODIS-Aqua and MERIS/OLCI [Chl-*a*] algorithms in the nBUS in comparison with *in situ* data

For both MODIS-Aqua and MERIS/OLCI sensors, the quality-controlled [Chl-*a*] match-up datasets were used for comparison (Figure 3.2), which covered the *in situ* [Chl-*a*] range of 0.18 – 36.25  $\mu\text{g l}^{-1}$ . The matchup datasets were reduced from  $n=56$  and 54 stations to  $n=36$  and 37 for MODIS-Aqua and MERIS/OLCI respectively, following the application of the stringent quality control measures outlined in Figure S3.2 in Annexure I. Scatter plots of the comparisons between *in situ* and satellite [Chl-*a*] are shown in Figures 3.2a-b with the data that passed quality control being easily identified from the raw data that did not. Statistical parameters of the linear regressions between the quality-controlled data showed a positive correlation between *in situ* Chl-*a* and satellite retrievals. The Pearson correlation coefficient was similar for both sensors, with MODIS-Aqua having a slightly lower correlation ( $r = 0.67$ ) than that of MERIS/OLCI ( $r = 0.68$ ) (Figure 3.2c).

Both sensors showed a similar [Chl-*a*] distribution when compared to co-located *in situ* [Chl-*a*] observations (Figures 3.2d and 2e), with MERIS/OLCI having a few data points outside the maximum range of the *in situ* Chl-*a* centred at  $\sim 2 \mu\text{g l}^{-1}$  (Figure 3.2e). In order to better understand the distribution between the datasets, the log-transformed  $[\text{Chl-}a]^{\text{in situ}} / [\text{Chl-}a]^{\text{satellite}}$  ratio was determined (Figure 3.2f) and showed that the apex of distribution for MODIS-Aqua was closer to zero (i.e., the 1:1 line), while the majority of the data was distributed within a positive ratio for both satellites. This positive distribution is indicative of a general tendency for both sensors to underestimate *in situ* Chl-*a*. This was similarly evident for both sensors in the negative mean relative error (MRE) (-44.6% and -38.7% for MERIS/OLCI and MODIS-Aqua respectively) and the negative median relative errors (-32.5% and -13.9% for MERIS/OLCI and MODIS-Aqua respectively) (Table 3.2). Similar findings (i.e., overestimation at lower [Chl-*a*] and underestimation at higher [Chl-*a*]) were reported by Dogliotti *et al.* (2009) for MODIS-Aqua when compared with SeaWiFS for the Argentinean Patagonian continental shelf between 38° S and 55° S, which they attributed to differences in phytoplankton composition across a similar range of [Chl-*a*].

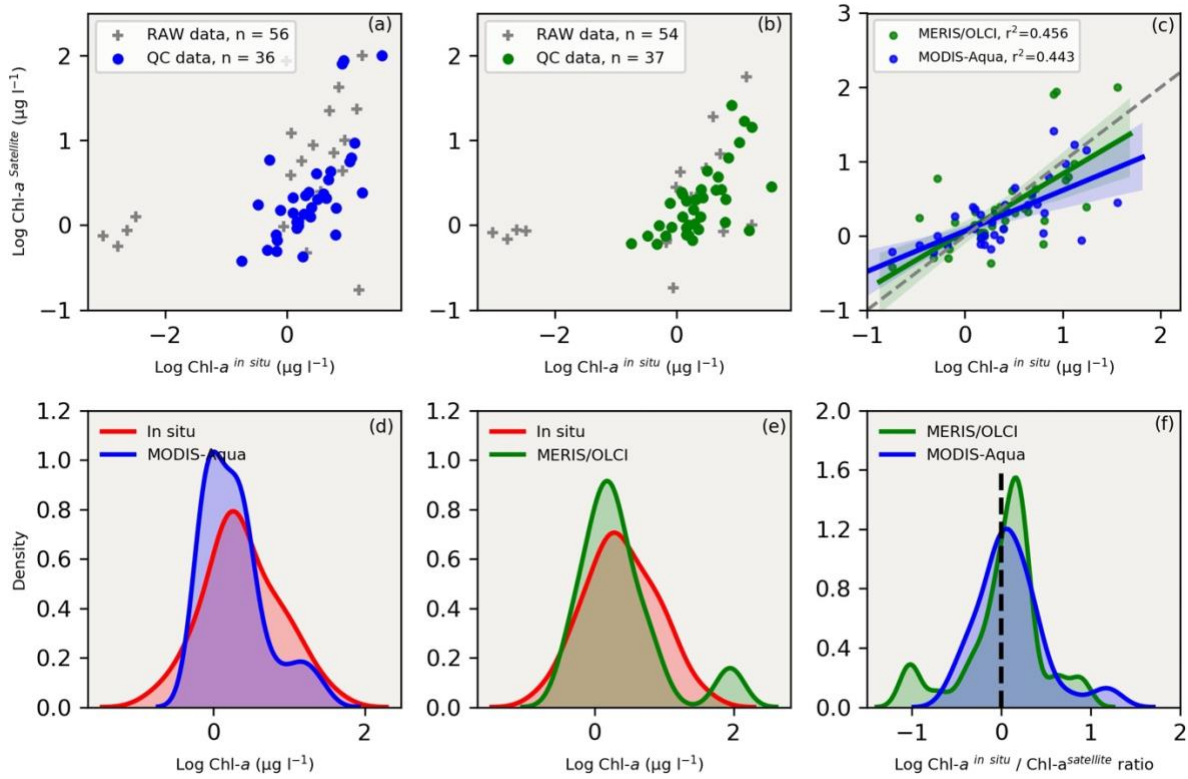


**Figure 3.1:** The top panel shows raw and quality-controlled (QC) *in situ* versus satellite Chl-*a* data for the MODIS-Aqua (blue dots) (a), MERIS/OLCI (green dots) (b) and linear regression statistics with 95% confidence intervals (shaded areas) for the QC Chl-*a* comparisons between MODIS-Aqua (blue shaded line) and MERIS/OLCI (green shaded line) (c). The number of QC datasets used for comparative analysis (n) are indicated. The bottom panel compares the data distribution between *in situ* (red) and satellite-derived Chl-*a* using the Kernel density estimation (KDE) plots for (d) MODIS-Aqua (blue) and (e) MERIS/OLCI (green). (f) is a direct comparison of the ratio of *in situ* to satellite Chl-*a* between the two sensors (blue: MODIS-Aqua; green: MERIS/OLCI). All datasets were log-transformed prior to plotting and statistical analysis.

Comparison of MODIS-Aqua to *in situ* [Chl-*a*] for the full dataset (n=179) (i.e., not limited to the time period that coincided with MERIS/OLCI), showed similar statistical results (data distribution and error margins) (Figure 3.3a). An overall [Chl-*a*] underestimation tendency is similarly observed as shown in Figures 3.3c (and 3.3c inset), the statistical metrics of which (MRE, MARE, RMSE, MedRD and Bias) are also summarized in Table 3.2, with a tendency to overestimate at very low Chl-*a* concentrations (Figure 3.3d). Overall, it can be observed from the log ratio distribution in Figure 3.3d that the MODIS-Aqua

satellite algorithm compared well with *in situ* measurements and that the error margins improved when the expanded full data matchups were used.

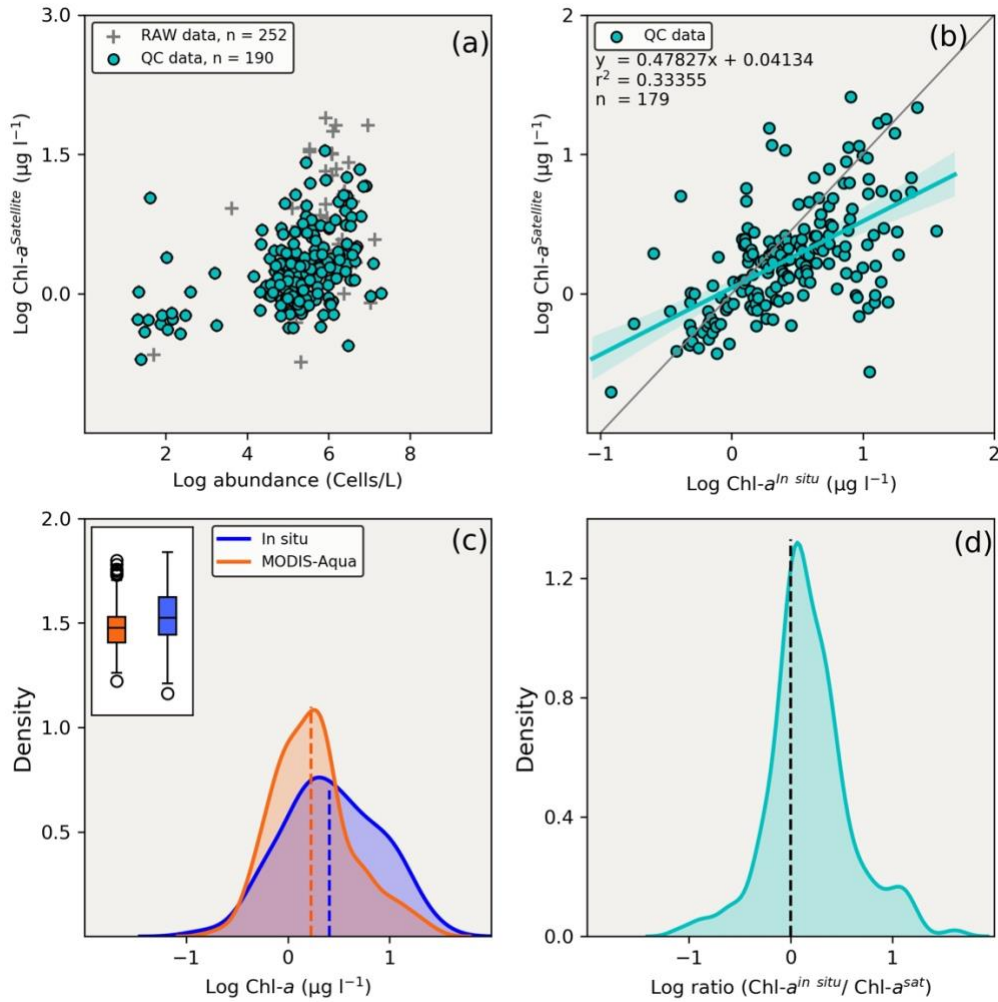


**Figure 3.3:** Comparison between full ( $n = 179$ ) *in situ* [Chl-*a*] dataset and MODIS-Aqua satellite matchup retrievals. **(a)** Raw and quality-controlled datasets, **(b)** Linear statistical regression of QC Chl-*a* between *in situ* and MODIS-Aqua matchups, **(c)** Comparative overview of Chl-*a* distribution from *in situ* and MODIS-Aqua using the Kernel density estimate plots and boxplots (inset). The dotted vertical lines indicate the mean Chl-*a* and **(d)** distribution plot of log-transformed Chl-*a*<sup>*in situ*</sup> / Chl-*a*<sup>*satellite*</sup> ratio.

**Table 3.2:** Statistical metrics used for comparison of satellite-derived and *in situ* Chl-*a* match-ups between the MODIS-Aqua and MERIS/OLCI sensors in the nBUS.

| Statistical metrics | Satellite sensor                              |                                               |                                               |
|---------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
|                     | MERIS/OLCI                                    | MODIS-Aqua                                    | Full MODIS-Aqua data                          |
| <i>n</i>            | 36                                            | 37                                            | 179                                           |
| MRE (%)             | -44.618                                       | -38.739                                       | -7.443                                        |
| MARE                | 0.803                                         | 0.279                                         | 0.429                                         |
| RMSE                | 0.445                                         | 0.393                                         | 0.320                                         |
| Median              | 0.332 <i>in situ</i> ; 0.224 <i>satellite</i> | 0.305 <i>in situ</i> ; 0.263 <i>satellite</i> | 0.408 <i>in situ</i> ; 0.227 <i>satellite</i> |
| MedRD (%)           | -32.354                                       | -13.902                                       | -44                                           |
| Ratio*              | 1.649                                         | 2.138                                         | 0.182                                         |
| Bias                | 0.009                                         | 0.008                                         | 0.002                                         |
| Slope               | 0.776                                         | 0.547                                         | 0.478                                         |

\* : mean Chl-*a* *in situ* / Chl-*a* <sup>sat</sup> ratio; *n*: number of data matchups

### 3.4.2. Deriving phytoplankton optical fingerprints from ocean colour remote sensing

#### 3.4.2.1. Remote sensing reflectance

Figure 3.4 shows the *Rrs* characteristics across 10 spectral wave bands in the visible range for oceanic waters dominated by different phytoplankton community groups, namely diatoms, HB and LB dinoflagellates, flagellates and mixed assemblage. These *Rrs* spectra showed considerable differences in magnitude and shape among the phytoplankton groups, which is subsequently exploited for deriving optical fingerprints that are characteristic for specific groups (Figure S3.1 of Annexure I). For example, the *Rrs* minima observed in the longer wavelengths (i.e., red region: 645, 667 and 678 nm) is evident for all phytoplankton groups except HB dinoflagellates, whose *Rrs* minima is in the shorter violet/blue region (412/443 nm) (Figure 3.4). LB dinoflagellates had a characteristic maxima in the violet/blue region (412/443 nm) of the spectra, while for both HB dinoflagellates and flagellates, the *Rrs* magnitude increased with increasing wavelength from violet/blue-to-green with the *Rrs* maxima located in the green spectral region (555 nm) for HB dinoflagellates and (547 nm) for flagellates.

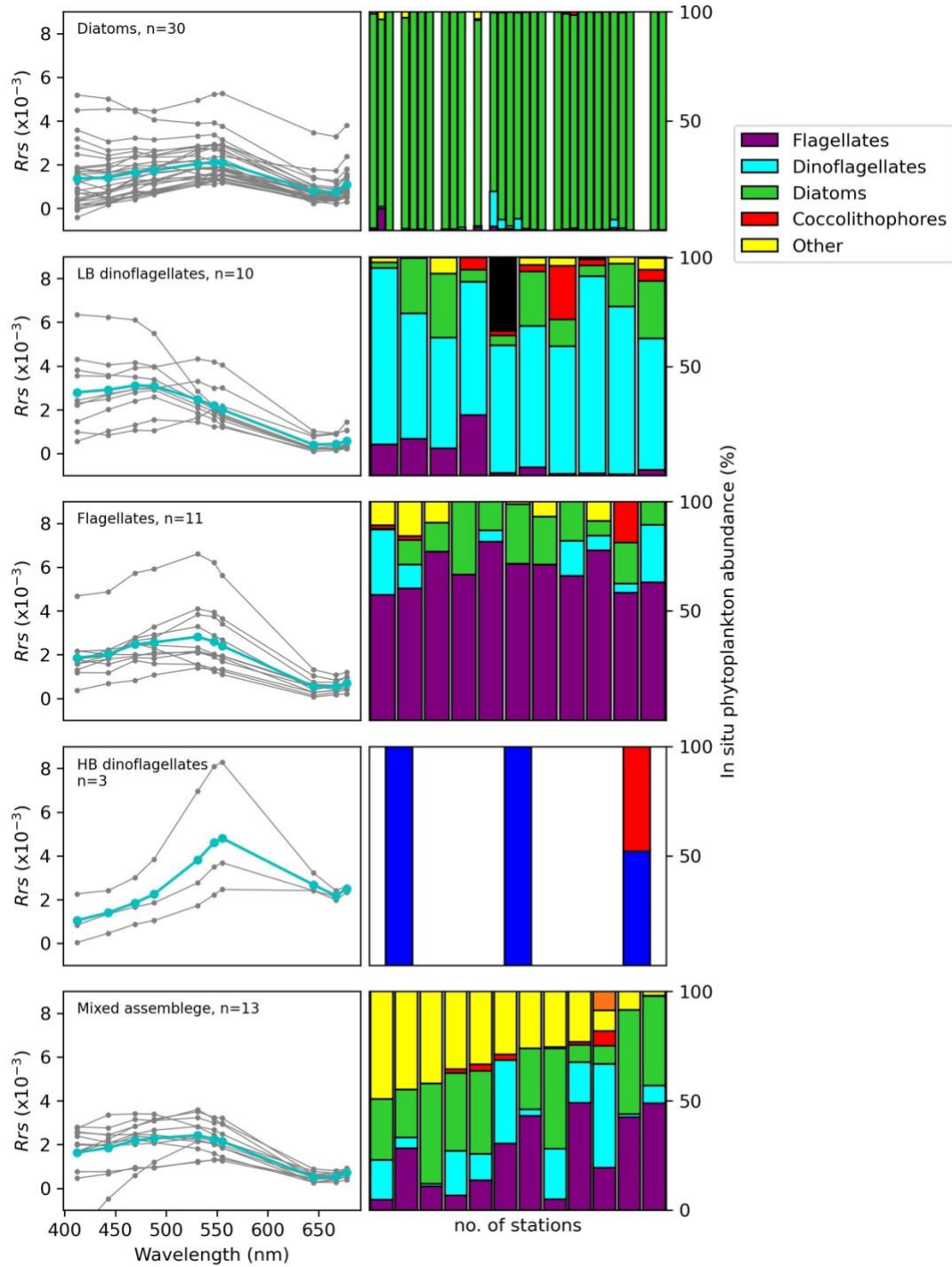


**Figure 3.4:** The Remote sensing spectral reflectance ( $Rrs$ ) in the visible range of the spectrum with wavebands at 412, 443, 469, 488, 531, 547, 555, 645, 667 and 678 for samples from the nBUS waters dominated by the phytoplankton groups (diatoms, flagellates, low (LB) and high (HB) biomass dinoflagellates and Mixed assemblage from the MODIS-Aqua satellite sensor are shown in the left panel. The cyan line indicates the mean  $Rrs$  at each spectral band and the number of matchups ( $n$ ) are indicated.

The coloured bars on the right panel represent the corresponding % phytoplankton community composition at each station per phytoplankton group. The colours refer to diatoms (green), LB dinoflagellates (turquoise), HB dinoflagellates (blue), flagellates (purple), coccolithophores (red), cryptophytes (orange), cyanobacteria (black) and other/unknown (yellow).

#### 3.4.2.2. Remote sensing reflectance spectral band-ratios

Multiple spectral band-ratios were investigated to identify optical signatures typical of waters dominated by the various phytoplankton groups under investigation. Boxplots of band-ratios were used to assign thresholds associated with the probability of dominance by each group based on the 25<sup>th</sup> and 75<sup>th</sup> percentiles of the datasets (Figure 3.5a-d). The *green/violet*, *blue/violet*, *violet/violet*, *blue/blue* and *red/violet* spectral band-ratios yielded no obvious unique spectral thresholds that may be assigned to dominance of any group as the data distribution (box plots) were within similar overlapping ranges (data not shown). However, characteristic dual spectral band-ratio thresholds were identified for *red/blue* ( $Rrs678/Rrs488$ ), *green/green* ( $Rrs547/Rrs531$ ), *red/red* ( $Rrs645/Rrs678$ ) and *green/blue* ( $Rrs555/Rrs488$ ) ratios that could describe a high probability for the presence of diatoms, LB dinoflagellates, HB dinoflagellates, flagellates and mixed communities. These differentiations are graphically represented in Figures 3.5a-d and the threshold values summarised in Table 3.3. The LB dinoflagellates had characteristically low *red/blue*, *green/green* and *green/blue* ratios, while diatoms occupied an intermediate *green/green* and *green/blue* band-ratios. The HB dinoflagellates had characteristically high *green/green*, *red/red* and *green/blue* band-ratios (Figures 3.5b-d blue shading). Although HB dinoflagellates typically had a higher *red/blue* ratio than diatoms they expressed a large overlap (Figure 3.5a teal shading). Flagellates overlapped the mixed assemblage in the *green/green* ratio (Figure 3.5b magenta shading) but occupied a relatively unique, yet narrow distribution band in the *red/blue* ratio (Figure 3.5a purple shading), while the mixed community had a distinct *red/red* band-ratio (Figure 3.5c orange shading).

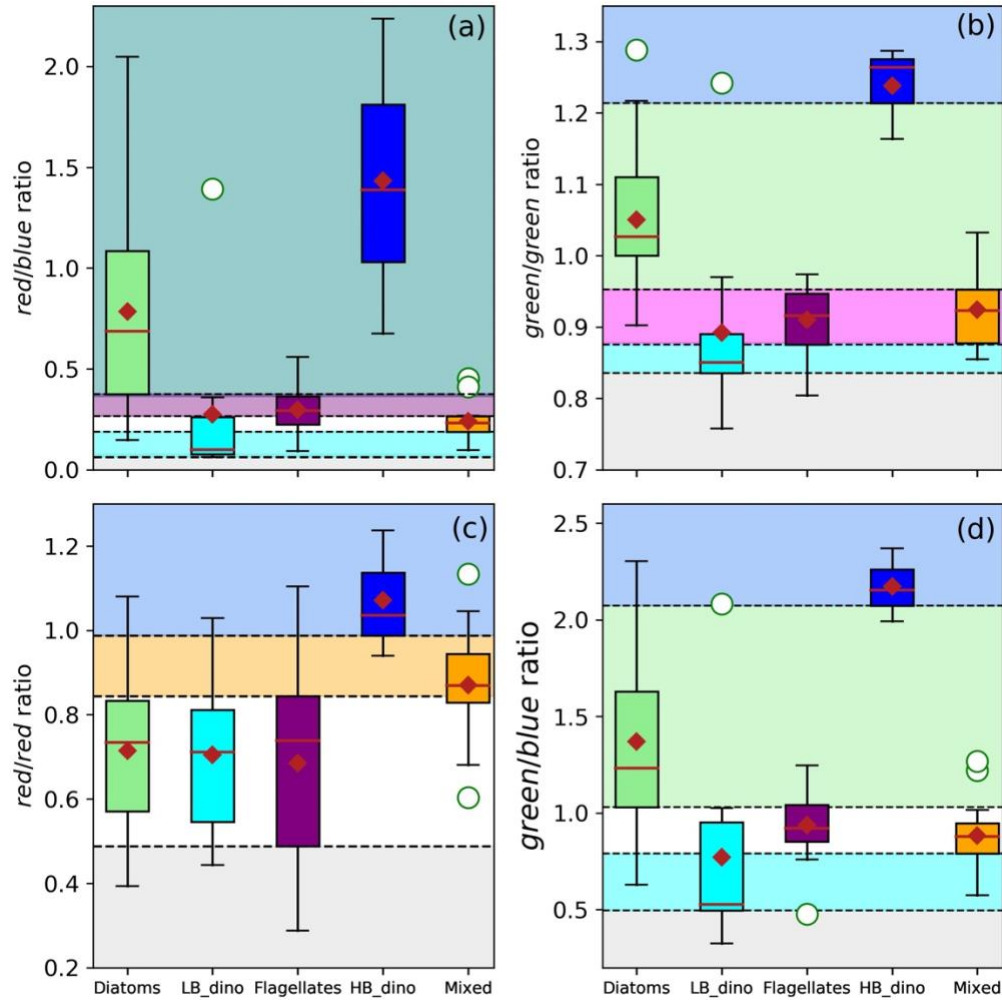


**Figure 3.5:** Boxplots of the dual-spectral band ratios for waters associated with dominance of diatoms, LB dinoflagellates (LB\_dino), flagellates, mixed community and HB dinoflagellates (HB\_dino). The thresholds of the *red/blue* ( $Rrs678/Rrs488$ ) (a), *green/green* ( $Rrs547/Rrs531$ ) (b), *red/red* ( $Rrs645/Rrs678$ ) (c) and (d) *green/blue* ( $Rrs555/Rrs488$ ) band-ratios are indicated by the dashed horizontal lines and colour shaded bands (light green = Diatoms; cyan = LB dinoflagellates, purple = Flagellates, blue = HB dinoflagellates, orange = Mixed, teal = Diatoms/HB dinoflagellates, magenta = Flagellates/Mixed). Statistical parameters such as the median, mean and outliers are indicated as the red line, red diamond and white circles respectively.

#### 3.4.2.3. Spectral band difference, RNR and [Chl-*a*]

The characteristic spectral band difference, RNR and [Chl-*a*] for detection of conditions associated with dominance of diatoms, LB dinoflagellates, HB dinoflagellates, flagellates and mixed communities were investigated and are graphically represented in Figure 3.6, with thresholds indicated. The threshold values

for spectral band difference are summarised in Table 3.3. Both diatom and HB dinoflagellate-dominated waters shared a characteristic of high nFLH (Figure 3.6a, grey shade), although diatoms displayed the highest nFLH by comparison. However, HB dinoflagellates had a higher RNR and [Chl-*a*] biomass and a lower line height at 531 nm (LH531) than diatoms (Figure 3.6b-d). Although generally having similar spectral features to other phytoplankton groups, the flagellate-dominated waters represent a discernible nFLH range between diatoms and dinoflagellates (Figure 3.6a, purple shade). Unlike their high biomass counterparts, the LB dinoflagellates had the lowest nFLH, RNR and were generally dominant in low [Chl-*a*] conditions (Figures 3.6a-c). The spectral band difference and Chl-*a* features of the mixed community showed no unique characteristics and were thus indistinguishable from other groups using these approaches. It should be noted that several line heights were calculated at various spectral wavelengths and were distributed similarly for all the groups (data not shown). Generally, variability in line height was observed in the green spectral regions (531, 547 and 555 nm) with a resolution between diatoms and HB dinoflagellates while the remaining groups showed no obvious line height thresholds unique to them. Important to note is that a final category was defined as “low *Rrs* signal”, where the *Rrs* signal was considered too low to confidently retrieve any discernible signal due to a low signal-to-noise ratio, these low *Rrs* criteria were defined by the lowest 25<sup>th</sup> percentile of the distribution of each *Rrs* variable and are summarised in Table 3.3.

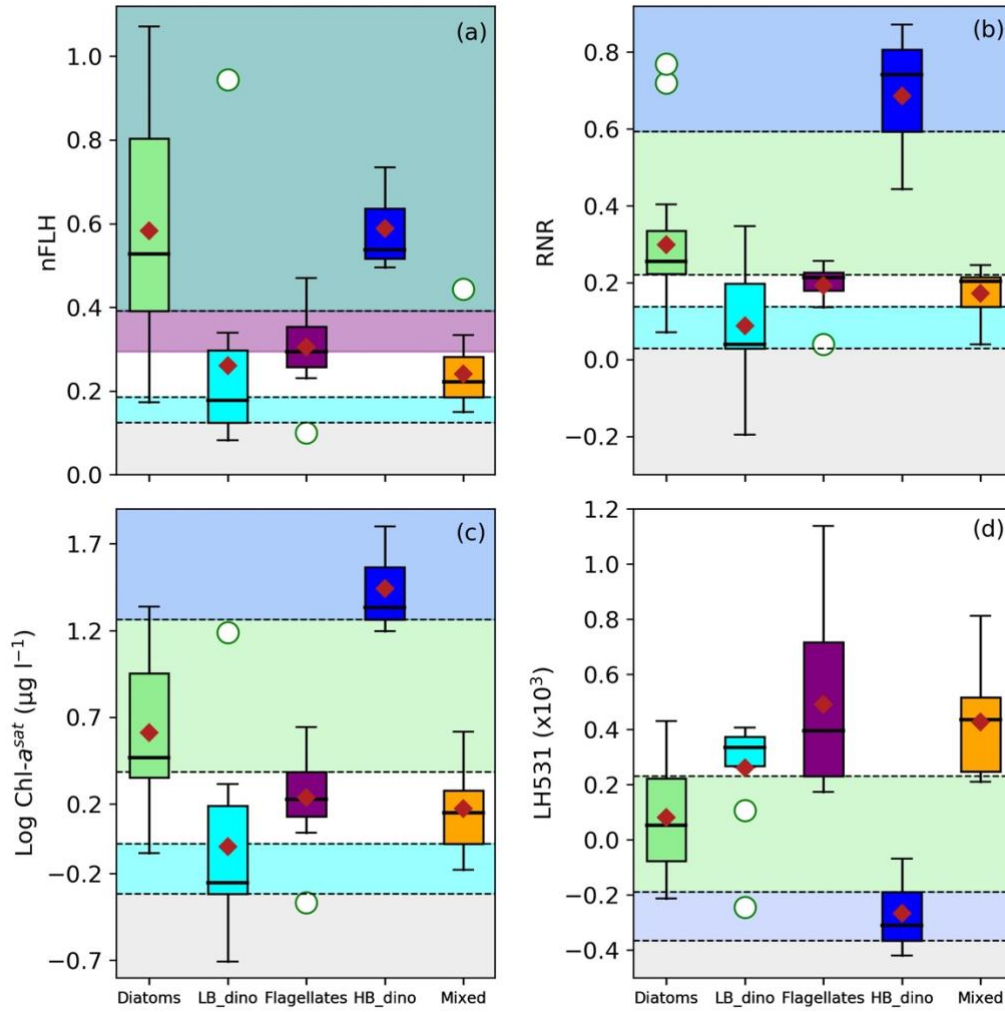


**Figure 3.6:** Boxplots of (a) nFLH, (b) RNR, (c) log-transformed [Chl-*a*] and (d) line height at 531 nm (LH531) for waters associated with dominance of Diatoms, LB dinoflagellates (LB\_dino), Flagellates, HB dinoflagellates (HB\_dino) and Mixed communities. The threshold ranges are indicated by the dotted horizontal lines and colour schemes (green = Diatoms; cyan = LB\_dino; purple = Flagellates; blue = HB\_dino; red = Mixed; grey scale = Diatoms/HB dinoflagellates). The median, mean and outliers are indicated as the bold black line, red diamond and white circles respectively.

**Table 3.3:** Summary of MODIS-Aqua spectral threshold characteristics for waters dominated by various phytoplankton groups in the nBUS.

| Phytoplankton group   | MODIS-Aqua remote sensing variables |                           |                       |                  |                          |                          |                    |                      |
|-----------------------|-------------------------------------|---------------------------|-----------------------|------------------|--------------------------|--------------------------|--------------------|----------------------|
|                       | Band-ratios                         |                           |                       |                  |                          | Spectral difference band |                    | Log [Chl- <i>a</i> ] |
|                       | Red: Blue<br>(488/678)              | Green: Green<br>(547/531) | Red: Red<br>(645/678) | RNR<br>(748/667) | Green: Blue<br>(555/488) | nFLH                     | LH531              |                      |
| Diatoms               | >0.363                              | >0.952<br><1.214          | -                     | >0.221<br><0.593 | >1.031<br><2.073         | >0.392                   | >-0.189<br>< 0.231 | >0.385<br>< 1.264    |
| LB dinoflagellates    | >0.064<br><0.189                    | >0.758<br><0.875          | -                     | >0.029<br><0.221 | >0.496<br><0.792         | >0.124<br><0.186         | -                  | >-0.030<br>< 0.189   |
| Flagellates           | >0.266<br><0.363                    | >0.875<br><0.952          | -                     | -                | -                        | >0.294<br><0.392         | -                  | -                    |
| Mixed community       | -                                   | >0.875<br><0.952          | >0.844<br><0.988      | -                | -                        | >0.186<br><0.294         | -                  | -                    |
| HB dinoflagellates    | >0.363                              | > 1.214                   | >0.988                | >0.593           | >2.073                   | >0.392                   | >-0.365<br><-0.189 | >1.264               |
| Low <i>Rrs</i> signal | <0.064                              | <0.758                    | -                     | <0.029           | <0.496                   | <0.124                   | <-0.365            | <-0.030              |

### 3.4.3. Algorithm development

Our approach to detecting phytoplankton community characteristics from space investigates statistical thresholds based on [Chl-*a*] biomass, dual band-ratios and spectral band differences to exploit small variations in the *Rrs* characteristics associated with dominance of specific phytoplankton groups. If the *Rrs* spectrum from a pixel is within a range defined by the threshold values for waters associated with the dominance of a particular phytoplankton group, then it is assigned to reflect the likelihood of that phytoplankton group being dominant. These thresholds are summarised in Table 3.3.

Given the identified thresholds for the various phytoplankton groups from the remote sensing variables indicated in Table 3.3, the next step was to determine the most suitable variables for algorithm development. To do this, the current study assesses 1) the algorithms' ability to confidently classify/distinguish multiple phytoplankton groups, 2) the characteristics of the linear relationship between the variables in Table 3.3 and [Chl-*a*], with the understanding that biomass is likely to influence the spectral characteristics of *Rrs* and 3) the range in [Chl-*a*] that is typical for each of the defined thresholds for the various phytoplankton groups, favouring variables that allow for the classification of a number of phytoplankton groups within a similar range of [Chl-*a*]. While some algorithms are suitable for detection of specific phytoplankton groups during high biomass blooms, this study embarks on developing an algorithm that is suitable for the detection of dominant groups even in low [Chl-*a*] (non-bloom) conditions. To assist with the assessment of these criteria, the linear relationship between the *Rrs* variables and [Chl-*a*] (Figure 3.7) is examined. Each of the three criteria is presented in detail below:

### 1) Can the *Rrs* variable confidently distinguish multiple PFTs?

In Figure 3.7a, the *red/blue* ratio defining flagellates and LB dinos are tightly clustered together with a low range of variability in the optical identifier making it difficult to distinguish them from each other. In addition, there was overlap in the range of diatoms and HB dinos. In Figure 3.7e, although more broad, it is clear that the majority of PFTs share a similar range of variability in the *red/red* ratio hampering an ability to identify the majority of PFTs.

### 2) Is variability in the *Rrs* signal biomass dependent?

A strong positive linear relationship and slope close to 1 was observed between [Chl-*a*] and the *red/blue* ( $R^2 = 0.721$ , slope = 0.784) and *green/blue* band-ratios ( $R^2 = 0.947$ , slope = 0.958) (Figures 3.7a and 3.7b respectively), suggesting that these optical signals were, for the most part, biomass-driven. This is not surprising as the global ocean colour remote sensing algorithms for [Chl-*a*] retrieval from the MODIS-Aqua are based on the ratio of the red, blue and green spectral bands. Using biomass as a criteria (or any other variable that is strongly dictated by biomass) constrains the algorithm's ability to detect a particular phytoplankton group outside of the assigned biomass range. This is highlighted by the absence of any overlap (i.e., vertical stacking) of the PFT boxes defined by the *green/blue* ratio in Figure 3.7b.

### 3) Is there overlap in the range of [Chl-*a*] for different PFTs?

Although the *green/green* band-ratio (Figure 3.7c) showed a similar positive linear relationship with [Chl-*a*] ( $R^2 = 0.784$ ), it had a much lower slope (slope = 0.207), while nFLH and RNR both displayed weak linear relationships and lower slopes ( $R^2 = 0.455$ , slope = 0.364, Figure 3.7d and  $R^2 = 0.415$ , slope = 0.236,

Figures 3.7f). When the slope is more gradual (i.e., Figure 3.7 c, d and f), the range in [Chl-*a*] encompassed for each *Rrs* identifier is broader. Moreover, for these optical signatures, there is a larger range of variability evident in the *Rrs* identifiers for a similar range in [Chl-*a*] concentration. This is highlighted by the overlap in [Chl-*a*] among the groups but with varying *Rrs* signatures (i.e., the vertical stacking of PFT boxes across a similar range of [Chl-*a*]).

Given the above, the red/blue (Figure 3.7a), green/blue (Figure 3.7b), and red/red (Figure 3.7e) band-ratios were not considered further and eliminated as viable variables for further algorithm formulation. On the other hand, nFLH and the *green/green* band-ratio were considered the most suitable candidates for further development of the phytoplankton PFT algorithm. In addition, the RNR spectral band-ratio was also considered, in particular as a means of discriminating dinoflagellates from diatoms under high biomass conditions (i.e., when [Chl-*a*] > 8 mg m<sup>-3</sup>).

Unsurprisingly, there are overlaps in some optical signatures of different phytoplankton groups. For instance, both diatoms and HB dinoflagellates have an overlapping nFLH range (0.392) (Figure 3.7a turquoise shading) and both flagellates and mixed communities share a similar range in the *green/green* ratio (Figure 3.7b pink shading). However, they have other unique signatures that allow a combination of criteria to be used to separate them out. For example, in the case of diatoms and HB dinoflagellates the *green/green* and RNR band-ratios are used to distinguish the two groups (Figure 3.8a). That is, if nFLH is >0.392 then that pixel can be classified as either a diatom or a HB dinoflagellate. However, if the RNR is >0.593 and the *green/green* ratio is >1.214 then that pixel is more likely to be dominated by HB dinoflagellates and as such is assigned that category. However, if the *green/green* ratio is <1.214 and the RNR is <0.593 then it is more likely a diatom and is assigned as such within the given nFLH range. The use of combined algorithms of spectral characteristics increases the robustness of the algorithm, while at the same time allowing groups to be detected across a broad range of [Chl-*a*]. For example, diatoms can be detected across the full range of their *green/green* and nFLH criteria, so long as the RNR is not high, in which case it is assigned to HB dinoflagellates.

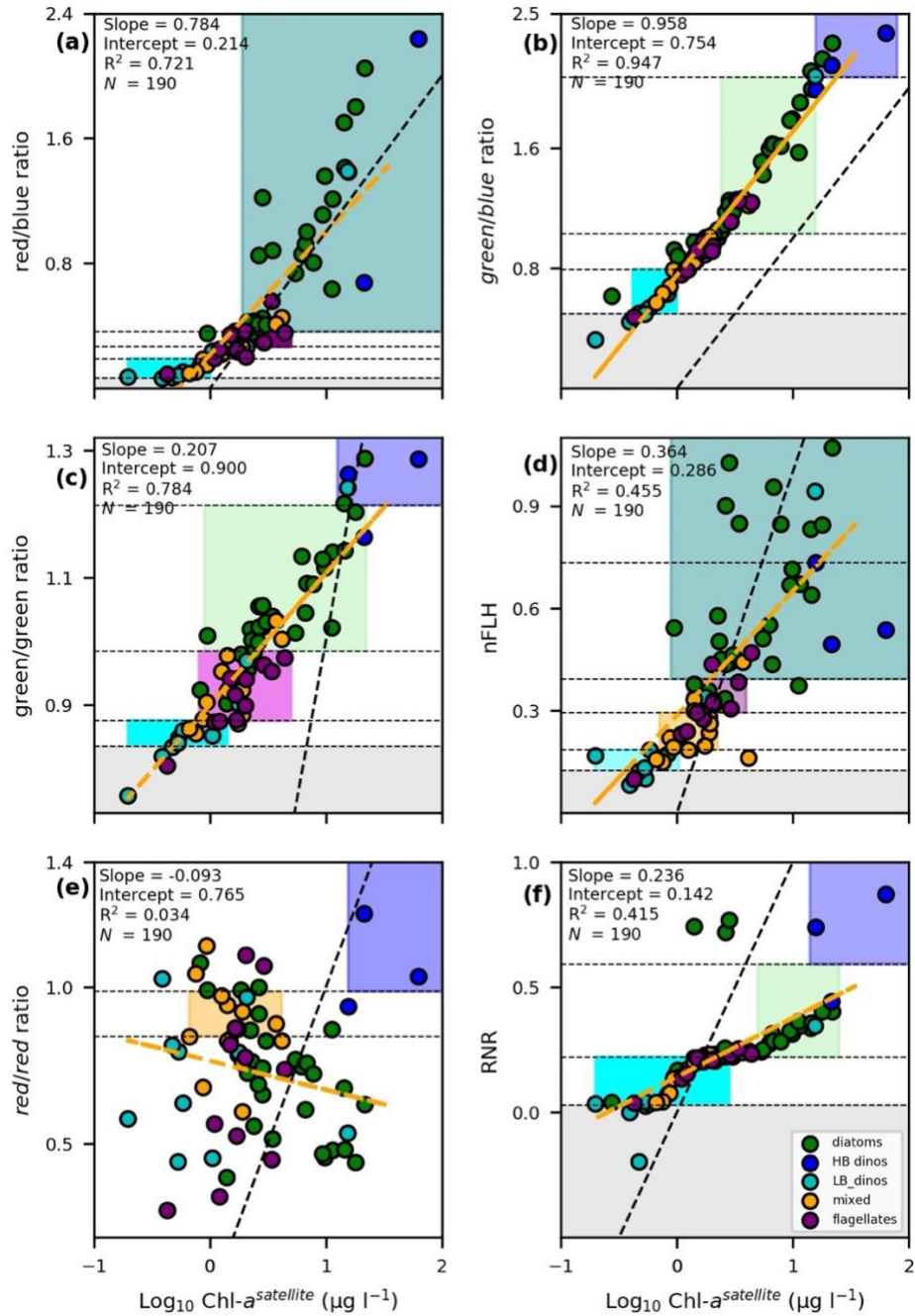


**Figure 3.7:** Linear regression analysis between Chl-*a* against the (a) red/blue, (b) green/blue, (c) green/green, (d) nFLH, (e) red/red and (f) RNR band-ratio, algorithms, [Chl-*a*] data was log-transformed prior to analysis. The linear regression is shown by the dashed orange line. The black dotted line represents the theoretical 1:1 relationship. The coefficient of determination ( $R^2$ ), slope, intercepts and number of samples ( $N$ ) are indicated. The samples representing dominance by diatoms, LB dinoflagellates (LB\_dino), HB dinoflagellates (HB\_dino), flagellates and mixed communities are indicated as green, cyan, blue, purple

and orange dots respectively. The shaded areas denote the unique spectral characteristic thresholds for each group (green = diatoms, cyan = LB dinoflagellates, orange = mixed, purple = flagellates, blue = HB dinoflagellates, magenta = mixed/flagellates, grey = diatoms/HB dinoflagellates).

Similarly, in the case of flagellates and mixed communities, despite an overlap in their *green/green* ratio, they could be distinguished from each other based on the unique statistical signature within their nFLH distribution (Figure 3.8b). That is, a pixel with a *green/green* band-ratio between 0.875 and 0.952 could be classified as either flagellate-dominated or a mixed community. However, if the nFLH is between 0.294 and 0.392 then it would be assigned to reflect flagellate dominance, whereas if the nFLH is between 0.186 and 0.294 it would reflect a mixed community. LB dinoflagellates on the other hand have a distinct *green/green* band-ratio and nFLH threshold, and unlike diatoms, HB dinoflagellates, flagellates and mixed community, were distinguished using individual thresholds of the *green/green* band-ratio and nFLH for their detection. Pixels are regarded as ‘other/unknown’ phytoplankton when no algorithm threshold criteria is met. A flowchart of the algorithm decision making tree (application) for discrimination and classification of the various phytoplankton groups in the nBUS is as shown in Figure 3.9 below.

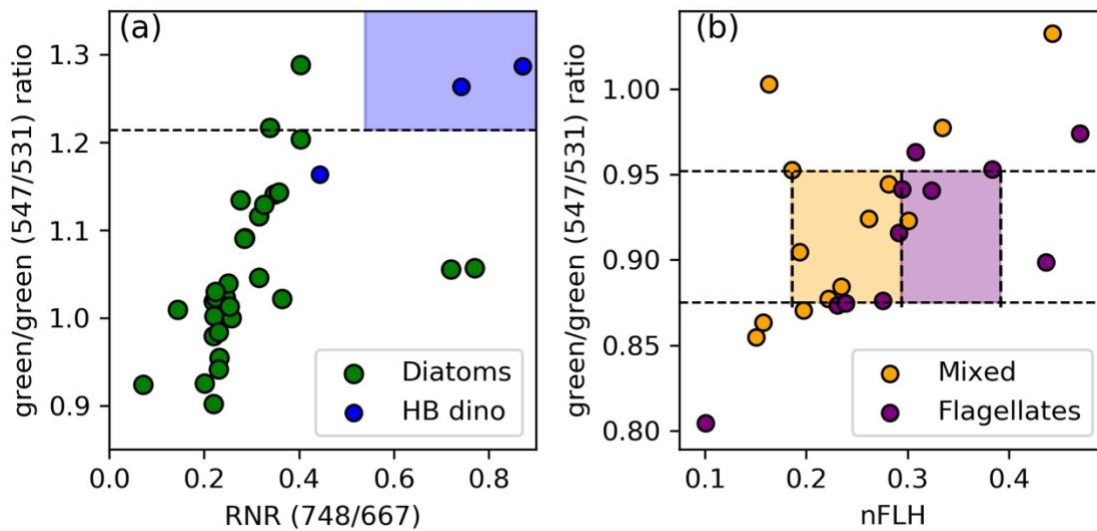


**Figure 3.8: a)** Discrimination of diatom from HB dinoflagellate blooms based on differences in their RNR signals given their shared high *green/green* ( $>1.214$ ) band-ratio and nFLH ( $>0.392$ ) spectral characteristics. **B)** The flagellates and mixed communities are distinguished based on their nFLH spectral characteristics given their similarities in their *green/green* characteristics. The blue, orange and purple colour shadings indicate the spectral characteristics unique to HB dinoflagellates, mixed community and flagellates respectively.

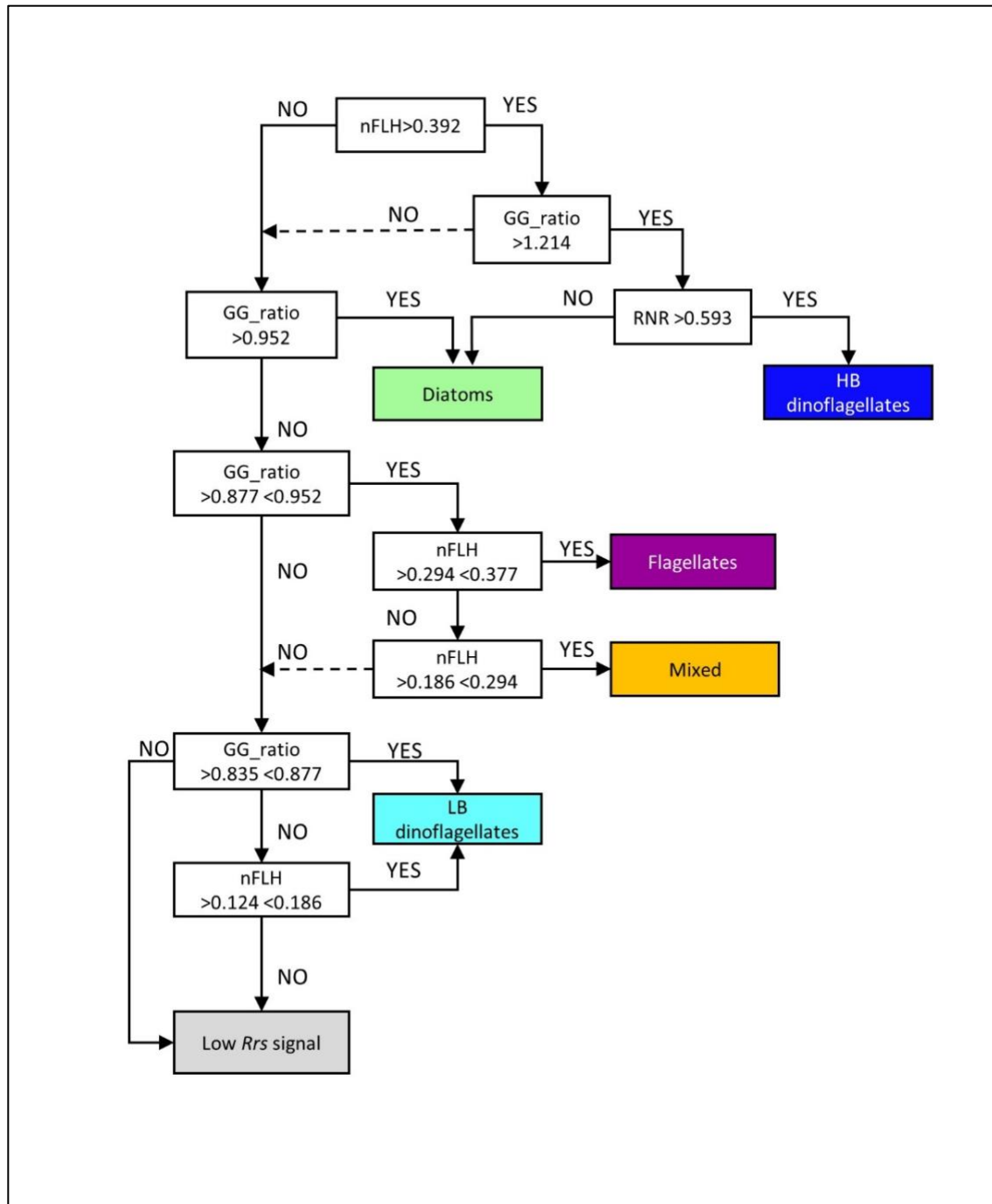


**Figure 3.9:** Schematic diagram showing the decision-making tree for classification of the various phytoplankton groups in the nBUS. The green/green (*Rrs547/Rrs531*) ratio (GG\_ratio), nFLH and RNR thresholds for each group are indicated.

#### 3.4.4. Algorithm validation

The algorithm was tested for accuracy and compared against randomly selected independent *in situ* datasets for diatoms. Unfortunately, this was only possible to do with diatoms, as this was the only phytoplankton group that dominated at enough stations to allow partitioning of the datasets into testing and validation groups. All other groups had so few stations in which they dominated that all had to be used to derive the most robust algorithm possible. The diatom validation was achieved by comparing observations with predictions (considered when *in situ* validation dataset's *Rrs* spectra fell within the algorithm detection thresholds). It should be noted that diatom dominance of validation datasets were similarly defined using the same criteria used to define diatom dominance for training datasets. A total of 7 datasets were used for validation of the diatom detection component of the algorithm for the nBUS. The quantitative validation results for diatoms, calculated as overall accuracy of the algorithm, was calculated as follows:

$$\text{Algorithm accuracy} = \frac{C_c}{T_c} \times 100\% \quad (5)$$

where  $C_c$  is the correct classifications and  $T_c$  is the total classification from the independent diatom dominance datasets not used in the algorithm training datasets.

The optical characteristics of the validation data for stations dominated by diatoms are compared against the algorithm thresholds and our algorithm compared well with the independent *in situ* observations of diatom dominance. Of the 7 stations, 5 matched with algorithm thresholds (i.e., were correctly classified by the algorithm). This translates to a percentage accuracy of 71.429 %. The validation results demonstrate the algorithm's ability to translate MODIS-Aqua *Rrs* observations to distributions of phytoplankton communities in the nBUS. The diatom-dominated stations that were not correctly classified had lower *green/green* and nFLH values that were below our algorithm's minimum detection thresholds. In addition, they occurred in waters with low [Chl-*a*] that were between 1-2  $\mu\text{g l}^{-1}$ . However, the method was able to correctly classify 3 stations of diatoms within the same [Chl-*a*] range based on their *Rrs* characteristics.

Although there were insufficient *in situ* HB dinoflagellate dominated station data to validate the algorithm, it was still possible to demonstrate its ability to detect a known dinoflagellate bloom identified in the southern Namaqua Benguela upwelling system 3.5km from Lambert's Bay (Cape Town, South Africa) in the sBUS (Fawcett *et al.*, 2007) (Figure 3.10).

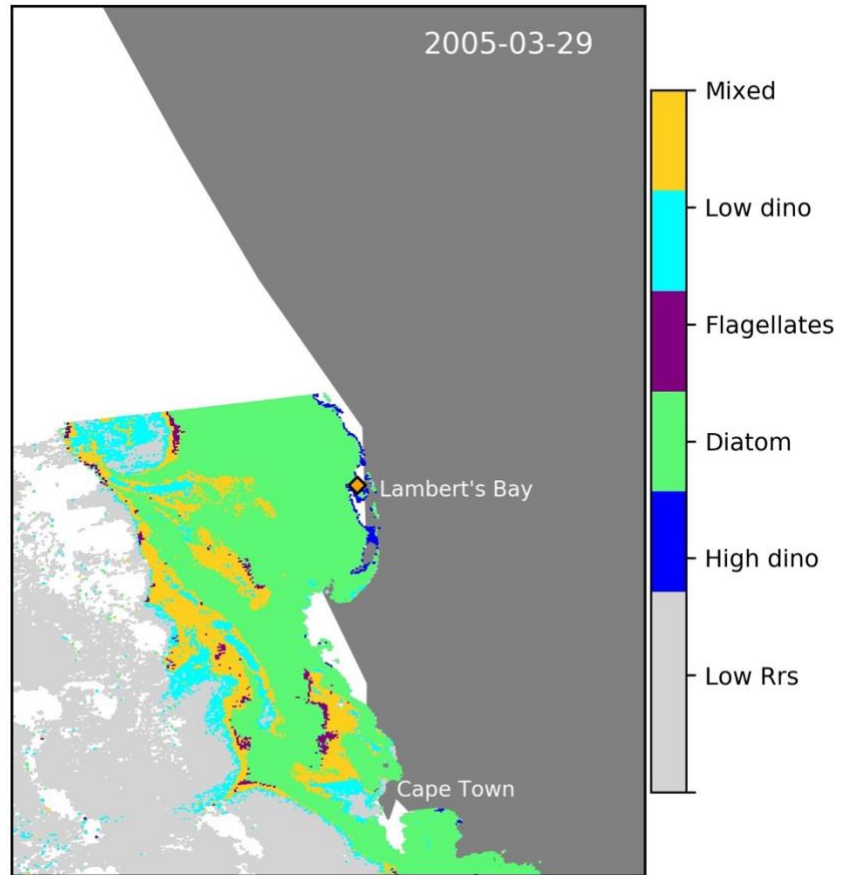


**Figure 3.10:** Evidence of the algorithm’s ability to detect a known harmful dinoflagellate bloom in the sBUS (Fawcett *et al.*, 2007). The sampled coastal station in Lambert’s Bay is indicated by the orange diamond.

### 3.5. Discussion

Forming the base of marine food webs, phytoplankton are key ecological role players in upwelling systems and the global ocean. Knowledge of their composition and their regional, seasonal and interannual distribution and trends is key to understanding possible climate-linked ecosystem changes with implications on ecosystem health, economy, food security and climate response. Satellite remote sensing is one of the only tools that can provide the spatial, temporal and multi-decadal data information on phytoplankton needed to adequately investigate their important role in ecosystem function. Thus, there is a need for ocean colour remote sensing algorithms that can discriminate between phytoplankton functional types. Discrimination between diatoms and dinoflagellates is particularly relevant to ecology, local aquaculture and recreational activities as some of the bloom-forming and toxin-producing species belonging to these groups have been reported in the nBUS (Dijerenge, 2015; Louw *et al.*, 2017; Gai *et al.*, 2018), which may be harmful to both marine life and humans. Substantial work has been done using ocean colour algorithms and modelling techniques to detect phytoplankton community structure in the southern Benguela (Bernard *et al.*, 2005; Aiken *et al.*, 2007; Evers-king, 2014; Smith and Bernard, 2020), but none as yet for the nBUS. This study is the first to derive an ocean colour remote sensing algorithm for the nBUS using a large compiled *in situ* microscopy dataset with satellite match-ups for detection and mapping of the most frequently encountered phytoplankton groups.

#### 3.5.1. Determining the most appropriate satellite sensor for algorithm development

The first step in this endeavour was to determine which satellite product to use based on the availability of spectral bands in the red and near infrared regions. This decision was approached by comparing the two available ocean colour remote sensing algorithms of [Chl-*a*] to *in situ* measurements in order to test how well they performed in the high biomass coastal waters of the nBUS. MODIS-Aqua provided more data near the 1:1 ratio than MERIS/OLCI, suggesting a good approximation of *in situ* Chl-*a* (Figure 3.3f). Although MERIS/OLCI had a higher slope (0.766) than MODIS-Aqua (0.547), it contained more statistical errors (MRD, MAE, RMSE, MARD) against *in situ* Chl-*a* than MODIS-Aqua (as summarised in Table 3.2). It should be noted that fluorometry-derived [Chl-*a*] may be biased towards higher concentrations when compared to high-performance liquid chromatography (HPLC), particularly in the presence of chlorophyll-*c* (Chl-*c*) due to potential overlap in emission spectra (Moutier *et al.*, 2019). It should however be noted that the [Chl-*a*] datasets used in the current study were measured using the non-acidification technique (Welschmeyer, 1994), which minimizes the fluorescence effects of Chl-*c*, chlorophyll-*b* (Chl-*b*) and phaeopigments while optimizing the sensitivity of [Chl-*a*]. Although both products performed admirably, the MODIS-Aqua sensor observations cover a larger temporal scale when compared to the now discontinued MERIS and recent OLCI satellite sensors, which allows for a much longer analysis of trend

detection in the nBUS, particularly for the period between 2012-2015 where there is a data gap during the transition from MERIS to OLCI sensors. The MODIS-Aqua product was thus selected for algorithm development and further investigations of optical fingerprints of the dominant phytoplankton taxonomic groups in the northern BUS. Although the MODIS-aqua ocean colour retrieval of Chl-*a* was determined to be statistically less erroneous than MERIS/OLCI for the nBUS, it should be noted that this step in our approach was not intended as a sensor validation study, which would instead involve the use of *in situ* radiometric reflectance measurements compared against concurrent satellite observations and is considered outside of the scope of this study.

The three most prominent drivers of variability between *in situ* and satellite derived [Chl-*a*] likely reflect the impact of atmospheric correction, different approaches to measuring *in situ* [Chl-*a*] and averaging across space and time. Atmospheric correction measures are necessary to overcome interference from atmospheric variables (e.g., aerosols, dust, clouds, scattered light etc.). The nBUS experiences dynamic annual, seasonal, and event scale atmospheric influences from terrestrial aerosol sources of dust plumes from the Namib desert (Shikwambana and Kganyago, 2022), intense fog (Spirig *et al.*, 2017) as well as coastal sulfur eruptions (Ohde and Dadou, 2018), which may interfere with accurate atmospheric correction, and subsequent Chl-*a* retrievals from satellite-derived reflectance adding to regular ocean-atmosphere contributions from moisture and aerosols (e.g., sea spray) (Mayer *et al.*, 2020). Additionally, discrepancies between [Chl-*a*] derived from fluorometry versus HPLC can impact the performance of the satellite algorithm. These discrepancies are likely to be region or season specific as they depend on the constituent pigments in the water that are in turn dictated by phytoplankton community dominance which varies both regionally and temporally. Another possible source of error is the scale difference between *in situ* sampling and match-up retrievals. The match-ups in the current study are derived from multi-pixel boxes which cover a spatial range of 13 – 25 km<sup>2</sup>. Ship-board measurements on the other hand are based on sampling 0.1 – 2 L of seawater from a specific latitude-longitude location. Given the small-scale spatial heterogeneity or patchiness of phytoplankton abundance in the ocean (Pei *et al.*, 2017; Scheinin and Asmala, 2020), averaging [Chl-*a*] over a multi-pixel box may produce discrepancies between measured and satellite derived [Chl-*a*]. Efforts are made to minimise the effects of this error by exclusion of multi-pixel boxes with mean values that have a coefficient of variation (CV) greater than 0.15 (Bailey and Werdell, 2006). Finally, it was challenging to obtain large numbers of match-ups in time and space in the relatively data-poor region of the nBUS. Although matchups within 12 hours of sampling were initially prioritised to minimise temporal discrepancies, the subsequent small number of match up stations that passed quality control (n=73) meant that the time window constraint had to be relaxed to 24 hours, which increased the database to n=190. A comparison of the relationships generated by the two data sets against *in situ* [Chl-*a*] (i.e., n=73

and  $n = 190$ ) showed differences in the statistical relationships (i.e., slopes degraded from 0.632 to 0.478 respectively, while the correlation coefficients similarly reduced from 0.744 to 0.578, but still remained comparable). It is possible that the above-mentioned variables, either in combination or on their own, as well as other factors not mentioned here, may have contributed to the observed discrepancies between satellite retrievals and *in situ* measurements of [Chl-*a*].

### 3.5.2. Phytoplankton optical fingerprints

Differences were observed in the *Rrs* spectral characteristics of waters dominated by different phytoplankton groups. These differences in optical characteristics can be attributed to differences in cellular pigment composition (and content), morphology, size and abundance (Vaillancourt *et al.*, 2004; Mao *et al.*, 2010). The size and pigment differences of various phytoplankton taxa in the nBUS have been shown previously (Hansen *et al.*, 2014; Barlow *et al.*, 2018). For example, Hansen *et al.* (2014) highlighted differences in water masses associated with different phytoplankton taxa and abundance at different upwelling stages from MODIS-aqua as testament to variability in *Rrs* (at 412 nm, 554 nm and 665 nm). Although differences in optical signatures can be exploited from space to distinguish different phytoplankton groups, there nonetheless remains the potential for overlap between different species that may occupy a similar size distribution and/or pigment content, and/or range of abundance. Optical indices from *Rrs* characteristics are complicated further by the complex interplay between the effects of cell size and abundance. For example, optical model simulations show that higher cell counts increase absorption and backscatter coefficients in smaller sized cells whereas these signals decrease with increasing cell size and lower cell abundance (Laiolo *et al.*, 2021). Furthermore, the pigment packaging effect (a reduction in light absorption from high intracellular [Chl-*a*], particularly in the blue wavelengths) increases with increasing cell size being more pronounced in larger cells ( $>10\ \mu\text{m}$ ) such as diatoms (Soja-wozniak *et al.*, 2020; Laiolo *et al.*, 2021). The observed optical signatures that are assigned in this study to different phytoplankton groups are generated from a net effect of the optical impacts from the communities' dominant size structure, pigment composition and biomass at which any one group commonly occurs. Regardless of the complexity of the inter-relationships between the multiple drivers of *Rrs* characteristics, our optical proxy accumulates these signals to statistically discern the band-ratio ranges typical of each group that may subsequently be used to identify them. In light of this, the band-ratios, RNR and nFLH fluorescence signals can still be recognized as effective signals for characterizing the presence of different phytoplankton groups. A purely abundance-based approach on the other hand makes the assumption that different species dominate at different typical biomass thresholds, and as such, is not able to distinguish between phytoplankton blooms of two different species with a similar abundance (Uitz *et al.*, 2006; Hirata *et al.*, 2011). Although four approaches were explored to derive optical fingerprints for the different

PFGs, the final algorithm used a combination of only 2 approaches: (1) the band-ratios (*green/green* and RNR) and (2) the spectral band difference approach (nFLH). The use of individual *Rrs* at different spectral bands and abundance-based approaches were excluded from the final algorithm. This multi-layered ocean colour remote sensing algorithm for PFG detection in the nBUS increases the robustness of the algorithm in that a pixel typically has to meet at least two criteria between the *green/green*, RNR and nFLH before it is assigned as either a diatom, dinoflagellate, flagellate or mixed community.

Band-ratio algorithms, particularly in the blue-green spectral bands, are typically designed for global applications over optically deep ocean waters for Chl-*a* retrievals (O'Reilly *et al.*, 2000). In coastal waters, optically active non-phytoplankton materials such as coloured dissolved organic matter (CDOM) are capable of light absorption in the blue and violet spectral regions in particular (Morel *et al.*, 2010; Coble, 2013). Their absorption in the blue spectral region typically dominates that of phytoplankton in estuarine and coastal areas (D'Sa and Kim, 2017; Isada *et al.*, 2021). As such, the blue-violet region of the *Rrs* spectra is likely to have a larger error associated with it that may undermine the ability to capture phytoplankton-driven characteristics. To overcome this limitation, spectral bands in the red-NIR (i.e., nFLH and RNR) and green (i.e., *green/green*) regions were used instead for phytoplankton group classification in the nBUS. Similarly, although the nFLH signal could also be influenced by CDOM, the absorption of CDOM in the red-NIR is very low and its influence on nFLH is considered negligible, making nFLH and other algorithms utilizing the red-NIR spectral bands ideal candidates for phytoplankton bloom detection and classification in optically complex coastal waters such as the dynamic nBUS. Such algorithms (i.e., those utilising the *Rrs*665/*Rrs*709 band-ratio) have previously been successfully developed, validated and applied in the sBUS for phytoplankton bloom detection (Bernard *et al.*, 2005). Smith and Bernard (2020) later discriminated HABs of diatoms from dinoflagellates using the maximum line height approach (MLH), a spectral band difference algorithm analogous to nFLH which computes the MLH between two line heights calculated at *Rrs*681 and *Rrs*709 spectral bands, coupled with the line height ratio (ratio of line heights calculated at 681 and 709 nm). In the current study, a similar approach (i.e., the use of products with spectral bands in the red and near infrared spectral regions) was adopted, but for different satellite products (i.e., nFLH) and used in combination with a *green/green* spectral band-ratio and thresholds that best suited the unique spectral characteristics of the resident phytoplankton communities in the nBUS.

It is recognized that the ability to distinguish different phytoplankton groups may be hampered by pixel averaging when their distribution is spatially heterogeneous (e.g., at the transition between inshore and offshore communities (e.g., Barlow *et al.*, 2018)). The 5x5 pixel match-up box centered around the *in situ* station in the current study spans an area of between 16 – 25 km<sup>2</sup>. It is thus possible that individual pixels

may be dominated by different groups, which can introduce errors in community identification when averaging across a 5x5 pixel box. As a precaution to minimize this effect, the standard deviation was used to identify boxes that express high variability and exclude them from further analysis.

### 3.5.3. Algorithm application

Using the algorithm as depicted in Figure S3.3 in Annexure I, the *green/green*, RNR band-ratios as well as nFLH data are translated from the MODIS-Aqua according to the thresholds listed in Table 3.3 to an example map of the distribution of the phytoplankton community in the nBUS for 28 April 2009 (Figure 3.11). From these maps (Figures 3.10b-d) it is clear how the spatial distribution of particular *Rrs* characteristics can be used to identify the phytoplankton groups. Diatoms were the most spatially abundant group, which is typical of high biomass inshore waters of the Benguela (Matlakala, 2019). Bloom conditions (Figure 3.11a; [Chl-*a*] > 2 ug l<sup>-1</sup>) were typically encountered inshore with a filament extending offshore at 22 °S. These blooms were primarily dominated by diatoms, which are the most frequently observed blooms in the nBUS (Hansen *et al.*, 2014; Louw *et al.*, 2017; Matlakala, 2019). Diatoms were easily distinguished from their high nFLH and high green/green ratios (Figure 3.11b and c, respectively). Dinoflagellates typically dominated in low [Chl-*a*] conditions and were generally distributed further offshore (>140 km from shore), where the waters are typically warmer and nutrient-limited (Mohrholz *et al.*, 2014). This is consistent with the literature (Hansen *et al.*, 2014; Wasmund *et al.*, 2014; Matlakala, 2019) and provides further confidence in the algorithm's abilities. Dinoflagellates were also evident in low [Chl-*a*] waters closer to shore (north of 22 °S latitude) near the A-B front, where the shelf is narrower and there is typically evidence of a warm water intrusion from the Angola current (Hutchings *et al.*, 2009; Rouault *et al.*, 2018). There was however some evidence of HB dinoflagellates within the inshore high [Chl-*a*] bloom, which have been observed to occur inshore typically in winter (Dijerenge, 2015; Matlakala, 2019). These dinoflagellate blooms are readily distinguished from diatoms by their characteristically high RNR signature (Figure 3.11d). Large patches of spatially cohesive flagellates were evident typically offshore (notably at ~23 °S and 25 °S) and identified by their unique green/green and nFLH combination. The most common flagellates identified in the Benguela are nanoflagellates, most commonly observed in the mid-shelf region and further offshore in the Namibian upwelling system (Barlow *et al.*, 2018; Hansen *et al.*, 2014), which agrees with our algorithm's predictions of the spatial distribution of this group from the example map. Very low [Chl-*a*] waters were coincident with extremely low values of nFLH, green/green and RNR and characterized as waters with an *Rrs* signal too low to confidently identify any phytoplankton group. Of note is that despite a clear [Chl-*a*] gradient (i.e., a typical decrease in biomass from inshore to offshore, Figure 3.11a), there is evidence of the algorithm being able to classify diatom, dinoflagellate and flagellate dominated communities as well as mixed community assemblages in both low and high [Chl-*a*]

conditions (Figures 3.10a and e). From this example image it is clear how the high spatial and temporal coverage of satellite remote sensing can be harnessed to our advantage to better understand the dynamics, distribution, phenology and trends in phytoplankton community composition.

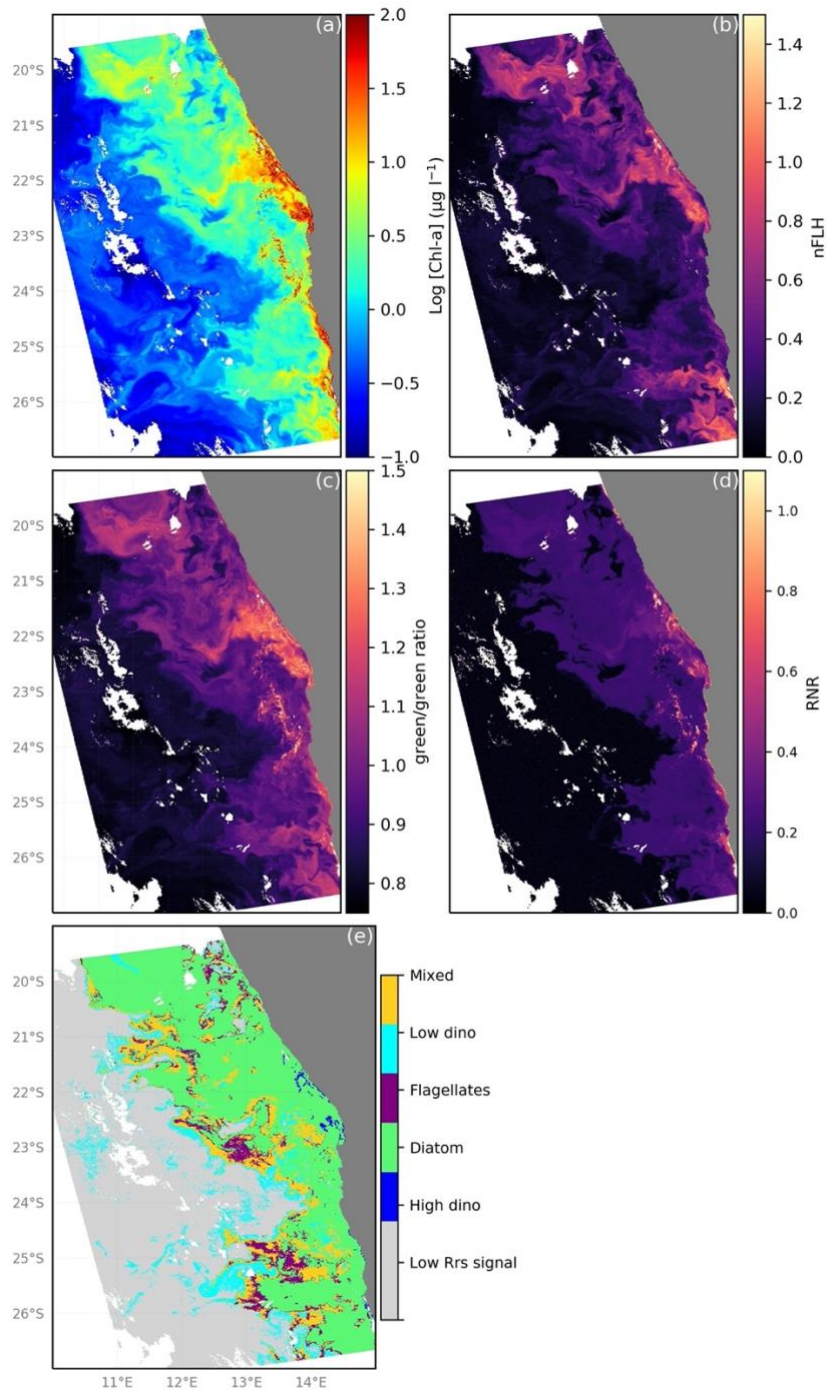


**Figure 3.11:** Demonstration of phytoplankton group dominance classification by the proposed ocean colour remote sensing algorithm for phytoplankton community from MODIS-Aqua observations for 11 March

2019 in the nBUS. (a) [Chl-*a*] distribution, (b) The observed nFLH, (c) green/green (*Rrs*547/*Rrs*531) band-ratio, (d) red/near-infrared (*Rrs*748/*Rrs*667) band-ratio and I application of the algorithm indicating the distribution of dominant phytoplankton groups in the nBUS.

### 3.5.4. Recognising algorithm limitations

#### 3.5.4.1. Use of microscopy data

*In situ* phytoplankton data is a prerequisite for ocean colour algorithm development and validation for satellite remote sensing of phytoplankton from space. Inaccurate or incomplete *in situ* data undermines our ability to correctly associate optical signatures to cells that aren't identified and may therefore lead to erroneous assignment of optical signatures to other phytoplankton groups, making accurate *in situ* measurements a scientific priority for increasing the accuracy and confidence of remote sensing and model development. Techniques such as microscopy are traditionally used in field observations for phytoplankton enumeration and taxonomic identification, providing valuable information for studying the diversity of phytoplankton taxa for assessing ecosystem health and balance, environmental monitoring and conservation, climatology and aiding aquaculture and fisheries industries with HABs detection among others (Anderson and Throndsen, 2004). Microscopic cell count techniques are particularly useful in that they provide identification of cells to species level. Although phytoplankton community information can be derived from these techniques, they have their limitations. For instance, analysis is dependent on highly trained and skilled people with thorough taxonomic expertise; these methods can be expensive, labour-intensive, time consuming, and may produce low precision unless a very large number of cells are counted (Anderson and Throndsen, 2004). Differential preservation of cells can lead to preferential cell loss and can thus introduce bias to sample classification (Williams *et al.*, 2016). The use of preservatives greatly affects the observed community composition depending on which preservative is used [e.g., Lugol's solution (either acidic or neutral) or formalin)] and for how long the samples were stored prior to analysis (Williams *et al.*, 2016). For instance, armored dinoflagellates are well preserved in all types of Lugols for up to 8 months whereas unarmored dinoflagellates are only well preserved in acid Lugols for the same period. Microflagellates and diatoms are well preserved in acid Lugols (3 months and ~4 months respectively), while diatoms can also be stored in neutral Lugols (up to 2 months). Coccolithophores on the other hand are poorly preserved in acid Lugols and instead require neutral Lugols (2 weeks) (Williams *et al.*, 2016). Phytoplankton samples from cruise campaigns in the current study were preserved in acidified (Meteor M153) and neutral (RGNO\_2019) Lugols and analyzed within 3 months of sampling. As such, coccolithophores may be misrepresented in both samples due to preferential preservation, this in addition to their small size which makes them harder to enumerate. Dinoflagellates (armored and naked), diatoms

and flagellates on the other hand are more likely to be well represented as they are generally well preserved in acidic Lugols even 225 days after sampling as opposed to the neutral Lugols with optimum preservation of samples for 28 days (Williams *et al.*, 2016). In this regard, samples preserved in neutral Lugol solution from the RGNO\_2022 cruise that were analyzed after a month (but within 3 months) may be underrepresenting some of these groups (i.e., diatoms, flagellates, coccolithophores). Furthermore, smaller (picophytoplankton) and fragile cells are not easy to identify and quantify, and as a result, may be underrepresented. Indeed, the absence of an occurrence of coccolithophore and cyanobacteria dominance in this study may be due to their relatively small size ( $< 2 \mu\text{m}$ ), which makes them challenging to detect and enumerate under conventional light microscopy. In addition, small cells tend to occur in high abundance but with low individual biomass, which further complicates counting and volume-based estimations. Preservation techniques involving Lugol's solution can also cause shrinkage or distortion of delicate picophytoplankton cells, leading to further underestimation (Williams *et al.*, 2016). Consequently, the contribution of smaller taxa may be underestimated in microscopy-based assessments, even though they can play a significant role in primary production and biogeochemical cycling. Finally, interpersonal differences from data analysed in different laboratories may also undermine the precision of microscopic analyses. Identification of pigment markers of phytoplankton groups using high-performance liquid chromatography (HPLC) has been adopted as an alternative proxy for phytoplankton community analysis (Kheirredine *et al.*, 2017; Kramer *et al.*, 2020). This method has some advantages against microscopic analysis such as being highly reproducible and allowing the quantification and identification of smaller and more fragile cells, including cells that would normally be degraded by sample preservation with Lugols (Paul *et al.*, 2021; Flander-Putrlle *et al.*, 2022). Advancements in the classification of phytoplankton groups has been made possible with the aid of specialised computer software such as CHEMTAX, which facilitates the classification of phytoplankton groups by means of pigment-to-Chl-*a* ratios (Mackey *et al.*, 1996). Because HPLC quantifies bulk pigment composition, which directly governs phytoplankton absorption properties and in turn shapes the spectral remote sensing reflectance signal, and because our algorithm exploits those spectral characteristics, it can be argued that HPLC provides a more functionally relevant basis for classifying community structure than microscopy, which often under-represents the smaller phytoplankton groups driving much of the optical signature. However, since historical HPLC data were not available for match-ups, our regional algorithm had to be derived from available microscopy data. which do, however, have some advantages over HPLC. For instance, pigment analysis is not able to provide the same level of detail as microscopy as they are not able to identify individual phytoplankton species. Also, similarities in photosynthetic pigments across multiple taxa make it difficult to distinguish different groups with confidence. Arguably, the future of phytoplankton enumeration lies within the realm of imaging with *in situ* cameras, holographic cameras and imaging flow cytometry. Although not without their own set of

challenges (Giering *et al.*, 2020), these approaches can generate images used to derive concentration and biodiversity information, as well as organism-specific size and shape (Boss *et al.*, 2022). Given the strengths and weaknesses of all the various approaches, it is clear that no one technique can be considered the holy grail for phytoplankton community analysis and it is generally recommended that different techniques are integrated in order to provide a more comprehensive analysis of phytoplankton communities.

#### *3.5.4.2. Limited datasets for development and validation*

Although there was arguably an adequate sample size for stations with diatom dominance ( $n = 37$ ) to allow this phytoplankton group to be more robustly characterised and partitioned into two sets of independent training ( $n=30$ ) and validation ( $n=7$ ), the number of matchup stations observing dominance of HB dinoflagellates ( $n=3$ ), LB dinoflagellates ( $n=10$ ), flagellates ( $n=11$ ) and mixed phytoplankton community ( $n=13$ ) were insufficient and constrained formal validation. The qualitative nature of our algorithm only allows an indication of the dominance of one group in the presence of others and does not estimate the relative composition of each group nor the abundance of each group. It is recognised that these small data sets (which are further constrained by the necessity for satellite matchups in a region that is characterized by a persistent stratocumulus cloud deck) severely limit the robustness of the algorithm being developed. Future work should consider the application of unsupervised approaches such as cluster analysis on reflectance spectra to identify optically distinct groups and assess their correspondence with taxonomic classifications. Such techniques could provide a more data-driven means of characterizing phytoplankton community structure and improving regional algorithm performance. The authors are nonetheless committed to working with currently available and accessible data to explore the expansion of this data set for the purposes of validation of the existing algorithm and for future refinement with improved statistics as more data becomes available over time. In spite of the recognised limitations, it is clear that there is a dire need for such an algorithm and that the one proposed here provides a good first approach that can be applied retrospectively to 20 years of ocean colour data for important investigations that characterise the distribution patterns, phenology and trends of key phytoplankton groups in the region.

### 3.6. Conclusions

In the majority of the studies of community structure dynamics in the nBUS to date, microscopy has been the most commonly used technique for identifying phytoplankton distribution (Hansen *et al.*, 2014; Dijerenge, 2015; Barlow *et al.*, 2018) and environmental monitoring (Louw *et al.*, 2017; Matlakala, 2019), although some studies used a combination of microscopy and pigment analysis (Barlow *et al.*, 2018), with the limitations of both being clear. Satellite-based remote sensing of ocean colour is the only observational capability that can provide synoptic views of upper ocean phytoplankton characteristics at high spatial and temporal resolution (~1 km, ~daily) and a high temporal extent (global scales, for years to decades). It is thus important that the value of remote sensing observations are maximised by developing ecosystem-appropriate, well characterised products. This study takes advantage of unique spectral features (reflectance, reflectance ratios and spectral band difference) of oceanic waters dominated by various phytoplankton groups to create an ocean colour remote sensing algorithm for phytoplankton classification. Our future work will focus on acquiring additional *in situ* data for improvement and validation of the algorithm while venturing into discrimination of bloom types (e.g., non-HABs from HABs of diatoms of *pseudo-nitzschia* species and dinoflagellates) and the detection of other key species (e.g., coccolithophores). Despite its limitations, the algorithm has enormous potential for mapping the distribution and phenology of phytoplankton groups on an unprecedented spatial and temporal scale in the nBUS. The intention is for this algorithm to be used for environmental monitoring of these phytoplankton types to better understand their spatial and temporal dynamics and environmental controls. In addition, application to the 20-year MODIS-aqua observation time series will allow an investigation of possible trends in community structure adjustments with important ecosystem implications for ocean-atmosphere exchange and energy transfer in support of the fisheries and aquaculture industries of Namibia.

### 3.7. References

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## Chapter 4: Seasonal patterns and multidecadal trends in PFGs in the Benguela upwelling system off Namibia.

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### 4.1. Abstract

Understanding the response of phytoplankton to climate change is crucial for predicting shifts in marine ecosystems. Despite the Benguela being the world's most productive eastern boundary upwelling system, the distribution and susceptibility of its PFGs to climate change remain poorly understood. Here, 20 years (2003–2022) of daily MODIS-Aqua satellite data are used to uncover distinct spatial and seasonal patterns and multi-decadal trends in key PFGs (diatoms, dinoflagellates, flagellates, coccolithophores). PFGs show regional and seasonal preferences in their *Spatial Extent* and *Frequency* of dominance, with evidence of niche conditions favoring particular PFGs. Despite regional and seasonal variability, PFGs overall increased in *Spatial Extent* and *Frequency* of dominance in the past two decades, except for declining coccolithophores. The link between  $W_{EQ}$  and PFG trends strongly suggests an altered nutrient supply-driven response. Diatoms, significant carbon exporters, exhibit pronounced adjustments, highlighting their sensitivity to environmental changes. These findings are indicative of potential impacts on biogeochemical cycling and higher trophic levels, affecting carbon export and marine services. These findings hold practical relevance for environmental management efforts in support of policy formulations and establishing marine protected areas for climate-resilient conservation strategies.

## 4.2. Introduction

Marine phytoplankton form the base of the aquatic food-web sustaining higher trophic levels and lucrative fisheries. In addition, phytoplankton production and export modulate biogeochemical cycling with important impacts on climate regulation (Charlson *et al.*, 1987; Falkowski *et al.*, 1998; Field *et al.*, 1998). These photosynthetic microorganisms are conceptually grouped into PFGs according to common ecological traits (Reynolds *et al.*, 2002). Diatoms are considered effective exporters of carbon to the deep ocean and to higher trophic levels (Allen *et al.*, 2005; Armbrust, 2009) while smaller dinoflagellates and calcifying coccolithophores are important producers of the climatically active DMS gas, which seeds aerosol and cloud formation and impacts climate (Charlson *et al.*, 1987; Yoch, 2002). Collectively, phytoplankton occupy key roles in ecosystem functioning, food security and climate, which makes them ideal indicators of overall ecosystem health and trophic status (Tweddle *et al.*, 2018). Phytoplankton community composition and succession are intricately tied to a complex interplay of physical and biogeochemical factors that dictate the characteristics of their environment (e.g., temperature, water column stability, light and nutrient availability) (Araújo *et al.*, 2022; Litchman *et al.*, 2012). Continued anthropogenic carbon emissions are altering many of these environmental forcing mechanisms that promote or constrain phytoplankton growth (Calvin *et al.*, 2023), with evidence of change already apparent in bloom phenology (Thomalla *et al.*, 2023), *Frequency* and spatial occupation (Dai *et al.*, 2023) and abundance (Behrenfeld *et al.*, 2006; Van Oostende *et al.*, 2023), with far reaching implications for marine ecosystem services. Understanding long-term spatiotemporal trends in phytoplankton dynamics, particularly in highly productive ocean regions, is fundamental to our ability to detect early ecosystem disturbances and predict the magnitude and direction of ecosystem shifts. Such knowledge is vital for informed decision-making and the implementation of effective conservation and management strategies for sustainable ecosystems and the preservation of the key services that they elicit.

Eastern Boundary Upwelling Systems (EBUS) are coastal oceanic regions characterized by equatorward wind-driven upwelling of cold nutrient-enriched subsurface waters to the euphotic zone where they fuel high rates of primary production that manifest as phytoplankton blooms (Kämpf and Chapman, 2016). Although comprising <7% of the global ocean, EBUS offer great socio-economic services by accounting for ~2% of global ocean production and ~20% of global fisheries yields (Carr and Kearns, 2003; Pauly and Christensen, 1995). The Benguela upwelling system (BUS) off South West Africa (Figure 4.1) is divided into its northern (nBUS) and southern (sBUS) components and is considered the most productive of the four main EBUS (Carr, 2001). The nBUS, off Namibia and Angola, is characterized by four main upwelling cells, viz.: the Kunene cell off Angola, and the Northern, Central and the largest and most intense Lüderitz cells (Figure 4.1a-c) off Namibia. The nBUS is progressively being impacted by climate change via

increasing SST (Figure 4.1d), intensifying  $W_{EQ}$  (Figure 4.1d), expanding oxygen-minimum zones (Monteiro *et al.*, 2008; Stramma *et al.*, 2008), decreasing vertical velocity (Polonsky and Serebrennikov, 2020) and altered wind-driven upwelling (Lamont *et al.*, 2018) in addition to human-induced activities such as overfishing (Cury and Shannon, 2004). Climate modes of extreme warm events, the so-called Benguela Niños, also impact the nBUS at decadal time scales (Imbol Koungue *et al.*, 2019). Plankton communities at the base of this key marine ecosystem are likely to be impacted by these altered climate dynamics with consequential changes expected in their composition and distribution patterns with cascading ramifications for ecosystem function. For example, increasing SST coupled with decreasing dissolved oxygen concentrations have been reported to constrain vertical plankton distributions and the survival of early life-cycle stages of fish (Auel and Verheye, 2007; Ekau and Verheye, 2005).

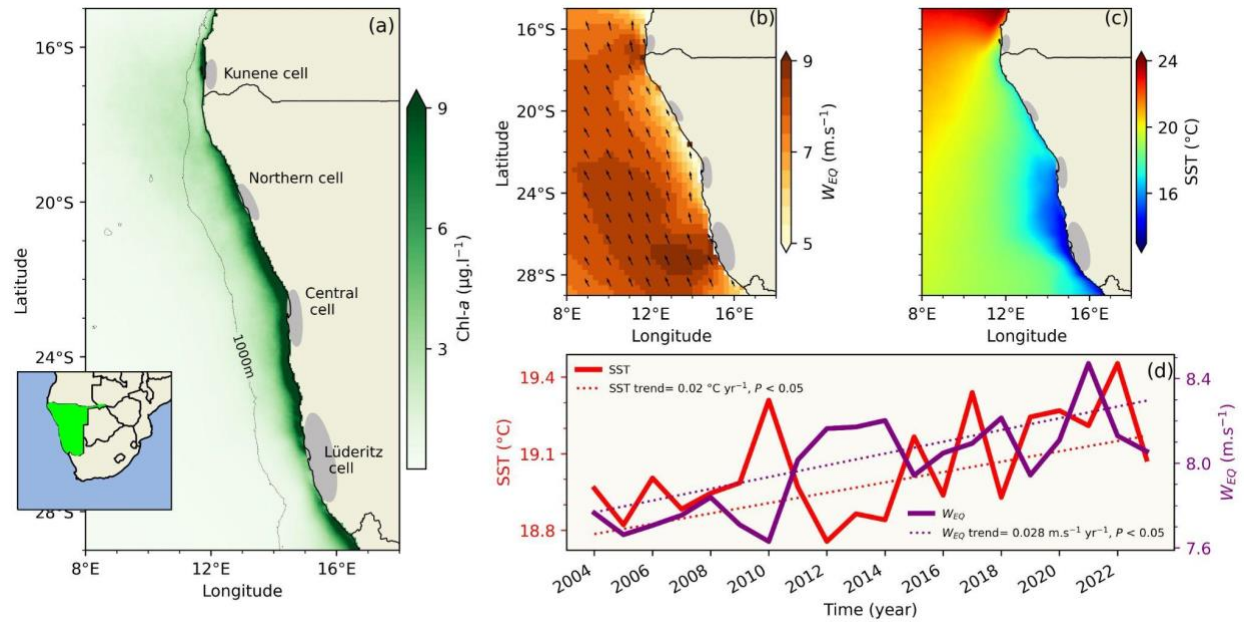


**Figure 4.1: Study area, mean phytoplankton abundance as well as long term dynamics of key climate drivers.** **a**, Map showing the northern Benguela upwelling system off Namibia (nBUS, inset) on the Southwest coast of Africa showing the mean chlorophyll *a* concentration (Chl-*a*, a phytoplankton biomass proxy) (MODIS-Aqua, Level-3, 4 km). The dotted line represents the GEBCO (GEBCO Bathymetric Compilation Group 2023, 2023) 1000 m isobath separating the Benguela shelf domain from the open ocean, with key upwelling centers indicated by gray shaded areas. **b**, Mean equatorward winds speed ( $W_{EQ}$ ) at 10 m above sea surface with wind direction (black arrows) overlaid, computed from the zonal (U) and meridional (V) wind components (European Union-Copernicus Marine Service, 2017). **c**, Sea surface temperature (SST) climatology (MODIS-Aqua, Level-3 4 km), with gray shaded areas in **b** and **c** also representing upwelling cells. **d**, Long-term trends in key climate drivers, SST and  $W_{EQ}$ , showing the imprint

of climate change manifested as warming and wind acceleration. The red and purple solid lines represent mean annual SSTs and  $W_{EQ}$ , respectively, with dotted lines indicating long-term annual trends. Trends are considered statistically significant when  $P < 0.05$ . Climatological means of Chl-*a*,  $W_{EQ}$  and SST (**a**, **b**, **c**) as well as annual means for trends analysis (**d**) were computed from daily satellite observations between 01 January 2003 – 31 December 2022.

Continuous environmental monitoring programs provide long-term datasets that are essential to ecosystem assessment for effective environmental management efforts (Benway *et al.*, 2019). Shipboard observations are severely constrained both spatially (distinct geographic transects) and temporally (monthly to seasonal occupations), making an ecosystem-wide response of phytoplankton communities to climate variability difficult to detect. Satellite remote sensing has advanced our ability to observe and monitor surface ocean dynamics at high temporal (daily, spanning years to decades) and spatial (300 m, global coverage) scales. Spatial and temporal trends in Chl concentration (Demarcq, 2009; Demarcq *et al.*, 2007, 2003), Chl-*a* size fractions (Lamont *et al.*, 2019) and bloom occurrence (Dai *et al.*, 2023) have been examined in the BUS, but phytoplankton communities in terms of PFGs dominance and their susceptibility to environmental change remain largely unexplored. Here, ocean colour satellite remote sensing algorithms (Moloto *et al.*, 2023; Smith *et al.*, 2023) are applied to 20 years (2003–2022) of daily MODIS-Aqua data to detect key PFGs (diatoms, flagellates, dinoflagellates and coccolithophores) and assess their spatial patterns and multi-decadal trends in the context of key environmental drivers of SST and  $W_{EQ}$ .

### 4.3. Methods

#### 4.3.1. Ocean colour satellite remote sensing data

Daily Level-3 (L3) ocean colour remote sensing data with 4 km spatial resolution from the Moderate Resolution Imaging Spectroradiometer aboard NASA's aqua satellite (MODIS-Aqua) were obtained from the NASA Ocean Color web (<https://oceancolor.gsfc.nasa.gov/>). Ocean colour data were obtained for the normalized fluorescence line height (nFLH,  $\text{mW m}^{-2} \mu\text{m}^{-1} \text{sr}^{-1}$ ), remote sensing reflectance ( $R_{rs}$ ,  $\lambda$ ;  $\text{sr}^{-1}$ ) at 443 ( $R_{rs443}$ ), 488 ( $R_{rs488}$ ), 531 ( $R_{rs531}$ ), 547 ( $R_{rs547}$ ), 667 ( $R_{rs667}$ ) and 678 ( $R_{rs678}$ ) nm wavebands as well as SST ( $^{\circ}\text{C}$ ) and Chl ( $\mu\text{g l}^{-1}$ ). The daily ocean colour remote sensing data spanned the period from January 2003 to December 2022, with a total of 65,619 daily satellite data files.

#### 4.3.2. PFG remote sensing detection proxies

The regional algorithm derived for MODIS-Aqua application of Moloto *et al.* (2023) was applied for the detection of PFG dominance (diatoms, flagellates, and low and high biomass dinoflagellates) in the nBUS. Dominance, according to the algorithm, is acquired when a PFG contributes more than 50% to the total phytoplankton community abundance at any given time and location. In cases where no single PFG contributes more than 50% to the total community, the algorithm classifies the assemblage as a 'mixed community'. The strength of this approach lies in its ability to represent ecologically plausible scenarios of co-dominance; however, a limitation is that it does not specify which groups comprise the mixed assemblage. The authors used statistical thresholds based on dual band ratios of spectral bands in the green, red and near-infrared regions (531, 547, 667 and 748 nm) as well as spectral band difference (nFLH) proxies to exploit small variations in  $R_{rs}$  characteristics of waters associated with dominance of PFGs. In the current study the low and high biomass dinoflagellates are combined and reported as one dinoflagellate PFG.

Coccolithophore blooms were detected using an adaptation of the Smith *et al.* (2023) algorithm, which utilizes the distinctive blue-green reflectance peak caused by coccolithophore blooms (Moore *et al.*, 2012). The original detection technique operates on the Sea-viewing Wide Field-of-view Sensor (SeaWiFS) data and calculates the integral of  $R_{rs}$  between 490 and 510 nm. SeaWiFS however has a limited temporal coverage (September 1997 to December 2010), thus limiting its suitability for this study. Accordingly, the algorithm was adopted for application to MODIS-Aqua observations. In the absence of MODIS-Aqua  $R_{rs490}$  and  $R_{rs510}$  wavebands, our adaptation instead calculates the integral of  $R_{rs}$  between 488 and 531 nm. An integral threshold of 0.26 was used since it corresponds to a minimum threshold of approximately  $2 \text{ mmol m}^{-3}$  of particulate inorganic carbon (PIC) in the MODIS-Aqua PIC product in confirmed offshore bloom areas (data not shown). A PIC of  $2 \text{ mmol m}^{-3}$  is often used as a threshold for detecting coccolithophore blooms (He *et al.*, 2022; Signorini and McClain, 2009). Additional classification criteria

included excluding pixels from potentially suspended sediment-laden waters with a peak in the green spectral band ( $Rrs488 > Rrs547$ ) and the exclusion of pixels potentially affected by anomalously elevated reflectance in the blue spectral band ( $Rrs488 > Rrs443$ ). Near-shore coccolithophore-like features in Namibia have been demonstrated to be a result of hydrogen sulfur ( $H_2S$ ) eruptions in the shelf (<200 m depth) (Ohde *et al.*, 2007; Ohde and Dadou, 2018), which have similar spectral features to coccolithophores (Siegel *et al.*, 2007). In order to avoid mis-classification of these events as coccolithophore blooms, the pixels where the bathymetry (GEBCO Bathymetric Compilation Group 2023, 2023) was less than 200 m were masked out.

#### 4.3.3. PFG quantitative indices

Two quantitative indices were derived following application of the PFG algorithms to allow for a spatiotemporal analysis of the 7291 daily satellite observations in the nBUS. These included 1) *Frequency* – calculated as the number of days of dominance per pixel by each PFG on an annual or seasonal time scale (days per year/season), and 2) *Spatial Extent* – defined as the area dominated by each PFG, calculated as the sum of all 4-km pixels dominated by each PFGs and converted to area ( $km^2$ ) by accounting for the spatial resolution of the MODIS-Aqua pixels.

#### 4.3.4. Equatorward Winds ( $W_{EQ}$ )

The Global Ocean Daily Gridded Reprocessed Level-3 (L3) Sea Surface Winds from Scatterometer (European Union-Copernicus Marine Service, 2017) was selected as the best (of four) wind data product for the region from a comparison with QuickSCAT (see Annexure II for detailed comparative study). The meridional (V) and zonal (U) wind vector components at 10 m above sea surface were used to compute  $W_{EQ}$ .

#### 4.3.5. Trends analysis

Annual and seasonal *Frequency*, *Spatial Extent*, SST and  $W_{EQ}$  time series datasets were computed from daily satellite observations and constitute the main material to compute linear trends analysis. Prior to trends analysis, quality control measures were applied to minimize error and bias following the approach of Ryan-Keogh *et al.*, 2023). Firstly, pixels with less than 50% of the total time series (i.e., <10 years) were excluded from any statistical trends analysis. Secondly, the datasets were tested for normality of their distribution. If the data were normally distributed, then linear regressions were performed using the robust Huber-Regression (epsilon ( $\epsilon$ ) = 1.35). The Huber regression analysis is robust as it is less sensitive to outliers and limits their impact on trends estimates. If the data were not normally distributed, then linear regression analysis was performed using the non-parametric Mann-Kendall (MK) test.

#### 4.3.6. Correlation of trends on PFGs with SST and $W_{EQ}$

To assess the correlation between long-term changes in key climate drivers of SST and  $W_{EQ}$  with PFGs,  $W_{EQ}$  was first regridded onto the 4 km MODIS-Aqua grid using the nested2gd method of the xESMF python package (version v0.8.2) (Jiawei Zhuang *et al.*, 2023). Then the PFG indices (i.e., *Spatial Extent*, *Frequency*) were linearly correlated against SST and  $W_{EQ}$  and quantified the strength of their association using Pearson's correlation coefficient ( $r$ ).

## 4.4. Results

### 4.4.1. Characterizing the climatological distribution patterns of PFGs in the context of key climate drivers

i.e.,

In this study, *Frequency* (days yr<sup>-1</sup>) and *Spatial Extent* (km<sup>2</sup>) are used as metrics to study spatiotemporal variability in PFG dominance. Dominance, according to the remote sensing algorithms (Moloto *et al.*, 2023; Smith *et al.*, 2023), is acquired when a PFG contributes more than 50% to the total phytoplankton community (see section 2.2. Of the Methods section). Climatological maps from the past 20 years of annual mean *Frequency* (Figure 4.2a) reveal that diatoms dominate most frequently ( $\leq 80$  days yr<sup>-1</sup>), followed by flagellates and mixed communities ( $\leq 30$  days yr<sup>-1</sup>) with moderate *Frequency* of dominance by dinoflagellates ( $\leq 16$  days yr<sup>-1</sup>) and infrequent coccolithophore dominance ( $< 2$  days yr<sup>-1</sup>). A poleward gradient of increasing *Frequency* is observed for all PFGs, with the highest frequencies occurring South of 20 °S (Figure 4.2a), consistent with a poleward decrease in SST (Figure 4.1c), that is typically aligned with increased nutrient supply to the euphotic zone from  $W_{EQ}$ -driven upwelling (Figure 4.1b). Diatoms show a classical inshore-offshore gradient (Figure 4.2a) that is consistent with Chl-*a* (Figure 4.1a), with the highest *Frequencies* observed in high Chl-*a* coastal waters. Diatoms are highly competitive in cold, nutrient-rich environments following upwelling and are regular blooming PFGs that, together with dinoflagellates, contribute the largest proportion to phytoplankton Chl-*a* biomass in the nBUS (Figure S4.1 in Annexure II), consistent with previous reports (Hansen *et al.*, 2014; Louw *et al.*, 2017, 2016). In contrast, flagellates, dinoflagellates, coccolithophores and mixed phytoplankton communities tend to dominate in offshore waters coincident with moderate to low Chl-*a* concentrations (Barlow *et al.*, 2018; Louw *et al.*, 2017) (Figure 4.2a, Figure S4.1 in Annexure II).

Examining PFGs *Frequency* in the context of SST and  $W_{EQ}$  (Figure 4.2b, Figure S4.2 in Annexure II) reveals evidence of niche conditions favoring different PFGs. Diatoms are more frequently associated with cold conditions and rarely dominate in temperatures greater than 17 °C. Although they occupy a broad range of  $W_{EQ}$ , their maximum frequencies are associated with less windy ( $< 7$  m s<sup>-1</sup>) conditions. In contrast, dinoflagellates most frequently dominate in warmer (16 – 19 °C) conditions, although a few instances of high *Frequency* were also evident in cold ( $< 14$  °C) and windy ( $> 8$  m s<sup>-1</sup>) conditions, corroborating previous shipboard findings of upwelling-induced dominance of dinoflagellates (Hansen *et al.*, 2014). Flagellates and mixed communities occupy a broad SST and  $W_{EQ}$  range but prevail in conditions that are relatively cooler than dinoflagellates ( $< 17$  °C) and windier than diatoms ( $> 7$  m s<sup>-1</sup>). The few occasions of coccolithophore dominance tend to coincide with moderate temperature (16-19 °C) and wind ( $> 6.5$  m s<sup>-1</sup>) conditions (Figure 4.2b, Figure S4.2 in Annexure II).

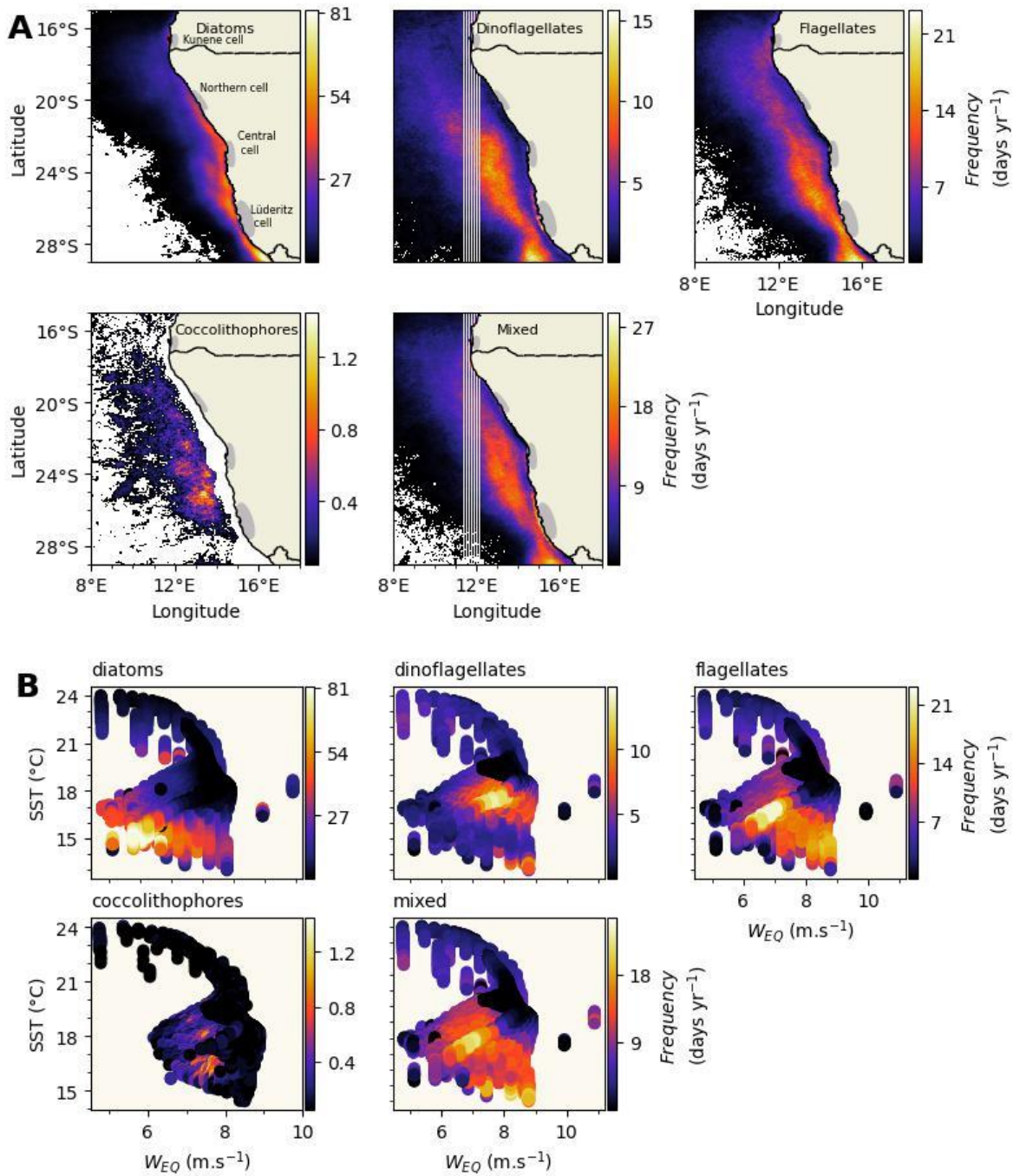


**Figure 4.2: Spatial climatological patterns of phytoplankton groups in the nBUS between 2003 and 2022.**

A, Spatial climatological annual mean *Frequency* of dominance by PFGs from daily MODIS-Aqua satellite observations. Only observations at depths  $>200$  m are shown for coccolithophores to the exclusion of coastal hydrogen sulfide ( $\text{H}_2\text{S}$ ) eruption plumes which have the same spectral features as offshore

coccolithophore blooms (Siegel *et al.*, 2007). **B**, Scatter plot of spatial climatological mean sea surface temperatures (SST, °C) and equatorward winds speed ( $W_{EQ}$ , m s<sup>-1</sup>) with annual mean *Frequency* overlaid (colour bar) to highlight mean PFG niche occupations of SST and  $W_{EQ}$  on 20-year climatological time scales.

All PFGs characteristically increase in *Spatial Extent* with increasing latitude from 15 °S to ~25 °S, consistent with decreasing SST and increasing  $W_{EQ}$  (Figure 4.3a). This is followed by a sharp decline at approximately 25 – 28 °S that coincides with maximum  $W_{EQ}$  speeds (>8.5 m s<sup>-1</sup>) near the Lüderitz upwelling cell (Figure 4.3a, Figure 4.1b). This decline in PFG *Spatial Extent* results from the cumulative effect of enhanced turbulence and dynamic circulation that acts as a biological boundary constraining phytoplankton growth and biomass accumulation (Agenbag and Shannon, 1988). An assessment of the seasonal cycle in *Spatial Extent* in the context of SST and  $W_{EQ}$  climatologies reveals differences in the magnitude and timing of PFG peaks (Figure 4.3b, red stars) that reflects a seasonal succession of community dominance. Dinoflagellates are the first to peak in April (early-autumn) during high  $W_{EQ}$  speeds (Figure 4.3b, blue line), followed by diatoms in May (late-Autumn) coinciding with a relaxation of  $W_{EQ}$  and declining temperatures. Flagellates peak in June (early-winter), while mixed communities in July (mid-winter) and finally coccolithophores in November (late-Spring). Except for coccolithophores, all PFGs exhibit a seasonal minimum between September and March (warmer periods) coinciding with peak summer SSTs and minimum  $W_{EQ}$  (Figure 4.3b). These results corroborate previous observations of diatoms and dinoflagellates thriving in cooler, upwelling periods, while coccolithophores flourish in warmer, more stratified summer waters (Hansen *et al.*, 2014; Louw *et al.*, 2017; Siegel *et al.*, 2007). Despite differences in the seasonal timing of *Spatial Extent* peaks, diatoms remain spatially dominant throughout the annual cycle and are not succeeded by any other PFG (Figure S4.3 in Annexure II). Seasonal succession in *Spatial Extent* is however observed in March and April when flagellate spatial dominance overtakes dinoflagellates and mixed populations respectively, with dinoflagellates recovering *Spatial Extent* dominance over flagellates in July (Figure S4.3 in Annexure II).

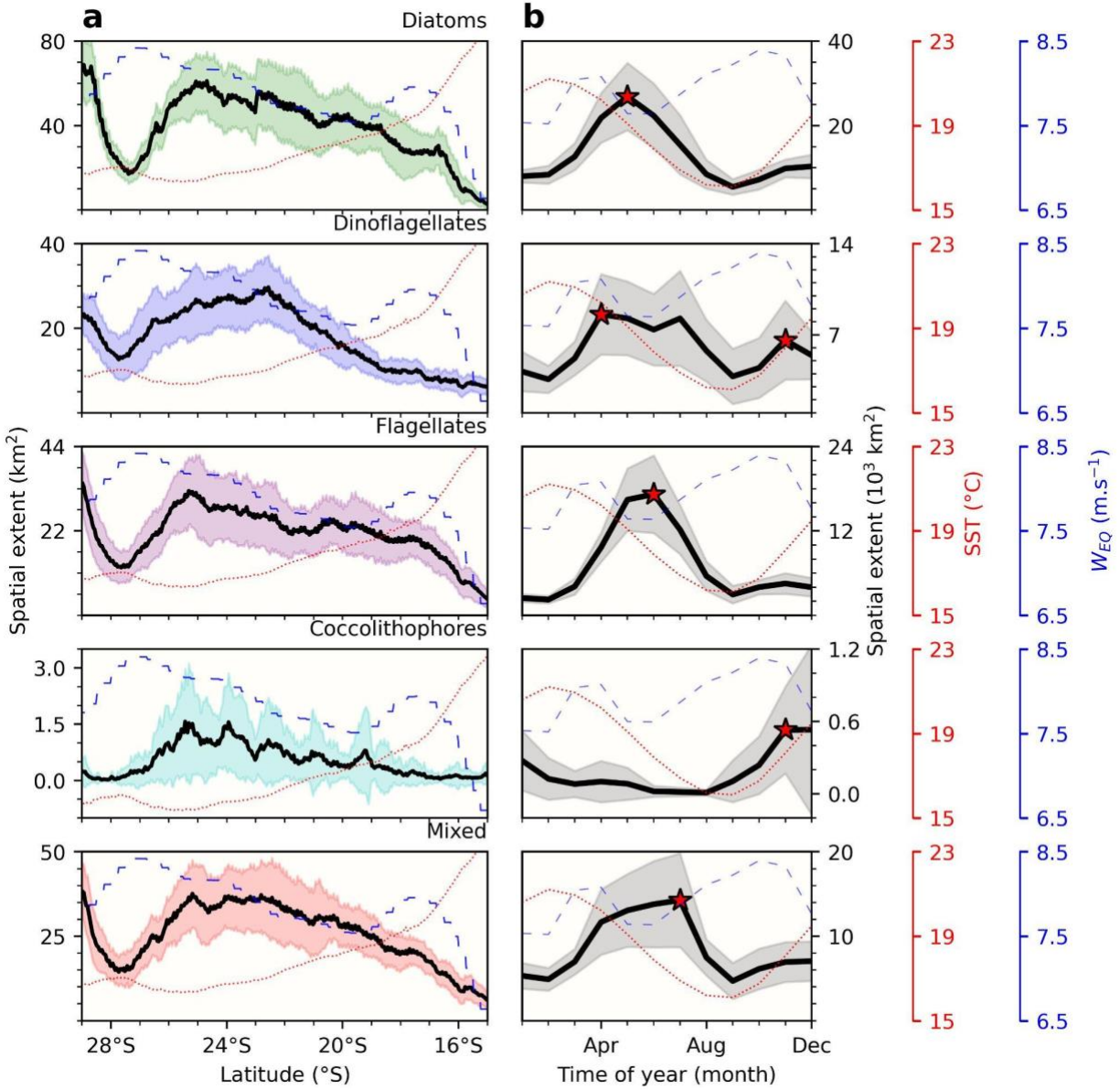


**Figure 4.3: PFGs *Spatial Extent* climatology in the past two decades (2003–2022).** **a**, Annual mean cross-shelf latitudinal distribution in *Spatial Extent* (solid black line) of PFG dominance. The shaded areas represent the degree of interannual variability in *Spatial Extent* calculated as the standard deviation. **b**, corresponding annual cycle of *Spatial Extent* in PFG dominance (solid black line) showing the typical PFG seasonal succession in the timing of peak *Spatial Extent* (red stars) and degree of variability (gray shaded areas, determined as standard deviation). The red (dotted) and blue (dashed) lines in panels **a** and **b** represent annual mean sea surface temperatures (SST) and equatorward winds speed ( $W_{EQ}$ ) respectively. All annual mean values were computed from daily satellite observations between January 2003 – December 2022. Note the varying scales of the *Spatial Extent* in panels **a** and **b** as well as among PFGs.

These results provide a more comprehensive and previously unobserved synoptic-scale account of regional and seasonal variability of key PFGs in the nBUS at unprecedented spatiotemporal scales. The observed regional and seasonal patterns reveal niche SST and  $W_{EQ}$  affinities that are favorable to the dominance of distinct PFGs in both time (seasonal succession) and space (north/south – inshore/offshore gradients). The ability to map the spatio-temporal variability in key PFGs allows for a more comprehensive understanding of ecosystem dynamics for effective monitoring and management of ocean health and associated services they provide.

#### **4.4.2. Evidence of warming and altered $W_{EQ}$**

Significant trends in SST and  $W_{EQ}$  (Figure 4.4) reflect substantial adjustments in key environmental variables that are known to impact phytoplankton production. The nBUS is impacted by general warming of  $0.02\text{ }^{\circ}\text{C yr}^{-1}$  (Figure 4.1d), with the most northerly region (near the Kunene cell) warming at a faster rate of up to  $0.1\text{ }^{\circ}\text{C yr}^{-1}$  (Figure 4.4a), amounting to maximum temperature changes of as much as  $2\text{ }^{\circ}\text{C}$  over the 20-year time period. These results are consistent with previous warming reports (Sweijd and Smit, 2020). This general warming trend is consistent across all seasons, however small patches of coastal cooling ( $-0.1\text{ }^{\circ}\text{C yr}^{-1}$ ) are observed off the Kunene cell in Summer and the Lüderitz cell in spring (Figure S4.4 in Annexure II). Trends in  $W_{EQ}$  are overwhelmingly positive (Figure 4.1d,  $0.028\text{ m s}^{-1}\text{ yr}^{-1}$ ), with coherent offshore increasing trends contrasting with the notable heterogeneity in alongshore trend patterns (Figure 4.4b). Strong positive  $W_{EQ}$  trends are observed inshore off Kunene and Central cells ( $<0.1\text{ m s}^{-1}\text{ yr}^{-1}$ ) while smaller regions of negative trends are constrained to the coastlines of the Northern and Lüderitz cells ( $<-0.5\text{ m s}^{-1}\text{ yr}^{-1}$ ) (Figure 4.4b). This spatial distribution in  $W_{EQ}$  trends is relatively consistent across all seasons but exacerbated in certain regions and seasons. For example, positive trends in  $W_{EQ}$  are dominant in Spring and Summer off the Kunene cell but in Autumn off the Central cell while the negative trends are largely absent in all seasons except Autumn (Figure S4.4 in Annexure II).

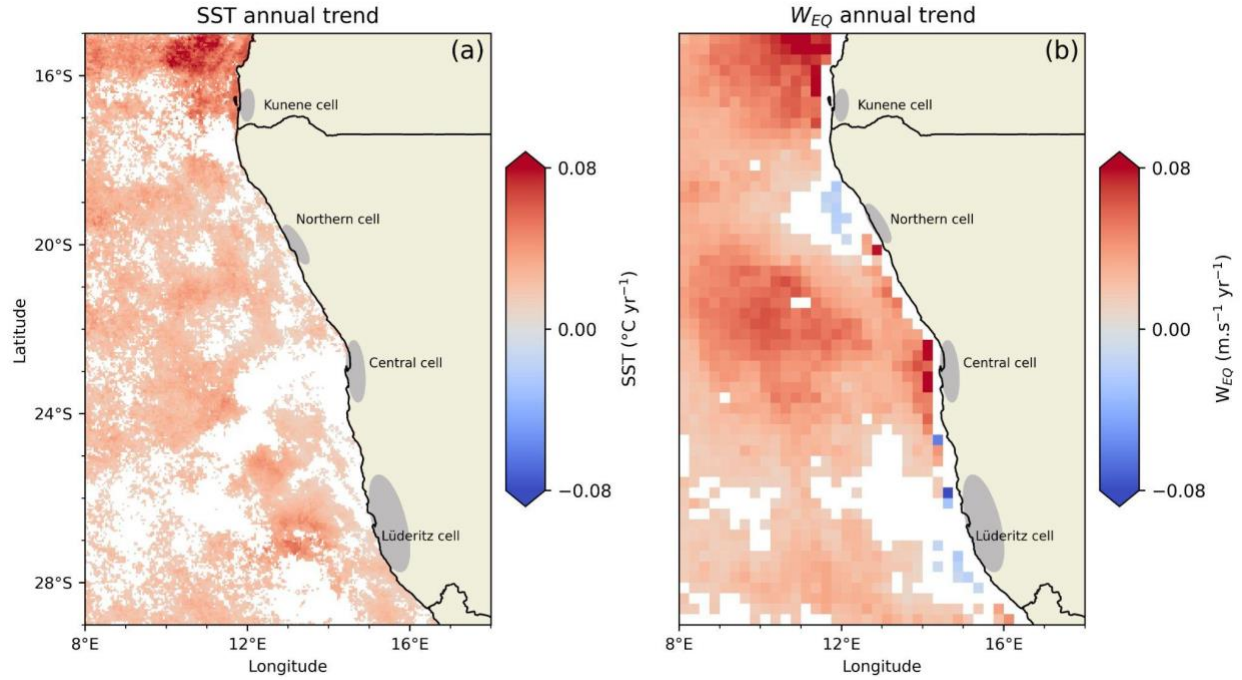


**Figure 4.4: Trends in key climate drivers in the nBUS**

Annual mean trends in **a)** sea surface temperatures (SST,  $^{\circ}\text{C yr}^{-1}$ ) and **b)** equatorward winds ( $W_{EQ}$ ,  $\text{m s}^{-1} \text{yr}^{-1}$ ) derived from daily satellite observations between 01 January 2003 – 31 December 2022. The gray shaded areas represent upwelling cells. Only statistically significant ( $P < 0.05$ ) trends are shown.

#### 4.4.3. Multidecadal trends in PFG dominance

With the application of PFT algorithms to satellite ocean colour data, it is possible to investigate the synoptic scale response of specific PFGs to adjustments in key environmental variables over two decades. A trends analysis of the annual *Frequency* ( $F_{trend}$ ) and *Spatial Extent* ( $SE_{trend}$ ) of PFGs reveals a heterogeneous distribution of significant ( $P < 0.05$ ) positive and negative trends, with evidence of regional cohesiveness in trend direction (Figure 4.5 and Figure 4.6). While  $F_{trend}$  reflects an increase or decrease in the *Frequency* of dominance of PFGs (Figure 4.5a), the  $SE_{trend}$  is indicative of a tendency to either expand (Figure 4.6a, red circles) or shrink (Figure 4.6a, blue circles) in spatial occupation. Over the region as a whole, there are equal areas affected by positive and negative trends in diatoms  $F_{trend}$  (Figure 4.5c). These trends are relatively consistent across inshore/offshore gradients (Figure 4.5a) but alternate with latitude between positive and negative trends (Figure 4.5b), with the Kunene and Central upwelling cells associated with increasing  $F_{trend}$  of diatom dominance, while the Northern and Lüderitz cells are instead associated with a decline. Notably, the increasing trends off the Kunene cell in the north are more prominent inshore, while the increasing trends further South (e.g., off the Central cell) are more conspicuous offshore. For  $SE_{trend}$ , the area impacted by positive trends surpass that of negative trends for diatoms (Figure 4.6b), with

the alternating latitudinal pattern still evident, most notably the decline in diatom  $SE_{trend}$  off the Northern Cell compared to a more typical increase in  $SE_{trend}$  off the Kunene and Central cells (Figure 4.6a).

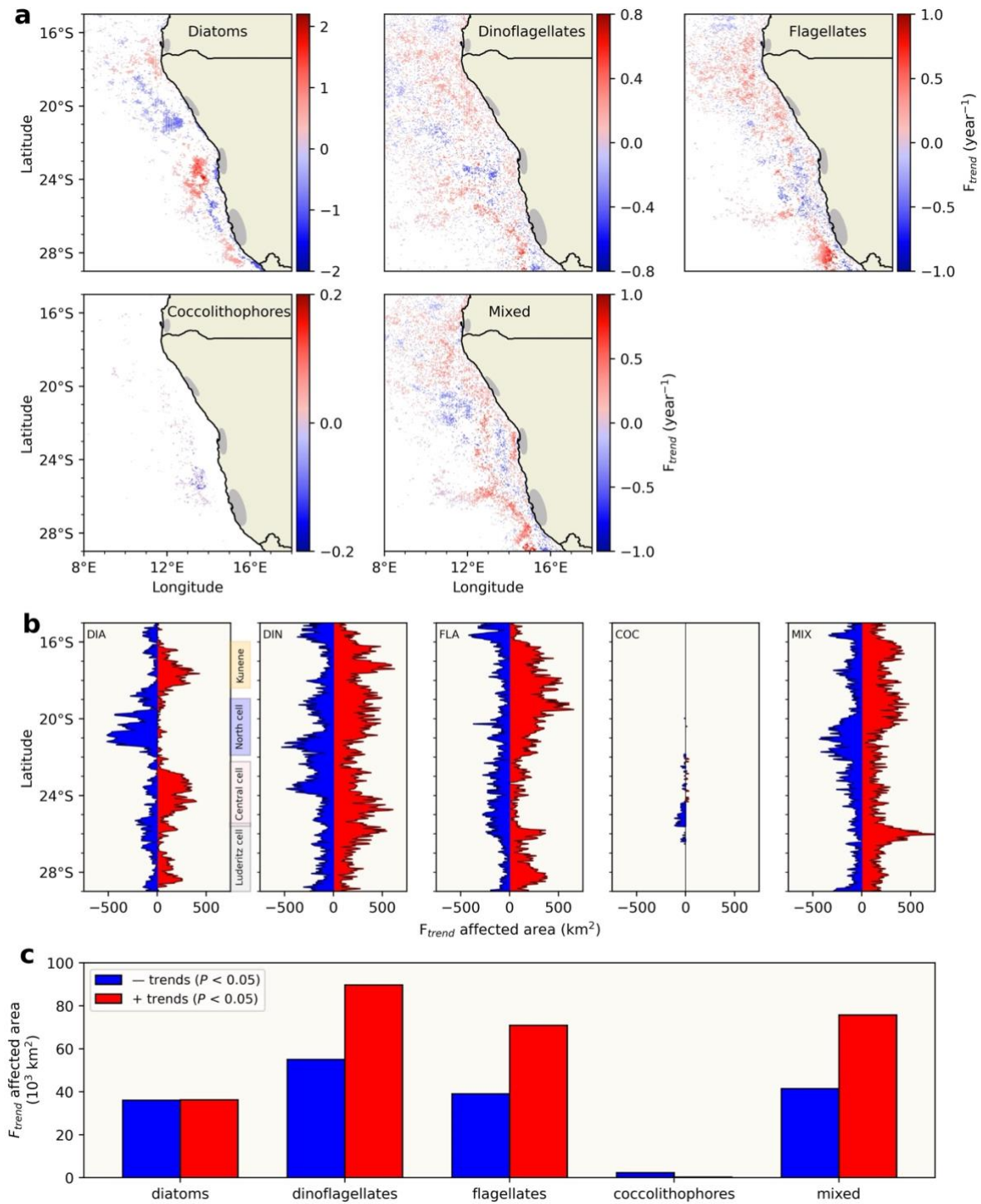


**Figure 4.5: Trends in PFGs *Frequency* of dominance in the past two decades (2003–2022).**

**a**, Spatial patterns of annual trends in *Frequency* of dominance ( $F_{trend}$ ) of key PFGs. Only statistically significant ( $P < 0.05$ )  $F_{trend}$  are shown. **b**, Latitudinal variation in the area ( $\text{km}^2$ ) affected by significant negative (blue) and positive (red)  $F_{trend}$  for diatoms (DIA), dinoflagellates (DIN), flagellates (FLA), coccolithophores (COC) and mixed (MIX) communities. Note the varying scales of the annual *Frequency* trends ( $F_{trend}$ ) colourbars in panel **a** among the PFGs. **c**, delineation of the total area ( $\text{km}^2$ ) impacted by statistically significant negative (blue) and positive (red) trends.

For dinoflagellates, flagellates and mixed communities, there is a dominance of positive *Frequency* trends over negative, which display both latitudinal (Figure 4.5b) and cross-shore (Figure 4.5a) variability. The dominance in positive trends for these PFGs is particularly prominent when looking at *Spatial Extent* (Figure 4.6b), which reflects the expansion of their regional occupation. Coccolithophores are the only PFG that show an overall decline in *Frequency* (Figure 4.5c) and a shrinkage in their *Spatial Extent* (Figure 4.6b), which is constrained to offshore waters (Figure 4.6a) in the south ( $\sim 24 - 27^\circ\text{S}$ ) (Figure 4.5b and Figure 4.6a). The observed  $F_{trend}$  imply a poleward offshore and equatorward inshore shifts in diatoms, equatorward shifts in dinoflagellates, flagellates and mixed communities with coccolithophores showing no obvious spatial shifting patterns. Perhaps the most striking result is that diatoms are adjusting at rates double (or more) that of other PFGs, underlining their sensitivity to changing environmental conditions. Such shifts signal possible major restructuring of the plankton community composition and diversity, whose magnitude cannot be assessed from changes in *Frequency* and *Spatial Extent* of dominance alone.

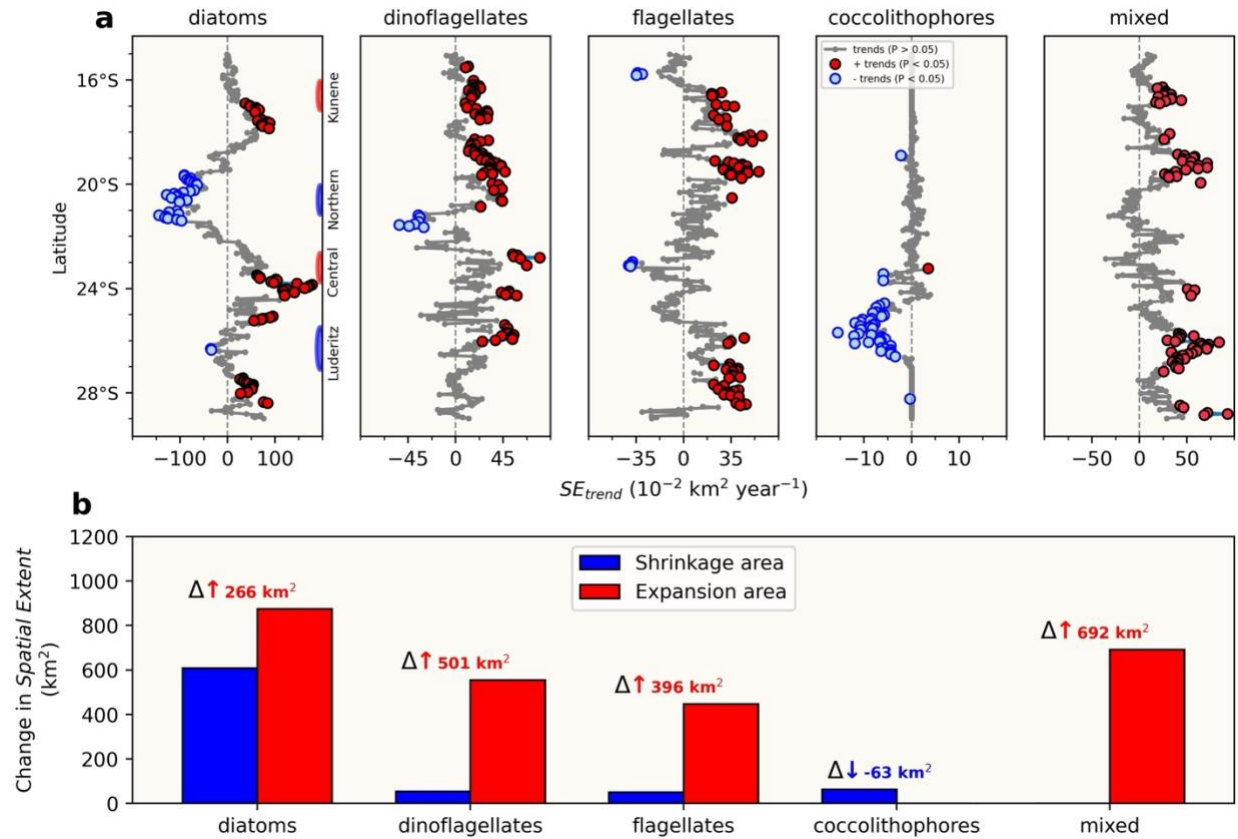


**Figure 4.6: Trends in PFGs *Spatial Extent* in the past two decades (2003–2022).**

**a**, Latitudinal patterns of annual trends in PFG *Spatial Extent* ( $SE_{trend}$ ). Regions impacted by statistically significant ( $P < 0.05$ ) positive (red dots) and negative (blue dots) indicate expansion and shrinkage in *Spatial Extent* respectively. The gray lines indicate statistically insignificant ( $P > 0.05$ ) trends. **b**, delineation of the total area (km<sup>2</sup>) impacted by statistically significant negative (blue) and positive (red) trends. Note the varying scales of the annual *Spatial Extent* trends ( $SE_{trend}$ ) in panel **a** among the PFGs.

Examining trends in *Frequency* and *Spatial Extent* in a seasonal context (as opposed to annually averaged) unveils discrepancies in where and when community adjustments in PFG dominance may be occurring (Figure S4.5, Figure S4.6 in Annexure II). For example, a latitudinal band may display both significant positive and negative trends for a particular PFG depending on the season, which partially offset each other when annually averaged. This is the case for  $SE_{trend}$  in diatoms which are positive in Autumn (~23 and 27 °S) but negative  $SE_{trend}$  for the same latitudinal band in Summer. Interrogating the trends through a seasonal lens also highlights instances of multi-decadal PFG succession. For example, in summer and winter there is a co-expansion and increase in  $F_{trend}$  between dinoflagellates, flagellates and mixed communities that coincides with decreasing diatoms. Conversely in Autumn, diatom expansion and an increase in *Frequency*

is coincident with decreasing  $F_{trend}$  and  $SE_{trend}$  (or no trends) in other PFGs. The dominance of decreasing  $F_{trend}$  and  $SE_{trend}$  trends for coccolithophores are most prevalent in Spring while increased trends in Summer (Figure S4.5, Figure S4.6 in Annexure II).

Overall, with the remarkable exception observed in coccolithophores, there is a net increase in *Frequency* and *Spatial Extent* of PFGs in the nBUS over the past 2 decades (Figure S4.7 in Annexure II). In this respect, our results (apart from coccolithophores) support the observations of Dai *et al.* (2023) who reported bloom intensification and expansion in the past 20 years (2003–2022) for the BUS region as part of a global coastal bloom analysis, albeit not resolving the blooms by PFGs. By focusing on PFGs, our study provides a more nuanced approach to disentangling phytoplankton multi-decadal dynamics, which is of particular importance given the varying ecological roles that different functional groups have for ecosystem services. The value of this approach is accentuated by an ability to discern the specific regions and seasons of varying trends in PFGs (Figure S4.5 and Figure S4.6 in Annexure II).

#### 4.4.4. PFGs adjustments in the context of warming and altered $W_{EQ}$

Evaluating phytoplankton community adjustments in the context of warming and altered  $W_{EQ}$  reveals strong positive and negative correlations that varied regionally (Figure S4.8, Figure S4.9 in Annexure II). It is worth noting that these analyses do not include additional physicochemical variables that may influence PFGs (e.g., river/land inputs, interactions with other biota and human-induced dynamics). In addition, different environmental variables may be acting antagonistically, additively or otherwise in driving PFG trends, making it challenging to identify the dominant driver of the observed multi-decadal variability. These relationships may also reflect correlation rather than causation, given the complex interactions and linkages between trophic levels in the upper ocean. With this in mind, a qualitative approach is used to examine the long-term driver-response relationships between PFGs against SST and  $W_{EQ}$ , achieved by grouping statistically significant ( $P < 0.05$ ) trends in PFGs ( $F_{trend}$  and  $SE_{trend}$ ) with their respective significant trends (or absence thereof) in SST and  $W_{EQ}$  (Figure 4.7). Each grouping is assigned a colour, with warm colours denoting an increasing trend in the PFG, while cool colours indicate a decline.

Coccolithophores aside, the largest coincident driver response in  $F_{trend}$  (Figure 4.7c) is an increase in PFGs coincident with warming and  $W_{EQ}$ , (most notably for dinoflagellates - orange bar; and less so for diatoms - blue bar). The same combination of drivers (i.e., warming and increased  $W_{EQ}$ ) is similarly coincident with a large decline in  $F_{trend}$  (Figure 4.7c), however the spatial distribution patterns differ considerably for each PFG (see Figure 4.7a; red dots versus dark green dots). Warming alone also coincides with a large proportion of increasing  $F_{trend}$  (Figure 4.7a; magenta dots). For driver response in  $SE_{trend}$ , there is an

overwhelming dominance of increasing trends for all PFGs (except coccolithophores) that are notably associated with both warming (magenta dots) and cooling (maroon dots), but with different regional expressions. A combination of warming and increased winds (red dots) also coincides with a large increase in *Spatial Extent* (Figure 4.7b, d), however less so for dinoflagellates (orange bar). Coccolithophores are the only PFG that show a dominance in decreasing  $SE_{trend}$  (Figure 4.7d; red bar), the majority of which are aligned with an increase in  $W_{EQ}$  together with warming (dark green dots) or an increase in  $W_{EQ}$  alone (black dots).

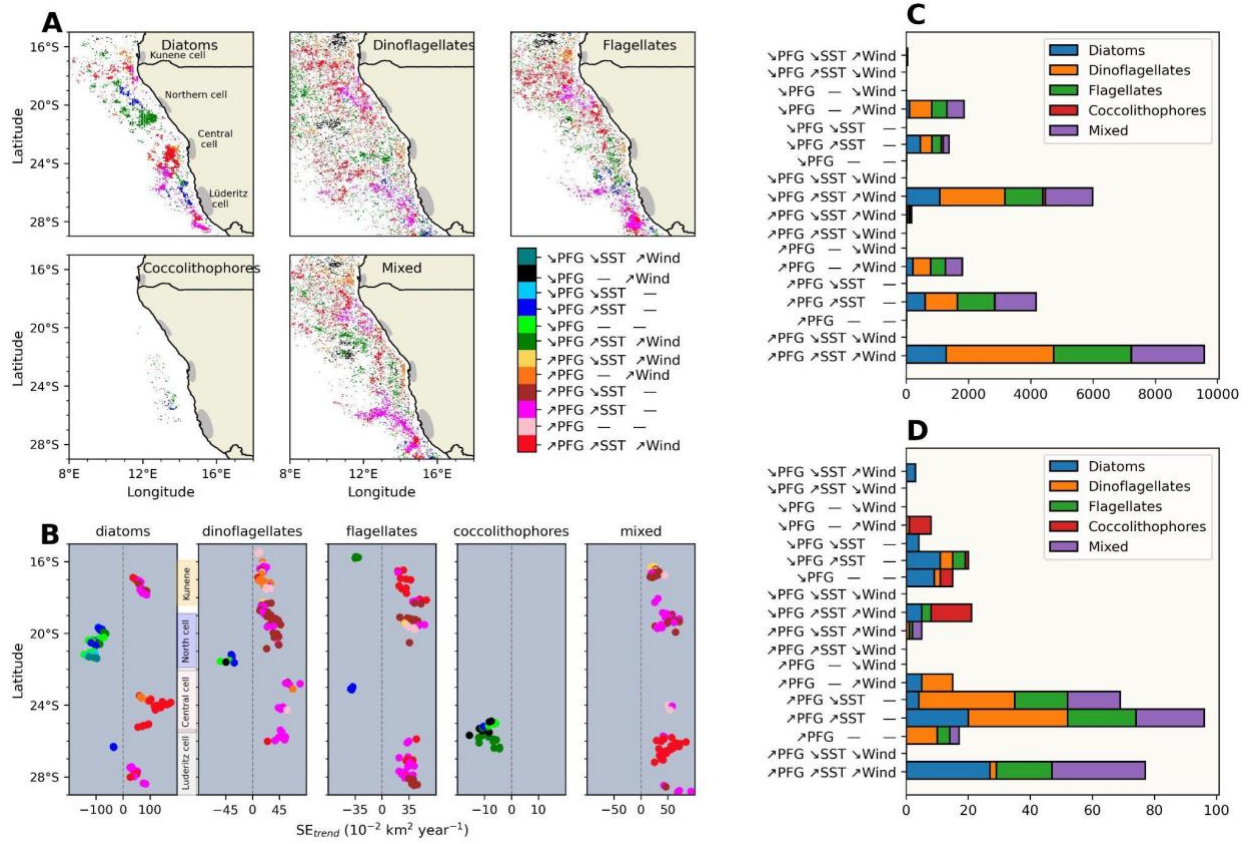


**Figure 4.7: Co-trends between PFGs against equatorward winds and sea surface temperatures.**

Spatial distribution of the classification of PFG response to SST and  $W_{EQ}$  between 2003–2022 in terms of *Frequency* (a) and *Spatial Extent* (b). The co-trends are indicated by different colour codes. The dashes indicate statistically insignificant ( $P > 0.05$ ) SST and equatorward wind trends whereas the arrows indicate significant directional trends. Only statistically significant  $F_{trend}$  and  $SE_{trend}$  were included. The counts of co-trends between PFG response ( $F_{trend}$  and  $SE_{trend}$ ) and SST and equatorward winds are shown in c and d, respectively.

## 4.5. Discussion

The occurrence and distribution of PFGs in the nBUS is primarily mediated by nutrient supply, temperature, light and turbulence (Hansen *et al.*, 2014; Mohrholz *et al.*, 2014). Equatorward winds drive coastal upwelling, which impacts temperature, turbulence, water column structure, nutrient and light supply. As such, these winds play a key role in determining the physicochemical environment that supports phytoplankton production, with different PFGs outcompeting others in the spectrum of conditions that vary both regionally (i.e., inshore/offshore, north/south) and temporally (i.e., on event/seasonal/annual and multi-decadal time scales) (Hansen *et al.*, 2014; Louw *et al.*, 2016; Mohrholz *et al.*, 2014; Siegel *et al.*, 2007).

The observed widespread adjustments in phytoplankton community dominance signify possible shifts in energy transfers and biogeochemical cycling within the ecosystem with significant multifaceted ecological implications. These changes can affect primary consumers and cascade to higher trophic levels such as krill, fish, marine mammals and birds, thereby impacting local biodiversity and fisheries yields that sustain local economies in this coastal region. In addition, given phytoplankton's roles in driving carbon export and air-sea gas exchanges, adjustments in community composition are likely to affect their role in climate regulation. Regions of increased trends in  $F_{trend}$  and  $SE_{trend}$  could potentially benefit commercial fish breeding grounds and food web biodiversity, depending on the functional group that is changing, while the opposite may be true for negative trends. Such adjustments may compel some species to adapt to new diets or result in migration of species that rely on specific phytoplankton to align with their preferred food source. For instance, decreases in energy transfer efficiencies have been associated with a collapse in anchovy larval fish populations in the California current upwelling system and vice versa, stressing the need for sustained quality foods for larval fish survival (Swalethorp *et al.*, 2023). In the current study,  $F_{trend}$  may also signal possible shifts in the phenology of PFGs since the *Frequency* metric relies on counting the number of days of PFG dominance. Increasing  $F_{trend}$  would thus imply PFG dominance that lasts longer and vice versa, which could reflect adjustments in PFGs phenology (e.g., through earlier or delayed bloom initiation, longer or shorter bloom durations). Such shifts in PFG phenologies (e.g., bloom initiation in particular) can potentially desynchronize the timing of food production and important life stages of higher trophic levels, affecting the survival of zooplankton and reproductive success of fish larvae (Cushing, 1990; Platt *et al.*, 2003). A phenology-focused study as a next step is necessary to fully constrain the occurrence and implications of these scenarios in the nBUS.

Diatoms are the most dominant PFG in the nBUS (Figure 4.2 and Figure 4.3) and key role players in the biological carbon pump (BCP) (Allen *et al.*, 2005). Our findings suggest that diatoms are particularly

sensitive to climate adjustments, raising concerns for the ecological impact that these changes may elicit. For instance, It is predicted that shifts away from diatom-dominated communities would negatively impact the efficiency of the BCP export and positively feedback into climate change dynamics (Cermeno *et al.*, 2008). Calcification and the downward flux of calcium carbonate ( $\text{CaCO}_3$ ) by coccolithophores also plays a key role in regulating the carbonate pump (Rost and Riebesell, 2004), which is likely to be negatively impacted by the significant decreasing trends in coccolithophores (Figure 4.5, 6 and Figure S4.7 in Annexure II). Coccolithophores and dinoflagellates also contribute to the global sulfur cycle as prominent DMSP producers (Yoch, 2002). DMSP supports up to 13% of bacterial carbon and sulfur demand while its cleavage to DMS gas enhances aerosol and cloud formation (Kiene *et al.*, 2000; Kiene and Taylor, 1988). As such, trends in these key species (declines in coccolithophores but notable increases in dinoflagellates) are likely to alter localized sulfur budgets and DMS emissions with impacts on albedo and climate regulation. Increasing trends in dinoflagellates are also of concern given their contributing role in the formation of Harmful Algal Blooms, which have the potential to cause devastating economic losses in the aquaculture and fisheries industries through accumulation of biotoxins and anoxia following collapse of high biomass blooms (Ndhlovu *et al.*, 2017).

Diatoms thrive in cold nutrient-enriched waters following upwelling events while dinoflagellates and flagellates can thrive in both cold, nutrient-rich as well as warmer stratified oligotrophic conditions (Hansen *et al.*, 2014). The observed shifts in diatoms towards areas of accelerating alongshore  $W_{EQ}$  (Kunene and Central cells) implies a shift to analogous environments of higher nutrient concentrations, while decreasing trends that align with decelerating alongshore  $W_{EQ}$  may be attributed to limited nutrient supply from decreased upwelling and/or an intensification of warming induced stratification. This is particularly evident in specific seasons where increasing  $F_{trend}$  and  $SE_{trend}$  in diatoms are coupled with decreasing  $F_{trend}$  and  $SE_{trend}$  in flagellates and dinoflagellates (e.g., Autumn) and vice versa (Summer) (Figure S4.6 in Annexure II), which can be attributed to competitive advantage (Hansen *et al.*, 2014; Pitcher *et al.*, 1991). These observations imply that competition for resources, particularly with diatoms, may be serving as a mechanism constraining flagellates and dinoflagellates intensification and expansion during periods of increased nutrient flux. On the other hand, coccolithophores thrive in stable and well stratified waters associated with low wind speeds and high solar radiation (Siegel *et al.*, 2007). It is not surprising that their declines are associated with increased offshore  $W_{EQ}$  (notably in Spring; Figure S4.6 in Annexure II), which may be amplifying turbulence and disrupting water column stability.

While there's general warming in the nBUS (Figure 4.1d, 4.6a and Figure S4.8 in Annexure II), the observed  $F_{trend}$  and  $SE_{trend}$  likely stem more from adjustments in alongshore  $W_{EQ}$  adjustments relative to

upwelling centers, highlighting the dominant role of wind-driven nutrient replenishment, while warming may increase their ability to exploit events of enhanced nutrient availability (Benedetti *et al.*, 2021) and likely drive changes in species diversity (Henson *et al.*, 2021). It should be noted, however, that the magnitude of long-term changes in SST and  $W_{EQ}$  may be insufficient to drive clear PFG compositional shifts. This is particularly plausible in the nBUS, where phytoplankton composition responds strongly to short-term upwelling variability, nutrient supply, and mesoscale processes (e.g., eddies) (Hansen *et al.*, 2014). For these reasons, it is possible that long-term ecosystem responses may be modulated by more frequent, short-term events that were beyond the temporal resolution of this trends analysis. Together, these results enrich our understanding of the underlying mechanisms steering community structure adjustments and highlights the complex associations and competitive interactions among PFGs, potentially serving as a driving force behind the observed spatiotemporal shifts and adjustments in PFG dominance.

Observed warming trends are likely to influence the metabolic rates of phytoplankton, with specific functional groups likely outcompeting others under warmer conditions (Soulié *et al.*, 2022). Similarly, trends in  $W_{EQ}$  bear profound implications for upwelling dynamics, a pivotal process governing nutrient replenishment to the euphotic zone which impacts phytoplankton productivity and community structure. Specifically, increasing alongshore  $W_{EQ}$  trends imply increased nutrient flux (through longer upwelling periods and/or increased upwelling strength) and vice versa for decreasing alongshore  $W_{EQ}$ , with downstream implications for the success of phytoplankton communities and the marine food web. Warmer conditions generally favor smaller-celled and motile phytoplankton such as dinoflagellates and coccolithophores which are better adapted to stratified, nutrient-depleted environments. In contrast, large diatoms, which depend on nutrient-rich conditions, are likely to be disadvantaged under sustained warming and reduced mixing. However, diatoms would be favoured in regions of increased nutrient-supply via wind-driven increased upwelling (Hansen *et al.*, 2014; Siegel *et al.*, 2007).

#### **4.6. Conclusions**

Our 20-year analysis of PFGs in the nBUS characterizes the regional and seasonal distribution of PFGs and reveals significant multidecadal shifts in response to changes in key physical drivers, notably upwelling-driving WEQ and SST. Seasonal expansions, contractions, and latitudinal redistributions in dominant PFGs highlight the dynamic and climate-sensitive nature of this ecosystem. These changes have major implications for biogeochemical cycling, food web dynamics, and the sustainability of ecosystem services. Comparisons with previous studies from the southern Benguela and other Atlantic upwelling systems suggest that similar phytoplankton community restructuring is occurring under broader global climate change. Our findings demonstrate the critical value of long-term, high-resolution satellite monitoring for detecting early ecological responses and emphasize the need for continued observation to guide adaptive management. Understanding phytoplankton responses to changing upwelling dynamics provides essential insight for conservation planning, and the development of climate-resilient marine protected areas. Insights into the changing upwelling dynamics and phytoplankton composition provide a scientific basis in support of informed decision-making in fisheries management and the development of effective policies aimed at ensuring sustainable practices and the preservation of marine resources within the context of climate change.

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## Chapter 5: Determining planktonic dimethyl sulfur compounds from space

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### 5.1. Abstract

Dimethyl sulfide gas and its precursor DMSP are significant sources of sulfur of biogenic origin in the upper ocean and atmosphere impacting marine microbial communities and climate dynamics. Here, *in situ* measurements of seawater DMS ( $\text{DMS}_{\text{sw}}$ ) and total DMSP ( $\text{DMSP}_t$ ) are used as a collective of dimethyl sulfur compounds (DMSc) in conjunction with colocated satellite estimates of SST and Chl, to develop a satellite remote sensing algorithm for estimation of  $\text{DMSP}_t$  in the upper ocean of the nBUS. DMSc observations were conducted from three cruise expeditions and one inshore anchor station, supplementing the dataset with previous DMSc records in the nBUS from the global sea surface DMS database and retrieving coincident satellite match-ups for the DMSc *in situ* observations. To develop a predictive algorithm, our dataset was randomly split into model training (70%, *in situ*) and validation (30%, satellite match-ups). Using the training dataset (*in situ* data), linear and quadratic relationships between DMSc, Chl, and SST, as well as between DMSc-to-Chl ratio and SST, were explored. Only strong ( $r > 0.5$ ) and significant ( $P < 0.05$ ) correlations were considered, which led to the development of 3 models: a quadratic multivariate approach incorporating both SST and Chl (Model A), a linear SST-dependent DMSc:Chl ratio model (Model B), and a quadratic SST-dependent DMSc:Chl ratio model (Model C). Regression analysis determined model coefficients using the training dataset, and performance was assessed through adjusted  $R^2$  and root mean squared error (RMSE). Further evaluation against the validation dataset, using RMSE, mean absolute percentage error (MAPE), mean relative bias (MRB), and median relative error (MedRE), identified Model A as the most accurate. Model A was thus selected for further analysis in the next chapter, where it will be applied to climatological datasets to assess seasonal patterns and multidecadal trends in DMSc.

## 5.2. Introduction

Dimethylsulfoniopropionate (DMSP) is a sulfur metabolite ubiquitous in the upper sunlit layer of the ocean produced primarily by marine phytoplankton and other microorganisms (Li *et al.*, 2010; Raina *et al.*, 2017; Yoch, 2002). DMSP accumulates intracellularly as particulate DMSP (DMSP<sub>p</sub>) in phytoplankton cells at high concentrations which vary between phytoplankton groups, with dinoflagellates, coccolithophores and some prokaryotes identified as DMSP hyper-producers (Belviso *et al.*, 1990; Saltzman and Cooper, 1989; Turner *et al.*, 1988). DMSP plays osmoregulatory, cryoprotectant and antioxidant roles in marine phytoplankton (Stefels, 2000; Sunda *et al.*, 2002; Van Alstyne and Puglisi, 2007). Cell disruption during death, aging (senescence), grazing by zooplankton and viral attacks on phytoplankton releases DMSP into the ocean environment as dissolved DMSP (DMSP<sub>d</sub>) (Brussaard *et al.*, 2005; Dacey and Wakeham, 1986; Wolfe *et al.*, 1994). Once released, DMSP<sub>d</sub> serves as a significant source of sulfur and carbon for bacterial communities, supporting between 5 to 15% of the bacterial carbon demand in surface waters (Kiene *et al.*, 2000). One of the DMSP degradation pathways involves its cleavage to the volatile DMS compound in a process mediated by DMSP lyase enzymes produced by some phytoplankton (diffuse release by DMSP<sub>p</sub> cleavage) and bacteria (cleavage of DMSP<sub>d</sub>) (Alcolombri *et al.*, 2015; Li *et al.*, 2021). (Franklin *et al.*, 2009; Kiene and Linn, 2000). DMS emissions from the ocean are a significant source of natural sulfur of biogenic origin to the atmosphere, with an estimated flux of  $\sim 28.1 \text{ Tg S yr}^{-1}$  (Lana *et al.*, 2011). Once released, DMS undergoes complex modifications leading to the formation of sulfate aerosols in the marine boundary layer. Such aerosols are capable of scattering incoming solar radiation, influencing cloud properties and act as cloud condensation nuclei (CCN), thus playing a critical role in regulating albedo and the Earth's climate (Bates *et al.*, 1987; Charlson *et al.*, 1987). Understanding and accurately quantifying DMS production is thus crucial for refining climate models, especially in highly productive marine regions like upwelling systems, where biological activity drives significant DMS production (Zindler *et al.*, 2012).

Eastern Boundary Upwelling Systems (EBUSs) are among the most productive oceanic regions globally that support large commercial fisheries (Carr and Kearns, 2003; Pauly and Christensen, 1995). The Benguela Upwelling System (BUS), partitioned into its northern (nBUS) and southern (sBUS) subsystems, is considered the world's most productive EBUSs (Carr, 2001). The nBUS experiences perennial coastal nutrient upwelling that supports high productivity that presents as sporadic phytoplankton blooms (Carr, 2001; Louw *et al.*, 2016; Matlakala, 2019). Upwelling zones such as those off the Peruvian, Mauritanian and Moroccan upwelling regions, as well as the North East Subarctic Pacific, are considered "hotspots" for DMS production due to their high primary productivity, dominance of high DMSP-producing dinoflagellates and prymnesiophytes following diatom bloom decline, iron (Fe) deposits from desert dust, supersaturation of oxygen (from newly upwelled water) and elevated DMSP-degrading microbial

communities (Andreae, 1985; Asher *et al.*, 2017; Belviso *et al.*, 2003; Franklin *et al.*, 2009; Royer *et al.*, 2010; Zindler *et al.*, 2012). The nBUS similarly experiences elevated phytoplankton blooms (Louw *et al.*, 2016), seasonal dust deposits from the Namib desert (Shikwambana and Kganyago, 2022), and seasonal (and event-scale) dominance of high-DMSP-producing coccolithophores (Hansen *et al.*, 2014; Siegel *et al.*, 2007) and dinoflagellates following declines in diatom blooms (Barlow *et al.*, 2018; Hansen *et al.*, 2014). As such, nBUS is expected to similarly behave as a “hotspot” for DMS production potentially contributing to the semi-permanent stratus cloud deck which has implications for albedo and climate regulation via radiative forcing.

Previous studies on DMS in the BUS focused on its regional variability and highlighted regional differences, with the more cooler subtropical productive Benguela waters (10 – 30 S) associated with larger DMS (>3 nM) compared to the warmer (30 N – 10 S) less productive regions (Andreae *et al.*, 1995; Bates *et al.*, 2001; Tanzer and Heumann, 1992). Nonetheless, a summary of the sea surface DMS observations collated from these Benguela research expeditions since 1980 (Table S5.1), highlights the scarcity of DMSP and DMS observations for the region. Existing environmental monitoring programs in the Benguela region focus primarily on physical and biological parameters like temperature, Chl as well as organisms at higher trophic levels (Barlow *et al.*, 2018; Cury and Shannon, 2004; Louw *et al.*, 2017, 2016; Matlakala, 2019) (see <https://www.dffe.gov.za> or <https://www.meft.gov.na> for full environmental reports), leaving DMSP and DMS dynamics largely unmonitored. This gap represents a critical oversight, particularly given the region’s potential contribution to regional sulfur cycling and the potential implications of DMS for climate regulation. The bottom line is that quantifying the spatiotemporal variability of DMSP and DMS concentrations in this highly productive region remains challenging with so few measurements. This observational gap highlights the need for technologies that extend our spatial and temporal sampling capabilities, with tools such as satellite ocean colour remote sensing at the forefront of practical application for continuous large-scale monitoring.

In recent years, several empirical approaches have been developed to estimate sea surface DMS concentrations and emissions at global scales (Belviso *et al.*, 2004; Galí *et al.*, 2018; Joge *et al.*, 2024; Simó and Dachs, 2002; Vallina and Simó, 2007). These models estimate DMS based on linear and multilinear regression methods using one or more ocean variables. The satellite algorithm approach of Galí *et al.* (2018), is to the best of our knowledge, the most recent algorithm that measures DMSP (Galí *et al.*, 2015) as the first step, and then predicts DMS from DMSP, allowing for the determination of both metabolites. While some of these models perform reasonably well globally, they generally find limited success at regional scales (Bell *et al.*, 2006) and tend to be outperformed by regional algorithms (Mansour *et al.*, 2023; McNabb

and Tortell, 2022). This underscores the necessity for developing regionally specific algorithms tailored to the distinct conditions of the nBUS, where unique upwelling dynamics and biological processes drive DMSP and DMS production.

This study aims to develop a satellite remote sensing algorithm for regional detection of DMSP and DMS as a collective (DMSc) in the nBUS upwelling region. By creating a regional model, this work will enhance our ability to estimate DMSc at large temporal and spatial scales to support an improved understanding of sulfur cycling in this ecologically vital area. Furthermore, the development of this algorithm will contribute to more comprehensive environmental monitoring systems, helping to inform climate models and conservation efforts, particularly as the impacts of climate change intensify in marine ecosystems.

## 5.3. Materials and methods

### 5.3.1. Data sources

#### 5.3.1.1. Cruise expeditions and sample analysis

This study focused on the nBUS off the coasts of Namibia and Angola within the latitudes and longitudes of 16–28° S and 9–15° E respectively (Figure 5.1a). Three cruise expeditions were carried out onboard the research vessel (RV) Meteor (M153, Feb – Mar 2019), RV Mirabilis (MIR2019, May 2019), Mirabilis (MIR2022, Apr – May 2022) and an inshore anchor station in Swakopmund (SWAK\_AS, Apr – May 2020) (Figure 5.1b). The geolocations of the stations sampled for all expeditions are as shown in Figure 5.1b. The author personally participated in all research expeditions mentioned above and was responsible for collecting the seawater samples used in this study.

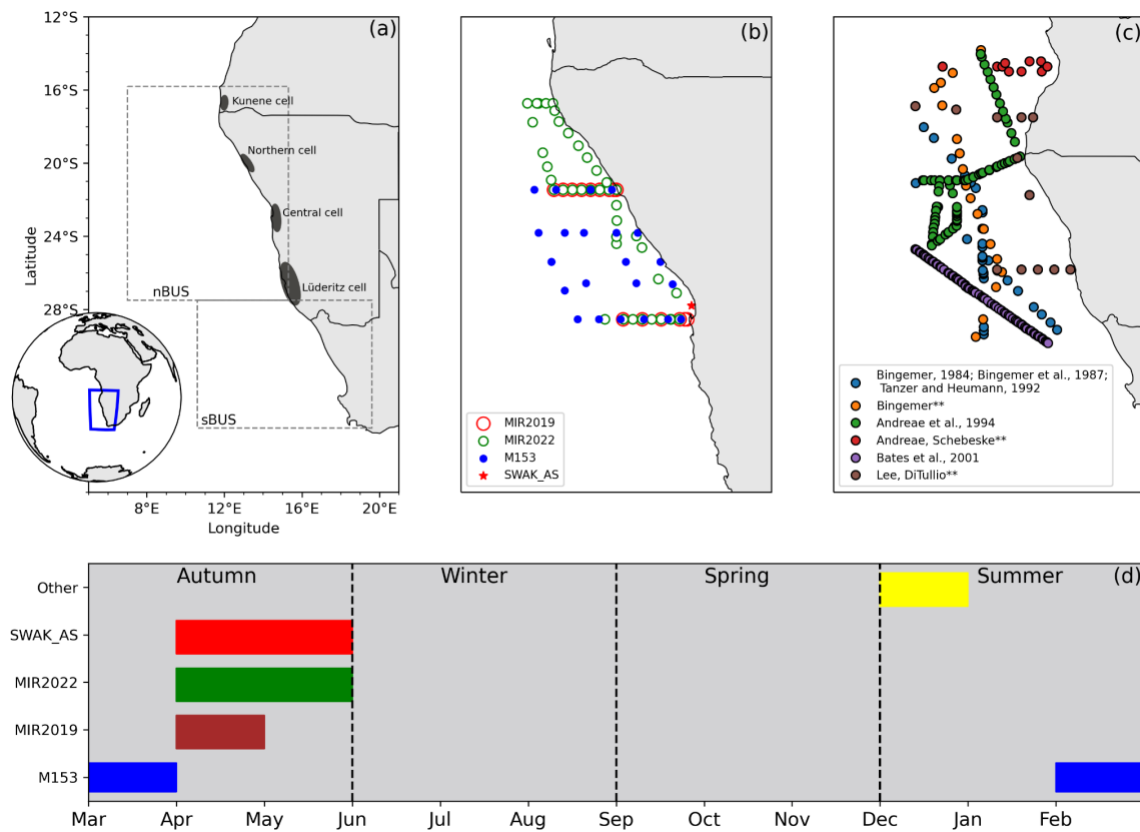


**Figure 5.1:** (a) The Benguela upwelling system along the southwestern tip of the African continent (inset) shared between South Africa, Namibia and Angola (shown in bold) with its northern (nBUS) and southern (sBUS) subsystems indicated by dashed gray boxes. Upwelling centers in the nBUS are indicated as gray shaded areas (b) Cruise expeditions that supported the collection of total DMSP (DMSPt) and/or DMS

observations from this study onboard the RVs *Mirabilis* (MIR2019, MIR2022, red and green circles respectively) and *Meteor* (M153, blue dots) as well as the inshore anchor station in Swakopmund (SWAK\_AS, red asterisk). **(c)** Historical research expeditions in the nBUS that supported the collection of DMSpt and/or DMS observations as obtained from the Global Sea Surface DMS database. **(d)** Temporal occupation of the various data sets used for algorithm development and validation.

#### 5.3.1.2. *Sampling and analysis*

For all cruise expeditions, seawater was sampled from Niskin bottles attached to a conductivity, temperature and depth (CTD) rosette in the surface ocean (0 – 3 m). For the inshore anchor station, a manually operated hand-held Niskin bottle was deployed from a jetty and used for seawater sampling from surface waters. Seawater was sampled from the Niskin bottles following the guidelines for sampling and analysis of seawater as recommended by (Stefels, 2009) for DMSP, DMS and DMSO analysis. Briefly, seawater was sampled gently into dark glass amber bottles using a teflon tube and allowed to overflow carefully without allowing any bubbling and then closed.

For total DMSP ( $\text{DMSPp} + \text{DMSPd} = \text{DMSPt}$ ) and DMS measurements, 10 mL of seawater was added to crimp-seal headspace sampling bottles. Then, Milli-Q water and a pellet of sodium hydroxide (NaOH) were added to convert DMSP to DMS. Duplicate samples were prepared for DMSP and DMS analysis. The sample bottles were immediately crimp-sealed and stored in the dark until analysis at a shore-based laboratory. Discrete DMSP–DMS (DMSc) measurements were analyzed by gas chromatography–mass spectrometry (GC–MS) coupled to a purge-and-trap system following the method described by (Zhou *et al.*, 2022). In this study, nitrogen gas was used as a carrier gas instead of helium. A new DMS standard was prepared for every analysis. For Chl samples, 200 ml of seawater was filtered through glass microfiber filters (Whatman GF/F, 25 mm diameter, 0.7  $\mu\text{m}$  pore size) and stored immediately in the freezer ( $-20\text{ }^{\circ}\text{C}$ ) for later analysis. A total of 79 discrete DMSc samples were collected from this study's cruise expeditions. Co-located total Chl was determined following the method of (Welschmeyer, 1994). Briefly, Chl was extracted from the GF/F filters by addition of 9 mL of 90% acetone for 24 hr in the dark at  $-20\text{ }^{\circ}\text{C}$ . These were then transferred into glass tubes and fluorescence was measured using a Turner (Model 10AU) fluorometer. Chl was determined from a seven-point calibration curve and represented as equivalents of Chl ( $\mu\text{g l}^{-1}$ ). The author personally participated in all research expeditions mentioned above and was responsible for collecting the seawater samples used and subsequent analysis of the DMSc and Chl samples used in this study.

#### 5.3.1.3. Additional data sources

The DMSP, DMS and Chl datasets from these cruises were complemented with additional *in situ* datasets from historical expeditions that were conducted in the nBUS obtained from the Global Surface Seawater (GSS) DMS database (<https://saga.pmel.noaa.gov/dms/>, last accessed: 30 April 2024) as summarized in Table 1. Data from the additional sources were considered only from samples collected in the top 10 m. The discrete DMSPt measurements in the GSS database were similarly obtained from alkaline hydrolysis of DMSP, a treatment resulting in the cleavage of DMSP to DMS that is subsequently analyzed by gas chromatography coupled to mass spectrometry. In some instances, DMSPt was partitioned into its particulate (DMSPp) and dissolved (DMSPd) fractions. As such, DMSPt was calculated as the sum of DMSPp and DMSPd when needed. DMSc was then computed as DMSPt + DMS. Ancillary data such as Chl and SST were also downloaded from the GSS database when available. The geolocations of the additional stations are shown in Figure 5.1c with the respective sampling dates and data sources are summarized in Table 1. A total of 247 data points were obtained. This supplementation with previous cruise datasets resulted in a total of 362 data points (Table 1).

**Table 5.1:** Past research expeditions in the Benguela upwelling system where *in situ* DMS and/or DMSP measurements were collected.

| Contributor        | Research Vessel / Platform | Start      | End        | No. of stations | Reference(s)                                  |
|--------------------|----------------------------|------------|------------|-----------------|-----------------------------------------------|
| Bingemer           | Polarstern                 | 1983/01/15 | 1983/01/18 | 12              | Bingemer, 1984; Bingemer <i>et al.</i> , 1987 |
| Kettle_D           | Polarstern                 | 1989/03/14 | 1989/03/17 | 21              | Tanzer and Heumann, 1992                      |
| Andreae            | Meteor                     | 1991/03/11 | 1991/03/20 | 87              | Andreae <i>et al.</i> , 1994                  |
| Bingemer           | Polarstern                 | 1993/11/08 | 1993/11/13 | 19              | unpublished                                   |
| Andreae, Schebeske | Meteor                     | 1994/04/30 | 1994/05/06 | 12              | unpublished                                   |
| Bates              | Ronald H. Brown            | 1999/02/04 | 1999/02/06 | 69              | Bates <i>et al.</i> , 2001                    |
| Lee, DiTullio      | RV Knorr                   | 2007/12/03 | 2007/12/11 | 27              | unpublished                                   |
| This study         | Meteor                     | 2019/02/02 | 2019/03/12 | 23              | This study                                    |
| This study         | Mirabilis                  | 2019/05/07 | 2019/05/09 | 15              | This study                                    |
| This study         | Mirabilis                  | 2022/04/25 | 2022/04/30 | 41              | This study                                    |

|            |                |            |            |    |            |
|------------|----------------|------------|------------|----|------------|
| This study | Anchor station | 2020/04/04 | 2020/05/13 | 36 | This study |
|------------|----------------|------------|------------|----|------------|

#### 5.3.1.4. Satellite data

Daily Level-2 (L2) 1km spatial resolution ocean colour satellite data from the Moderate Resolution Imaging Spectroradiometer on board the Aqua satellite (MODIS-Aqua) were obtained from the National Aeronautics and Space Administration (NASA) Ocean Color Web (<https://oceancolor.gsfc.nasa.gov/>, last accessed 30 April 2024). The standard MODIS-Aqua Chl product, based on an empirical relationship derived from remote sensing reflectance ( $R_{rs}$ ) between 440 and 670 nm was retrieved. This product is a combination of the standard OC3 algorithm (O'Reilly and Werdell, 2019) and the colour index (CI) algorithm (Hu *et al.*, 2012), where the OC3 algorithm is applied at Chl  $>0.2 \text{ mg m}^{-3}$ , whereas the CI algorithm is applied at Chl  $<0.15 \text{ mg m}^{-3}$ , and a weighted blending approach is applied between 0.15 and  $0.2 \text{ mg m}^{-3}$ . Other products obtained from MODIS L2 include the SST and L2 flags.

#### 5.3.1.5. Satellite matchups with *in situ* data

For satellite retrievals coinciding with *in situ* observations of DMSP (from this study and from the historical GSS DMS database), the highest available resolution observations (temporal: daily, spatial: 1km) L2 satellite retrievals from MODIS-Aqua were used. These were co-located in time and space ("matchups") against *in situ* observations following the steps outlined by Moloto *et al.* (2023). Retrievals of satellite Chl and SST are henceforth designated with the SAT subscript (i.e., Chl<sub>SAT</sub>, SST<sub>SAT</sub>).

#### 5.3.1.6. Data quality control

Quality control measures were implemented to minimize the inclusion of potentially erroneous and/or invalid *in situ* and satellite datasets following steps outlined by Moloto *et al.* (2023) in order to ensure consistency of the datasets and facilitate algorithm development. For datasets obtained from the GSS DMS database, only samples with concurrent DMSP<sub>t</sub> and DMS<sub>sw</sub> measurements were considered for this study. The quality-control measures applied resulted in a total of 106 (from 362) data points considered for algorithm development and validation, noting the dominance of autumn and the absence of winter and spring (Figure 5.1d).

### 5.3.2. Algorithm development using *in situ* datasets

Prior to algorithm development, the dataset containing co-located DMSc, Chl and SST were first randomly split into two subsets: a set for model training and cross-validation (70 % of the total points;  $n = 74$ ) and a set for model validation and evaluation (30 % of the total points;  $n = 32$ ) (Figure 5.2a). Secondly, in order to reduce skewness and variance of the datasets, especially those containing outlying observations, the

datasets were log-transformed (base 10) such that it mimics a normal distribution as is often considered to stabilize the variance of a series. The normality of the datasets was tested using the traditional 0.05  $P$  value cut-off. If the  $P$  value was less than 0.05, then the dataset is considered skewed (normal distribution is not assumed) and vice-versa if the  $P$  value was equal to or greater than 0.05. Variables with a skewed approximate distribution entered statistical analyses after log-normalization, including Chl and DMSc, whereas SST was not log-normalized (Figure 5.2b).

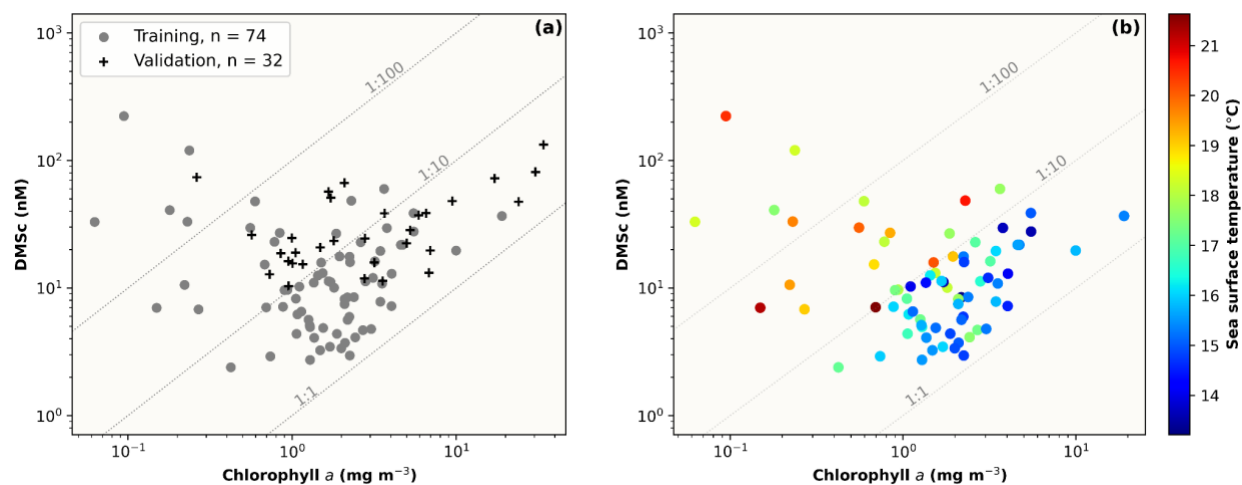


**Figure 5.2:** (a) Subsetting the quality-controlled *in situ* DMSc and chlorophyll  $a$  data into training (gray circles) and validation (black crosses) datasets based on random selection. (b) DMSc–Chl scatterplot (training subset) with the value of sea surface temperature (SST) shown in colour. The diagonal dotted gray lines in both (a) and (b) represent constant DMSc:Chl ratios.

To develop the DMSc algorithm, the relationships between DMSc (chemical), Chl (biological) and SST (environmental) were first analyzed to determine their suitability as possible predictors of DMSc from *in situ* datasets. Simple regression fits were conducted on possible predictors to explore the predictive skill of each variable separately (univariate) and as co-drivers (multivariate) as an exploratory analysis based on the calculation of Pearson (linear regression) and Spearman rank (nonlinear) correlation coefficients. Several base linear and quadratic regression models that predict either DMSc or DMSc-to-Chl ratio as functions of either Chl, SST or both, were built. These base models are defined by equations (2a) – (2h). Models were selected based on their regression results, with the strongest ( $r > 0.5$ ) and significant ( $P < 0.05$ ) predictors considered for further development and evaluation. Model performance was assessed based on their adjusted  $r$  squared ( $R^2$  adj) and the root-mean squared error (RMSE) when tested against the respective training datasets used in their development.

$$\log_{10}\text{DMSc} = \alpha + \beta_1 \log_{10}\text{Chl} \quad (2a)$$

$$\log_{10}\text{DMSc} = \alpha + \beta_1 \log_{10}\text{Chl}^2 + \beta_2 \log_{10}\text{Chl} \quad (2b)$$

$$\log_{10}\text{DMSc} = \alpha + \beta_1 \text{SST} \quad (2c)$$

$$\log_{10}\text{DMSc} = \alpha + \beta_1 \text{SST}^2 + \beta_2 \text{SST} \quad (2d)$$

$$\log_{10}\text{DMSc} = \alpha + \beta \text{SST} + \gamma \log_{10}\text{Chl} \quad (2e)$$

$$\log_{10}\text{DMSc} = \alpha + \beta_1 \text{SST}^2 + \beta_2 \text{SST} + \gamma_1 \log_{10}\text{Chl}^2 + \gamma_2 \log_{10}\text{Chl} \quad (2f)$$

$$\log_{10}\text{DMSc}-\text{Chl ratio} = \alpha + \beta_1 \text{SST} \quad (2g)$$

$$\log_{10}\text{DMSc}-\text{Chl ratio} = \alpha + \beta_1 \text{SST}^2 + \beta_2 \text{SST} \quad (2h)$$

### 5.3.3. Algorithm validation using satellite matchup datasets

Selected algorithms were validated using an independent data subset composed of satellite matchups ( $\text{Chl}_{\text{SAT}}$  and  $\text{SST}_{\text{SAT}}$ ). Log-normalization of DMSc, DMSc:Chl ratio and Chl was applied prior to cross-validation to avoid skewing the statistics toward the largest values. The algorithm performance, whereby DMSc measured *in situ* was compared to the DMSc predicted from remotely sensed  $\text{Chl}_{\text{SAT}}$  and  $\text{SST}_{\text{SAT}}$ , was evaluated using an array of statistical error metrics defined in Table 5.2 [squared correlation coefficient ( $R^2$ ), root mean squared error (RMSE), mean relative bias (MRB), median relative error (MedRE) and mean absolute percentage error (MAPE)].

**Table 5.2:** Statistical error metrics for model validation using independent datasets that were not part of the model development.  $\text{DMSc}_{\text{SAT}}$  and  $\text{DMSc}_{\text{obs}}$  denote satellite predictions and *in situ* observations of DMSc respectively. Statistics were performed on log-transformed DMS and Chl datasets for both observations and satellite estimations.

| Statistical metric                       | Mathematical equation                                                                                                                                                    |
|------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Root mean squared error<br>(RMSE)        | $\sqrt{\frac{\sum_{i=1}^N (\log_{10}\text{DMSc}_{\text{SAT}} - \log_{10}\text{DMSc}_{\text{obs}})^2}{N}}$                                                                |
| Mean relative bias<br>(MRB)              | $\sum_{i=1}^N \left( \frac{\log_{10}\text{DMSc}_{\text{SAT}} - \log_{10}\text{DMSc}_{\text{obs}}}{\log_{10}\text{DMSc}_{\text{obs}}} \right)$                            |
| Mean absolute percentage error<br>(MAPE) | $100 \frac{1}{N} \sum_{i=1}^N \text{abs} \left( \frac{\log_{10}\text{DMSc}_{\text{SAT}} - \log_{10}\text{DMSc}_{\text{obs}}}{\log_{10}\text{DMSc}_{\text{obs}}} \right)$ |

|                                                |                                                                                                                                         |
|------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------|
| <b>R-squared</b><br><b>(R<sup>2</sup>)</b>     | $1 - \frac{\sum_{i=1}^N (\log_{10} DMSc_{SAT} - \log_{10} DMSc_{obs})^2}{\sum_{i=1}^N (\log_{10} DMSc_{SAT} - \log_{10} DMSc_{obs})^2}$ |
| <b>Median relative error</b><br><b>(MedRE)</b> | $\frac{\log_{10} DMSc_{median_{SAT}} - \log_{10} DMSc_{median_{obs}}}{\log_{10} DMSc_{median_{obs}}}$                                   |

## 5.4. Results and discussion

### 5.4.1. Algorithm development and evaluation

Pearson (linear) and Spearman (non-linear) correlations were used to assess the relationships between potential predictor variables (log-normalized Chl and SST) and log-normalized DMSc or the DMSc:Chl ratio as shown in Figure 5.3. This analysis showed both positive and negative correlations between DMSc and the DMSc:Chl ratio against predictor variables which ranged in strength ( $r$  range = -0.6 to +0.63), with some relationships being statistically significant ( $P < 0.05$ ) (Figure 5.3). In general, these correlations were stronger for linear than for non-linear regressions (Figure 5.3).

Chl showed weak negative (linear;  $r = -0.13$ ) and positive (non-linear;  $r = 0.09$ ) correlations against DMSc, with statistically insignificant ( $P > 0.05$ ) contribution observed (Figures 5.3a–b, respectively). These weak correlations between Chl and DMSc have been observed previously for the Peruvian (Zhao *et al.*, 2022) and Mauritanian (Zindler *et al.*, 2012) upwelling systems as well as in global data sets (Galí *et al.* 2018, 2015). When interrogating the relationships in terms of degree of variance, Chl alone could only explain  $\leq 2\%$  of the variability in DMSc (Figure 5.3c, d). In this regard, Chl as an individual predictor of DMSc (Equations 2a and 2b) was not considered an effective predictor of DMSc and was disregarded for further model development.

SST on the other hand, although weakly positively correlated with DMSc ( $r = 0.33$  and  $0.28$  for linear and non-linear regressions respectively), these correlations were statistically significant (Figures 3a, b). As such, the environmental variable of SST alone could explain  $<11\%$  of the variability in DMSc (Figure 5.3c–d), which is substantially more than the biological variable of Chl. There are two possible explanations for the above-observed contrasting correlations with DMSc between Chl and SST: (1) *in situ* observations have shown, at limited spatial scales, that sea surface DMSP and DMS concentrations and variability are closely related to PFGs as opposed to abundance (using Chl as a proxy). This has been shown to be a result of differences in DMSP-producing capacity of phytoplankton, with the frequently blooming diatoms (in cold nutrient-rich environments) associated with higher Chl concentrations known for not producing high concentrations of intracellular DMSP, while DMSP-hyperproducing coccolithophores and dinoflagellates (which thrive in warm nutrient-deficit environments) more typically associated with low biomass (Chl) being important producers of DMSP and DMS (Masotti *et al.*, 2010; McParland and Levine, 2019; Zhou *et al.*, 2009). The nBUS is associated with the above-mentioned phytoplankton groups, with diatoms being the regular blooming species associated with high Chl biomass in cold nearshore waters while coccolithophores and dinoflagellates dominate in warm low-Chl oligotrophic waters following diatom

bloom collapse (Barlow *et al.*, 2018; Hansen *et al.*, 2014; Louw *et al.*, 2017; Siegel *et al.*, 2007). It is thus not surprising to observe relatively high DMSc concentrations across the full range of Chl observed (Figures 2b, 3a), which could possibly be a result of differences in phytoplankton communities under different biomass conditions as observed previously for the nBUS. (2) In the nBUS, SST dynamics have been shown to be directly related to phytoplankton group dominance. In the previous study (Chapter 4, manuscript in review) that corroborated the *in situ* observations of (Hansen *et al.*, 2014), different PFGs were shown to have different niche SST and  $W_{EQ}$  occupations. With regards to SST, dinoflagellates thrive in two conditions associated with low Chl: 1) cold and turbulent and 2) warm waters, diatoms (which are typically low DMSP-producing algae) are more common in cold eutrophic waters (high Chl associated with blooms) while flagellates, dinoflagellates and coccolithophores (hyper-producers of intracellular DMSP) thrive in warm (low Chl) oligotrophic waters. The observed correlation (or lack thereof for Chl) between SST vs DMSc may reflect how species composition (i.e., dominance succession) may be more important for DMSc variability than Chl in this region, as is previously been observed in subtropical, temperate and subpolar open-ocean areas (Galí and Simó, 2015; Simó and Pedrós-Alió, 1999; Vila-Costa *et al.*, 2008) from shipboard measurements globally. SST in this instance is thus more likely able to reflect aspects of community succession in the nBUS, which may explain the observed weak ( $r < 0.5$ ) but significant ( $P < 0.05$ ) positive correlation between SST and DMSc (Figure 5.3a, b).

Chlorophyll is strongly ( $r = 0.6$ ) and significantly negatively correlated with SST (Figure 5.3a, b). This is to be expected as diatom blooms (using Chl as a proxy) in the nBUS are typically observed in colder (nutrients rich) waters and collapse with increasing SST as nutrients are depleted in a phenomenon accompanied by phytoplankton community dominance succession (Hansen *et al.*, 2014; Louw *et al.*, 2016). With this in mind, the predictive power of the relationship between SST and the ratio between DMSc and Chl was interrogated. This ratio reflects the coupling and decoupling between biology (Chl) and DMSc in the region with varying SST. It was found that SST had the strongest and most significant correlation ( $r = 0.63$ ) with the DMSc-to-Chl ratio. Given the above, SST was subsequently considered for algorithm development as a predictor of both DMSc and the DMSc-to-Chl ratio, represented as equations (base models) 2(c), 2(d), 2(g) and 2(h). Models 2(g) and 2(h) that predict the DMSc-to-Chl ratio using SST, can subsequently be used to determine the total DMSc concentration by multiplying the ratio with co-located Chl. Shipboard observations, despite spatial limitations, have previously shown that sea surface DMS-to-Chl ratios are dependent on the composition of phytoplankton groups (Masotti *et al.*, 2010). Since phytoplankton succession in the nBUS is driven by upwelling events associated with varying SST, the use of SST for algorithm development in this study thus inherently considers the succession of dominant algal species in this region.

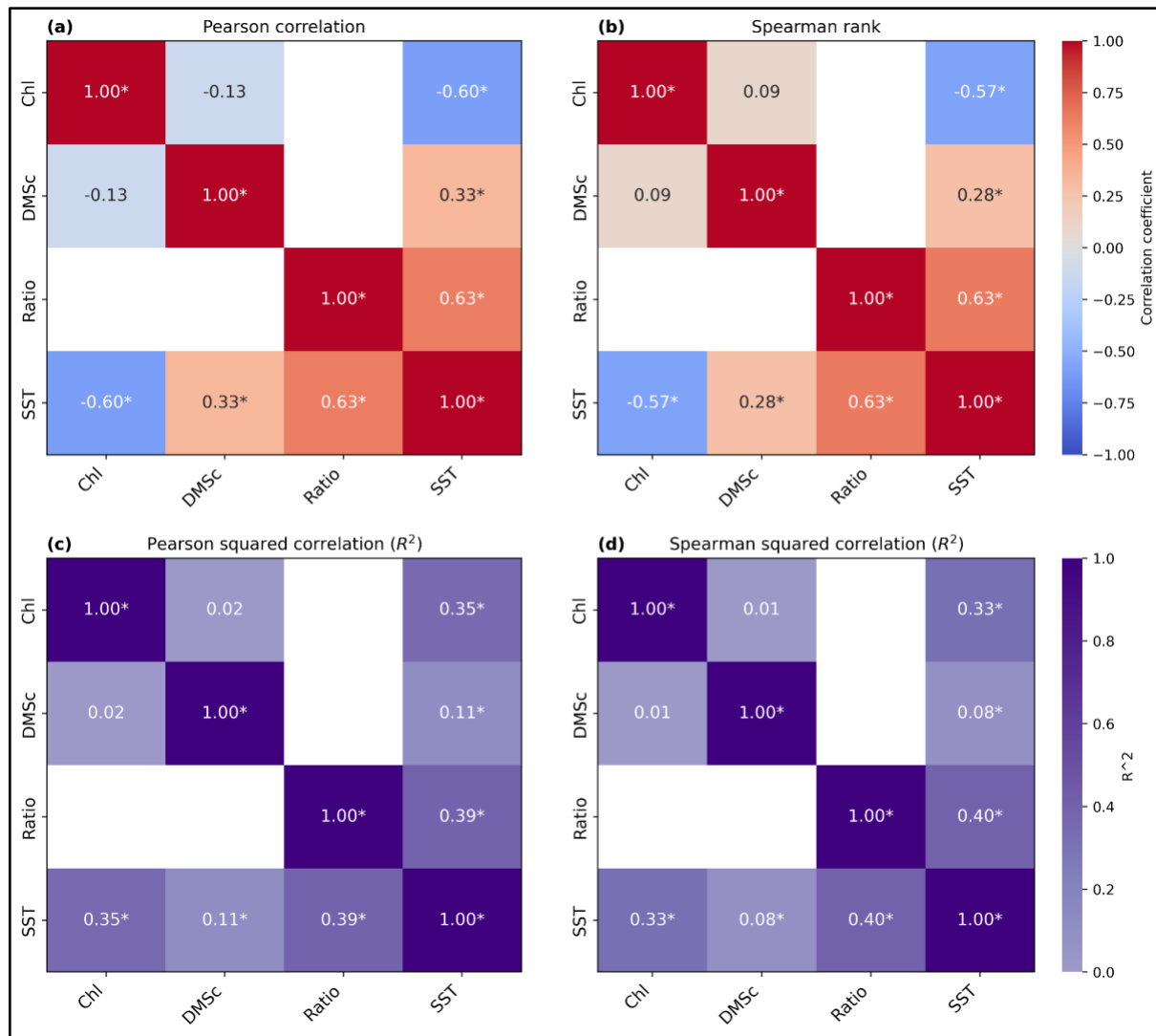


**Figure 5.3:** Heatmaps of the Pearson (a) and Spearman (b) rank correlations showing the degree of linear and non-linear correlations between DMSc and its proposed predictors of Chl and SST. Correlations between the DMSc:Chl ratio against SST were also tested. The colourbar indicates the direction (negative in shades of blue and positive in shades of red) and strength of the correlation. The coefficients of determination ( $R^2$ , the square of the correlation metrics), which shows the variance in DMSc or DMSc:Chl that can be explained by their respective predictor(s) are shown in (c) and (d). The blank cells in all figures mask the correlations between DMSc:Chl against Chl and DMSc. Self-self-correlations are indicated by the perfect correlations of 1. The asterisks indicate statistically significant ( $P < 0.05$ ) correlations.

The predictive ability of Chl and SST together were also tested in a multivariate analysis against DMSc (Figure 5.4). In this instance positive statistically significant regressions were observed for linear ( $r = 0.34$ )

and nonlinear ( $r = 0.59$ ) fits against DMSc, explaining up to 18% and 35% of the variance in DMSc for linear and non-linear fits respectively (Figure 5.4). The ability for Chl and SST to be used together as a multivariate predictor of DMSPt at a global scale was described previously by Galí *et al* (2018) using a quadratic fit. However, this relationship only held under certain physical conditions: namely in a “stratified” water column [based on the quotient between light penetration depth (*Zeu*) and mixed layer depth (MLD)]. In their study, these conditions were said to be related to saturation of phytoplankton (DMS producers) in shallow MLD’s under stratified conditions as opposed to deeper MLD’s of well mixed water columns (where the multivariate relationship did not hold), which were instead characterized by a more uniform distribution of nutrients, SST and other dissolved material across the water column. Our datasets were collected between December and May (i.e., during the warmer Summer and Autumn periods that are more susceptible to stratification) (Figure 5.1d). However, the nBUS experiences regular upwelling events throughout the seasonal cycle that intermittently bring cold subsurface waters to the surface inducing event scale well—mixed water columns throughout the year. The range of SST in our study (13.21 – 21.63 °C) reflects this event scale variability suggesting that our region was unlikely to typically meet the stratified criteria of Galí *et al* (2018) It is possible that the Chl—SST dynamics may be strongly related to DMSc irrespective of the water column structure, but it is more likely that the observed relationships under stratified conditions are responding to community structure adjustments that reflect community shifts during the quiescent stratified periods that follow an upwelling event.

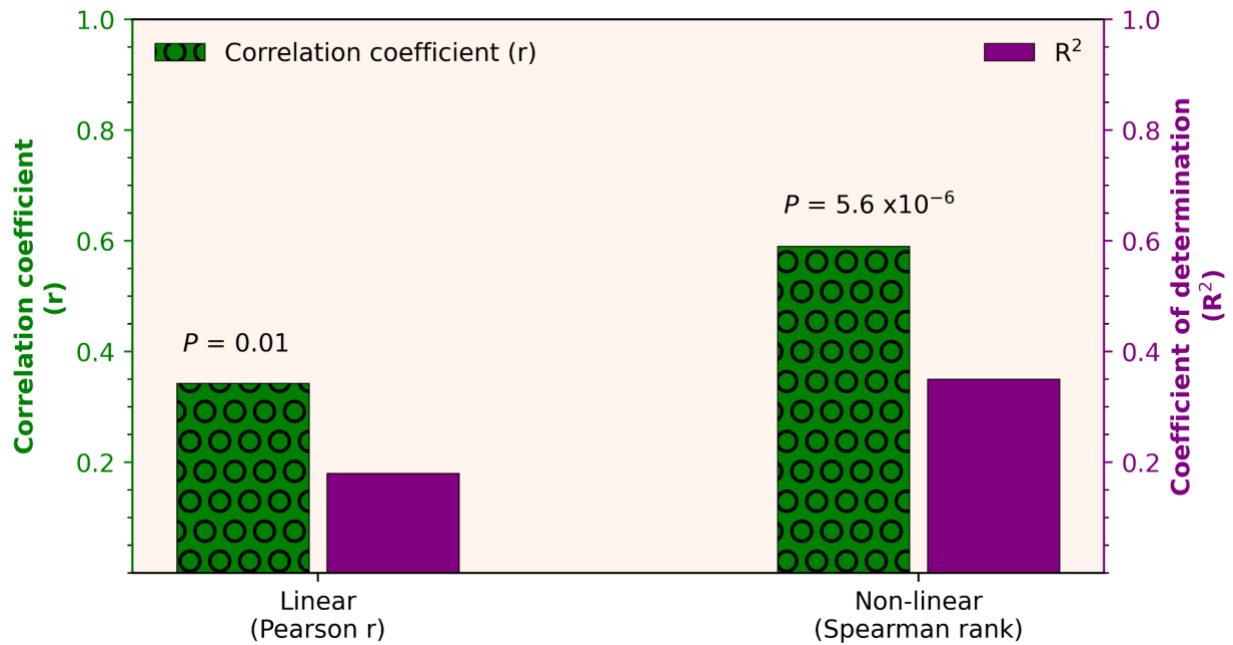


**Figure 5.4:** Linear and non-linear regression coefficients and coefficients of determination ( $R^2$ ) for multivariate regression between DMSc (target variable) against chlorophyll and sea surface temperature (predictors). The correlation coefficients are indicated by the green bars with circle hatches while coefficients of determination by cyan unhatched bars. The  $P$  values for each regression, indicative of statistical significance ( $P < 0.05$ ), are indicated as  $P$  above the correlation bar graphs.

Guided by the above-observed correlation patterns (Figures 5.3 and 5.4), the 3 best base models ( $r > 0.5$ ;  $P < 0.05$ ) were selected for further model development represented by equations 2(f) (quadratic model using both SST and Chl as predictors of DMSc), 2(g) and 2(h) (linear and quadratic models, respectively, using SST as a predictor of DMSc-to-Chl ratio, which is then multiplied by Chl to reveal the DMSc concentration). The coefficients of each model were determined from a regression analysis (Figure 5.5) and their significance (measured as  $P$  value) are summarized in Table 3. The statistical metrics, RMSE and  $R^2$ , were used to evaluate the performance of each model against the training dataset.

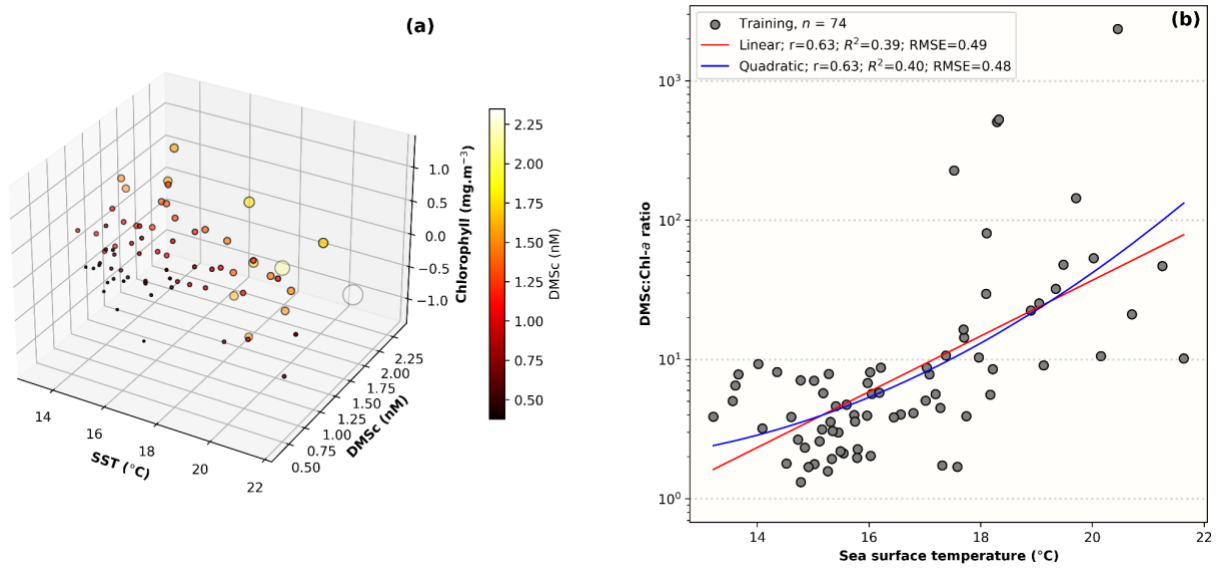


**Figure 5.5:** Regression analysis between DMSc, Chl and SST. **(a)** 3D scatter plot of the multivariate quadratic regression analysis between DMSc against both Chl and SST as predictors of its variability (equation 2f). The colourbar as well as the size range of the circles indicate the variability in DMSc. **(b)** Linear (red line) and quadratic (blue line) regressions between the DMSc:Chl ratio and SST (equations 2g and 2h respectively). The gray dots represent the training datasets ( $n = 74$ ). All variables except SST were log-transformed prior to analysis.

**Table 3:** Summary of fitted model coefficients and goodness-of-fit statistical metrics obtained when fitting the linear and quadratic regressions (Equations 2f - 2h) using *in situ* training data set observations of DMSc, SST and DMSc:Chl ratio). DMSc, Chl and DMSc:Chl were log-normalized prior to analysis.

| Model | Equation | Coefficients |           |           |            |            | Model evaluation |      |
|-------|----------|--------------|-----------|-----------|------------|------------|------------------|------|
|       |          | $\alpha$     | $\beta_1$ | $\beta_2$ | $\gamma_1$ | $\gamma_2$ | $R^2_{adjusted}$ | RMSE |
| A     | (2f)     | 1.58         | 0.01      | -0.15     | 0.60*      | 0.09       | 0.35             | 0.56 |

|                                     |      |        |       |       |                    |      |      |      |
|-------------------------------------|------|--------|-------|-------|--------------------|------|------|------|
| B                                   | (2g) | -2.43* | 0.2*  | –     | –                  | –    | 0.38 | 0.49 |
| C                                   | (2h) | 1.83   | 0.01  | -0.30 | –                  | –    | 0.38 | 0.48 |
| <i>P</i> values of the coefficients |      |        |       |       |                    |      |      |      |
| A                                   | (2f) | 0.54   | 0.47  | 0.62  | 1x10 <sup>-6</sup> | 0.39 | –    | –    |
| B                                   | (2g) | 0.000  | 0.000 | –     | –                  | –    | –    | –    |
| C                                   | (2h) | 0.300  | 0.383 | 0.287 | –                  | –    | –    | –    |

The asterisk and bold font denote coefficients that are statistically significant ( $P < 0.05$ ).

The resulting equations for the three selected model fits are as follows:

Model A:

$$\log_{10}\text{DMSc} = 1.58 + 0.01\text{SST}^2 - 0.15\text{SST} + 0.6\log_{10}\text{Chl}^2 + 0.09\log_{10}\text{Chl} \quad (2f)$$

Where only one of the Chl coefficients (0.61) is significant ( $P < 0.05$ ).

Model B:

$$\log_{10}\text{DMSc} = (-2.43 + 0.2\text{SST}) * \log_{10}\text{Chl} \quad (2g)$$

Where both the intercept (-2.43) and SST coefficient (0.2) are significant ( $P < 0.05$ ).

and

Model C:

$$\log_{10}\text{DMSc} = (1.83 + 0.01\text{SST}^2 - 0.30\text{SST}) * \log_{10}\text{Chl} \quad (2h)$$

Where the intercept and both SST coefficients are insignificant ( $P > 0.05$ ).

All three of the models showed similar  $R^2$  and RMSE values when evaluated against the training datasets (Tables 3). However, only Models A and B had statistically significant intercepts and coefficients of the predictor variables whereas model C coefficients showed no statistical significance towards DMSc determination. Nonetheless, all 3 models were validated against the test dataset (not used in model development) for further model validation.

#### 5.4.2. Algorithm validation

The three models (Models A, B, and C) were assessed for their ability to reproduce observed DMS concentrations in the validation data set from the Benguela upwelling region using RMSE, MAPE, MRB,

and MRE as evaluation metrics (Figure 5.6). Model A demonstrated the highest predictive accuracy, with a RMSE of  $0.34 \text{ nmol m}^{-3}$  and a MAPE of 18%, outperforming Models B (RMSE =  $0.39 \text{ nmol m}^{-3}$ , MAPE = 22%) and C (RMSE =  $0.38 \text{ nmol m}^{-3}$ , MAPE = 22%) (Figure 5.6). Notably, Model A's RMSE improved when validated against independent observations compared to the training dataset, underscoring its strong generalizability. In contrast, the RMSE values of Models B and C did not improve, indicating potential overfitting or incomplete representation of DMSc variability. Analysis of model biases revealed that Model A exhibits a mean relative bias (MRB) of  $-0.17 \text{ nmol m}^{-3}$ , suggesting a tendency to underestimate observations, while Models B and C showed positive MRB values of 0.06 and 0.03  $\text{nmol m}^{-3}$ , respectively, indicating an overall tendency to overestimation (Figure 5.6). Median relative error (MedRE) analysis further reinforced these findings, with Model A showing a net negative error (-0.24) compared to Models B (0.04) and C (0.04) (Figure 5.6). The models shows good agreement with observations at moderate to high DMS concentrations but tend to underestimate values below 30 nM. This underestimation is likely due to increased relative uncertainty in low-concentration measurements, reduced model sensitivity in the lower range, and limited representation of low-DMS samples in the training dataset. Together, these results establish Model A as the most accurate and robust of the three models for DMSc estimation in the region while highlighting areas for further refinement, in particular to address its underestimation tendencies. Together, these results establish Model A as the most accurate and robust of the three models for DMSc estimation in the region while highlighting areas for further refinement, in particular, to address its underestimation tendencies.

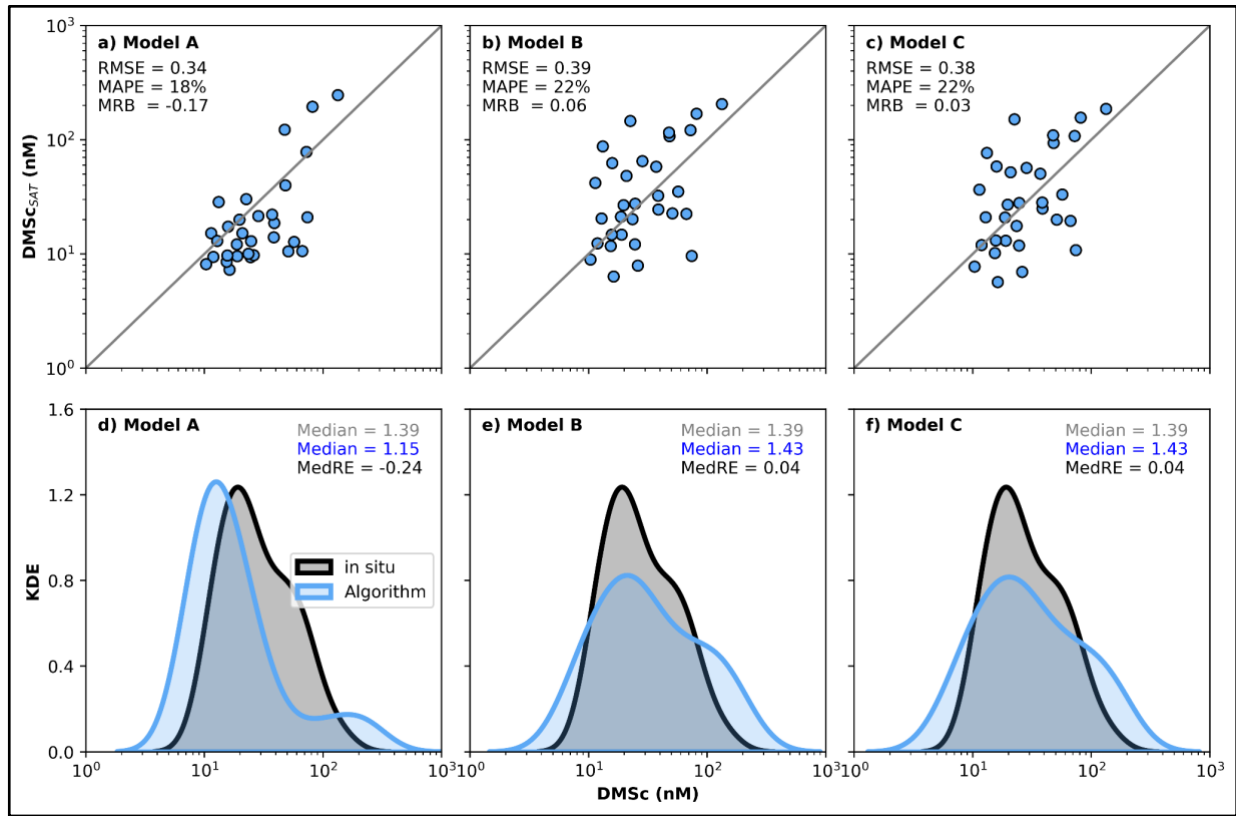


**Figure 5.6:** (a) - (c) Validation of the algorithms using satellite match-up datasets of chlorophyll and sea surface temperatures ( $\text{Chl}_{\text{SAT}}$ ,  $\text{SST}_{\text{SAT}}$  respectively). (d) - (f) Kernel density estimation (KDE) comparing the distribution between *in situ* observations of DMSc (gray shade, validation datasets,  $n = 31$ ) and satellite-derived DMSc estimations (blue shade). All statistics, the root mean squared error (RMSE), mean absolute percentage error (MAPE), mean relative bias (MRB), median and median relative error (MedRE) were calculated on log-transformed (base 10) datasets.

In what follows, some of the weaknesses of this novel approach are addressed, focusing on two aspects. Firstly, a key limitation in the development of remote sensing algorithms is data scarcity, particularly in under-observed regions such as the nBUS. Inadequate data coverage both regionally and seasonally limits the ability to accurately capture variability, and extreme events, all of which are critical for robust algorithm development and validation. This data shortage can introduce biases and reduce the model's ability to generalize. Moreover, sparse data complicates the calibration and validation of models, as insufficient data may cause overfitting, where models learn noise rather than genuine patterns. Secondly, the satellite algorithm developed here relies on only a few predictor variables, specifically Chl and SST. While these variables provide valuable insight into surface-level biological and thermal conditions, DMSc production is a complex process influenced by a broader range of factors, including phytoplankton community composition, chemical interactions, physical oceanographic processes, and the activity of other

microorganisms. Complex interactions between biological and physical processes, such as nutrient availability, vertical mixing, solar radiation dose, and microbial degradation, are not represented by Chl and SST alone, potentially leading to oversimplified predictions of DMSc concentrations. A recommendation for future work includes the need for additional *in situ* datasets with broader spatial and seasonal coverage. It is also recommended that future research efforts incorporate additional variables or proxy data sources that better capture the complex interplay driving DMSc. Together these approaches could assist in improving algorithm performance and enhance the accuracy of DMSc monitoring in this key region.

## 5.5. Conclusions

Understanding seasonal and regional dynamics and long term trends of DMSc in the Benguela upwelling system is essential for studying ocean-atmosphere-climate interactions due to its significant role in marine biogeochemical cycles, cloud formation and albedo (Bates *et al.*, 1987; Charlson *et al.*, 1987; Saltzman and Cooper, 1989). The Benguela, one of the most productive upwelling regions globally (Carr, 2001; Carr and Kearns, 2003), is a potential hotspot for DMSc production, yet its spatial and temporal variability and long term trends remains poorly characterized. By leveraging satellite-derived variables, remote sensing algorithms of DMSc can capture the dynamics of this key compound across spatial and temporal scales that are otherwise challenging to observe with shipboard observations alone. Such advancements are important for improving climate models and assessing the regional impacts of biogeochemical feedbacks on global climate systems. Here a satellite algorithm is developed specifically tailored to the region and aimed at filling a critical observational gap. The approach was to use co-located SST, Chl and DMSc training datasets to fit some models and to validate the best one using a smaller validation subset. The best results were achieved with a model that used both SST and Chl in a quadratic form. Although this algorithm had the best performance (RMSE 0.34 and MAPE 18%), it should be acknowledged that it tended to underestimate (with a bias of  $-0.17 \log_{10}$  space). The inherent limitations of this algorithm include its limited predictor variables, coupled with uncertainties in satellite measurements and the scarcity of *in situ* data for calibration and validation, constrain its accuracy and applicability. Despite its limitations, this satellite algorithm will prove invaluable in addressing critical environmental questions surrounding planktonic DMSc in the nBUS, offering insights into patterns and processes that are otherwise inaccessible with traditional *in situ* observations. Continued investment in algorithm refinement, enhanced data integration (such as solar radiation dose or photosynthetically active radiation, windiness, mixed layer depth), and expanded *in situ* validation efforts will ensure that this algorithm remains pivotal in tackling pressing challenges such as ecosystem management and the impacts of climate change in the nBUS.

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## Chapter 6: Unveiling seasonal patterns and multidecadal trends in planktonic dimethyl sulfur compounds from space

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### 6.1. Abstract

Planktonic dimethyl sulfur compounds (DMSc) are ubiquitous in the global surface ocean and play important roles in the sulfur cycle in support of marine communities and modulating climate dynamics. Here the seasonal and regional patterns and long-term trends of DMS and its precursor DMSP are investigated in relation to associated biophysical factors in the nBUS using 20 years (2003 – 2022) of daily MODIS-Aqua satellite observations. The DMSc seasonal cycle in the nBUS displays a classical “summer DMS paradox” in which the DMSc peak in Summer coincides with minimum Chl concentrations and maximum SST. Averaged across the nBUS region, the climatological DMSc seasonal cycle follows the pattern Summer ( $63.12 \text{ nmol m}^{-3}$ ) > Autumn ( $46.77 \text{ nmol m}^{-3}$ ) > Spring ( $17.26 \text{ nmol m}^{-3}$ ) > Winter ( $16.65 \text{ nmol m}^{-3}$ ). Our results suggest that this annual cycle is strongly influenced by temperature, windiness and phytoplankton community succession, with coccolithophore blooms and minimum winds coinciding with the Summer DMSc peak while minimum DMSc conditions in Winter are instead aligned with maximum Chl concentrations as well as blooms of diatoms and flagellates. Although DMSc shows an overall increasing annual trend of  $0.39 \text{ nmol m}^{-3} \text{ yr}^{-1}$ , notable regional and seasonal differences emerge upon closer examination. Annual trends in DMSc show a coherent increase offshore, with strongest positive trends observed in Summer and Autumn. This contrasts with the notable heterogeneity observed in inshore trends, with positive trends occurring in Winter, while negative trends are observed Spring and Autumn. Warming, along with the substantial overall expansion in dinoflagellates, one of the prominent groups of DMSc producing algae, can potentially explain the observed long-term increase in DMSc. This analysis represents the first attempt to reveal the previously unobserved spatially extensive seasonal cycle and multidecadal trends in DMSc concentrations in the nBUS.

## 6.2. Introduction

Planktonic dimethyl sulfur compounds, DMSP and DMS, are ubiquitous in the upper global ocean. DMSP has been a focus of many studies in the past decades, largely due to its osmoregulatory, antioxidant and cryoprotective roles in phytoplankton as well as serves as a significant source of carbon and sulfur to microbial communities in seawater (Kiene *et al.*, 2000; Kiene and Linn, 2000; McParland and Levine, 2019). Moreover, its cleavage to DMS contributes to aerosol and cloud formation thereby contributing to climate regulation via radiative forcing (Bates *et al.*, 1987; Charlson *et al.*, 1987). The roles of DMSP and DMS in phytoplankton, their biogeochemical and climatic importance as well as the key factors controlling their variability in marine environments have been extensively discussed in **Chapter 2 (section 2.5 of this thesis)** [also see thorough reviews by Kiene *et al* (2000) and Yoch (2002)]. Eastern Boundary Upwelling Systems (EBUS) are recognized as potential hotspots for DMSP and DMS production (Zindler *et al.*, 2012) due to their exceptionally high biological productivity (Carr, 2001; Carr and Kearns, 2003). Despite the Benguela upwelling system being the world's most productive EBUS (Carr, 2001), a comprehensive understanding of the regional distribution, seasonal cycle and long-term patterns of dimethyl sulfur compounds (DMSP and DMS, henceforth abbreviated as DMSc) remain elusive. This is primarily due to sparse *in situ* observations from shipboard surveys that typically occupy repeat monitoring lines with limited spatial, seasonal and temporal coverage. The application of satellite remote sensing of DMSc offers a transformative approach to addressing this problem by providing continuous and spatially extensive observations at high resolution that enable new insights into the spatiotemporal variability of these compounds and their interactions with climate drivers.

The nBUS has experienced significant climate-driven change in recent decades, with notable impacts on its physical and biogeochemical characteristics. Observations indicate a general warming of SST (Sweijd and Smit, 2020) and acceleration of trade winds (Polonsky and Serebrennikov, 2020). There is also evidence of shifts in the timing, duration and intensity of upwelling (Bordbar *et al.*, 2021; Lamont *et al.*, 2018; Santos *et al.*, 2012), potentially disrupting nutrient delivery to surface waters. Concurrently, the oxygen-minimum zones (OMZs) in the nBUS have expanded and exacerbate deoxygenation conditions in subsurface waters (Monteiro *et al.*, 2008). This deoxygenation, coupled with warming, and altered nutrient supply has implications for marine productivity, as plankton dynamics and trophic interactions are altered in response to varying physicochemical conditions (Auel and Ekau, 2009; Auel and Verheye, 2007; Ekau and Verheye, 2005; Wishner *et al.*, 2018). Any subsequent adjustments in primary productivity or shifts in dominant PFGs could cascade through the food web, threatening the ecosystem services they provide to the nBUS, such as the support of fisheries and climate feedbacks through carbon sequestration and the production of cloud precursor molecules via DMS. The role of cloud precursor molecules in the nBUS is

particularly relevant given the semi-permanent stratocumulus cloud deck that is characteristic of the region and has a large impact on albedo and global climate (Che *et al.*, 2022).

In **Chapter 4**, satellite observations of PFGs highlighted their large-scale seasonal, regional, and long-term shifts in response to climate drivers over the past two decades (2003–2022). Building on this foundation, this chapter aims to investigate the seasonal, regional and long-term variability of DMSc and investigate how these align with environmental and biological variability in the nBUS. To achieve this, this chapter seeks to (1) apply the regional DMSc satellite algorithm developed in **Chapter 5** to the same 20-year climatology in **Chapter 4**, (2) examine linkages between DMSc variability and satellite-derived Chl, SST, and  $W_{EQ}$ , and (3) assess how the dominance patterns and trends of different PFGs align with observed DMSc patterns and trends. Collectively, these objectives provide the first regional-scale assessment of DMSc variability in the nBUS and its relevance for understanding sulfur cycling under changing climate conditions. Understanding these interactions is critical for projecting how DMSc production in the nBUS may evolve under changing climate conditions, with implications for sulfur cycling impacting microbial communities and radiative forcing from cloud formation at both regional and global scales.

### 6.3. Materials and methods

#### 6.3.1. Ocean colour satellite remote sensing data

Daily L3 ocean colour remote sensing data with 4-km spatial resolution from the MODIS-Aqua were obtained as described in Chapter 4 (Section 4.3.1) and spanned the period from January 2003 to December 2022 for the region depicted in Figure 6.1.

#### 6.3.2. Equatorward winds

The Global Ocean Daily Gridded Reprocessed Level-3 (L3) Sea Surface Winds from Scatterometer data were obtained from the (European Union-Copernicus Marine Service, 2017). The meridional (V) and zonal (U) wind vector components at 10 m above sea surface were used to compute  $W_{EQ}$ .

#### 6.3.3. DMSc algorithm application

The satellite remote sensing algorithm for detection of DMSc in the nBUS derived in **Chapter 5**, shown by equation (1) below, was applied to 20 years of daily SST and Chl data from MODIS-Aqua to derive spatial and temporal distributions of DMSc for the period and region of interest.

$$\log_{10}\text{DMSc} = 1.58 + 0.01\text{SST}^2 - 0.15\text{SST} + 0.6\log_{10}\text{Chl}^2 + 0.09\log_{10}\text{Chl} \quad (1)$$

#### 6.3.4. PFG algorithm application

The ocean colour remote sensing algorithm for detection of dominant PFGs described in **Chapter 3** was similarly applied to 20 years of daily MODIS-Aqua ocean colour observation datasets. Following application of the algorithm, the *Spatial Extent* and *Frequency* metrics were computed to quantify the PFGs and used for further analysis.

#### 6.3.5. Regional and Seasonal Climatology

To assess the long-term mean spatial distributions of DMSc, PFGs (*Frequency*), Chl, SST and  $W_{EQ}$ , a 20-year climatology was derived from the satellite dataset covering the period 2003–2022. Daily DMSc, Chl,  $W_{EQ}$  and SST estimates were averaged across the entire 20-year time span to generate a spatially resolved climatological mean, providing an overview of the regional distribution of DMSc, Chl, SST and  $W_{EQ}$  in the nBUS. For PFGs, daily observations were counted for the 20-year period for each PFG, then the PFG with the highest count per pixel was assigned as being climatologically dominant.

To examine how regional distributions in DMSc, Chl, SST and  $W_{EQ}$  varied seasonally, daily estimates were averaged over each season: Summer (December–February), Autumn (March–May), Winter (June–August), and Spring (September–November). Spatial maps of the seasonal climatologies were computed by

averaging all days within the corresponding months over the full time period to highlight seasonal adjustments in regional patterns. Spatial maps of the seasonal climatologies for PFGs were computed in terms of *Frequency*, by counting the number of pixels dominated by each PFG for every season. Each pixel was assigned a dominance by a particular PFG when the seasonal counts (days per season) of that particular PFG were greater than all others over the 20-year period.

To examine the seasonal cycle of DMSc, Chl, SST and  $W_{EQ}$  averaged across the entire nBUS, daily satellite-derived estimates were aggregated into monthly mean values. For PFGs, monthly averages were created from their *Spatial Extent*, which reduces the impact of short-term fluctuations and instead emphasizes temporal adjustments in the seasonal cycle. The resulting monthly climatology provides insights into the typical seasonal cycle of DMSc in the nBUS over the study period and how this cycle aligns with biological and environmental factors.

#### **6.3.6. Trends analysis**

Annual mean DMSc were computed from daily satellite-derived DMSc estimations. Spatial linear trends analyses were determined on the annual time series following the method of Ryan-Keogh *et al.* (2022) as described in Chapter 4 (Section 2.5). In brief, pixels with less than 50% of the total time series (i.e., <10 years) were excluded from statistical trends analysis. Secondly, the datasets were tested for normality of their distribution. If the data were normally distributed, then linear regressions were performed using the robust Huber-Regression (epsilon ( $\epsilon$ ) = 1.35), whereas if data were not normally distributed, then linear regression analysis was performed using the Mann-Kendall (MK) test. Temporal trends in DMSc were calculated by 1) annual anomaly detection via subtracting the overall climatological mean from the individual annual mean values, and 2) annual mean DMSc which enables the investigation of the interannual variations in sea surface DMSc concentration.

## 6.4. Results

### 6.4.1. Climatological sea surface distribution of DMSc in relation to Chl, PFGs, SST and $W_{EQ}$

Here, the dynamics of DMSc in surface waters were evaluated from satellite observations using the algorithm developed in **Chapter 5** to document spatial and temporal variations based on 20 years (2003 – 2022) of daily MODIS-Aqua satellite observations. Regional climatological mean values of DMSc were analyzed in the context of associated biophysical variables (i.e., Chl as a proxy for phytoplankton biomass, PFGs as an indicator of dominant community composition, SST and  $W_{EQ}$ ) (Figure 6.1).

Regional variability was observed in the climatological distribution of DMSc across the nBUS that ranged from low values of  $<10 \text{ nmol m}^{-3}$  to high values of  $>200 \text{ nmol m}^{-3}$  (Figure 6.1a). However, occasional instances of extremely high DMSc were observed with a maximum recorded instance of  $1828.63 \text{ nmol m}^{-3}$ . This regional variability was aligned with varying physical (SST,  $W_{EQ}$ ) and biological (Chl and PFG) conditions. High concentrations of DMSc ( $>100 \text{ nmol m}^{-3}$ ) are observed in the alongshore region between  $16 - 26^\circ \text{ S}$  associated with high Chl ( $>10 \text{ mg m}^{-3}$ ) (Figure 6.1b) that was frequently dominated by diatoms (Figure 6.1c), weak winds ( $<7 \text{ m s}^{-1}$ ) (Figure 6.1e), and cooler conditions (Figure 6.1d) resulting from nutrient-enrichment of the sunlit surface ocean from wind driven upwelling (Louw *et al.*, 2016; Mohrholz *et al.*, 2014). High, more spatially homogenous DMSc concentrations ( $>100 \text{ nmol m}^{-3}$ ) are present north of  $16^\circ \text{ S}$  (Figure 6.1a) and associated with much warmer ( $>20^\circ \text{ C}$ ) conditions (Figure 6.1d), Chl ranging between  $0.5$  and  $7 \text{ mg m}^{-3}$  (Figure 6.1b), and a diverse phytoplankton community dominated by a combination of diatoms inshore, followed by flagellates, then mixed communities and lastly dinoflagellates further offshore (Figure 6.1c). Finally, high DMSc concentrations ( $>100 \text{ nmol m}^{-3}$ ) were also evident in the open ocean region West of  $11^\circ \text{ E}$  and South of  $24^\circ \text{ S}$  (Figure 6.1a), where Chl concentrations were particularly low (Figure 6.1b) and dominated by dinoflagellates (Figure 6.1c).

Low DMSc concentrations ( $<19.8 \text{ nmol m}^{-3}$ , indicated by the contour in Figure 6.1a) concentrations are observed in an offshore band South of  $20^\circ \text{ S}$  and East of  $12^\circ \text{ E}$ . Within the low DMSc band there is a decreasing gradient in DMSc with increasing latitude, with lowest concentrations further south (Figure 6.1a). This Low DMSc band is associated with cold conditions (SST  $<15^\circ \text{ C}$ ), moderate to strong winds ( $>7 \text{ m s}^{-1}$ ) and moderate to high Chl concentrations ( $>1 \text{ mg m}^{-3}$ ) with a strong inshore-offshore gradient that is dominated by diatoms.

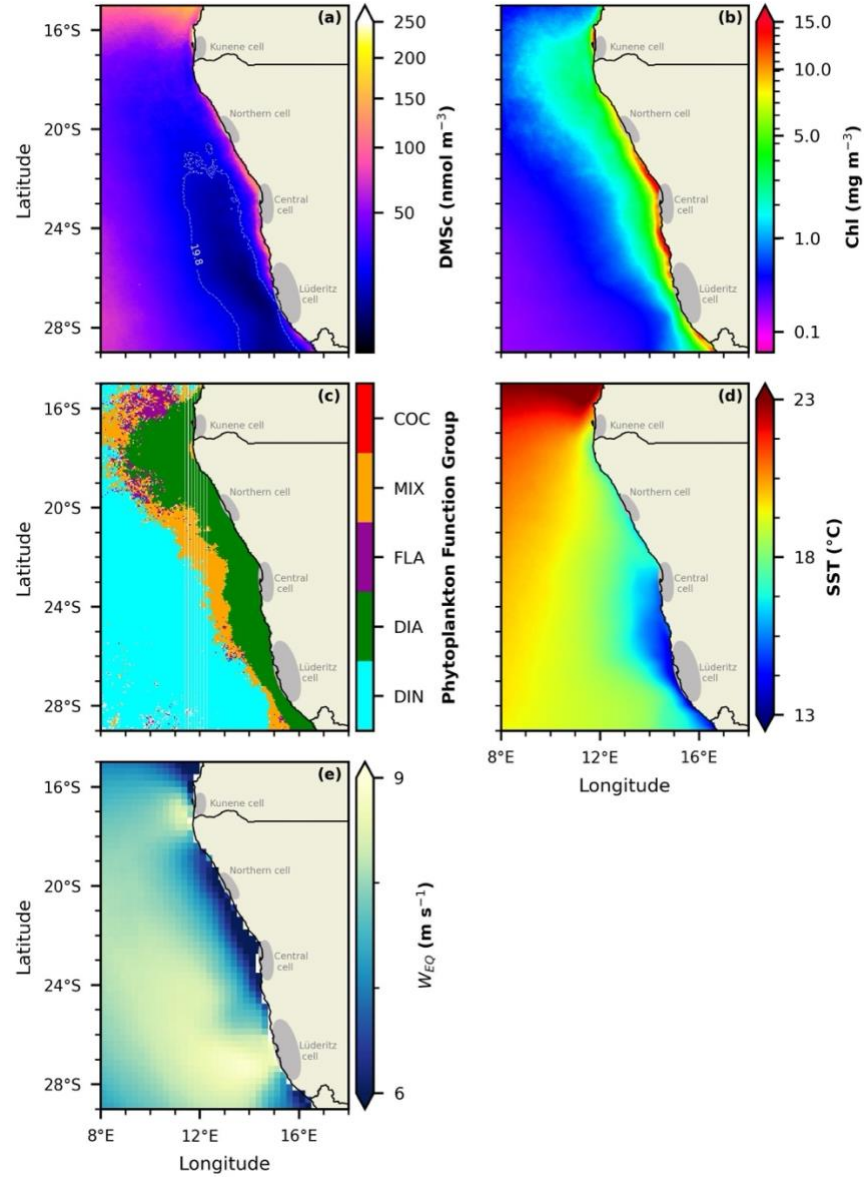


**Figure 6.1:** Regional map of the nBUS showing the climatological mean of planktonic dimethyl sulfur compounds (DMSc) (a), chlorophyll-a (Chl) (b), PFG dominance of dinoflagellates (DIN), diatoms (DIA), flagellates (FLA), mixed communities (MIX) and coccolithophores (COC) (c), sea surface temperature (SST) (d) and equatorward winds ( $W_{EQ}$ ) (e). All values were calculated from daily satellite observations between 2003–2022. The algorithms developed in Chapters 5 and 3 were used for DMSc and PFG analysis

respectively. The dotted white line in (a) represents the 19.8 mmol m<sup>-3</sup> DMSc isobar (determined as the 25th percentile).

#### 6.4.2. Seasonal changes in regional variability of sea surface DMSc in the context of Chl, PFG, SST and $W_{EQ}$

Significant seasonal variability was observed in the regional distribution of sea surface DMSc and other physical (SST,  $W_{EQ}$ ) and biological (Chl, PFGs) factors in the nBUS (Figure 6.2). The elevated coastal DMSc concentrations were observed across all seasons (Figure 6.2A) and associated with high phytoplankton biomass (Chl) (Figure 6.2b), dominance of diatoms (Figure 6.2C), moderate (<18 °C) SST (Figure 6.2D) and weak (<7 m s<sup>-1</sup>)  $W_{EQ}$  (Figure 6.2E). Seasonal variations were only evident in the offshore region (Figure 6.2) where consistently low DMSc is observed in Winter and Spring whereas the elevated DMSc concentrations (found north of 16 °S and West of 11 °E and South of 24 °S) occur in Summer and Autumn (Figure 6.2A).

While Summer and Autumn have similar DMSc, Chl and SST spatial distribution patterns, key differences are evident in their  $W_{EQ}$  and PFG patterns (Figures 6.2A-E, and Figure S6.1 in Annexure IV). Summer is the only season with evidence of coccolithophore dominance (Figures 6.2C and S6.1 in Annexure IV), albeit in small patches (Figure 6.2C) with almost no instances of flagellate dominances. In Autumn, there are no instances of coccolithophore dominance, and there are more regions dominated by flagellates and diatoms (Figures 6.2C and S1 in Annexure IV). In terms of the  $W_{EQ}$  patterns, Summer has the lowest winds (when averaged over the nBUS region, Figure S6.1 in Annexure IV) and a uniform distribution of moderate to strong (>8 m s<sup>-1</sup>) winds whereas strong (>10 m s<sup>-1</sup>)  $W_{EQ}$  are found at ~26.6 S in Summer while the region north of 16 °S has moderate to weak (<8 m s<sup>-1</sup>) (Figure 6.2E). Similarly, Winter and Spring have similar spatial DMSc, Chl and SST and  $W_{EQ}$  distribution patterns (Figures 6.2A-E), but there are key differences in PFG distributions characterized by a larger proportion of dinoflagellates in Spring than in Winter and a larger proportion of flagellates in Winter than in Spring (Figure 6.2C and Figure S6.2 in Annexure IV). In terms of  $W_{EQ}$  amplitude, spring exhibits stronger winds (>9 m s<sup>-1</sup>) compared to winter (Figure 2E).

The low DMSc band observed offshore in the annual climatology (Figure 6.1a) persists across all seasons (Figure 6.2A) and can be regarded as a “DMSc-minimum-zone”. Here, colder conditions (~ <14 °C) prevail throughout all seasons with variable Chl, PFG dominance and  $W_{EQ}$  patterns (Figure 6.2b-d) .

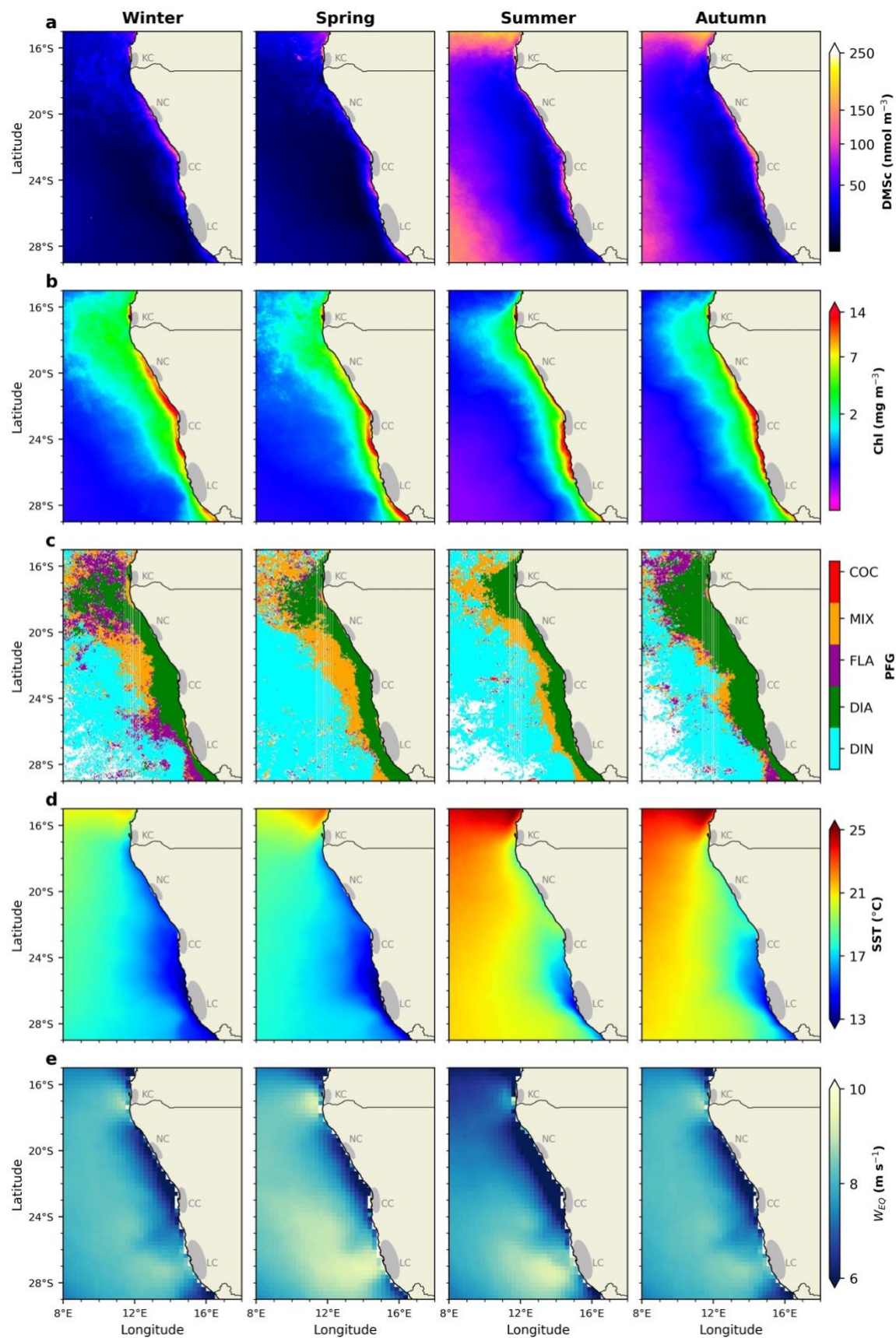


**Figure 6.2:** Seasonal changes in regional variability for **A)** dimethyl sulfur compounds (DMSc), **B)** Chlorophyll (Chl), **C)** PFG *Frequency* of dominance for dinoflagellates (DIN), diatoms (DIA), flagellates (FLA), mixed communities (MIX) and coccolithophores (COC), **D)** sea surface temperature (SST) as well as in **E)** equatorward winds ( $W_{EQ}$ ) for Winter (June, July, August), Spring (September, October, November), and Summer (December, January, February) and Autumn (March, April, May). All values were computed from 20 years (2003–2022) of daily satellite observations. The Kunene (KC), Northern (NC), Central (CC) and Lüderitz (LC) upwelling cells are indicated by the grey shadings.

#### 6.4.3. Seasonal cycle of regionally averaged sea surface DMSc in the context of Chl, PFG, SST and $W_{EQ}$

Here, monthly averages were utilized across the entire nBUS region to explore the mean seasonal cycle of sea surface DMSc and in the context of seasonal adjustments in Chl, SST,  $W_{EQ}$  and PFGs from *Spatial Extent* (Figure 6.3). Highest DMSc was observed in Summer (mean =  $63.12 \text{ nmol m}^{-3}$ ), followed by Autumn (mean =  $46.77 \text{ nmol m}^{-3}$ ), with low DMSc in Spring and Winter (mean =  $17.26$  and  $16.65 \text{ nmol m}^{-3}$  respectively) (Figure 6.3). The low DMSc concentrations in Winter and Spring coincides with periods of maximum phytoplankton biomass (Chl) and low SST (Figure 6.3a), with strong  $W_{EQ}$  (Figure 6.3b) and *vice versa* for high DMSc conditions observed in Summer.

It is understood that during the growing season, phytoplankton not only accumulate biomass but also expand in their spatial coverage. With this in mind, an examination of the seasonal cycle of *Spatial Extent* ( $\text{km}^2$ ) allows for the determination of the blooming period for each PFG, defined as the period when the *Spatial Extent* increases above its climatological mean (Figure S6.2 in Annexure IV). These results show that there is overlap in the blooming season for diatoms, dinoflagellates, flagellates and mixed communities, whereas coccolithophores instead typically bloom in late spring and summer which coincides with a secondary bloom in dinoflagellates (Figure S6.2 in Annexure IV). When examining the seasonal cycle of DMSc in the context of the phenology of the various PFG's (Figure 6.3c), it becomes clear that periods of minimum DMSc are associated with bloom peak timing periods of diatoms (May, late Autumn), flagellates (June, early Winter), mixed communities (July, late Winter) and dinoflagellates (April, mid-autumn). On the other hand, an increase in DMSc concentrations towards the summer maxima coincide with the timing of coccolithophore blooming period (December, early Summer) (Figure 6.3c).

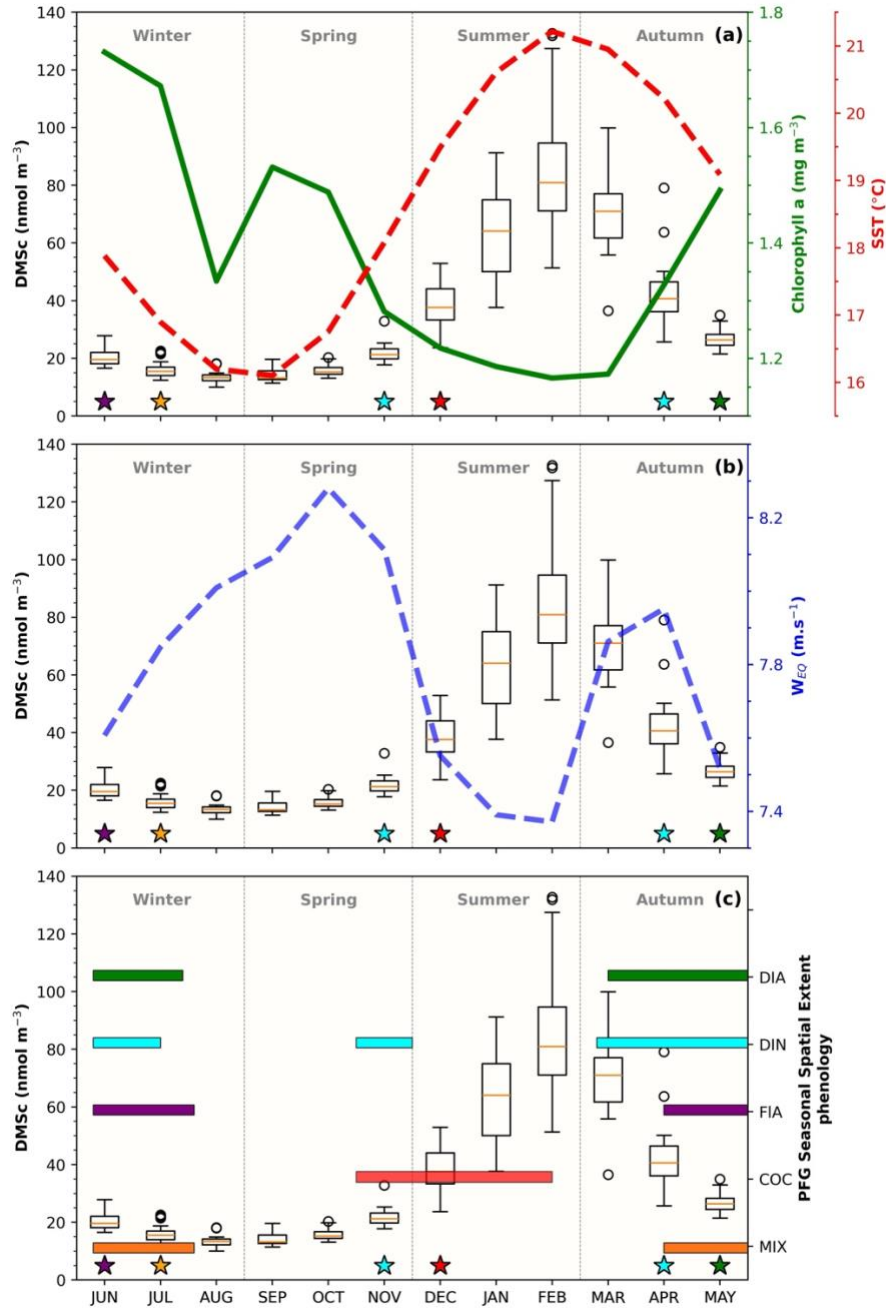


**Figure 6.3:** Seasonal cycle of DMSc (boxplot) in the nBUS with the mean value shown by the orange line and outliers by white circles (a)–(c). Seasonal cycles of chlorophyll (green solid line), sea surface temperature (SST, dotted red line) (a) as well as of equatorward winds ( $W_{EQ}$ , blue dotted line) (b) are also shown. The blooming period of each PFG (defined as the period when the *Spatial Extent* of that PFG increases above its climatological mean) is presented in (c) as horizontal bars for diatoms (DIA, green), dinoflagellates (DIN, cyan), flagellates (FLA, purple), coccolithophores (COC, red) and mixed communities (MIX, orange). The stars in (a)–(c) indicate the period (month) of peak (maximum) *Spatial Extent* for each PFG.

#### 6.4.4. Multidecadal trends in sea surface DMSc

The multi-decadal (20 year) annual and seasonal trends in DMSc spanning the period from 2003 to 2022 for the nBUS are as shown in Figures 6.4 and 6.5. Here, the regional annual trends analysis reveals a more heterogeneous distribution of significant ( $P < 0.05$ ) positive and negative trends in inshore waters (Figure 6.4a), which alternate with latitude. Coastal areas adjacent to the Kunene and Central upwelling cells are associated with increasing trends, while the region between the Northern and Central cells as well as the Lüderitz cell are instead associated with declining trends in DMSc (Figure 6.4a). In offshore waters, a more homogenous zone of significant positive trends of increasing DMSc is observed (Figure 6.4a). There are however areas where no significant trends are evident, with small patches of negative trends identified offshore off the Kunene cell (Figure 6.4a). When averaged over the whole of the nBUS region (Figures 6.4b-c), both the trends in anomalies and the trends in the annual means highlight the dominance of an increase in DMSc of  $0.37\text{--}0.39\text{ nmol m}^{-3}\text{ yr}^{-1}$ , over the past 20 years (2003–2022).

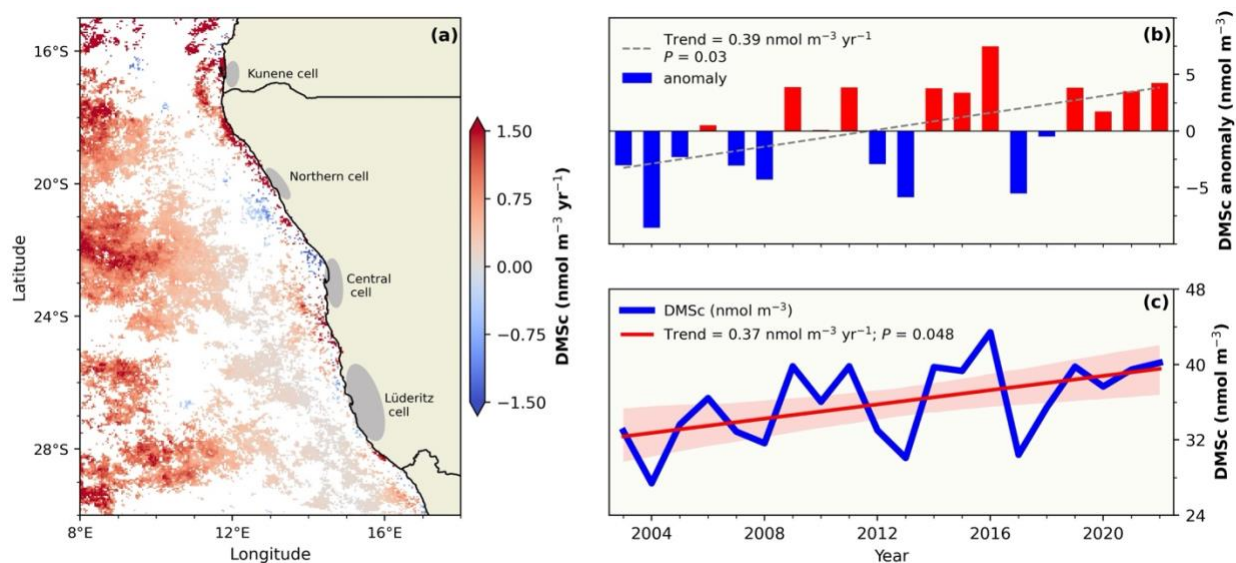


**Figure 6.4:** Multi-decadal trends in dimethyl sulfur compounds (DMSc) in the nBUS based on 20 years of daily MODIS-Aqua observations. (a) Spatial variability in statistically significant ( $P < 0.05$ ) trends (log space), (b) shows the interannual variability in DMSc anomalies (blue and red bars, indicating anomalously low or high DMSc respectively) and the linear trend (dotted grey line) whereas (c) shows the annual mean DMSc (blue solid line) and the linear trend (red line). The shaded area (red) in (c) indicates the 95% confidence level.

When the trends in DMSc are interrogated on a seasonal basis, it is possible to identify both regional and seasonal discrepancies in where and when these changes are occurring (Figure 6.5). Strong positive ( $>4 \text{ nmol m}^{-3} \text{ yr}^{-1}$ ,  $P < 0.05$ ) trends were observed offshore during the relatively warmer Summer and Autumn seasons (Figure 6.5c–d). Strong positive ( $>0.8 \text{ nmol m}^{-3} \text{ yr}^{-1}$ ) trends were also detected in Winter (Figure 6.5a), predominantly along the inshore regions of the coastline. An exception is the negative trend in DMSc observed inshore in Winter off the northern upwelling cell. In Spring (Figure 6.5b), the majority of the nBUS exhibited moderate to weak positive trends ( $<0.8 \text{ nmol m}^{-3} \text{ yr}^{-1}$ ,  $P < 0.05$ ) except for the inshore region near the Kunene cell that displayed strong positive ( $>0.8 \text{ nmol m}^{-3} \text{ yr}^{-1}$ ,  $P < 0.05$ ) trends and predominantly negative trends in the near coastal waters, most notably off the Lüderitz cell. Additionally, negative trends were generally more pronounced in Autumn inshore near the Central and Northern upwelling cells and offshore off the Kunene cell (Figure 6.5d). These seasonal discrepancies in the distribution of the trends, with negative trends occurring most frequently in winter and positive trends in summer, is confirmed in the trend distribution plots (Figure S6.3A in Annexure IV). However, when the affected area of these trends is taken into consideration (Figure S6.3B in Annexure IV) it is clear that the nBUS region is overwhelmingly dominated by positive trends, with the largest affected area occurring in Summer and Autumn. Averaging the trends in DMSc across the whole nBUS and over each season shows that Autumn has the strongest mean increase in DMSc ( $1.55 \text{ nmol m}^{-3} \text{ yr}^{-1}$ ), followed by Summer ( $1.43 \text{ nmol m}^{-3} \text{ yr}^{-1}$ ), then Winter ( $0.30 \text{ nmol m}^{-3} \text{ yr}^{-1}$ ) and lastly Spring ( $0.17 \text{ nmol m}^{-3} \text{ yr}^{-1}$ ) (Figure S6.4 in Annexure IV).

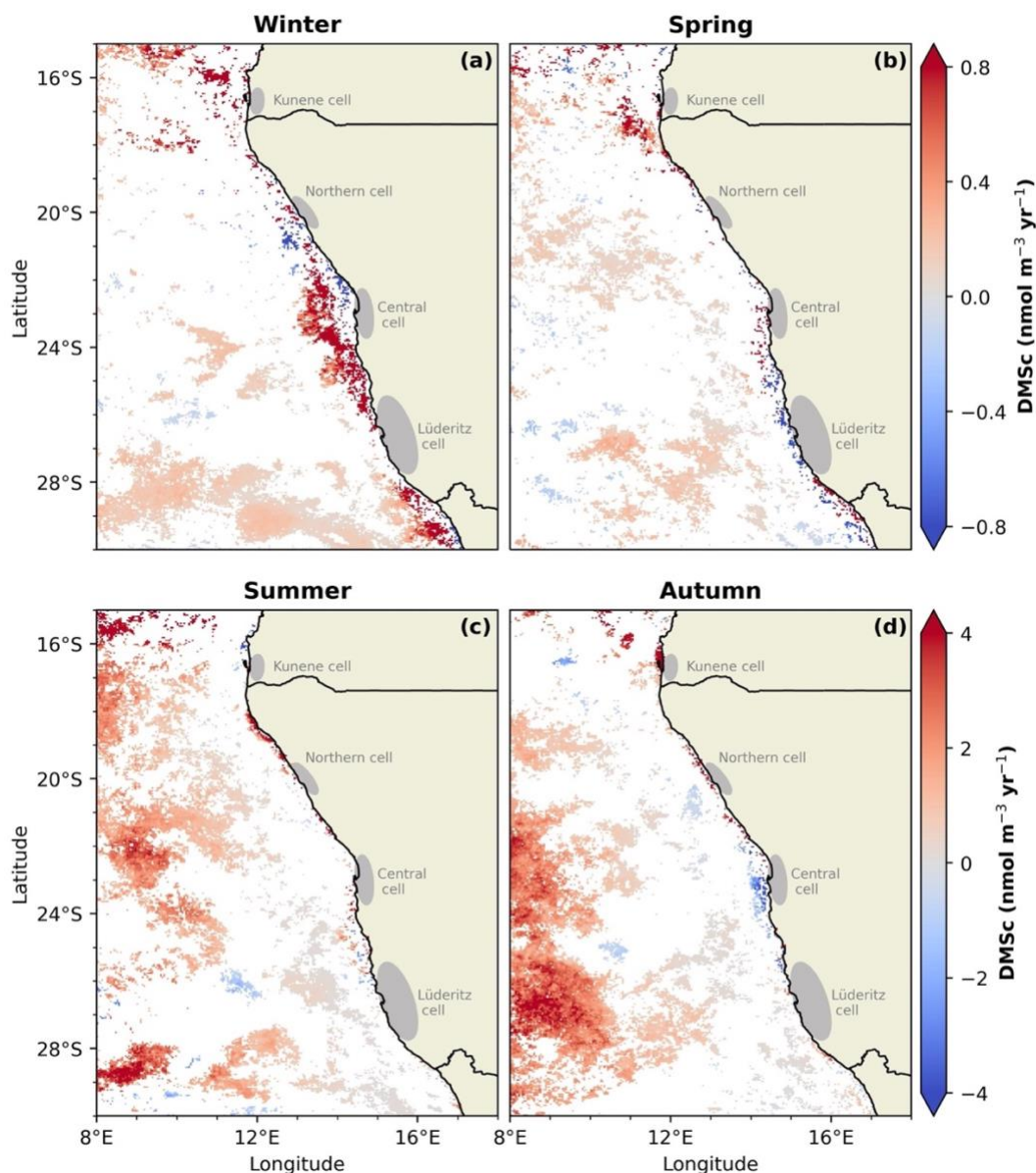


**Figure 6.5:** Seasonal disparities in long-term trends in dimethyl sulfur compounds (DMSc) in the nBUS for (a) Winter, (b) Spring, (c) Summer and (d) Autumn. Only statistically significant ( $P < 0.05$ ) trends are displayed. Notice the discrepancies in the scale of the colour bars between Winter and Spring (a–b) and Summer and Autumn (c–d).

#### 6.4.5. Multidecadal trends in DMSc in the context of adjustments in Chl, SST, $W_{EQ}$ and PFGs

Here, DMSc trends (Figure 6.4a) were evaluated in the context of phytoplankton response to climate change via altered phytoplankton abundance (Chl), warming and altered  $W_{EQ}$  (Figures 6.6a, 6.6c and 6.6e, respectively). Phytoplankton abundance trends (Chl, Figure 6.6a) exhibit significant variability, generally confined to high-biomass nearshore regions, with clear regional coherence in both positive and negative

trends. The nBUS is dominated by warming trends with no notable decreasing SST trends, with the strongest warming trends observed in the inshore region north of 17 °S (Figure 6.6b). Trends in  $W_{EQ}$  are overwhelmingly positive, with coherent offshore increasing trends (Figure 6.6e). The strongest positive  $W_{EQ}$  trends are observed inshore off the Kunene and Central cells and north of 17 °S. Smaller regions of negative trends do however exist but are constrained to the nearshore waters off the Northern and Lüderitz cells (Figure 6.6e).

Although relatively infrequent, decreasing trends in DMSc coincide with declines in Chl and increases in SST and  $W_{EQ}$ , particularly in the inshore waters off the Northern Cell. In contrast, the more widespread positive trends in DMSc correspond to decreasing offshore Chl, increasing inshore Chl, warming SST, and rising  $W_{EQ}$ . Two smaller inshore regions, around ~19 °S and near the Lüderitz Cell, exhibit increased DMSc that are instead associated with decreasing wind trends (Figure 6.6).

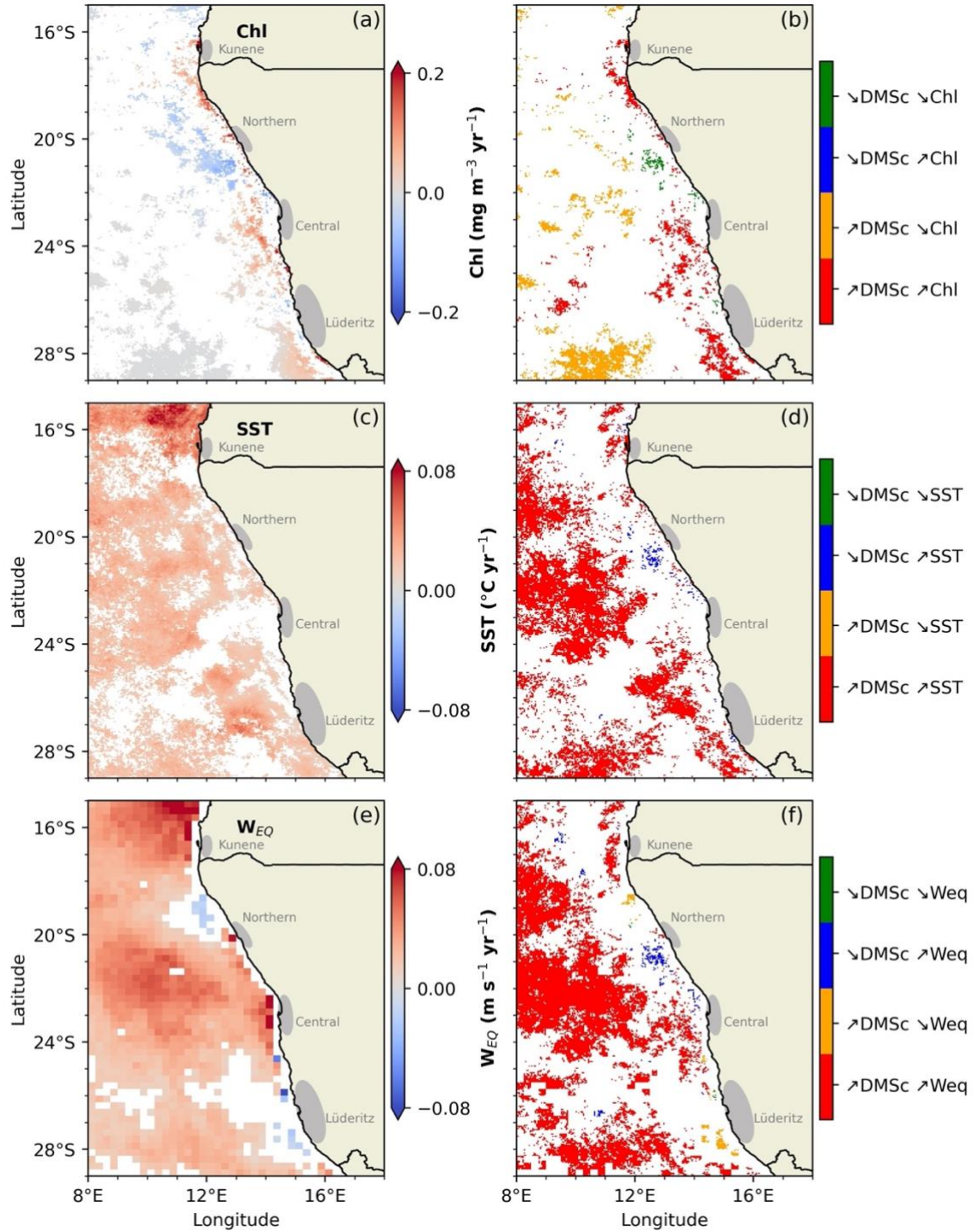


**Figure 6.6:** Regional distribution of statistically significant ( $P < 0.05$ ) annual trends in Chl (a), SST (c) and  $W_{EQ}$  (e) over the past 2 decades (2003–2022) based on daily satellite observations are shown on the maps. Regions of coincident significant trends ( $P < 0.05$ ) between DMSc and Chl, SST and  $W_{EQ}$  are depicted in (b), (d) and (f), respectively, highlighting how changes in Chl, SST and  $W_{EQ}$  align with changes in DMSc (or not).

What follows is an investigation on how phytoplankton community adjustments may have impacted DMSc trends. This is achieved by applying the PFG algorithm of Moloto *et al.* (2023) to assign each pixel to a specific PFG dominance. The DMSc algorithm was then applied to PFG-specific assigned pixels to determine the trends in DMSc that are associated with specific PFGs (Figure 6.7a). No clear spatial pattern emerges in DMSc trends across PFG-specific pixels (Figure 6.7a), as both positive and negative trends are observed for each PFG. While the maps may visually suggest a slight dominance of positive (red) trends, a closer examination of the magnitude of these trends - averaged separately for positive and negative values within each PFG - reveals minimal net change ( $<1.78 \text{ nmol m}^{-3}$  over the 20 years) for diatoms, flagellates, and mixed communities. Only dinoflagellates exhibit a notable net increase, with a dominant positive trend in DMSc amounting to  $103.86 \text{ nmol m}^{-3}$  over the same period (Figure 6.7b).

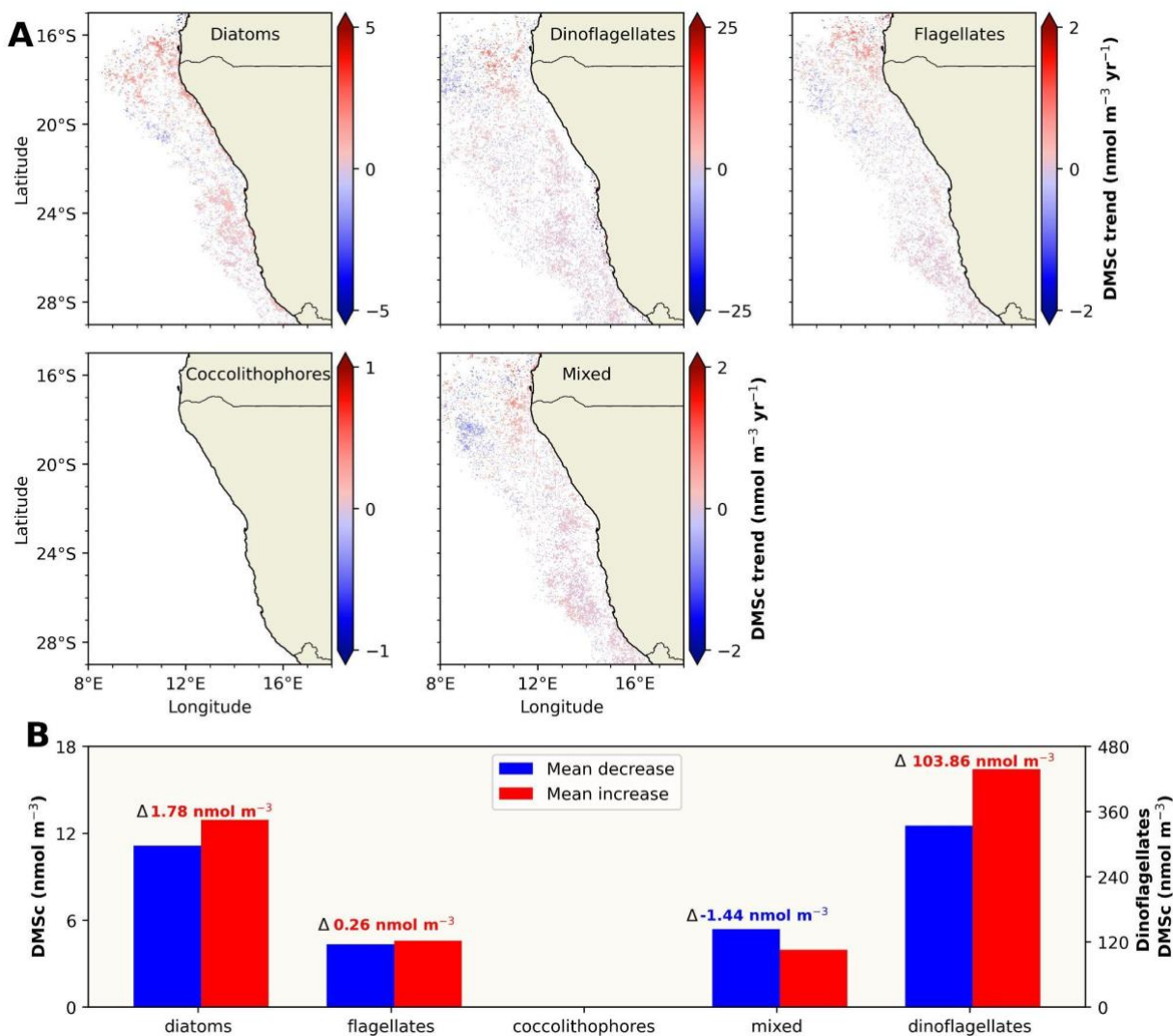


**Figure 6.7: a:** Regional maps of PFG-specific annual trends in DMSc over the 20-year period in the nBUS. Only statistically significant ( $P < 0.05$ ) positive (red) and negative (blue) annual trends are shown. Notice the discrepancies in the magnitude of trends (colourbar) among the PFGs. **b:** Mean positive (red) and negative (blue) changes in DMSc in 20 years based on the trends in **a**, determined by calculating the mean annual negative and positive trends and multiplying by 20 years. The delta sign indicates the net change in DMSc associated with each PFG, with positive values (red) indicating a net increase in DMSc and *vice versa* for negative (blue) values. Note the scale of dinoflagellates is indicated on the right of **b**.

## 6.5. Discussion

### 6.5.1. Regional and Seasonal variability

The concentration of DMSc in marine ecosystems is influenced by a complex interplay of physical, biological, and chemical processes and their interactions are not yet fully understood (Stefels *et al.*, 2007). These processes fluctuate over temporal (e.g., seasonal, annual, decadal) and regional (e.g., coastal upwelling versus offshore) gradients, leading to significant variations in DMSc levels (Masotti *et al.*, 2010; McParland and Levine, 2019; Zhou *et al.*, 2009). The nBUS is a highly dynamic and exceptionally productive region of the world's ocean, where the complex interplay between wind patterns, SST, nutrient availability, and phytoplankton community structure drives significant variability in DMSc concentrations. These interconnected factors shape the seasonal, regional, and long-term fluctuations in DMSc, influencing both local biogeochemical cycles and broader climate-related feedback mechanisms. Here, the regional, seasonal and multidecadal variability in DMSc in the nBUS is investigated in the context of Chl (as a proxy for biomass), SST,  $W_{EQ}$  and PFGs (phytoplankton community structure).

Generally, the climatological mean DMSc concentrations were  $<250 \text{ nmol m}^{-3}$ , with occasional occurrences of more extreme concentrations, with one instance reaching a maximum of  $1828.63 \text{ nmol m}^{-3}$ . These concentrations are within a similar order of magnitude as those reported from *in situ* measurements for the Mauritanian ( $1015 \text{ nmol m}^{-3}$ , determined as DMSPp+DMSPd+DMS) (Franklin *et al.*, 2009; Zindler *et al.*, 2012), West Indian ( $1440 \text{ nmol m}^{-3}$ ) (Shenoy and Kumar, 2007), Peruvian ( $359 \text{ nmol m}^{-3}$ ) (Zhao *et al.*, 2022), and the Moroccan ( $166 \text{ nmol m}^{-3}$ ) (Belviso *et al.*, 2003) upwelling systems. These regionally and seasonally dependent instances of high DMSc concentrations are perhaps not surprising when considering that the Benguela upwelling system is not only the most productive of the 4 main EBUS (Carr, 2001) but also experiences occurrence of high DMSc-producing coccolithophores and dinoflagellates (Hansen *et al.*, 2014; Siegel *et al.*, 2007).

There was no obvious regional relationship observed between the spatial distribution of Chl and DMSc except for the narrow strip of the coast where high DMSc was associated with particularly high Chl ( $>14 \text{ mg m}^{-3}$ ), which was dominated by diatoms and persistent across all seasons (Figure 6.2). Regular blooms of diatoms are known to frequently occur in coastal waters off the Namibian coastline (Louw *et al.*, 2017, 2016) where they may be associated with an increase in the amount of DMSP in the water, leading to increased DMS production (Bell *et al.*, 2015; Nguyen *et al.*, 1988). These coastal blooms likely explain the observed persistent elevated DMSc in the nBUS coastal region, despite being dominated by diatoms. Although diatoms are not typically high DMSc producing algae, their substantial biomass may nonetheless

contribute positively to DMSc concentrations due to the exceptionally high abundances at which they occur close to the coast. From a temporal perspective, the observed seasonal cycle of DMSc with respect to Chl (i.e., maximum accumulation in Summer coupled with minimum Chl concentrations and vice versa) (Figure 6.3), has previously been observed in subtropical, temperate and subpolar open-ocean areas (Galí and Simó, 2015; Simó and Pedrós-Alió, 1999; Vila-Costa *et al.*, 2008) as well as in the Sargasso sea (Polimene *et al.*, 2012). This typical decoupling between DMSc and Chl strongly suggests that seasonal blooms do not drive the DMSc cycle in the nBUS. This counterintuitive phenomenon is widespread across most of the ocean (Polimene *et al.*, 2012; Simó and Pedrós-Alió, 1999; Vila-Costa *et al.*, 2008) and difficulty in explaining it has led some authors to describe it as the so-called “summer DMS paradox” (Simó and Pedrós-Alió, 1999).

There appears to be a regional relationship between the distribution of DMSc and SST, with colder waters associated with low DMSc and *vice versa*. This is not only true in a purely regional sense (Figures 6.1 and 6.2) but also on a seasonal perspective (Figures 6.2 and 6.3a) where the warmer seasons (Summer and Autumn) are associated with higher concentrations of DMSc, notably offshore (Figure 6.2). Warmer SSTs are generally thought to increase the metabolic activity of phytoplankton (varies between species, some may benefit from warming while others may be negatively impacted) (Barton *et al.*, 2020; Kremer *et al.*, 2017) thereby possibly leading to increased DMSP production. However, the observed decoupling between Chl and DMSc concentrations suggests that increased metabolic activity is unlikely to be a primary driver of DMSc distribution. On the other hand, warming decreases microbial DMS consumption and has previously been suggested to explain the “summer DMS paradox” (Galí and Simó, 2015; Polimene *et al.*, 2012).

The regional minima in DMSc coincides with maxima in  $W_{EQ}$  and vice versa, this in addition to the DMSc seasonal cycle also being out of phase with the seasonal cycle of  $W_{EQ}$ , with the seasonal maximum in DMSc coinciding with the seasonal minima in  $W_{EQ}$  in Summer (Figures 6.2, 6.3b and S6.1 in Annexure IV). Wind has been shown to be the most influencing factor driving sea–air fluxes of DMS from the surface ocean acting as a strong removal process of seawater DMS (Bell *et al.*, 2017; Joge *et al.*, 2024; Zhang *et al.*, 2008), which far exceeded its bacterial consumption (Zhang *et al.*, 2008). The observed anti-correlation between DMSc and  $W_{EQ}$  in this study (Figure 6.3b, S6.1 in Annexure IV) suggest that wind-mediated removal of DMS strongly subsides in Summer when winds are at their minimum, thereby contributing to DMS accumulation, whereas its removal (sea-air flux) is at a maximum in Spring, when winds are strong, thus contributing to minimum DMSc concentrations. The seasonal mean wind speeds are also well below 11 m s<sup>-1</sup> (Figure 6.3b), a suggested threshold above which a decrease in gas transfer is observed (Bell *et al.*, 2013), suggesting maximum wind-mediated sea surface DMS removal in Spring in the nBUS. The observed

high DMSc along the coast (north of 23 °S) (Figure 6.2a) coincides with minimum wind speeds across all seasons (Figure 6.2e) in addition to high Chl (Figure 6.2b), suggesting minimized wind-driven DMS removal/sea-air flux and thus contributing to the accumulation of DMSc along the coast.

From a PFG perspective, the offshore regions were typically dominated by dinoflagellates across all seasons, with regional instances of coccolithophores dominance in Summer. Both of these functional groups are known hyper-producers of DMSP/DMS in marine environments (Belviso *et al.*, 1990; Saltzman and Cooper, 1989; Turner *et al.*, 1988). As such, their dominance is a likely contributor to the regional and seasonal distribution patterns of DMSc. The seasonal cycle of coccolithophores *Spatial Extent* is also in-phase with that of DMSc (Figure 6.3c). However, considering that coccolithophores only constitute a minimal portion of the phytoplankton community (Figure S6.1 in Annexure IV), it is unlikely that their presence is the dominant driver of the DMSc seasonal cycle. It is possible that, although coccolithophores rarely dominate when diatoms are prevalent, their relative abundance may still be sufficient to influence the DMSc signal. However, because the current algorithm identifies only periods of dominance rather than relative changes in coccolithophore abundance over space and time, it cannot fully capture their contribution to DMSc variability. In this context, an algorithm capable of resolving relative shifts in species composition and relative abundance would be better suited to assess the co-evolution of phytoplankton community dynamics and DMS trends.

Overall, our findings highlight the intricate interplay between PFGs, SST, Chl and  $W_{EQ}$  in shaping the spatial and seasonal DMSc variability. The coupled and decoupled relationships between DMSc against SST, Chl, and DMSc further reinforce the idea that DMSc dynamics are not solely dictated by bulk phytoplankton biomass but are instead governed by a combination of region-specific ecological and biogeochemical factors. These include an optimal combination of meteorological, physical and biological factors such as low winds [minimize DMS sea-air exchange (Bell *et al.*, 2013)], warm SSTs [enhance near-surface stratification (Siegel *et al.*, 2007) leading to accumulation of DMSP/DMS in the upper mixed layer (Galí *et al.*, 2015), altering phytoplankton metabolic rates (Kremer *et al.*, 2017) and decrease microbial DMS consumption (Galí and Simó, 2015; Polimene *et al.*, 2012)], and phytoplankton community succession from flagellates to blooms of high-DMSc-producing coccolithophores and dinoflagellates. Together, these conditions result in significant DMSc enrichment in surface waters in the nBUS in Summer and Autumn (notably offshore), whereas these conditions are not experienced in Winter and Spring, and low DMSc concentrations persist over the entire region (except for a very narrow coastal band of higher DMSc) (Figures 6.1, 6.2, 6.3 and Figures S6.1, S6.2 in Annexure IV).

### 6.5.2. Multidecadal trends and drivers of DMSc

The DMSc trends are overwhelmingly positive with only a small region of negative trends inshore off the northern cell and offshore off the Kunene cell. The positive trends tend to overlap substantially with warming and increasing winds, but less so with Chl (Figure 6.6). While SST may promote phytoplankton DMSc production and inhibit bacterial DMS consumption, increasing winds are expected to lead to enhanced sea-air DMS outgassing, thus leading to substantial long-term loss in DMS in the sea surface. However, this expected DMS loss from windier conditions is not reflected in the observed DMSc trends. One possible explanation is that warming promotes DMSP production while simultaneously inhibiting bacterial DMS consumption, a process requiring bacterial conversion of DMSP to DMS. By inhibiting bacterial activity, there's less conversion of DMSP to DMS, resulting in reduced availability for DMS outgassing and a subsequent accumulation of DMSP in surface waters. Since DMSP is not subject to direct wind-driven outgassing from the surface ocean, the observed increasing wind speeds may have little to no effect on the observed DMSc trends, consistent with continued accumulation of DMSP over time (and minimal DMS) in the ocean surface.

The positive DMSc trends observed offshore are evident primarily in the warmer seasons (Summer and Autumn), which is the seasonal max period of DMSc, whereas the inshore positive trends are primarily observed in Winter (Figure 6.5). These observed seasonal shifts in DMSc trends indicate that DMS production and removal processes are influenced by seasonally variable oceanographic and biological dynamics. The observed offshore trends in warmer seasons (Figure 6.5) could possibly be linked to increased stratification and biological activity as a result of climate warming. The small patch of negative trends in DMSc off the northern cell (Figure 6.4) are primarily evident in winter and autumn (Figure 6.5). This region of negative trends coincides with a negative trend in Chl, suggesting that here the decline in DMSc may specifically be linked to declines in Chl despite warming. The differential trends across upwelling cells highlights localized drivers of DMSc variability. The Kunene cell experiences persistent positive trends in spring, whereas the northern cell exhibits negative trends across all seasons, suggesting regional differences in DMSc cycling and phytoplankton dynamics. The persistent negative trends relative to the northern upwelling cell across all seasons may indicate a long-term reduction in DMSc production or increased removal processes, potentially influencing regional sulfur fluxes and climate feedback mechanisms.

The findings of this study reveal a complex interplay between SST, Chl, and DMSc trends, with SST and Chl showing both coupled and decoupled relationships in driving DMSc trends (Figure 6.7). This highlights the region-specific dynamics governing DMSc production. Although the methods were unable to estimate

DMSc in coccolithophore-dominated pixels (Figure 6.7), due to their association with particularly low Chl concentrations, coccolithophores were shown to shrink in their *Spatial Extent* and decrease in their *Frequency* of dominance in the nBUS in Chapter 4. Given that coccolithophores are known hyper-producers of DMSc, is it likely that their decline could impact observed trends in DMSc. The remarkable net increase in DMSc associated with dinoflagellates highlights their potential as key contributors to DMSc production, possibly through expansion in *Spatial Extent* and increasing *Frequency* of dominance (Chapter 4). These findings suggest that dinoflagellates may be important drivers of increasing DMSc trends in the region, with warming potentially amplifying their metabolic DMSc production while simultaneously inhibiting microbial DMS consumption (Galí and Simó, 2015).

### 6.5.3. Limitations of the study

Given that the present study employed a remote sensing methodology to examine some of the physical and biological drives associated with the spatiotemporal variability of DMSc, it was necessary to adopt certain assumptions and simplifications in the methodological framework. Numerous other potential factors, which are similarly evolving on both seasonal and long-term scales due to climate change, may impact the cycling (production and removal) of DMSc, including bacterial consumption of DMS, conversion of DMSP to methanethiol (MeSH), zooplankton grazing (DMSP is reconstituted in fecal pellets and sinks), oxidation to dimethyl sulfoxide (DMSO) and other physical processes (e.g., water column stratification) that are known to influence DMS concentration in the surface ocean. The current study thus oversimplifies the drivers of seasonal variability and trends in DMSc. In addition, coccolithophore-dominated regions tend to be associated with extremely low or undetectable Chl concentrations (Galí *et al.*, 2015; Siegel *et al.*, 2007). Since Chl is an input variable into the algorithm used to estimate DMSc concentration, it likely leads to underestimations of the role of coccolithophores in driving DMSc distribution. Additionally, the current approach does not distinguish between DMSP and DMS independently, as *in situ* sampling measured both metabolites simultaneously. Individual determination of DMSP and DMS are necessary for disentangling the coupling and decoupling between the two metabolites to better understand their cycling as well as for measuring seasonal, annual and long-term trends in sea-to-air fluxes of DMS.

An additional key limitation of this study lies in the interpretation of DMSP patterns in relation to drivers of SST and Chl, which are themselves input variables in the empirical algorithm used to estimate DMSP. As a result, any observed relationships between DMSP and these variables must be viewed with caution, as they may partly reflect the mathematical structure of the algorithm rather than independent biogeochemical interactions. This built-in dependency limits the ability to disentangle cause-and-effect relationships and introduces an element of circular reasoning, particularly in attributing variability in DMSP

to SST or Chl changes. Nonetheless, because the algorithm includes a non-linear (quadratic) relationship with SST while the observed spatial and temporal patterns appear more linear, some insight can still be gained into the coupled or decoupled nature of their distributions beyond what is structurally imposed by the algorithm. Future studies using direct DMSP observations or alternative modelling approaches will be important for validating and refining these inferences.

## 6.6. Conclusions

Remote sensing presents a robust and powerful methodology facilitating the examination of variability, trends, and drivers of ocean phenomena across both regional and temporal scales. This study leverages satellite observations to unveil the previously unobserved regional distribution, seasonal cycle and multidecadal trends in dimethyl sulfur compounds in the nBUS in relation to climate drivers (SST and  $W_{EQ}$ ) and phytoplankton adjustments (biomass and community dominance). The annual DMSc peak in Summer (notably in the northerly and offshore extremes) coincides with minimum Chl and maximum SST, resembling the so-called “summer DMSc paradox”. In this study, the seasonal cycle of DMSc appears to be influenced by a combination of elevated SST, reduced WEQ and phytoplankton community succession from flagellates and diatoms to coccolithophores and dinoflagellates. While dinoflagellates are dominant in Summer, coccolithophores also reach their seasonal maximum during this time (and dominate in certain offshore pixels). Together, these conditions contribute to the summer peak in DMSc. In terms of long-term trends, there is an overall increase in DMSc, which may be linked to regional warming, the offshore expansion of dinoflagellates and the intensification of coastal dinoflagellate blooms. The findings of this study address a key knowledge gap by characterizing the spatial and temporal patterns of DMSc variability within the context of key environmental drivers in the world’s most productive EBUS. Additionally, this work contributes to broader scientific efforts to incorporate satellite-derived DMSc estimates into climate and biogeochemical models for improved predictions of stratocumulus cloud formation and associated albedo. Such advancements are essential for improving the ability to monitor and predict climate-biogeochemical interactions, offering a clearer understanding of how marine ecosystems may respond to future environmental changes.

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## Chapter 7: Main findings and conclusions, limitations and recommendations

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Oceanic PFGs, which form the base of marine ecosystems, play diverse and critical roles in driving primary production, supporting nutrient cycling, shaping food web dynamics and impacting climate (Tweddle *et al.*, 2018). Among these, certain groups are particularly important for the marine sulfur cycle through their production of DMSP, a key compound that supports microbial communities' sulfur and carbon demands (Kiene *et al.*, 2000) and serves as a precursor to DMS gas (Belviso *et al.*, 1990). DMS, in turn, plays a crucial role in climate regulation by influencing cloud formation and albedo (Bates *et al.*, 1987; Charlson *et al.*, 1987). However, climate change is altering the physicochemical properties that regulate phytoplankton dynamics, with potential consequences for biogeochemical cycles, ecosystem functioning and associated services they provide to mankind. In light of these changes, continuous monitoring of the marine environment is essential for detecting early ecosystem changes for informed mitigation strategies. In the context of the nBUS, the Namibian National Marine Information and Research Centre (NatMIRC) undertakes quasi-monthly monitoring surveys using shipboard observations, which provide long-term datasets for ecosystem assessment for effective environmental management efforts (Louw *et al.*, 2016). However, such efforts are limited in their spatial and temporal coverage, making an ecosystem-wide response of phytoplankton communities to climate variability difficult to detect.

This study set out to advance our understanding of phytoplankton distribution patterns and associated DMSP and DMS concentrations in the nBUS by leveraging satellite observations that have superior spatial and temporal coverage. The key research questions being addressed in this thesis are as follows: 1) What is the regional and seasonal distribution of PFGs in the nBUS and how do they vary in the context of key environmental drivers 2) How are these PFGs responding to climate change, and how do their responses to climate variability influence planktonic DMSP production? In order to address these pressing questions, four objectives were set to achieve these aims: (1) Develop a robust, regionally specific ocean colour satellite algorithm for detecting PFGs in the nBUS (Chapter 3), (2) apply the PFG algorithm to examine regional, seasonal and long-term patterns over the past 20 years in the context of temperature and  $W_{EQ}$  (Chapter 4), (3) develop a regionally specific satellite remote sensing algorithm for the detection of DMSP concentrations (Chapter 5), and (4) apply the DMSP algorithm to investigate regional and seasonal distributions and long-term trends in DMSP in the context of biophysical drivers such as chlorophyll-*a* (Chl, proxy for phytoplankton biomass), PFGs, SST as well as upwelling-favourable  $W_{EQ}$  (Chapter 6). This chapter revisits the objectives, summarizing the methods used, key conclusions drawn from the findings, as well as the study's limitations and recommendations for future research.

### 7.1. Summary of methods

To address the above-mentioned research objectives, this study employed a combination of *in situ* observations, satellite remote sensing, and statistical modelling. Chapter 3 demonstrated the detection of PFGs through the use of ocean colour remote sensing reflectance products from the Moderate Resolution Imaging Spectroradiometer (MODIS). Relationships between the normalised fluorescence line height (nFLH), red-near infrared (RNR) as well as the green/green spectral band-ratios were examined, using the 25th and 75th percentiles to determine thresholds for identifying waters dominated by each PFG (i.e., diatoms, dinoflagellates, flagellates and mixed communities). For coccolithophore detection, a modification of the remote sensing method of Smith *et al.* (2023) was applied to MODIS data.

To estimate DMSP and DMS (collectively as DMSc, dimethyl sulfur compounds), empirical relationships linking these sulfur compounds to Chl and SST were assessed in Chapter 5. The strongest variability in DMSc was explained by the multivariate analysis using Chl and SST in a quadratic fit, and was subsequently used for algorithm development. Both algorithms were validated using independent datasets not used in their development. These approaches provide a novel means of studying PFG and DMSc dynamics in the nBUS at scales that are impossible to achieve using traditional ship-based sampling alone. Daily satellite observations spanning the period between 2003–2022 were used to determine seasonal and multidecadal trends following the approach of Ryan-Keogh *et al.* (2023), which applied linear regressions to seasonal and annual means and anomalies. For driver-response analysis, Pearson correlation coefficients were determined between biochemical variables (PFGs, Chl and DMSc) and climate drivers (SST,  $W_{EQ}$ ). This in addition to determining coincidence in significant trends between climate drivers (SST and  $W_{EQ}$ ), phytoplankton (PFGs, Chl) as well as planktonic metabolites (DMSc).

### 7.2. Summary of key findings

The development of a novel ocean colour satellite remote sensing algorithm for detecting key PFGs in the nBUS from the MODIS-Aqua satellite represents a significant advancement in regional environmental monitoring. The MODIS-Aqua satellite provides the most temporally consistent datasets from a single sensor of coincident ocean colour, SST and Chl measurements spanning the period between 2003–2023, thereby enabling large-scale, synoptic assessments of both trends and drivers of spatiotemporal variability. Through this novel method, our study demonstrated that PFGs in the nBUS exhibit distinct seasonal patterns in their *Spatial Extent* and *Frequency* of dominance, with niche conditions associated with varying combinations of gradients in SST and  $W_{EQ}$  favouring particular groups at different times of the year. When examining seasonal and regional trends in PFG dynamics, strong seasonal and regional variability in PFG trends were observed, with diatoms expanding their *Spatial Extent* in Autumn but contracting in Summer,

while dinoflagellates and flagellates exhibited the opposite trend, increasing in Summer and decreasing in Autumn. Diatoms exhibited strongest multidecadal trends (in terms of magnitude) and given their role as key carbon exporters, the observed diatom trends highlight their sensitivity to climate variability, with implications for carbon sequestration and energy transfer to higher trophic levels. The study further identified a strong link between diatom dominance and alongshore  $W_{EQ}$ , with regions experiencing increasing  $W_{EQ}$  corresponding with a rise in diatom prevalence, while weakening winds instead exhibited a decrease in diatom dominance. These results suggest that changes in nutrient supply driven by wind driven-upwelling variability are shaping PFG distributions in the region. Additionally, warming trends characterizing the nBUS are likely enhancing phytoplankton's ability to exploit intermittent nutrient pulses. Offshore declines in coccolithophores, key producers of DMSP, were associated with accelerating  $W_{EQ}$ , reflecting shifts in environmental conditions that may negatively impact sulfur cycling in the region.

The application of the DMSc satellite algorithm provided the first spatially and temporally comprehensive assessment of the seasonal cycle and multidecadal trends in DMSc production within the nBUS. A characteristic “summer DMS paradox” was observed, where the summer DMSc peak coincided with seasonal minimum Chl concentrations and maximum SST. The blooming period of coccolithophores coincides with the timing of the seasonal maximum in DMSc concentrations in Summer, whereas the winter DMSc minimum coincided with a Chl maximum and dominance of diatoms and flagellates. These observations suggest that the seasonal cycle of DMSc peak is influenced by a combination of elevated SST, reduced  $W_{EQ}$  and phytoplankton community succession from flagellates and diatoms to dominance of high-DMSc-producing coccolithophores and dinoflagellates. Long-term DMSc trends revealed a coherent offshore increase, contrasting with a more heterogeneous distribution pattern inshore. This increasing offshore trend was associated with warming and an expanding *Spatial Extent* of dinoflagellates, reinforcing the role of phytoplankton succession in shaping DMSc variability. These findings provide new insights into the spatial and temporal dynamics of PFGs, strengthening our large-scale understanding of the links between environmental forcing, phytoplankton community structure, and sulfur cycling in the nBUS. This study further lays the groundwork for refining biogeochemical models that integrate phytoplankton-driven DMSc production in upwelling systems.

### **7.3. Limitations and challenges**

While this study has advanced the capability of satellite-based detection of PFGs and their associated sulfur compounds, several limitations must be acknowledged. The PFG detection algorithm was constrained by the availability of *in situ* datasets, though publicly available datasets were incorporated to supplement the analysis. Additionally, while the algorithm successfully identified dominant PFGs, it was unable to resolve

community structure beyond dominance, meaning that co-occurring groups could not be fully characterized. Furthermore, the algorithm could not differentiate between harmful and non-harmful species, which is particularly relevant for monitoring harmful algal blooms (HABs). The inability to resolve phytoplankton at the species level also limits its application for studying finer-scale ecological dynamics.

Similarly, the DMSc detection algorithm faced challenges due to limited datasets, restricting the extent of training efforts. The algorithm was also developed using a subset of environmental variables, SST and Chl in particular, as certain unexplored variables had been shown in previous studies to have no significant correlation with DMSc production both globally (Galí *et al.*, 2018, 2015) and in upwelling systems (Andreae, 1985; Franklin *et al.*, 2009; Zhao *et al.*, 2022; Zindler *et al.*, 2012). However, this oversimplification may introduce some uncertainty as the controls of DMSc variability are not fully understood. Additionally, the algorithm exhibited limitations in detecting DMSc production in coccolithophore-dominated waters, which could impact estimates of total sulfur production in offshore regions where these taxa are prevalent (Siegel *et al.*, 2007). Another key limitation was the inability to account for microbial consumption of DMS and wind-driven sea-air fluxes, which play a critical role in regulating the net flux of sulfur from the ocean to the atmosphere (Galí and Simó, 2015; Polimene *et al.*, 2012). Furthermore, our algorithm does not resolve DMSP and DMS independently, as both compounds were concurrently quantified during *in situ* sampling. Discrete measurements of DMSP and DMS would enable a more accurate assessment of their coupling and decoupling dynamics. This distinction is particularly important for quantifying the temporal variability and long-term trends in DMS sea-to-air fluxes, which are key to understanding sulfur cycling and its climate feedback mechanisms (Charlson *et al.*, 1987).

More broadly, the application of both algorithms was affected by inherent limitations of satellite remote sensing, particularly the influence of cloud cover and other atmospheric interferences on data availability. The nBUS is frequently characterized by persistent clouds, fog, and seasonal dust deposits (Shikwambana and Kganyago, 2022; Spirig *et al.*, 2019), all of which impact satellite signal quality and contribute to data gaps. This limitation likely resulted in underestimations of both PFG and DMSc distributions, especially in regions with persistent high cloud cover. Furthermore, it is important to note that satellite ocean colour sensors provide information limited to the near-surface layer (approximately the first optical depth) and therefore cannot detect subsurface distribution of phytoplankton and other optically active material in the euphotic zone depth ( $Z_{eu}$ ), which may influence the reflectance signal observed by the satellite. This is particularly the case when the subsurface Chl maximum is not at the sampled depth within the euphotic zone depth and is within the depth observed by the satellite. A study by Louw *et al* (2016) showed

subsurface Chl maxima to be common in the nBUS. The subsurface Chl maxima may influence the water-leaving reflectance, which may affect Chl estimation by ocean colour remote sensing algorithms (Matthes *et al.*, 2023). As such, our satellite-based classification may misrepresent the true vertically integrated PFG dominance, particularly in regions when a different phytoplankton population dominates within a deep subsurface Chl maxima. In addition, it is important to note that long-term trends derived from satellite observations may vary depending on the dataset used, as differences in sensor calibration and retrieval algorithms can influence both the magnitude and direction of the observed changes. In this study, we mitigated these uncertainties by selecting the most accurate products for each variable and using MODIS as a single-sensor dataset where possible; however, residual discrepancies between satellite products remain a potential source of uncertainty in the trend estimates. Despite these challenges, this study demonstrated the potential of satellite-based techniques for advancing our understanding of large-scale phytoplankton and planktonic dimethyl sulfur cycling in upwelling systems, while highlighting areas where future improvements can enhance detection capabilities.

#### **7.4. Recommendations for future research**

To address the limitations identified in this study and improve the accuracy and applicability of PFG and DMSc detection algorithms, several key recommendations for future research are proposed. First, addressing data limitations is critical for improving algorithm performance. Continued ship-based cruise surveys should be conducted to collect *in situ* phytoplankton and DMSc measurements, which can be used to further train and validate satellite-based algorithms and reduce uncertainties in PFG and sulfur cycle estimations. Advancing PFG detection techniques requires improved satellite-based proxies for differentiating between functional groups. Future research should explore the use of hyperspectral satellite observations, such as those from NASA's recently launched PACE (Plankton, Aerosol, Cloud, ocean Ecosystem) mission, which offers enhanced spectral resolution capable of distinguishing subtle variations in phytoplankton optical properties. Hyperspectral data could allow for more precise classification of PFGs, reducing the current limitation of only detecting dominant groups and providing deeper insights into community structure.

To improve satellite estimates of DMSc in the nBUS, future studies should explore additional environmental variables that may influence DMSc production and incorporate them into algorithm development. These include solar radiation dose and mixed layer depth (MLD), which are strongly positively correlated with DMS irrespective of latitude, Chl or SST in the upper mixed layer over the global ocean (Miles *et al.*, 2009; Vallina and Simó, 2007). In addition, phytoplankton community structure influences DMSc production, with different PFGs having been shown to produce different amounts of

DMSc (Belviso *et al.*, 1990; Saltzman and Cooper, 1989; Turner *et al.*, 1988). As such, future studies should explore the development of algorithms that integrate dominant PFG composition to improve predictions of DMS concentrations. The current algorithm could also benefit from the integration of a dedicated sub-model tailored to coccolithophore-dominated waters, similar to the approach of Galí *et al* (2015), as the current framework lacks the capacity to accurately estimate DMS concentrations in regions where coccolithophores dominate. This would require concurrent, high-resolution measurements of DMSP and DMS concentrations and phytoplankton community structure to establish robust empirical relationships. Such an approach could significantly enhance the accuracy of DMS estimations. In terms of model evaluation, in addition to the statistical metrics used in this study (RMSE, MAPE, MRB, and MRE), future evaluations of the DMS model would include the slope of the regression between observed and modelled DMS values. Although simple, this metric provides an effective measure of systematic bias by quantifying the degree to which model predictions deviate from a 1:1 relationship, thereby offering additional insight into model generalisation and robustness.

In terms of establishing empirical relationships between DMSc and predictor variables, machine learning techniques, such those based on Gaussian process regression (GPR) (Mansour *et al.*, 2023), artificial neural networks (ANN) and random forest regression (RFR) (McNabb and Tortell, 2022), should be considered as alternative approaches to traditional parameterization methods (e.g., regression). In addition, generalized additive models allow nonlinear relationships between DMS, environmental drivers, and biological variables to be captured without imposing strict functional forms, and should also be explored in future analysis. These techniques have been demonstrated to improve predictive accuracy at regional scales and may better capture the complex, nonlinear relationships governing sulfur cycling in upwelling systems. Ultimately, improving our understanding of phytoplankton-sulfur interactions will not only enhance climate models but also inform marine ecosystem management strategies in response to ongoing environmental change. Furthermore, future studies of *in situ* DMSc dynamics in the nBUS should focus on independent measurements of DMSP and DMS which would allow their estimates independently from satellite. Independent quantification of DMSP and DMS will enable a clearer understanding of their individual dynamics, facilitate assessments of their coupling or decoupling under varying environmental conditions, and improve estimates of seasonal and long-term trends in DMS sea-to-air fluxes.

Lastly, while the current DMSc algorithm is calibrated specifically for the nBUS, future efforts should aim to expand and validate the algorithm across the entire Benguela upwelling region to enhance its spatial applicability and support basin-scale assessments of sulfur cycling.

## 7.5. References

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## Annexure I: Supplementary Material data for Chapter 3

This is Supplementary Material data for

### Chapter 3: Ocean colour satellite remote sensing of phytoplankton functional groups

The statistics used for comparison were the mean relative error (MRE), mean absolute relative difference (MARD), median relative difference (MedRD), root mean squared error (RMSE) and relative bias. These were calculated as follows:

$$MRE = \frac{\log_{10}Chl_{sat} - \log_{10}Chl_{field}}{\log_{10}Chl_{field}} \times 100\% \quad (S1)$$

$$MARD = \frac{|\log_{10}Chl_{sat} - \log_{10}Chl_{field}|}{\log_{10}Chl_{field}} \times 100\% \quad (S2)$$

$$MedRD = \frac{\log_{10}Sat_{median} - \log_{10}Field_{median}}{\log_{10}Field_{median}} \times 100\% \quad (S3)$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^N (\log_{10}Chl_{field} - \log_{10}Chl_{sat})^2}{N}} \quad (S4)$$

$$Bias = \sum_{i=1}^N \frac{|\log_{10}Chl_{sat} - \log_{10}Chl_{field}|}{N} \quad (S5)$$

Where  $Chl_{sat}$ ,  $Chl_{field}$  and  $N$  are satellite-derived [Chl-*a*], *in situ* fluorometric derived [Chl-*a*] measurements and the number of data points respectively.

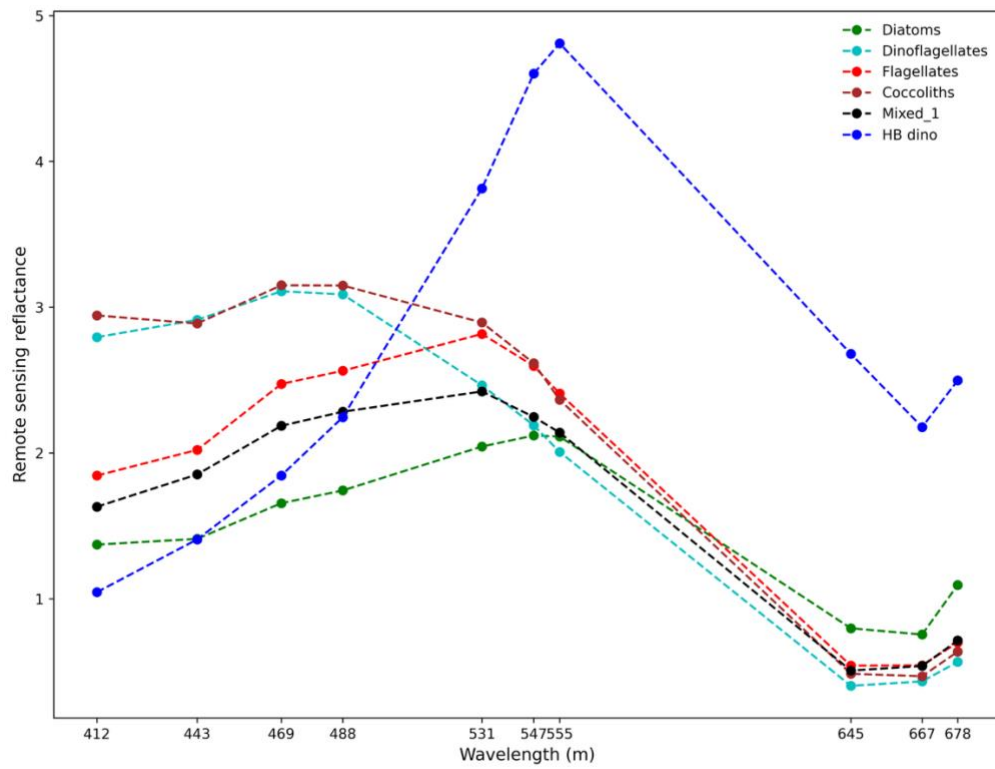


**Figure S3.1:** Mean remote sensing reflectance characteristics for waters associated with dominance of various phytoplankton groups in the northern Benguela upwelling system.

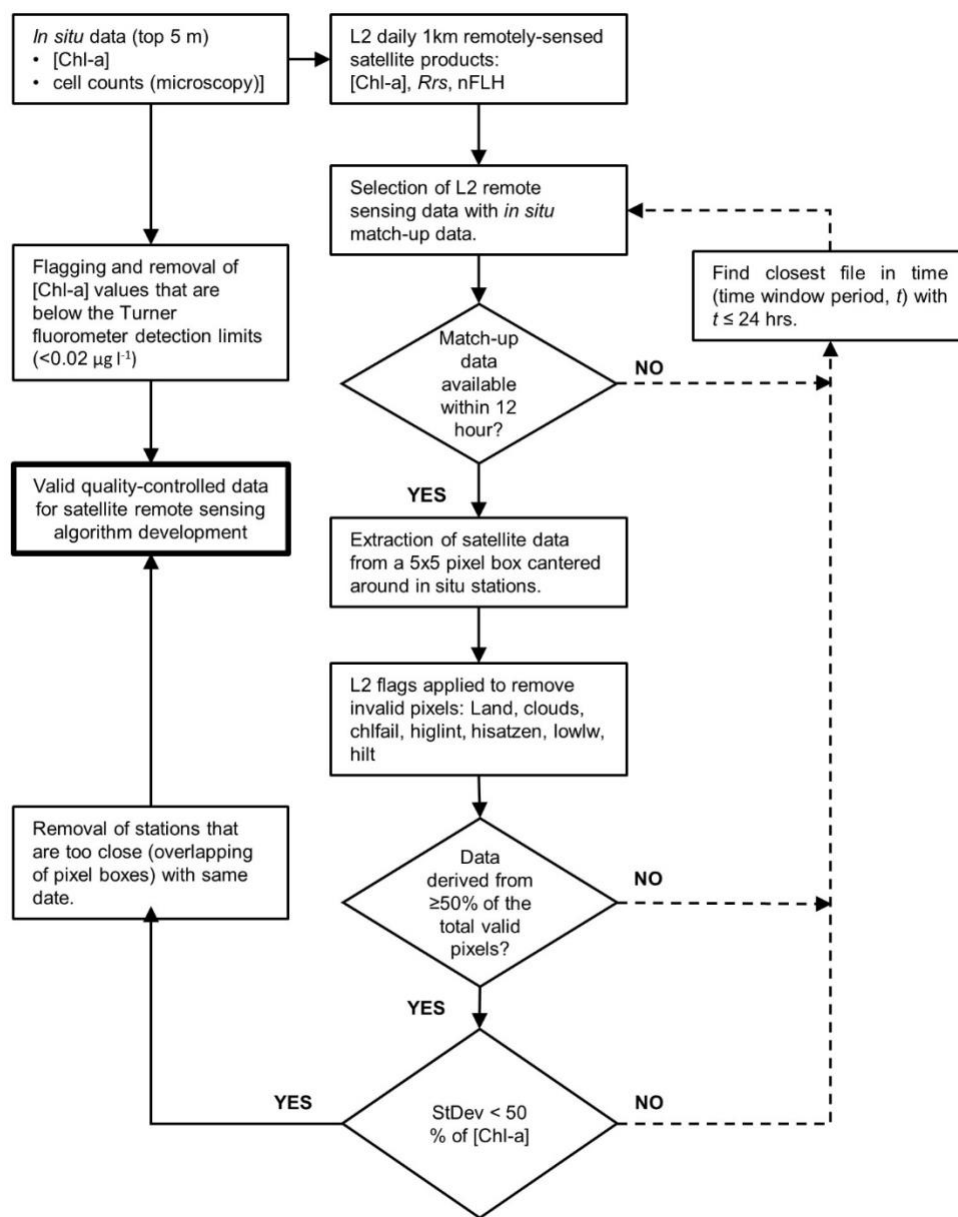


**Figure S3.2:** Flowchart of steps followed, and quality-control measures applied to determine extraction for satellite values that match up with *in situ* data.

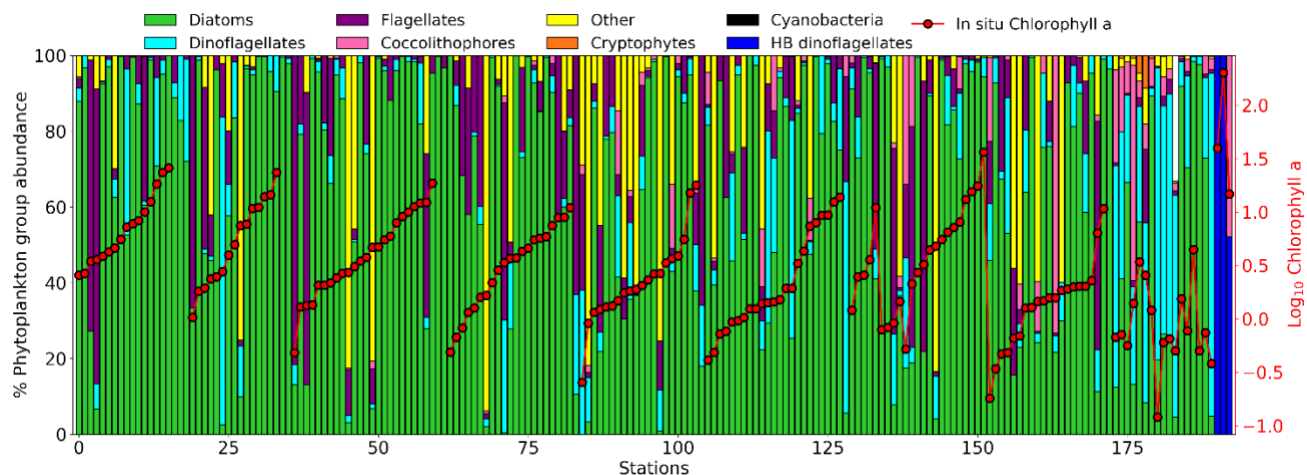


**Figure S3.3:** Quality-controlled microscopy datasets showing phytoplankton community cell concentrations (% composition) and associated biomass (Chl-*a*) in the nBUS spanning the period between 2001 – 2019 from various cruise expeditions.

## Annexure II: Supplementary Material data for Chapter 4

This is Supplementary Material data for:

### Chapter 4: Seasonal patterns and multidecadal trends in phytoplankton functional groups in the Benguela upwelling system off Namibia.

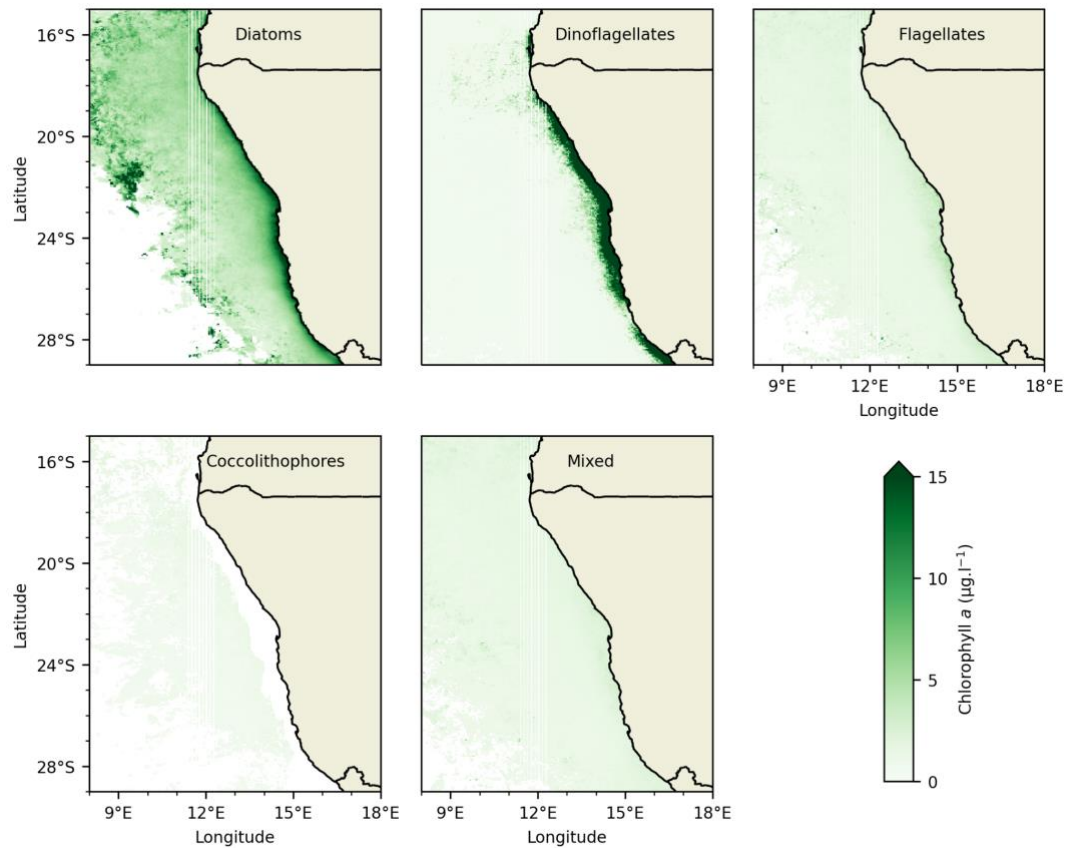


**Figure S4.1: Two-decade (2003-2022) mean phytoplankton-specific biomass (chlorophyll *a*)**

Spatial distribution of climatological mean biomass (Chlorophyll *a*,  $\mu\text{g l}^{-1}$ ) of key phytoplankton functional groups (PFGs, viz.: diatoms, dinoflagellates, flagellates, coccolithophores and mixed communities) in the nBUS based on 20 years (2003–2022) of daily MODIS-Aqua observations.

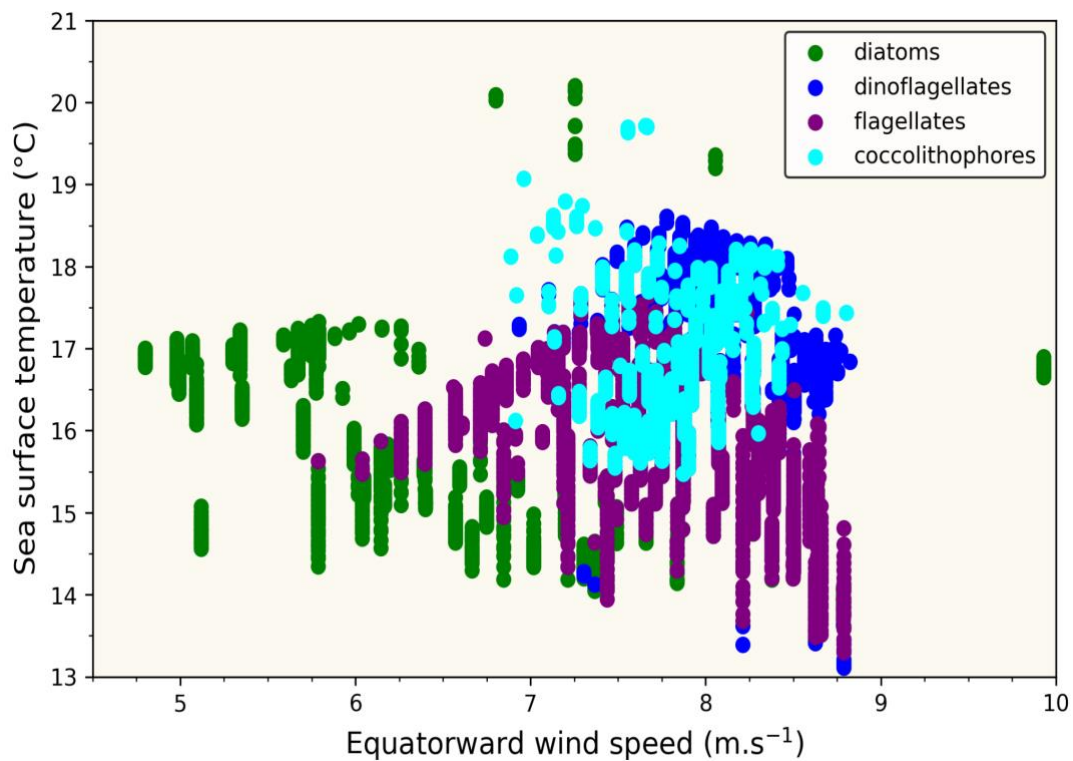


**Figure S4.2: Niche Sea surface temperature and equatorward winds speed occupations for PFGs.**

The top 25% annual mean PFG *Frequency* of dominance for diatoms (green), dinoflagellates (blue), flagellates (purple) as well as coccolithophores (cyan) showing the typical SST (°C) and equatorward winds speed (m s<sup>-1</sup>) associated with their dominance.

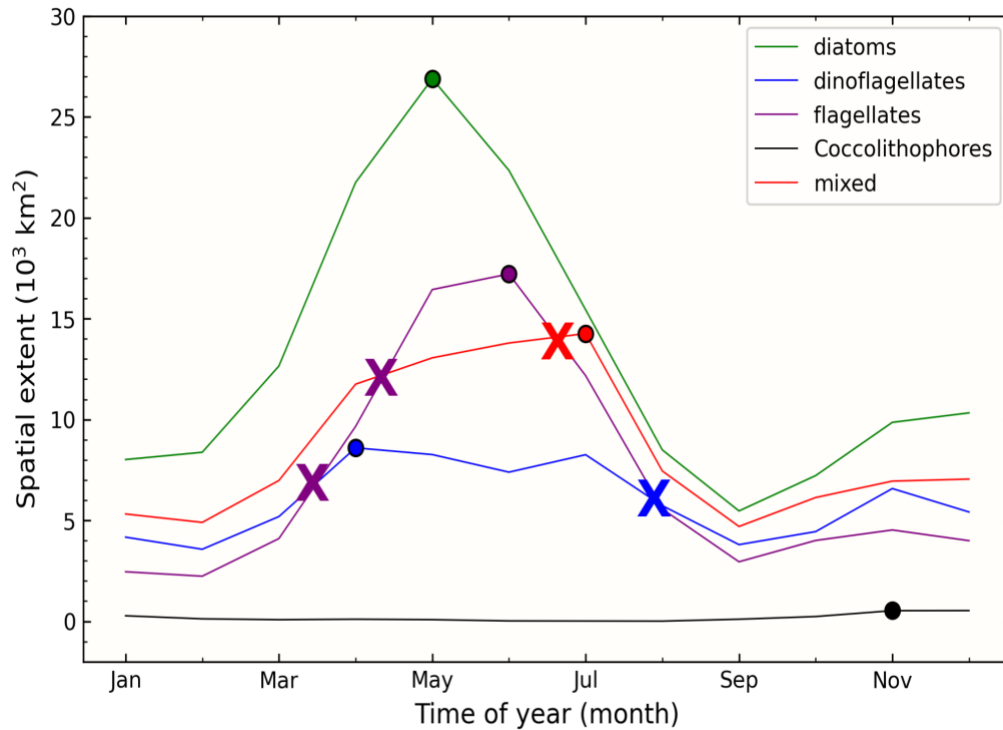


**Figure S4.3: Seasonal succession of PFGs in terms of *Spatial Extent*.**

Annual cycle of *Spatial Extent* ( $\text{km}^2$ ) of diatoms (green), dinoflagellates (blue), flagellates (purple), coccolithophores (black) and mixed community (red) showing seasonal succession in the timing of maximum *Spatial Extent* between the phytoplankton functional groups (PFGs). The coloured dots indicate the seasonal maximum *Spatial Extent* for each PFG whereas the crosses indicate the timing (time of year, month) of the onset of succession among the phytoplankton groups, with the purple, red and blue crosses indicating succession by flagellates, mixed community and dinoflagellates, respectively. Of note, diatoms (green) are not succeeded by any PFG throughout the year while in contrast, coccolithophores do not succeed any PFG and occupy the least *Spatial Extent*.

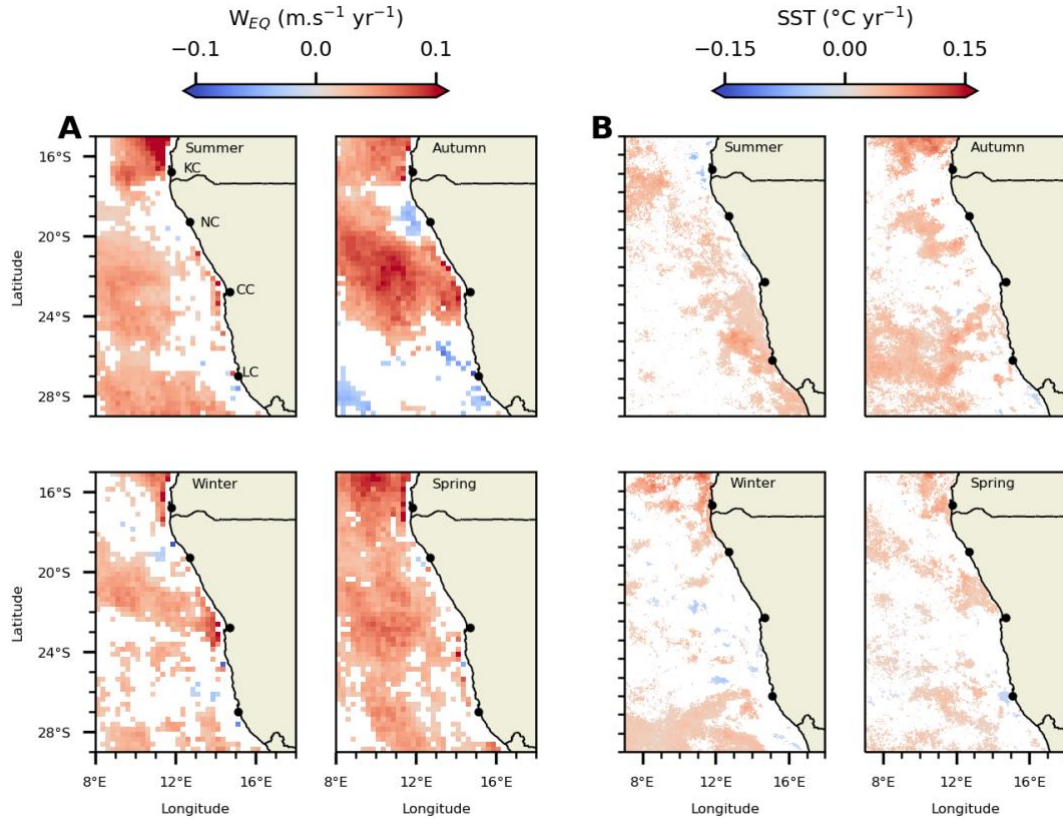


**Figure S4.4: Seasonal trends in key environmental drivers between 2003–2022**

Seasonal variability in the annual trends in equatorward winds speed (a) and sea surface temperatures (b) in the past two decades (2003–2022), showing the Summer, Autumn, Winter and Spring seasonal trends. The black dots represent key upwelling centers, viz.: Kunene (KC), Northern (NC), Central (CC) and the Lüderitz (LC) upwelling cells. Only statistically significant ( $P < 0.05$ ) trends are shown.

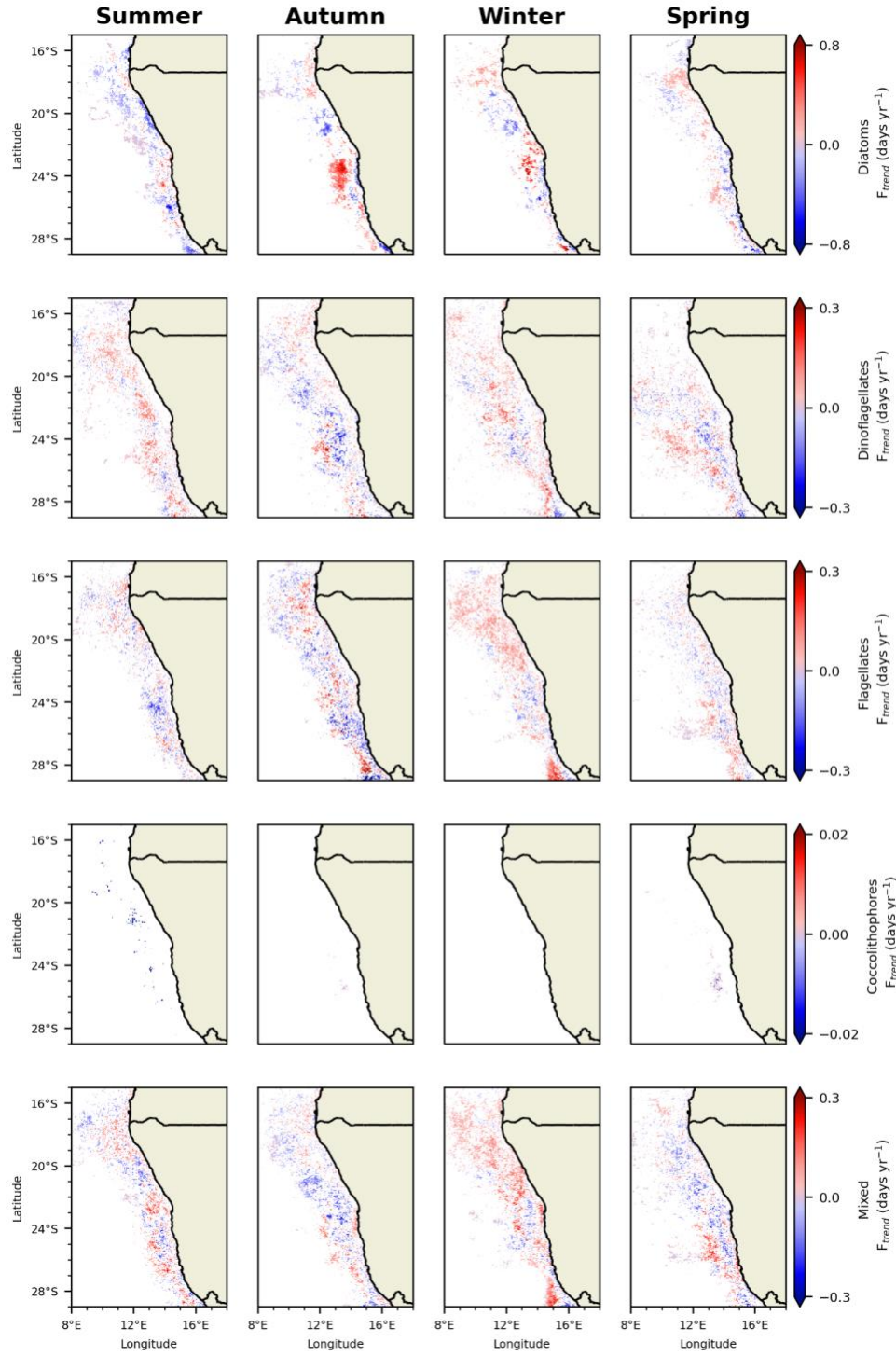


**Figure S4.5: Seasonal frequency trends ( $F_{trend}$ ) of PFGs between 2003 – 2022.**

Spatial patterns of seasonal trends in PFG Frequency of dominance ( $F_{trend}$ ) for Summer, Autumn, Winter and Spring. Only statistically significant ( $P < 0.05$ )  $F_{trend}$  are shown.

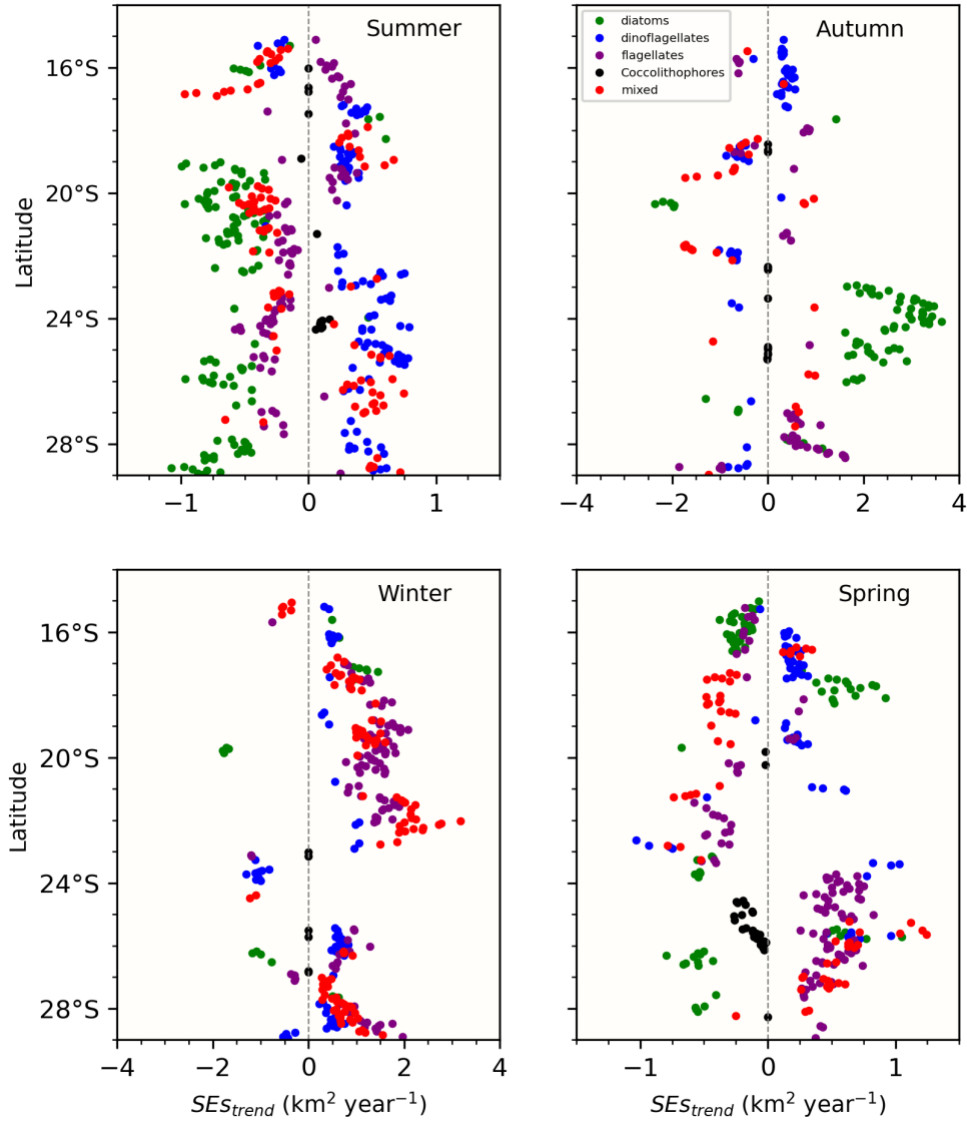


**Figure S4.6: Seasonal latitudinal *Spatial Extent* trends ( $SEStrend$ ) of PFGs.**

Temporal timing and zonal variability in PFG spatial expansion and shrinkage in the past two decades (2003–2022), showing the Summer, Autumn, Winter and Spring seasonal trends. PFGs are indicated as the coloured dots (blue: dinoflagellates; green: diatoms; purple: flagellates; red: mixed; black: coccolithophores). Only statistically significant ( $P < 0.05$ ) trends are shown.

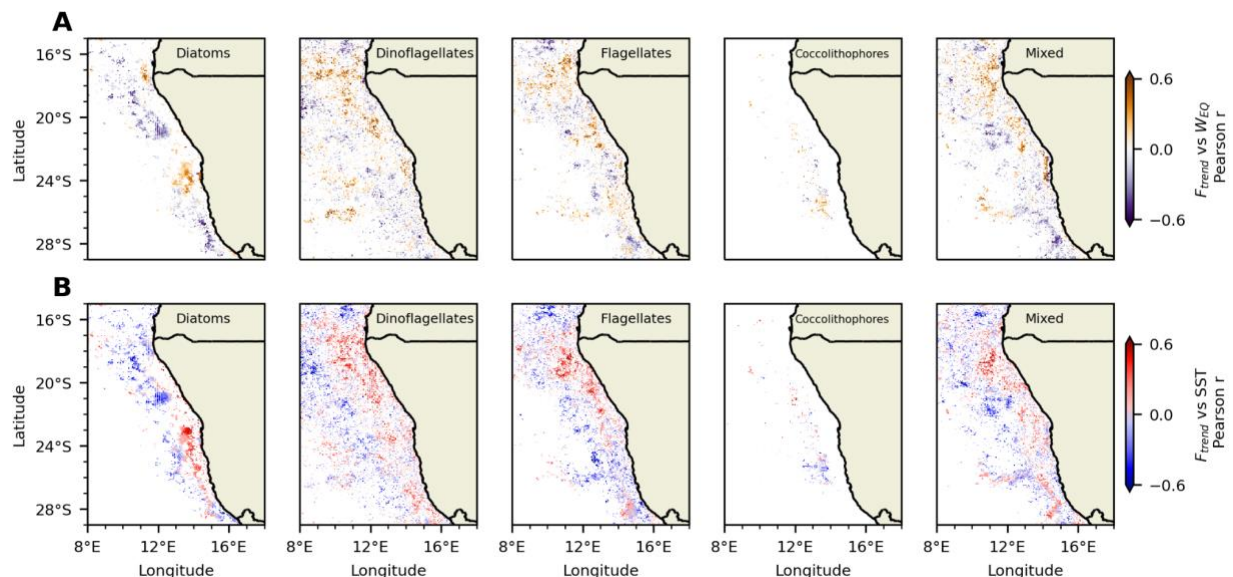


**Figure S4.7: Correlation between trends in PFGs  $F_{trend}$  and key climate drivers**

Long-term changes in PFG *Frequency* of dominance and their linear relationship with equatorward winds speed ( $W_{EQ}$ ) (a) and sea surface temperatures (SST) (b). The colour bars indicate the strength of linear association, determined as the Pearson correlation coefficient (r).

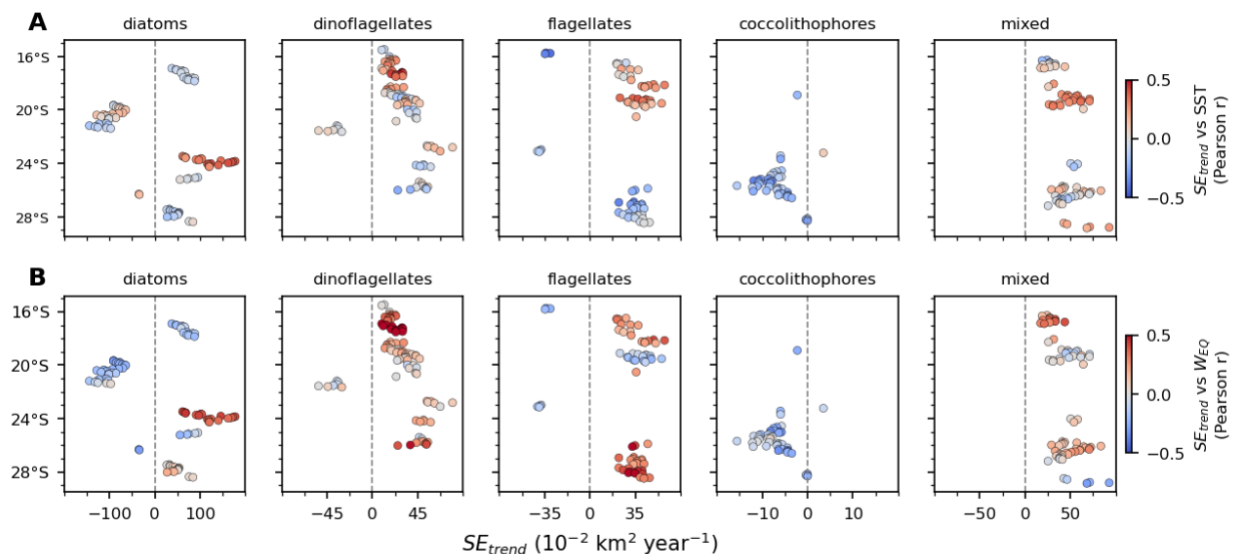


**Figure S4.8: Correlation between trends in PFGs  $SE_{trend}$  and key climate drivers.**

Linear relationship between PFG  $SE_{trend}$  against sea surface temperature (SST, panel a) and equatorward winds speed ( $W_{EQ}$ , panel b). The colour bars indicate the strength of linear association, determined as the Pearson correlation coefficient (r).

## Comparative analysis of wind reanalysis products against satellite observations

### **Introduction**

The SeaWinds scatterometer of surface ocean winds data onboard the QuickSCAT satellite have previously been used to characterize equatorward and upwelling-favorable wind climatology (Louw *et al.*, 2016) and trends (Demarcq, 2009) in the nBUS. Satellite scatterometer sensor failures however hamper their ability to provide temporally consistent datasets from a single sensor. Reanalysis products on the other hand provide the most complete and coherent past climate datasets as they are typically a blend of short-range scatterometer observations rerun with weather forecasting models to provide “gap-free” climatological datasets, making them ideal candidates for long-term climate studies. Here, four wind reanalysis products are compared against the QuickSCAT ocean winds datasets to determine the best product that best represents wind dynamics in the nBUS region. These included 1) datasets obtained from the fifth generation European Centre for Medium-Range Weather Forecasts (ECMWF) reanalysis for global climate and weather (ERA5, Hersbach *et al.* (2020), available at <https://cds.climate.copernicus.eu/>), 2) the Japanese 55-year Reanalysis (JRA-55, Kobayashi *et al.* (2015), available at <https://jra.kishou.go.jp/JRA-55/>), 3) the NCEP-DOE Reanalysis 2 (NCEP-DOE AMIP-II, Kanamitsu *et al.* (2002), found at <https://psl.noaa.gov/data/gridded/data.ncep.reanalysis2.html>) and 4) the Global Ocean Daily Gridded Reprocessed level 3 (L3) Sea Surface Winds from Scatterometer (European Union-Copernicus Marine Service, 2017) (GOD-GSSWS, from the E.U. Copernicus Marine Service Information, available at <https://doi.org/10.48670/moi-00183>). The QuickSCAT SeaWinds scatterometer wind vector datasets were obtained at <ftp://ftp.ifremer.fr/ifremer/cersat/products/gridded/MWF/L3/QuikSCAT/Daily/>.

## **Methods**

The meridional (V) and zonal (U) wind vector components as well as equatorward winds (computed from both wind vectors) at 10 m above sea surface datasets were used for comparison of reanalysis products against QuickSCAT observations. Prior to analysis, the hourly datasets from reanalysis products were resampled to monthly means for the period between 2000 – 2009 when QuickScat data were available. Multiple data points (pixels within the ocean area of the northern BUS, Figure M1 gray dotted box) were selected for comparison of datasets. The statistical metrics used for comparison were the mean absolute percentage error (MAPE) and the root mean squared error (RMSE). In addition, linear regression was used to assess the degree of agreement between the reanalysis datasets and QuickScat which included the intercept, slope and the correlation coefficients (Pearson's  $r$ ).

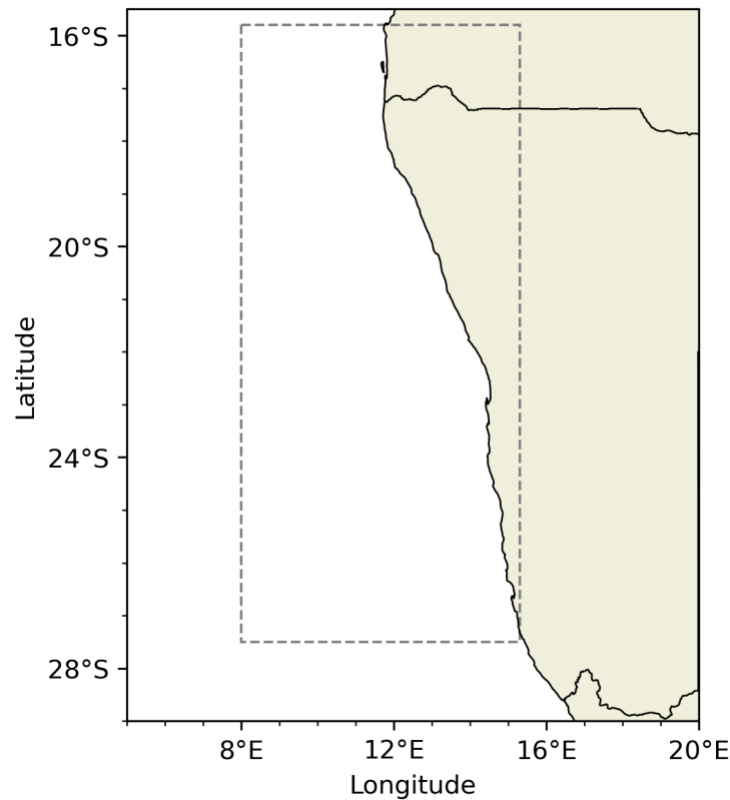


**Figure M1:** Map of the nBUS off Namibia showing the bounding box (gray dotted lines) within which pixels over the ocean were used for comparative analysis between reanalysis products and QuickSCAT satellite observations.

## Results

Besides the GOD-GSSWS, other reanalysis products generally underestimated the meridional (V) wind component (Figure M2A). In contrast, the zonal (U) wind component is overestimated by reanalysis products with the exception of GOD-GSSWS, which underestimated the U component (Figure M2B). With respect to equatorward winds, reanalysis products generally underestimated QuickSCAT observations (Figure M3), with the exception of the GOD-GSSWS product which compared well with QuickSCAT. The lowest RMSE and MAPE were observed for GOD-GSSWS when compared against QuickSCAT wind components (U and V) and equatorward winds (Table M1). In addition, correlation coefficients were highest for GOD-GSSWS (Table M1). In general, the GOD-GSSWS compares well with satellite observations for the nBUS and was chosen for further analysis in this study.

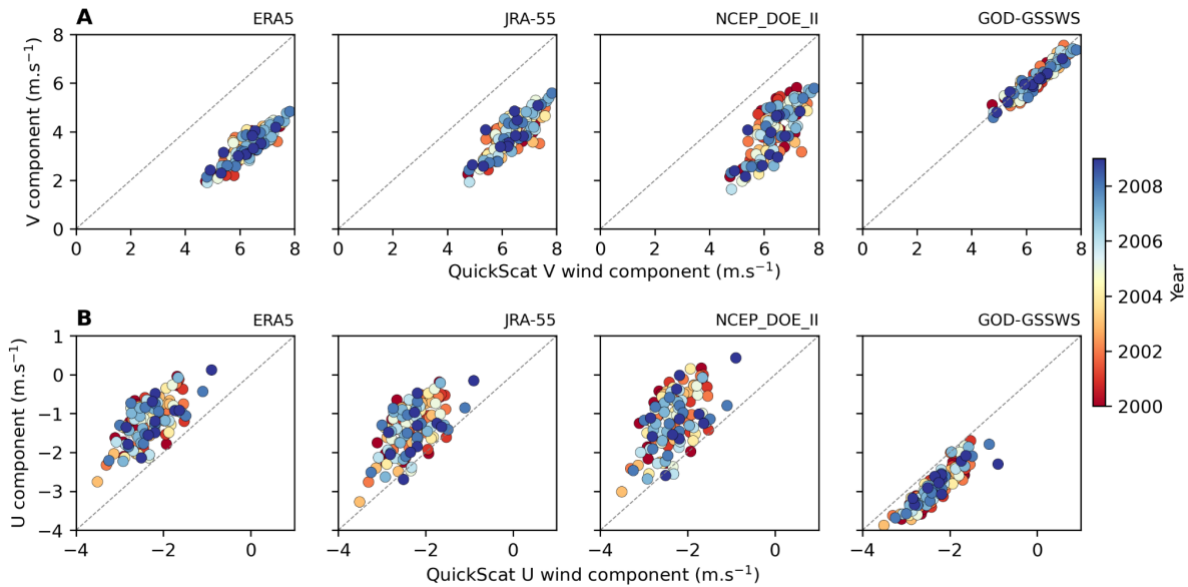


**Figure M2:** **A**, mean monthly meridional (V) wind speed from QuickSCAT compared to reanalysis products for the nBUS for the period between 2000 and 2009. **B**, same as in **A** but for the zonal (U) wind component. The dotted black line shows the theoretical 1:1 ratio.

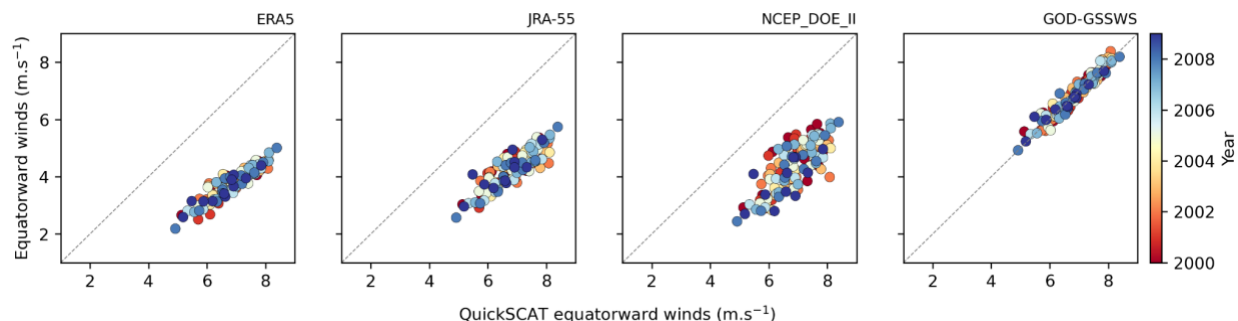


**Figure M3:** Mean monthly equatorward winds (computed from U and V components to the exclusion of poleward winds) from QuickSCAT compared to reanalysis products for the nBUS for the period between 2000 and 2009. The dotted black line shows the theoretical 1:1 ratio.

**Table M1:** Results of the statistical metrics used to compare reanalysis products against QuickSCAT observations for the nBUS region between 2000 and 2009 when QuickSCAT observations are available. Statistical metrics were calculated from monthly mean datasets. The bold numbers highlighted in green indicate a product that is better by comparison.

| Wind product                  | Statistical Metric |             |             |             |             |
|-------------------------------|--------------------|-------------|-------------|-------------|-------------|
|                               | MAPE               | RMSE        | Slope       | Intercept   | Pearson's r |
| Meridional wind (V component) |                    |             |             |             |             |
| ERA5                          | 0.46               | 2.94        | 0.84        | -1.92       | 0.88        |
| JRA-55                        | 0.39               | 2.5         | <b>0.95</b> | -2.12       | 0.82        |
| NCEP_DOE_II                   | 0.37               | 2.43        | 1.16        | -3.35       | 0.77        |
| GOD-GSSWS                     | <b>0.04</b>        | <b>0.32</b> | 0.89        | <b>0.49</b> | <b>0.95</b> |
| Zonal wind (U component)      |                    |             |             |             |             |
| ERA5                          | 0.5                | 1.22        | 0.79        | 0.67        | 0.66        |
| JRA-55                        | 0.42               | 1.08        | 0.78        | <b>0.43</b> | 0.58        |
| NCEP_DOE_II                   | 0.52               | 1.32        | 0.85        | 0.81        | 0.54        |
| GOD-GSSWS                     | <b>0.26</b>        | <b>0.61</b> | <b>0.92</b> | -0.77       | <b>0.89</b> |
| Equatorward winds             |                    |             |             |             |             |
| ERA5                          | 0.45               | 3.11        | 0.68        | -0.88       | 0.92        |

|             |             |            |             |             |             |
|-------------|-------------|------------|-------------|-------------|-------------|
| JRA-55      | 0.38        | 2.6        | 0.73        | -0.69       | 0.87        |
| NCEP_DOE_II | 0.37        | 2.54       | 0.86        | -1.5        | 0.77        |
| GOD-GSSWS   | <b>0.02</b> | <b>0.2</b> | <b>0.95</b> | <b>0.34</b> | <b>0.97</b> |

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### Annexure III: Supplementary Material data for Chapter 5

This is Supplementary Material data for:

#### Chapter 5: Determining planktonic dimethyl sulfur compounds from space

**Table S5.1:** Past research expeditions in the Benguela upwelling system where *in situ* DMS and/or DMSP measurements were collected.

| Contributor           | Research Vessel / Platform | Start      | End        | No. of stations | Reference(s)                                  |
|-----------------------|----------------------------|------------|------------|-----------------|-----------------------------------------------|
| Bingemer              | Polarstern                 | 1983/01/15 | 1983/01/18 | 12              | Bingemer, 1984; Bingemer <i>et al.</i> , 1987 |
| Kettle_D              | Polarstern                 | 1989/03/14 | 1989/03/17 | 21              | Tanzer and Heumann, 1992                      |
| Andreae               | Meteor                     | 1991/03/11 | 1991/03/20 | 87              | Andreae <i>et al.</i> , 1994                  |
| Bingemer              | Polarstern                 | 1993/11/08 | 1993/11/13 | 19              | unpublished                                   |
| Andreae,<br>Schebeske | Meteor                     | 1994/04/30 | 1994/05/06 | 12              | unpublished                                   |
| Bates                 | Ronald H. Brown            | 1999/02/04 | 1999/02/06 | 69              | Bates <i>et al.</i> , 2001                    |

## Annexure IV: Supplementary Material data for Chapter 6

This is Supplementary Material data for:

### Chapter 6: Unveiling seasonal patterns and multidecadal trends in planktonic dimethyl sulfur compounds from space

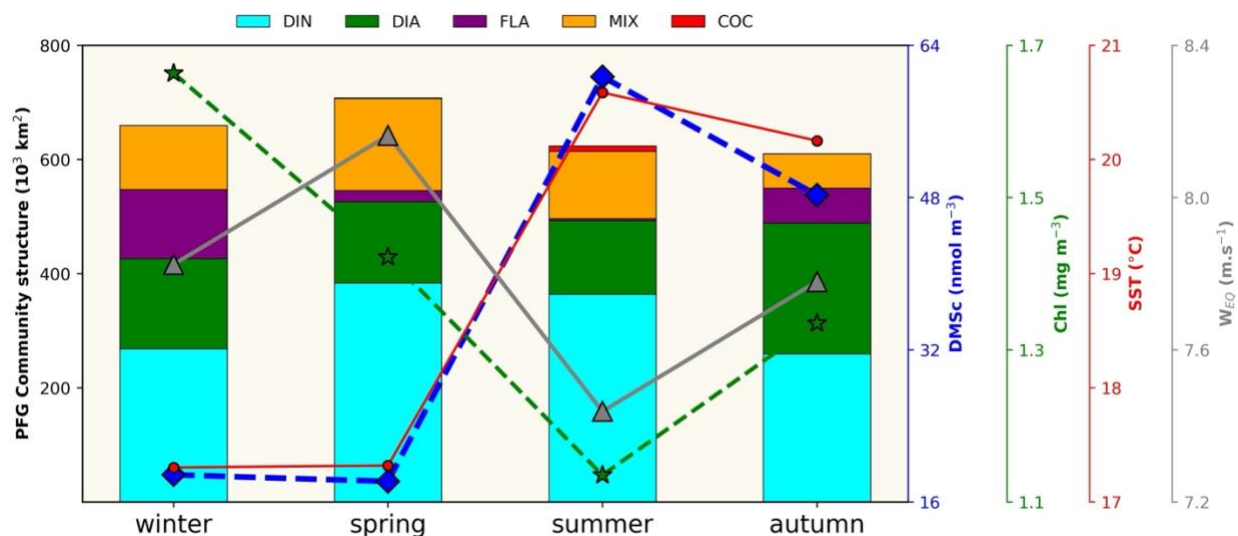


**Figure S6.1:** Climatological seasonal mean dimethyl sulfur compounds (DMSc, blue diamonds) in the nBUS. The seasonal mean community dominance structure (coloured bars) for dinoflagellates (DIN), diatoms (DIA), flagellates (FLA), mixed community (MIX) and coccolithophores (COC) computed by counting the number of pixels in **Figure 6.2** for each community and translated to *Spatial Extent* (km<sup>2</sup>) after accounting for the MODIS-Aqua resolution, as well as mean chlorophyll (Chl, green stars), sea surface temperature (SST, red circles) and equatorward winds ( $W_{EQ}$ , grey triangles) associated with DMSc are shown.

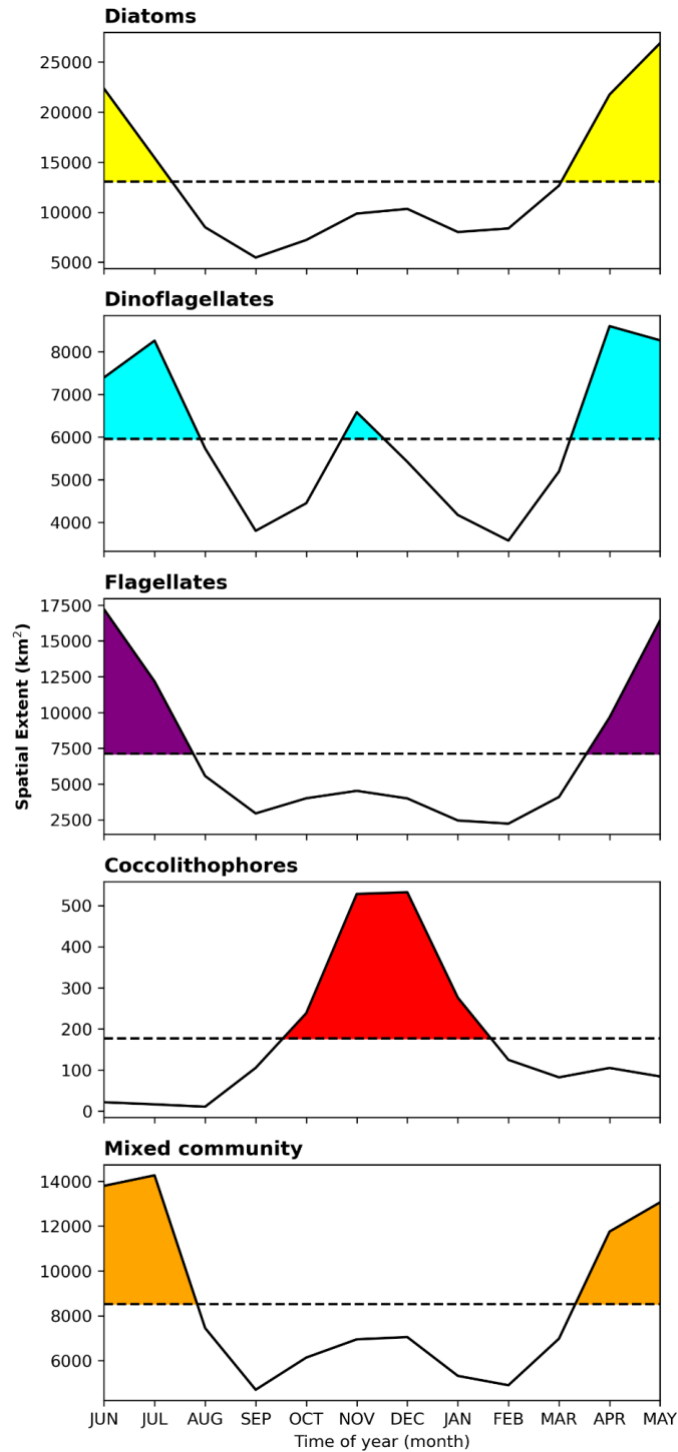


**Figure S6.2:** Seasonal cycle of the *Spatial Extent* for phytoplankton functional groups (PFGs) in the nBUS based on application of the PFG algorithm of Moloto *et al* (2023) using 20 years (2003–2022) of daily MODIS-Aqua observations. The horizontal dotted line shows the climatological mean *Spatial Extent*. The

shaded areas indicate the timing of the growing season, defined as the period when the *Spatial Extent* of each PFG is above the climatological mean *Spatial Extent*.

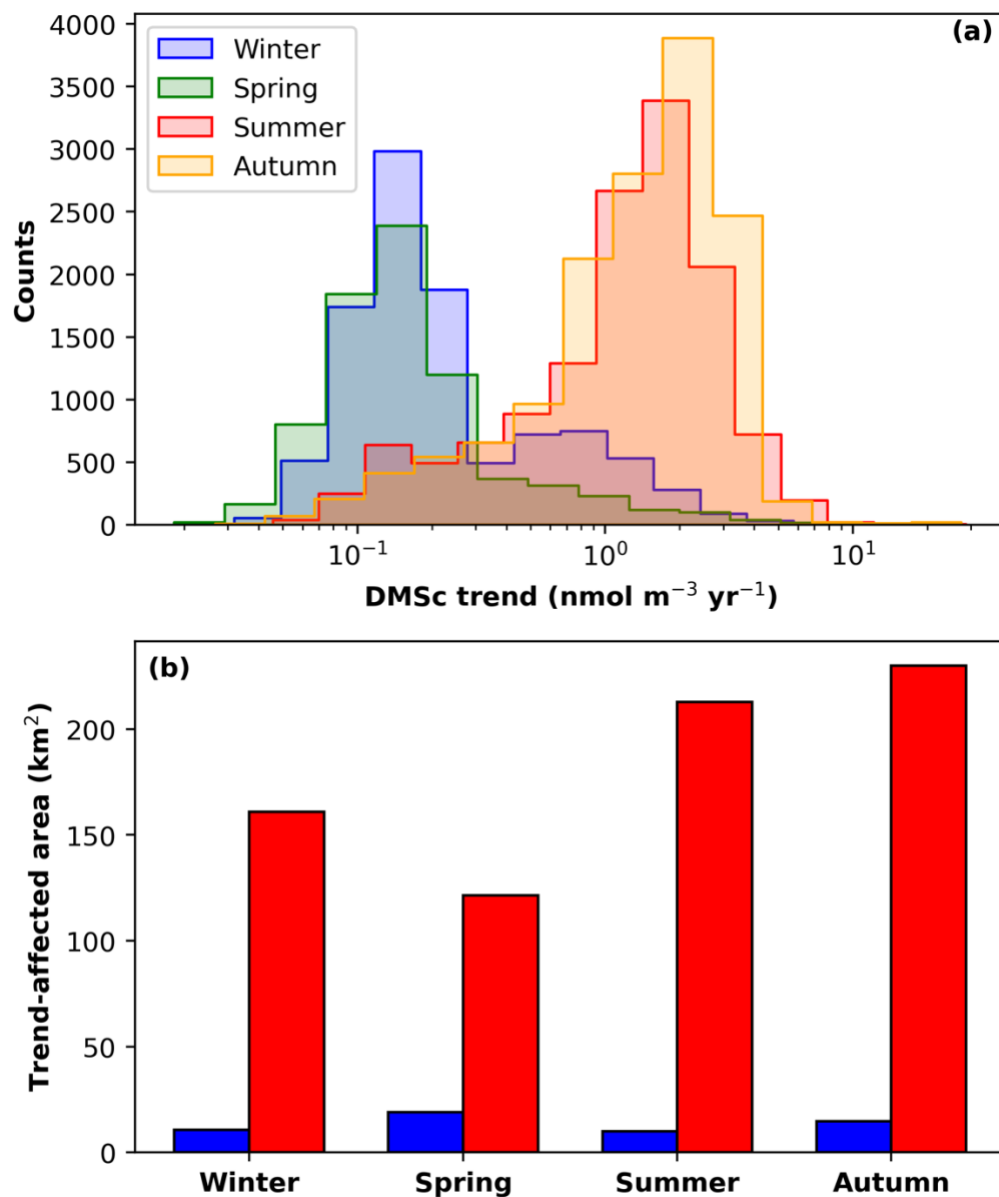


**Figure S6.3:** **a)** Distribution of the trends in DMSc across the Winter (blue), Spring (green), Summer (red) and Autumn (orange) seasons. **b)** Bar graph showing the area impacted by positive (red) and negative (blue) trends between the different seasons.

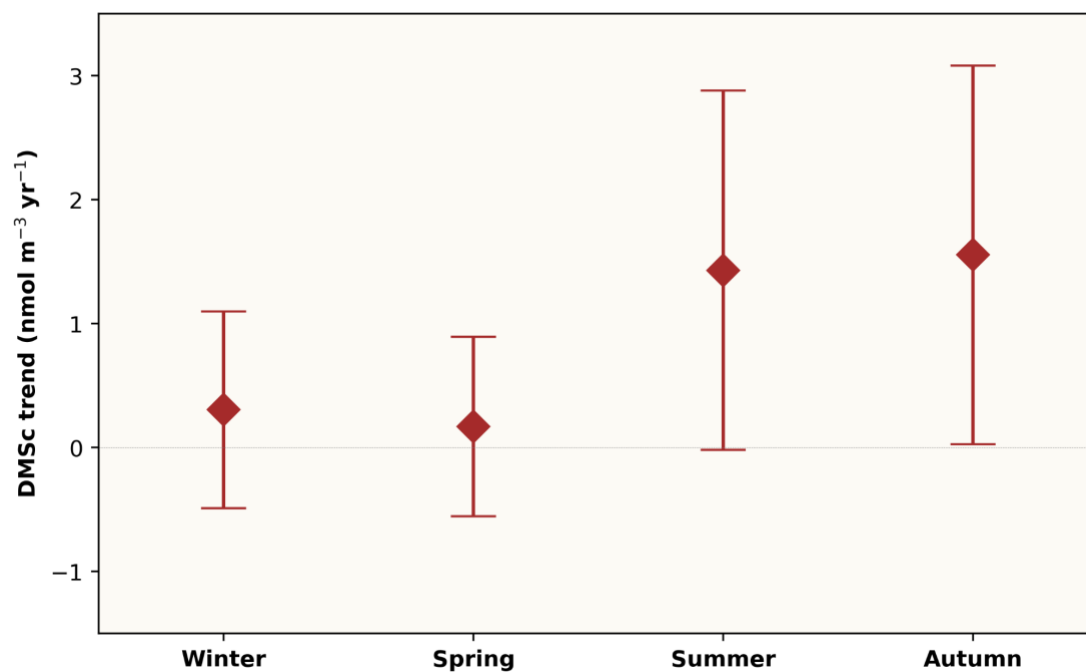


**Figure S6.4:** Seasonal mean annual trends in DMSc in the nBUS indicated by the diamonds, with the standard deviation shown by the error bars.