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SOLAS Virtual Summer School 2022

13 – 17 June 2022
Online

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Figure 1: Screen shot of students, lecturers, and organising committee members of the SOLAS virtual Summer School 2022

We all have felt the effects of the Corona Virus Disease (COVID) pandemic over the last two years, not only in our private lives, but also in our professional spheres. SOLAS made the difficult decision to take our summer school – well known for its intensive two-week, hands-on approach – to the virtual realm. This was a difficult decision that ultimately came down to the idea that we did not want the current cohort of SOLAS early career researchers to miss an opportunity to broaden the context of their research, as well as meet each other and leaders in their fields. However, this was no easy task. The organising committee knew that there was no way to replicate the in-person school, but we wanted to offer an enriching and fun event, nonetheless. We engaged the help of Mindfully Wired to support our online interactions using Whova and Zoom.

The virtual SOLAS Summer School took place on 13-17 June, 2022. A total of 62 students from 24 countries were accepted and the content was delivered by 29 international and interdisciplinary experts (Figure 1). The students were offered a carefully selected mix of lectures, discussions and workshops over five days (see the full programme here). As in previous SOLAS Summer Schools, one focus of this virtual summer school was on communication and networking. As we now know after more than two years of the pandemic, virtual events pose a very special challenge when it comes to communication and networking. Thanks to the great students, lecturers, and the team of Mindfully Wired, the hurdles of virtual events were skillfully overcome and transformed into a lively experience that will be remembered by the participants. We hope that fruitful collaborations will emerge in the future and we saw, through the Whova platform interactions, that the students mobilised to meet even after the school finished.

The virtual summer school concluded with the awarding of work-related travel and publication monetary prizes to selected students. This year, the best posters, the most liked uploaded photo, and the most creative/engaged social media post were awarded. A total of 12 prizes found happy recipients (see their work in the scientific highlights section). SOLAS would like to thank The Gordon and Betty Moore Foundation, The Partnership for the Observation of the Global Oceans (POGO), and the Xiamen Marine International Cooperation Center for their generous financial support. Furthermore, we would like to point out that the contents of the first virtual SOLAS Summer School are available to the interested public.

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Anna Lunde Hermansson is a PhD student at Chalmers University of Technology, Sweden, where her research focuses the marine environmental effects from shipping. Anna holds a MSc degree in marine sciences and chemistry from University of Gothenburg, Sweden, and University of Otago, New Zealand.

Ship exhaust scrubbers – a primary polluter of the sea. Based on the paper *Comparing emissions of polyaromatic hydrocarbons and metals from marine fuels and scrubbers* by Lunde Hermansson *et al.* 2021

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In January 2020, the International Maritime Organization (IMO) implemented new global regulations to limit the maximum sulphur content in marine fuels (IMO Annex VI of MARPOL, Regulations for the Prevention of Air Pollution from Ships). Instead of switching to compliant fuels, e.g. distillate low-sulphur fuels such as marine gas oil (MGO), ships may install exhaust gas cleaning systems, so called scrubbers, that enable a continued use of less expensive heavy fuel oils (HFOs).

Scrubbers are developed to reduce sulphur oxide (SO_X) emissions; the exhausts are led through a fine spray of water where SO_X readily dissolve and as a result, the water then becomes acidified (Karle and Turner, 2007). Also, the scrubber removes other contaminants from the ship's exhaust and the scrubber water, seawater in an open loop system and freshwater in the closed loop system, turns into a toxic cocktail (Tao *et al.*, 2013; Turner *et al.*, 2017). Chemical characterisation of scrubber discharge water shows that the acidified water becomes enriched with metals and polyaromatic hydrocarbons (PAHs) that are then discharged directly to the marine environment. For open loop systems, hundreds of cubic meters contaminated water are discharged directly back to the sea every hour, while the closed loop system recirculates the water, discharging smaller volumes (5 m^3/h) from the holding tank.

The aim of the study is to compare the emission factors from the previously dominating combustion of HFO, with two available alternative strategies to meet the new global sulphur cap. Emission factors of a selection of 3 metals and 3 PAHs from the combustion of different marine fuels are compared to the emission factors derived from the use of open and closed loop scrubbers (Figure 2). Additionally, contaminant-specific loads to the marine environment and to the atmosphere are estimated and compared with respect to different fuel-use and exhaust gas cleaning scenarios (Figure 3).

The results show that HFO, with and without scrubbers installed, generates higher emission factors of both metals and PAHs compared to

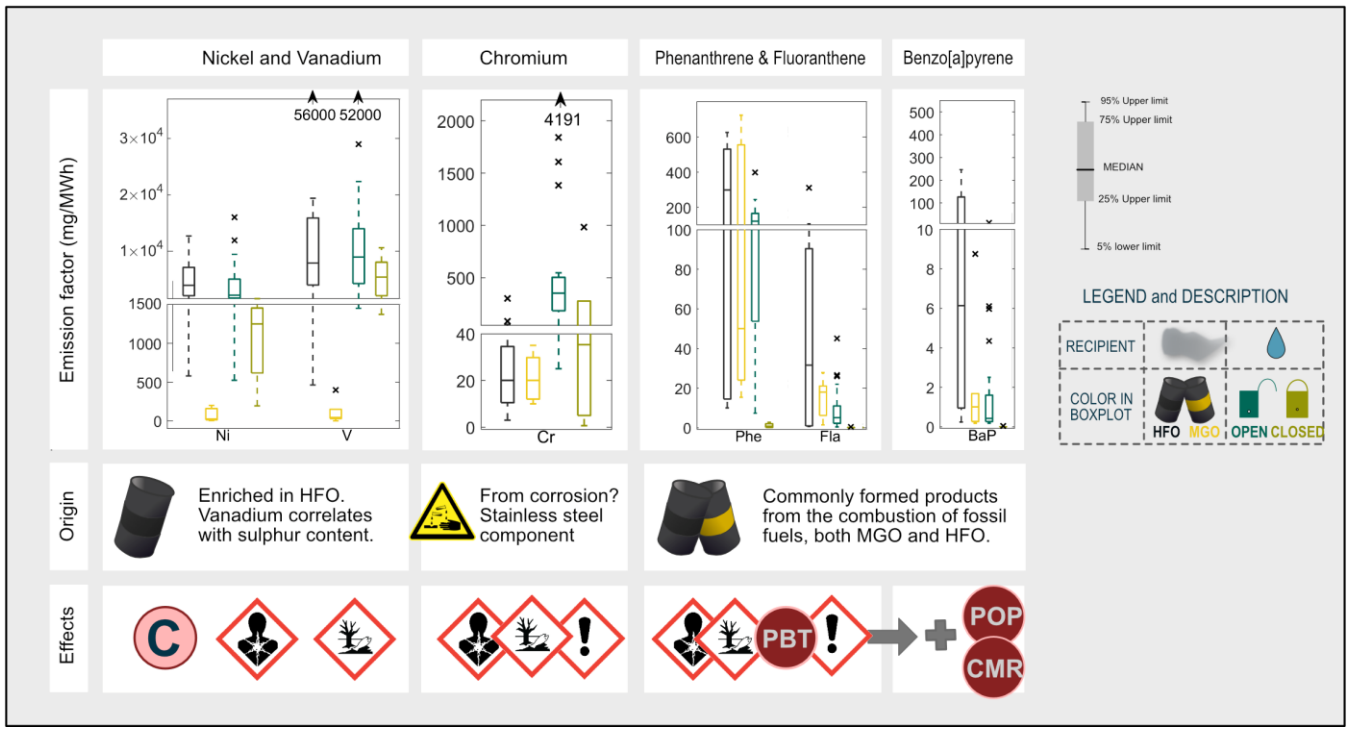

Figure 2: Emission factors (mg/MWh) of a selection of metals and polyaromatic hydrocarbons (PAHs) where heavy fuel oils (HFO) and marine gas oil (MGO) represent the emission factors to the atmosphere while open and closed loop represent emission factors to water. The box represents the 25th (bottom) and 75th (top) percentile with the mid-line being the median. The whiskers show the range of min and max values and the outliers are marked as crosses (if not visible within the range of the plot they are marked with an arrow and the corresponding value of the outlier). The scale differs between compounds. Also shown are possible origins and potential effects based on the European Union REACH classification system.

MGO (Figure 2). Also, the use of open loop scrubbers results in even higher emissions of for example chromium than HFO combustion alone. Although the emission factors of the PAHs appear to be reduced with scrubbers, these emission factors only include the emissions to water. The total emissions from vessels equipped with scrubbers, remain uncertain but the results suggest that contaminants are emitted to both the air and water recipient.

Comparing the relative loads based on different future scenarios of fuel-use and scrubber operations show that the chromium input may increase 5-fold if 22% of the fleet use scrubbers (Figure 3). The baseline scenario (dashed line) reflects the load prior to the new sulphur cap while scenario 1-3 correspond to future scenarios where the new regulations are implemented. The results from the different scenarios show that a shift to MGO would reduce the load of the selected metals and PAHs.

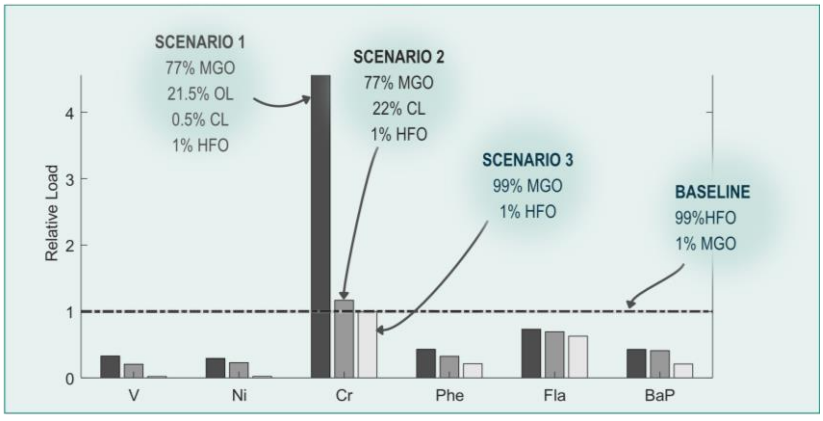

Figure 3: The environmental load of metals and polyaromatic hydrocarbons (PAHs) from the different combustion scenarios (presented within the bubbles) relative to the Pre-2020 sulphur cap scenario (dashed line, relative load = 1).

The use of scrubbers potentially introduces a new mode-of-entry for HFO combustion products, where the atmospheric processes are bypassed, and the contaminants are being discharged directly to the water column instead. As PAHs and their derivatives are toxic to marine organisms, some being mutagenic and carcinogenic (Achten and Andersson, 2015; Honda and Suzuki, 2020) and metals can cause adverse effects (Morales *et al.*, 2016), changing the primary recipient, from air to water, will also alter the environmental impact. In addition, previous ecotoxicological studies on marine organisms show that exposure to scrubber discharge water results in adverse effects, and that the mixture itself is more toxic than what could be predicted evaluating the toxicity of each individual compound (Koski *et al.*, 2017; Magnusson *et al.*, 2018).

Several PAHs (e.g. benzo[*a*]pyrene) and metals (e.g. nickel) found in scrubber discharge water are listed as priority substances under the European Union Water Framework Directive (WFD) and under regional conventions such as the Helsinki convention (HELCOM) and the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR). The result of this study thus implies that allowing discharge of scrubber wash water to the marine environment is in direct conflict with the European Union's goal to achieve Good Environmental Status in European waters (through the Marine Strategy Framework Directive and the WFD).

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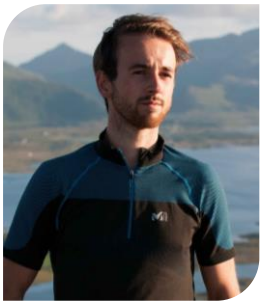
This short scientific article is based on the paper Comparing emissions of polyaromatic hydrocarbons and metals from marine fuels and scrubbers by Lunde Hermansson *et al.* 2021 (https://doi.org/10.1016/j.trd.2021.102912).



Benjamin Heutte obtained a BSc and MSc in environmental sciences at the Swiss Federal Institute of Technology Lausanne (EPFL), Switzerland, and continues with a PhD at the same university since 2021. His research is focused on aerosol sources and mechanisms in remote polar environments, especially in the central Arctic Ocean.

Annual aerosol chemical composition retrieved with an aerosol mass spectrometer in the central Arctic

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The Arctic environment is changing rapidly due to climate change, which induces several feedback processes such as retreating sea ice, changing atmospheric transport patterns and cloud formation. Atmospheric aerosols have an important impact on the Earth's surface energy budget, through scattering or absorption of incoming solar radiation (direct effect) or through aerosol-cloud interactions (indirect effect). Both effects strongly depend on the physico-chemical properties of these aerosols and remain the largest uncertainties in our estimations of future climates (Intergovernmental Panel on Climate Change, 2021), especially for natural aerosols (Carslaw *et al.*, 2013). While the overall seasonality of aerosol mass concentrations and chemical compositions at Arctic ground-based surface observatories is relatively well known (Schmale *et al.*, 2022; Willis *et al.*, 2018), it remains unclear whether these observations are representative for the central Arctic. In addition, short extreme events such as storms, warm-air mass intrusions or intense pollution episodes from ship emissions have been less studied, mostly due to a lack of comprehensive, high-time resolution chemical composition datasets.

In September 2019, R/V Polarstern left Tromsø harbour, Norway, towards the central Arctic Ocean for a year-long measurements campaign. The Multidisciplinary drifting Observatory for the Study of Arctic Climate (MOSAiC) expedition was the most comprehensive expedition of this kind in the central Arctic in history, and aimed at closing some of the knowledge gaps in various interlinked processes at play in this region. Figure 4 shows the expedition track from September 2019 to October 2020 (Shupe *et al.*, 2022).

We measured the chemical composition of submicron aerosols using a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne Research Inc., USA). Additionally, measurements of equivalent black carbon (eBC) were performed using an aethalometer (AE33, Magee Scientific, USA). The AMS dataset was cleaned for local pollution (e.g., exhaust by Polar stern's engine and vents,

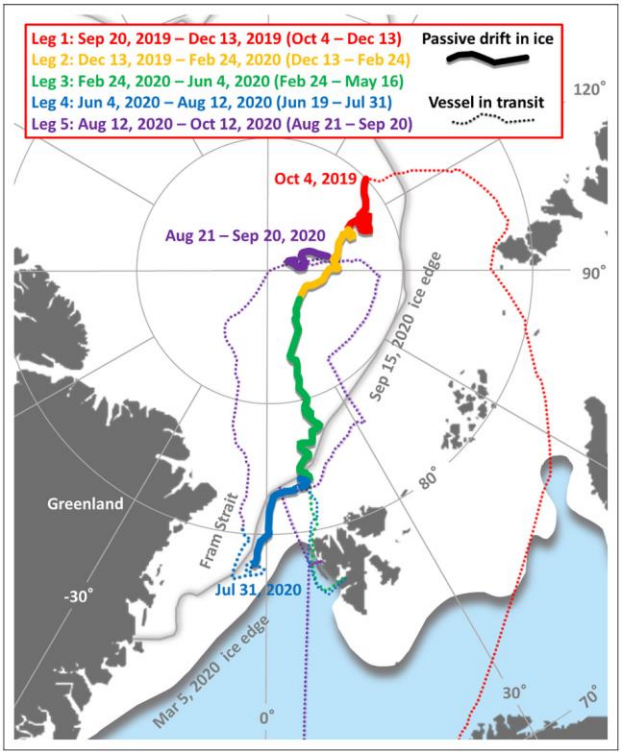

Figure 4: Expedition track color-coded by cruise leg during MOSAiC Periods of passive drift by Polarstern (solid) and periods of transit when the vessel was underway (dotted) are distinguished. The inclusive dates for each of the 5 legs are given in the legend, with the second set of dates in parentheses being the dates spent in passive drift. The approximate sea ice edge at the annual maximum (March 5, 2020) and minimum (September 15, 2020) is also provided (Shupe *et al.*, 2022).

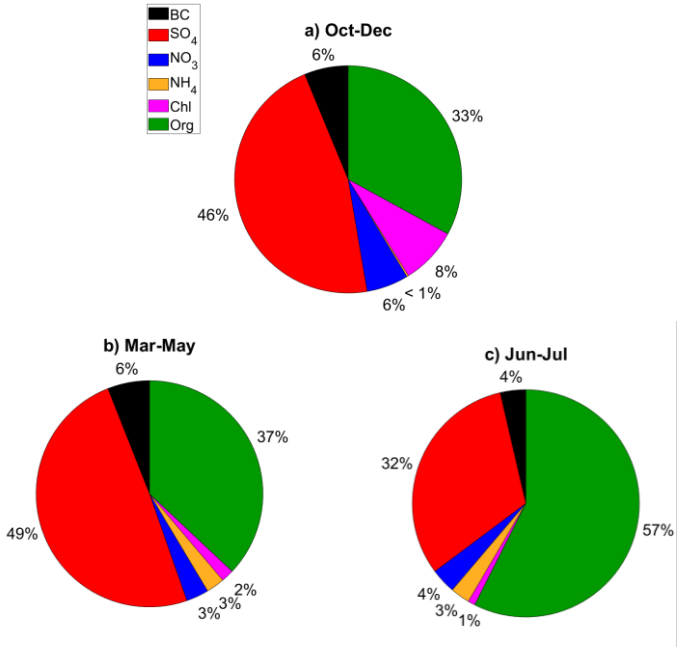

Figure 5: Relative contribution of the main aerosol species for (a) October to December, (b) March to May and (c) June to July, during MOSAiC expedition. Note that the Aerosol Mass Spectrometer (AMS) dataset was cleaned for local pollution.

skidoos, on-ice diesel generators) following the cosine similarity method described by Dada *et al.* (accepted), while the aethalometer dataset was cleaned with a pollution flag derived from applying a Pollution Detection Algorithm (PDA) on a collocated Condensation Particle Counter (CPC) dataset (Beck *et al.*, 2022).

The dataset was separated into three periods, from October to December 2019, from March to May 2020, and from June to July 2020 (note there is no data for other months). We found median [25th, 75th percentiles] submicron non-refractory aerosol mass concentration of 0.22 [0.14, 0.32], 0.98 [0.79, 1.21] and 0.24 [0.14, 0.57] µg/m^3, for the three periods, respectively. The autumn period (October-December) is characterised by pristine conditions and low aerosol mass concentration, with a dominance of particulate sulfate (46% SO_4, Figure 5). The spring period (March-May) is characteristic of the Arctic haze season, with the highest annual aerosol mass concentration and sulfate contribution. These can be associated with an expansion of the polar dome leading to enhanced long-range transport from mid-latitudes and increased particles lifetime through diminished removal processes. Finally, the summer period (June-July) shows the highest organic aerosols contribution (57% organic), from local/regional emissions of biogenic precursor gases (e.g. dimethyl sulfide) that can contribute to the formation of secondary organic aerosols (SOA) or directly with emissions of primary organic aerosols (POA). The mean aerosol mass concentration is also decreased, predominantly due to enhanced aerosol removal processes (via wet and dry deposition) and a contraction of the polar dome that reduces long-range transport.

In the context of my PhD, I will aim at characterising the main chemical and geographical sources of organic aerosols in the central Arctic ocean, using a source apportionment method applied on the AMS dataset, called positive matrix factorisation (PMF,

Paatero & Tapper, 1994). These results should also benefit the modelling community, by providing unique year-long, chemically-resolved, high-resolution observations of both natural and anthropogenic aerosols at these remote latitudes and pristine environments.

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Data used in this study was produced as part of the international Multidisciplinary drifting Observatory for the Study of Arctic Climate (MOSAiC) with the tag MOSAiC20192020.

Philippa Rickard is a postdoctoral research associate in Marine Biogeochemistry in the Carbon-Water Dynamics group at Heriot-Watt University, UK. Philippa previously worked at a Postdoc, and completed her PhD, at Newcastle University, UK, where she investigated environmental variability of surfactants in the surface microlayer in coastal and freshwater systems.

Surfactant control of air-water gas exchange in a freshwater lake

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The surface microlayer (SML) is operationally defined as the uppermost 10-100 µm of surface water, and covers ~70% of Earth's surface (Engel *et al.*, 2017). Accumulation of surfactants in the SML is ubiquitous (Sabbaghzadeh *et al.*, 2018; Wurl *et al.*, 2011) and at this interface they are a control of mass transfer between the air and water phases. SML surfactant enrichment greatly reduces the air-water exchange rate of carbon dioxide (CO_2) at the ocean basin scale (Pereira *et al.*, 2018), however, this conclusion cannot be generalised to freshwater systems because relevant studies are absent. Given the major contribution of the freshwater system to the global carbon cycle (O'Reilly, 2015, Verpoorter, *et al.*, 2014), this is a critical omission.

This work aims to address the deficiency of freshwater studies by coupling total surfactant measurements in the SML and corresponding subsurface water (SSW) with direct gas transfer velocity estimates for CO_2 by eddy covariance (EC) at a freshwater lake: Lake Erken, Sweden (Figure 6a). The Erken Laboratory at Lake Erken is an active Swedish Infrastructure for Ecosystem

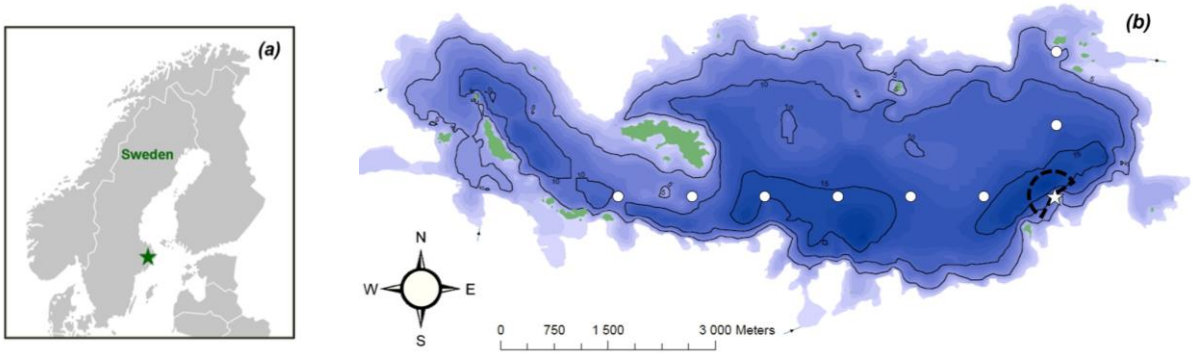

Figure 6: Lake Erken is located in upland Eastern Central Sweden (59.835°N, 18.633°E, green star; (a), with an eddy covariance tower and a CO_2 sensor located on and near Malma Island (white; b) respectively, close to the south-east shore of the lake. The approximate tower footprint (~400 m ENE to SSW) is depicted by the black dashed line; SML and SSW samples were collected from transects within the tower footprint into the prevailing wind direction at the time of sampling, and also from lake-wide sampling sites (white dots) spaced at 1 km intervals.

Science (SITES) field station, with continuing longitudinal datasets for a suite of biogeochemical variables. An EC tower is located on Malma Island, close to the south-east shore of the lake (Esters *et al.*, 2021), and partial pressure of CO_2 in the water (0.5 m depth) is measured with a Submersible Autonomous Moored Instrument (SAMI2-CO2), located ~100 m northwest from Malma Island.

Throughout ~20-day field campaigns during boreal summer (June 2021) and autumn (October 2021), the SML (< 1000 µm; Garret Screen; Cunliffe and Wurl, 2014; Garrett, 1965) and SSW (~20 cm; hand dipped bottles) were sampled during approximate daily transects within the footprint of the EC tower (~400 m) into the prevailing wind, and during one lake-wide survey per campaign (Figure 6b). Total surfactant activity (SA) is expressed as equivalents of model surfactant Triton-X-100 (mg l^{-1} T-X-100 eq.); enrichment factor (EF) = SASML/SASSW, where surfactants are considered enriched when EF >1.

Surfactants were largely enriched in the microlayer throughout the low to very high wind regimes sampled (up to ~11 m s^{-1}; Figure 7a), which is in agreement with previous oceanic studies (Sabbaghzadeh *et al.*, 2018; Wurl *et al.*, 2011). Extensive surfactant slick conditions (> 1 mg l^{-1} T-X-100 eq.; 7b) were present during June 2021, where SML SA varied (0.7-1.7 mg l^{-1} T-X-100 eq.) with windspeed and followed the same, but lagged, trend as SSW SA (0.6-1.5 mg l^{-1} T-X-100 eq.; Figure 7c). The evident decoupled process is likely due to initial turbulent mixing of the SML with SSW, which ultimately induces bubble scavenging and consequently increases SA (Mustaffa *et al.*, 2020) with increasing windspeed. This process was not observed during October 2021, where there was no trend evident in SML or SSW SA (0.6-0.9 mg l^{-1} T-X-100 eq. and 0.6-0.8 mg l^{-1} T-X-100 eq. respectively) throughout low to very high wind regimes.

The seasonal difference in SA behaviour observed is possibly due to compositional

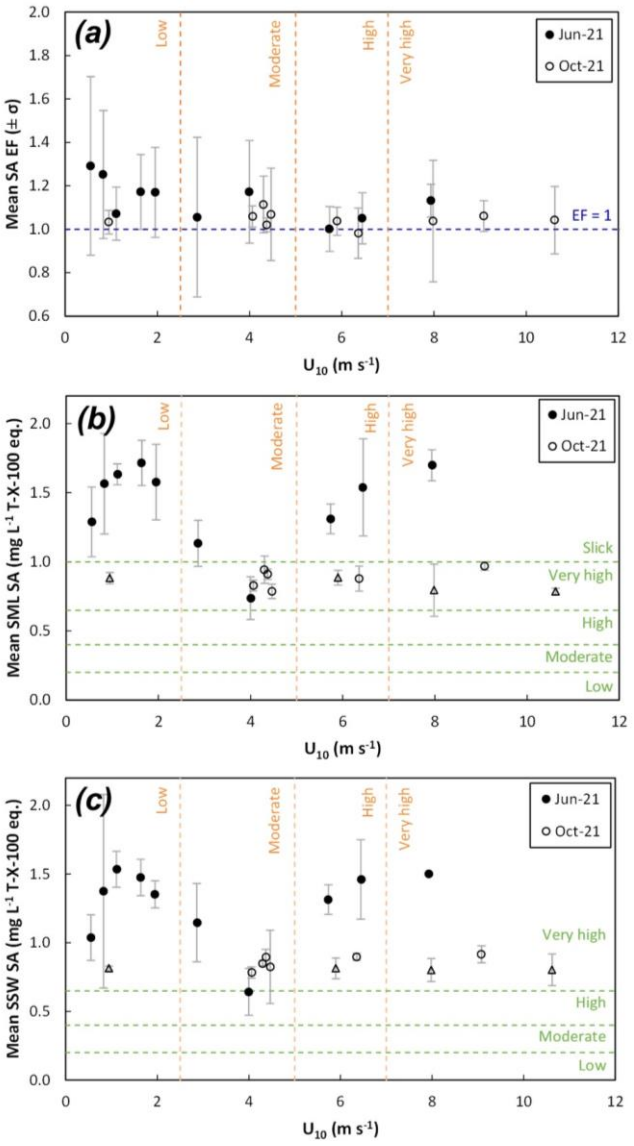

Figure 7: Mean (± σ) SA enrichment factors (EF = SASML/SASSW; a), and surface microlayer (SML) and sub-surface water (SSW) total surfactant activity (SA; mg l-1 T-X-100 eq.), against windspeed at 10 m (U10) for eddy co-variance tower footprint transects. The orange and green dotted lines show the boundaries of wind and surfactant re-gimes (Mustaffa *et al.*, 2020; Pierson and Moskowitz, 1964) respectively; the blue dotted line shows EF = 1.

differences in the total surfactant pool. The next stage of this work is to explore any seasonal differences in dissolved organic matter (DOM) composition in the SML and SSW samples, using data produced from size-exclusion chromatography (SEC; HW50S, Tosoh, Japan; Huber *et al.*, 2011). The resulting data set will be correlated with the gas flux estimations from the EC tower, and will enable the first ever assessment of gas exchange across the surface

of a freshwater body, as impacted by varying amounts of total surfactant activity and indices of the organic composition of the total surfactant pool.

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Samira Moussa Idrissa studied marine science and climate change in Niger and then moved to Cape Verde in 2020 to conduct her master studies. The topic of her master thesis is to investigate on the aerosol's optical properties profile characterisation over São Vicente, Cabo Verde, during the ASKOS campaign.

Aerosols optical properties profile characterisation over São Vicente, Cabo Verde, during the ASKOS campaign

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Aerosols are essential components of the climate system (Knippertz & Todd, 2012). They can influence climate in various ways. Due to their optical, radiative properties and their potential to act as cloud condensation nuclei (CCN) and ice nucleating (IN) particles, they play a central role in Earth's energy budget and hydrological cycle (Ramanathan *et al.*, 2007). Additionally, the role of aerosol particles in the global terrestrial and oceanic biogeochemical cycles is vital (Winckler *et al.*, 2008). However, despite their importance and relevance in the climate system, they are still considered a major source of uncertainty to our understanding of climate processes and, consequently, in the Earth system and climate models simulations (Stocker *et al.*, 2013).To reduce these uncertainties, coordinated and strategic integration of data from multiple platforms (e.g., ground-based networks, satellite, ship, and aircraft) (Wang *et al.*, 2014, Thomas *et al.*, 2007, Holben *et al.*, 1998) and techniques (e.g., *in-situ* measurement, remote sensing, numerical modelling, and data assimilation) are highly required.

Within this perspective, one objective of my master thesis was to investigate the atmosphere columns by using sun photometer data (AERONET) during the ASKOS experiment, which took place from July to September 2021 at São Vicente Island of Cabo Verde. The instantaneous retrievals of aerosol optical depth from Aerosol Robotic Network (AERONET) at 500 nm (AOD) were analysed and are represented in Figure 8. The AOD over Mindelo varied from values of 0.2 to 2.0 during extreme dust transport events. These events occurred throughout the year, with significantly higher values based on AERONET retrievals. That indicates a hazy aspect of the atmosphere. In addition, a reduction in the value of the Angstrom coefficient ($\alpha_{440\text{-}870}$) is usually recorded whenever a substantial increase in AOD occurs. In particular, the period from July to mid-September experienced the lowest values of $\alpha_{440\text{-}870}$, over Mindelo, fluctuating between 0.2 and 0.6. This fluctuating suggests an increase of the coarse particles in the atmosphere column above Mindelo, mainly transported from Saharan regions to the island and with the contribution of marine coarse mode aerosols from the Atlantic.

The analysis of the lidar ratio reveals a lowering in its variability (40 - 80 sr) compared to the ending of the year (40 - 110 sr) similar to that seen for $\alpha_{440\text{-}870}$. Identical patterns can be distinguished for

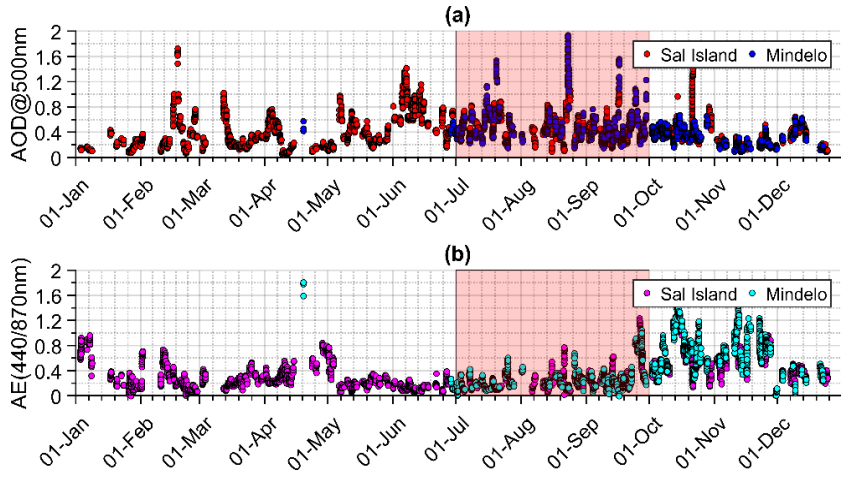

Figure 8: Variability of Aerosol Optical Depth at 500 nm (AOD@500nm) and Angström Exponent based on 440 and 870 nm (AE 440/870 nm) over Mindelo and Sal Island for the year of 2021 based on Aerosol Robotic Network (AERONET) sun photometer retrievals. The ASKOS campaign period is highlighted in red.

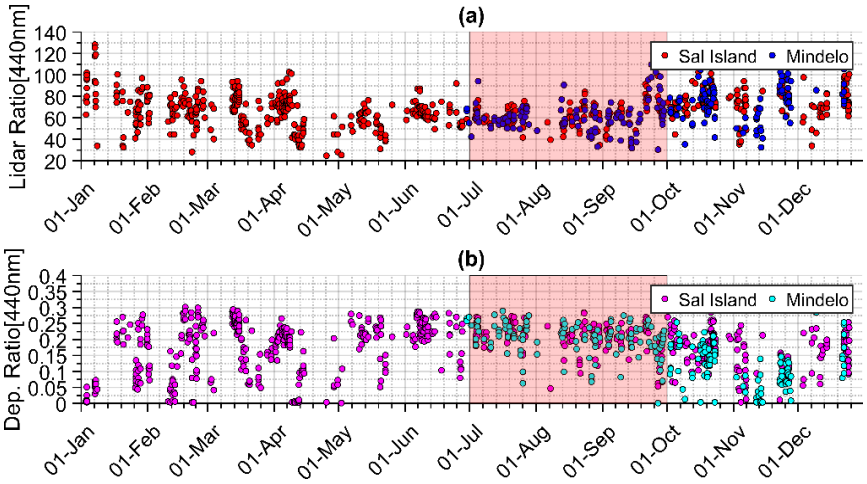

Figure 9: Variability of columnar Lidar ratio and particles depolarisation ratio at 440 nm over Mindelo and Sal Island for 2021 based on Aerosol Robotic Network (AERONET) sun photometer retrievals. The ASKOS campaign period is highlighted in light red.

the depolarisation ratio, which recorded mostly high values from the beginning of the summer season until mid-September as can be seen in Figure 9. This situation indicates the presence of an air mass with non–spherical scatterers such as mineral particles (almost-pure dust conditions) as indicated by an increase in the particle depolarisation ratio, and some spherics species involved in a mixing state of the atmosphere such as dust and pure marine, dust and pollution or another type of particle-like volcano origin.

Under the conditions described, it is possible to characterise distinct scenarios of the aerosol mixture over Mindelo, and to have a good understanding of the atmosphere composition in term of particles.

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This study was totally funding by the institution of WASCAL. I would also like to express my gratitude to my supervisors Prof. Dr. Nilton Évora do Rosario and Dr. Nikolaos Siomos, who have accompanied me throughout this learning process.

Tiera-Brandy Robinson moved to Germany in 2016 to start her PhD in Oliver Wurls marine interface group at University of Oldenburg, Germany, and then continued as a postdoc. She is now starting a new postdoc position at GEOMAR Helmholtz Centre for Ocean Research Kiel, Germany, utilising marine sensors to detect biogeochemical changes and nutrient limitation in the ocean.

Transparent exopolymer particles and Coomassie stainable particle concentrations and enrichment in the sea surface microlayer of a central Arctic open lead

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The surface microlayer (SML) is the boundary layer between the ocean and atmosphere (Hardy, 1982). It acts as a physical boundary layer, and typically becomes enriched – compared to the underlying bulk water – in organic matter and surface-active material (Cunliffe *et al.*, 2013; Wurl *et al.*, 2016). Extracellular polymeric substances (EPS) are important surface-active components of the SML, which help to aggregate and transport organic matter in the water and contribute to the role of the ocean as a carbon sink (Mari *et al.*, 2017; Yamada *et al.*, 2017) as well as help to bind and stabilise the SML layer. Two types of gel-like EPS have attracted particular attention in marine biogeochemical studies: transparent exopolymer particles (TEP), acidic polysaccharides (Alldredge *et al.*, 1993), and Coomassie stainable particles (CSP), proteinaceous particles (Long and Azam, 1996), both useful in their relative ease of collection via staining. In this study we characterised the concentration of TEP, CSP and surfactants in the SML and underlying water (ULW) at 1 m depth of an Arctic open lead, in combination with meteorological parameters and an assessment of near surface turbulence, during three weeks spanning the transition from summer melt into autumnal freeze-up. Concentrations of chlorophyll-a (Chl-a), and particulate matter were also collected to help identify shifts in production/consumption mechanisms for TEP, CSP, and surfactants.

A catamaran outfitted with six partially immersed rotating glass discs and peristaltic pumps was deployed in a central Arctic open lead and sampled the SML through the physical phenomena of surface tension (Ribas-Ribas *et al.* 2017). In addition, ULW at one metre depth (the standard depth for ULW collected in open ocean environments) was collected for comparison. Measurements began on 18.08.2018 and the open lead remained largely unfrozen for 21 days until 08.09.2018, when much of the lead was frozen over, and sampling was no longer possible. The period from 26.08.-05.09.2018 was characterised by the movement of several storm systems with higher winds. Based on a change in meteorological data and EPS data, and for the purpose of improved intra and intercomparison,

results have been split into two categories of "period 1" from 18.08.-25.08.2018 and "period 2" from 26.08.-05.09.2018.

The SML was found to be enriched with EPS and surfactants for most of the study even as EPS concentrations decreased by 73% for TEP and 50% for CSP in period 2, which corresponded to the onset of the autumn freeze up and shifting winds giving longer fetch conditions at our measurement location (Figure 10). Average CSP:TEP ratios of 2.96 in the SML and 2.77 in the ULW suggest a proteinaceous gel matrix, orroborating previous findings sampled from Arctic melt ponds and open leads, but also showed an increase in this ratio over time as temperatures in the open lead decreased. This is a unique finding to the Arctic environment and suggests a differing EPS production/consumption system than is seen in open ocean environments. While not significant, an interestingly negative correlation was found between EPS and Chl-a and particulate organic carbon (POC, Figure 11) in which both, TEP and CSP, decreased during period 2, while Chl-a and POC increased, suggesting that TEP did not make up a large part of the organic carbon pool and changes occurred to the local production and degradation processes between period 1 and 2.

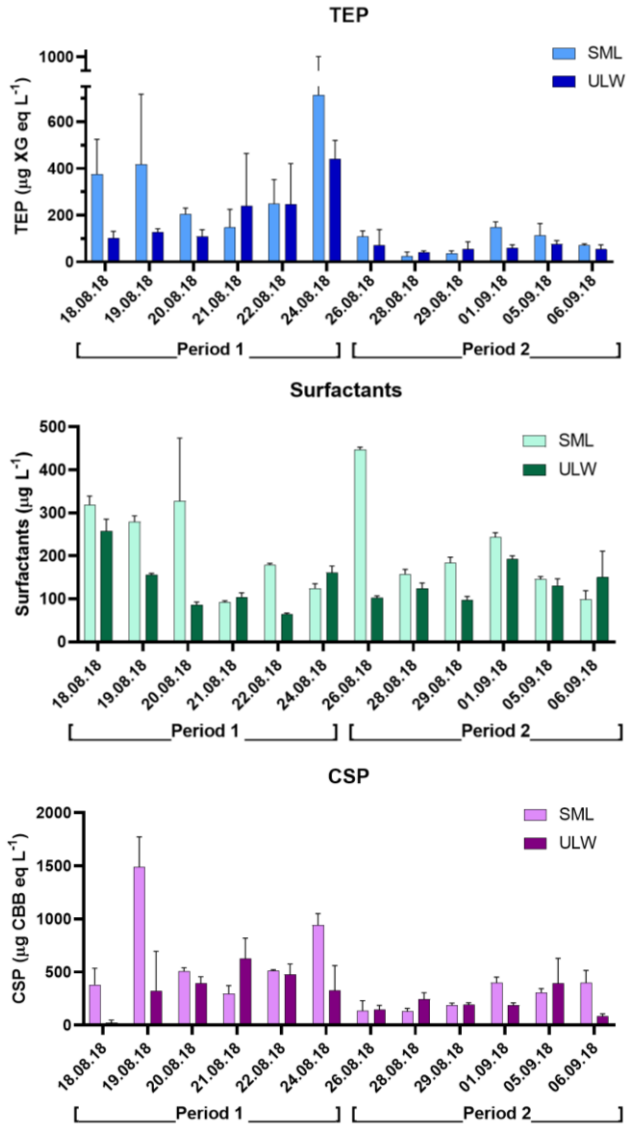

Figure 10: Time series of concentrations in the sea surface microlayer (SML, lighter bars) and underlying water (ULW, darker bars) for: transparent exopolymer particles (TEP), Coomassie stainable particles (CSP) and surfactants with indications for the two periods defined.

Additional data on phytoplankton and bacterial community composition is needed in order to further understand the local biogeochemical process involved in EPS enrichment of the SML. However, this study shows that shifts in EPS concentration in the SML can occur separately from the surfactant pool and do occur during the freeze-up of open lead systems.

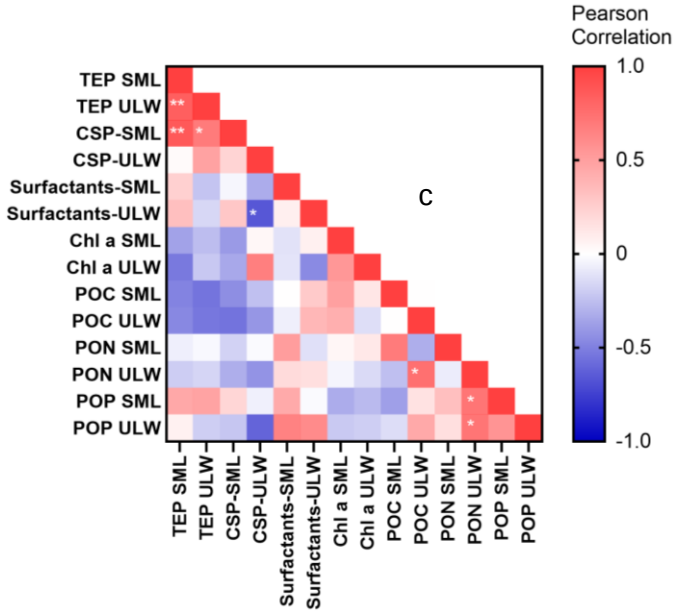

Figure 11: Heatmap of Pearson correlation matrix between all 14 variables sampled in both, the sea surface microlayer (SML) and underlaying water (ULW), over the entire sampling period. Significant correlations are marked by **(p < 0.01) and *(p < 0.05). Colour bar indicates correlation coefficient.

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Axelle Brusselman is a PhD candidate in Chemical Oceanography Unit at the University of Liège, Belgium. She got her Master degree in Oceanography at the University of Liège in 2021. Her project focuses on the study of carbon dioxide (CO_2) and methane (CH_4) fluxes along the atmosphere –sea ice-water column – sediment continuum in Antarctica.

CO_2 and CH_4 fluxes along the atmosphere – sea ice-water column – sediment continuum

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Carbon dioxide (CO_2) and methane (CH_4) are two potent anthropogenic long-lived greenhouse gases (GHGs) that contribute to about 81% of the total radiative forcing of the Earth (Arias *et al.*, 2021). Predicting their future atmospheric concentration is quite challenging because of the lack of knowledge existing on the contribution of their natural sources and sinks to the atmosphere (Nisbet *et al.*, 2014). Polar regions, well-known as the most affected by environmental changes, still represent one of the largest uncertainties in the understanding of the GHGs cycles. How the sea ice cover affects these cycles remains one of the greatest unknowns (Parmentier *et al.*, 2013).

Since the early 90's, carbon fluxes in the Southern Ocean (SO) are a long-lived critical question for the ocean science community. The ventilation of the ocean interior is predominantly occurring through the SO surface. As a result, SO is estimated to store roughly 75% of the global oceanic uptake of excess heat and 43% of the global uptake of excess carbon from the atmosphere (Frölicher *et al.*, 2015).

Sea ice cover is one of the main controls on polar ocean physical and biogeochemical processes, and its extent is predicted to be reduced by the end of the century. Reduction of ice extent has been predicted to increase CO_2 fluxes and SO water productivity (Bopp *et al.*, 2013). However, in these approaches, little attention is paid to sea ice internal physical and biogeochemical processes and their impact on carbon fluxes (Stephens and Keeling, 2000). However, the coupling between sea ice, and pelagic and benthic environment regarding nutrients, organic matter and carbon are poorly quantified, so that to date, it is difficult to assess the impact of sea ice processes on the SO primary production.

CH_4 is the second most important GHG after CO_2. If the CH_4 dynamics in the Arctic Ocean currently receives growing attention, contrastingly, the SO has received far less attention as seen in Figure 12. The only studies to have documented the surface distribution show contrasting results (Lamontagne *et al.*, 1974; Jacques *et al.*, 2021). Some areas exhibit a general CH_4 undersaturation with CH_4 distribution reflecting the age of the water mass (with some exceptions). In contrast, some observed a rapid increase of the surface concentration in the marginal ice zone. Higher values near the Antarctic continent are

also observed and it is suggested that the Ross Sea is oversaturated in CH_4, and therefore can act as a source of CH_4 for the atmosphere.

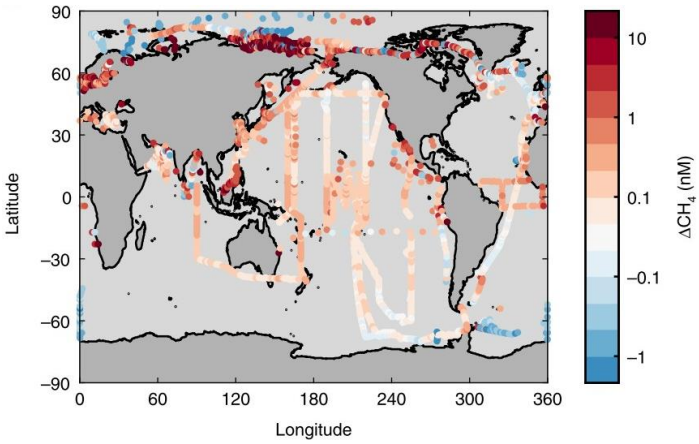

Figure 12: Most recent global variabilities in methane (ΔCH_4) climatology. Note the lack of data in most of the Southern Ocean.

The project will develop an innovative, integrated approach of sea ice, water column, and sediment components of the Antarctic marine ecosystem to identify sources and sinks of CO_2 and CH_4 across the atmosphere-sediment vertical continuum in the West Antarctic Peninsula (WAP). Using this novel approach, we want to address two overarching questions: What is the role of sea ice in carbon fluxes in the WAP in the context of predicted sea ice reduction? What is the current status of the WAP waters as a source or sink of atmospheric CH_4?

The WAP is a crucial area for our surveys since it is the most impacted by climate change in Antarctica. WAP encompasses large, shallow areas connecting the sediment and the atmosphere and diverse sea ice landscapes. Sea ice sampling sites will be chosen depending on the sea ice cover and its seasonal persistence to highlight sea ice's impact on the underlying water column and sediment in terms of carbon fluxes. The fluxes will be analysed with various instruments and technics including CO_2 chamber systems, gas chromatography, sediment traps, core incubation. The integrated vertical approach developed in the project will allow us to assess the main contributions along the vertical, including the sediment that is most likely a significant contributor, but also sea ice that can consume or produce CH_4.

Documenting CH_4 dynamics in sea ice will be facilitated by improving our capability to work on low amounts of gas available in sea ice samples compared to the water column. This improvement will be based on implementing a new sea ice extraction device presented in Figure 13, currently under testing for continental ice samples.

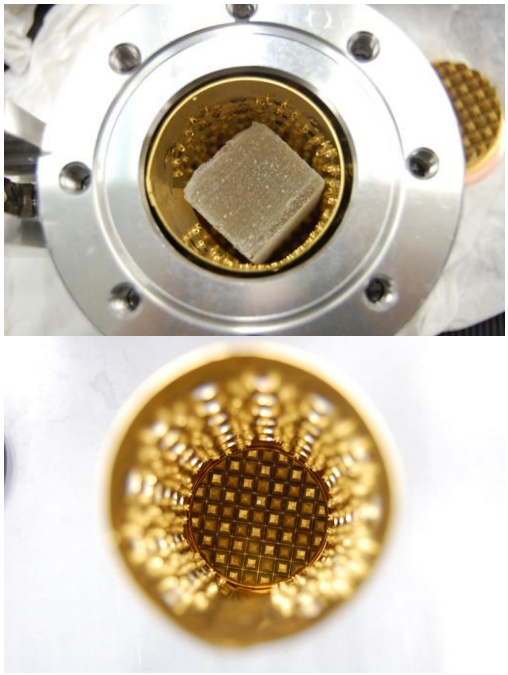

Figure 13: Top: Vessel of the new extraction system with the grater and an ice sample. Bottom: details of the grater.

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Samantha Rush completed a Bachelor in Chemistry at the University of South Carolina in Columbia, South Carolina, USA, in 2022. She is beginning her Chemical Oceanography PhD programme at the University of Connecticut- Avery Point, Connecticut, USA, in the northern hemisphere fall of 2022, which will focus on alkalinity in the Arctic.

Primary production estimates in the US Bering and Arctic Seas through chlorophyll-a fluorescence measurements on 2019 Saildrone missions

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The Arctic Ocean represents one of the most rapidly changing environments on the planet as a result of increasing anthropogenic carbon release (Urban, 2020). Ice in the Arctic plays an essential role in sunlight reflection, global warming mitigation, carbon dioxide (CO_2) glacial containment, weather pattern regulation, and biogeochemical cycling; however, Arctic sea ice volume has decreased by 40% compared to 40 years ago (Urban, 2020). Beyond the mere ice cover decline, sea ice thickness is also decreasing (Van Leeuwe *et al.*, 2018). Declining sea ice raises significant concerns regarding the buffering capacity of water, the global carbon cycle, and biological productivity (Zhang *et al.*, 2022).

Productivity forms the basis of the marine food webs as autotrophs, namely phytoplankton, convert inorganic CO_2 into organic carbon and molecular oxygen. Primary production rates represent oceanic photosynthesis and depend on both, light and nutrient availability (Frey *et al.*, 2017). As such, the Arctic Seas have tended to experience highly productive periods as the ice melts and light increases in the summer months (Frey *et al.*, 2017). However, the unprecedented climate changes marked by increased temperatures, reduced ice, and altered seasonality have changed primary production trends in the Arctic. Typical sea ice algae and under-ice phytoplankton bloom phenomena moreover have the potential to be distorted given substantial sea ice changes (Frey *et al.*, 2017).

Traditional oceanic in-situ measurements to understand the rapidly changing Arctic environment along oceanographic transects have insufficient temporal and spatial resolution to measure in remote, ice-covered areas, especially in conjunction with unpredictable ice sheet movements. By utilising saildrones, a type of uncrewed surface vehicle (USV) powered by wind and solar energy, real-time measurements of oceanic and atmospheric conditions can be made at finer scale (Cokelet *et al.*, 2015). Thus, saildrones provide a modern, technologically feasible way to capture oceanic and atmospheric data in the Arctic (Cokelet *et al.*, 2015).

To better understand the Arctic environmental changes, the National Oceanic and Atmospheric Administration (NOAA) partnered with Saildrone Inc. to deploy six saildrones in the Bering and Chukchi Seas following the 2019 seasonal ice retreat. The goal of this study was to evaluate the spatial and temporal variability of chlorophyll-a biomass and primary production in the Arctic Seas using the saildrone-collected data.

Because the saildrones travelled across different water masses, primary production was estimated from measurements made by a chlorophyll-a fluorescence sensor. Since most oceanic photosynthesis occurs through algae containing the chlorophyll-a pigment, chlorophyll-a serves as an estimate of phytoplankton biomass.

By comparing chlorophyll-a estimates in open water and ice, primary productivity was investigated in three saildrones that encountered sea ice during the mission. Saildrone interactions with ice were confirmed by measurements of reduced salinity near sea ice indicating freshening due to thawing. Evaluations of saildrone events in ice and open water showed no statistical difference in chlorophyll-a measurements indicating the absence of an ice-edge bloom at 1-meter depth near the sea ice (Figure 14). The lacking detection of an ice bloom may reflect no true bloom or be a result of thinning ice, incorrect mission timing, or the bloom occurring below 1-meter in the water column.

The primary productivity estimates for all six saildrones in the mission were then computed using chlorophyll-a concentrations via the original Behrenfeld & Falkowski equation (Behrenfeld *et al.*, 1997) with the Kameda growth term (Kameda *et al.*, 2005). Results indicated that the highest production occurred in spring, with reduced production over summer, and a slight increase in fall (Figure 15). One saildrone consistently reported higher production values, likely spatial in nature due to its location in the Green Belt and Bering Sea, an area known for elevated production due to light and nutrient content provided by mixing (Springer 1996).

Given that the saildrones only collect chlorophyll fluorescence data in the upper 1-meter of the water column, the primary production calculation is representative of only the surface of the water column. Therefore, estimates of primary production from saildrones provide valuable spatial context but do not fully resolve processes occurring throughout the water column. Nonetheless, saildrones do provide unique opportunities for data collection now and in the future, especially in the Arctic Oceans.

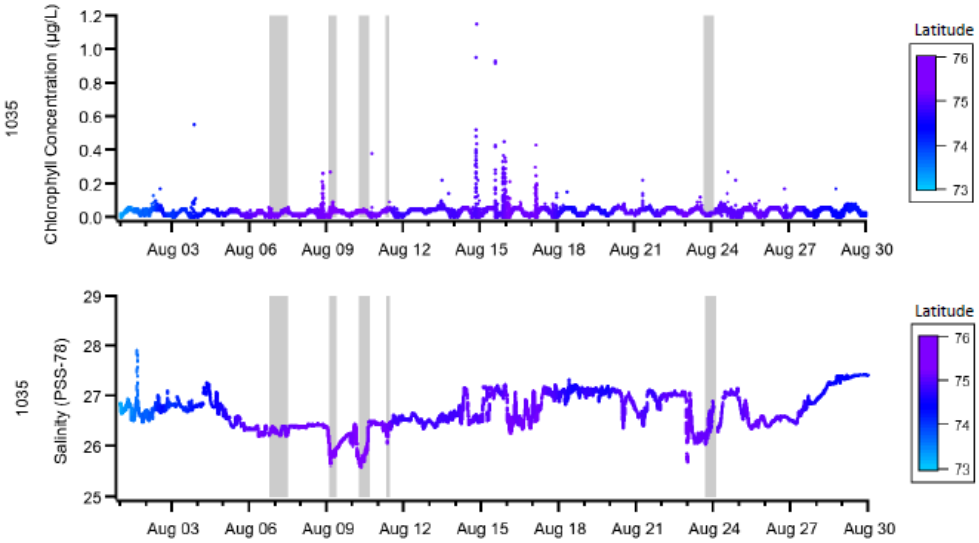

Figure 14: One selected saildrone chlorophyll-a timeseries (top) and salinity timeseries (bottom) coloured by latitude during a time period of both open water and ice conditions. The regions shaded in grey correspond to times when the saildrone was in the ice.

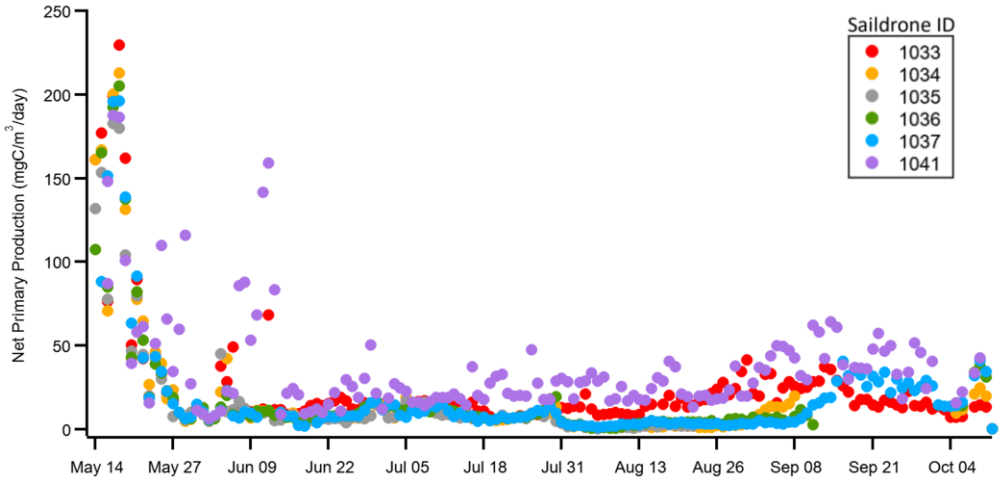

Figure 15: Net primary production estimate from chlorophyll-a observations coloured by saildrone ID over the course of the entire mission.

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Acknowledgements

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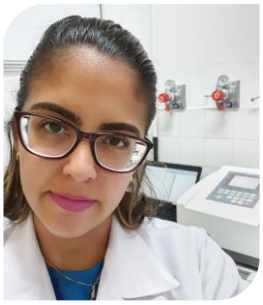

Raisa de Siqueira Alves Chielle is an oceanographer and PhD candidate at the Federal University of Ceará, Brazil, studying the carbon cycle dynamics and origin of organic matter in a large mangrove-dominated delta in Brazil, the Parnaíba River Delta.

Carbon dynamics in the water-atmosphere interface of the Parnaíba Delta, Brazil

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In the context of climate change, many studies focus on knowledge of the global carbon cycle, in order to understand its dynamics in its various reservoirs and to quantify the fluxes between them. The open ocean is one of the most studied carbon reservoirs, given its significant importance in the global carbon cycle as a large anthropogenic carbon sink, responsible for the absorption of about 26% of carbon dioxide (CO_2) emitted by human activities (Friedlingstein *et al.*, 2022). However, coastal systems, such as estuaries, are still often neglected in these studies.

Estuarine ecosystems are important environments in biogeochemical cycles, as they receive a large amount of material from the continent, exchange it with the coastal ocean, and are one of the most active areas in the exchange of materials and energy fluxes (Gattuso *et al.*, 1998). The heterotrophy of most of these environments, together with the entry of pCO_2 enriched river waters, are the main reasons that estuaries are, in general, super saturated in CO_2 in relation to the atmosphere (Abril and Borges, 2004). However, there is large inconsistency and variability in the emissions of CO_2 by these systems, in general, due to the lack of studies in these environments, mainly in tropical and southern hemisphere ones, and due to the great diversity of environments.

The Parnaíba Delta is the largest open sea delta in the Americas, covering an area of 3138 km^2, located on a climatic transitional coast with two marked seasons. The delta is formed by a complex system with more than 70 islands, multiple tidal channels, and fluvial-marine plains, which harbor around 1500 km^2 of mangrove. The establishment of the Environment Protection Area in 1996, and the low population density of the area allow the delta to be an almost pristine environment, with little industrial development, and with ecotourism and agriculture as the main economic activities. Therefore, the delta is a key environment in understanding the carbon cycle in natural environments, and how climate change may influence its dynamics.

In this study, we aimed to detail the seasonal and spatial variability of CO_2 levels and fluxes in the large Parnaíba Delta, to assess the effects of different morphological scenarios under tidal changes and different rainfall levels on the

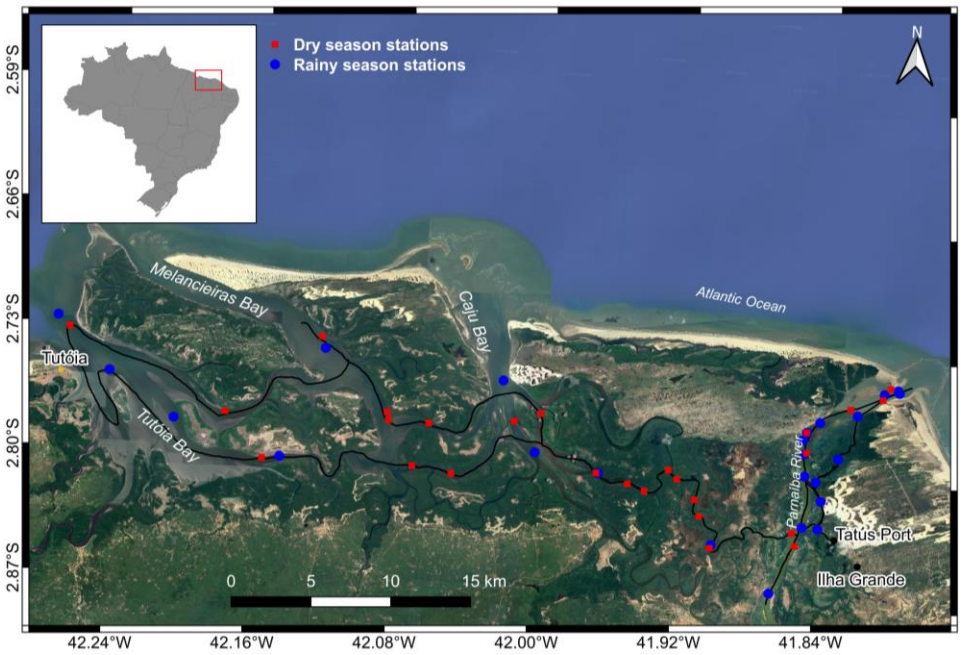

Figure 16: Map of the area sampled, highlighting the sample points (red - dry season; blue – rainy season), and the vessel trajectory along four channels of the Parnaíba delta: Parnaíba River, Caju, Melancieiras, and Tutóia.

biogeochemical carbon cycle. In addition, we aimed to verify the contribution of the different sources of organic matter and their relation to the variability of CO_2 in this environment. For that, major channels and bays of the Parnaíba delta were sampled during dry and wet seasons (Figure 16) for continuous measurements of pCO_2, temperature, salinity, and wind velocity, and also subsurface water samples were collected in discrete stations to analyze pH, total alkalinity (TA), dissolved inorganic carbon (DIC), dissolved oxygen, and chlorophyll-a.

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Maliha Zareen Khan obtained her doctorate degree in geology from China University of Geosciences, China, and started her post-doctorate research at Xiamen University, China, in 2020. Her research project is based on deciphering the role of diatoms and dynamics of biogenic silica in oligotrophic North Pacific subtropical gyre with respect to mesoscale eddies.

Influences of cyclonic eddies on biogenic silica dynamics in the oligotrophic Northwest Pacific subtropical gyre

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Mesoscale eddies play a significant role in the transportation of biogeochemical elements, as well as deliver episodic pulses of deep-layer nutrients to the euphotic zone (McGillicuddy *et al.*, 2003); thus, impacting biological productivity (Benitez-Nelson *et al.*, 2007) and structural composition of phytoplankton community (Wang *et al.*, 2016).

Eddies demonstrate characteristic spatial and temporal changes (Chelton *et al.*, 2011), influencing subsequent particle flux through eddy lifespan resulting from variations in physical mixing (Sweeney *et al.,* 2003). Field observations suggest that significant differences in the magnitude and composition of eddy-induced particle export are dependent on the formation mechanism, sampling relative to eddy age, location of sampling within a mesoscale feature, and appropriate non-eddy references (Benitez-Nelson *et al.*, 2007; McGillicuddy *et al.*, 2007; Zhou *et al.*, 2020). In-situ studies of cyclonic eddies have documented increased primary productivity and biomass in the Sargasso Sea (Sweeney *et al.,* 2003) and in the subtropical Pacific (Benitez-Nelson *et al.*, 2007).

Research suggested that large phytoplankton such as diatoms are more likely to play an important role in the global biological pump; consequently, diatoms related biogenic silica (BSi) play a crucial role in the active interaction between Si and carbon (C) cycles during their production in the upper ocean (Ragueneau *et al.*, 2006). However, little attention has been paid to the response of siliceous phytoplankton in oligotrophic regimes, direct measurements of varying BSi dynamics and export fluxes through the euphotic zone (Ez) in North Pacific Subtropical Gyre (NPSG) with respect to mesoscale processes and its comparison with the ambient surroundings.

In the North Pacific, the Kuroshio Extension and the Subtropical Counter Current (Figure 17A) are two of the most eddy-energetic regions with dynamic interactions between eddies and the time-mean flow (Cheng *et al.*, 2014).The present study was designed to investigate the responses of large phytoplankton related to eddy evolution i.e., diatom bloom to anticipated nutrient injection in a cold-core, cyclonic eddy (CE2) as well as comparing our investigations with the reference station in

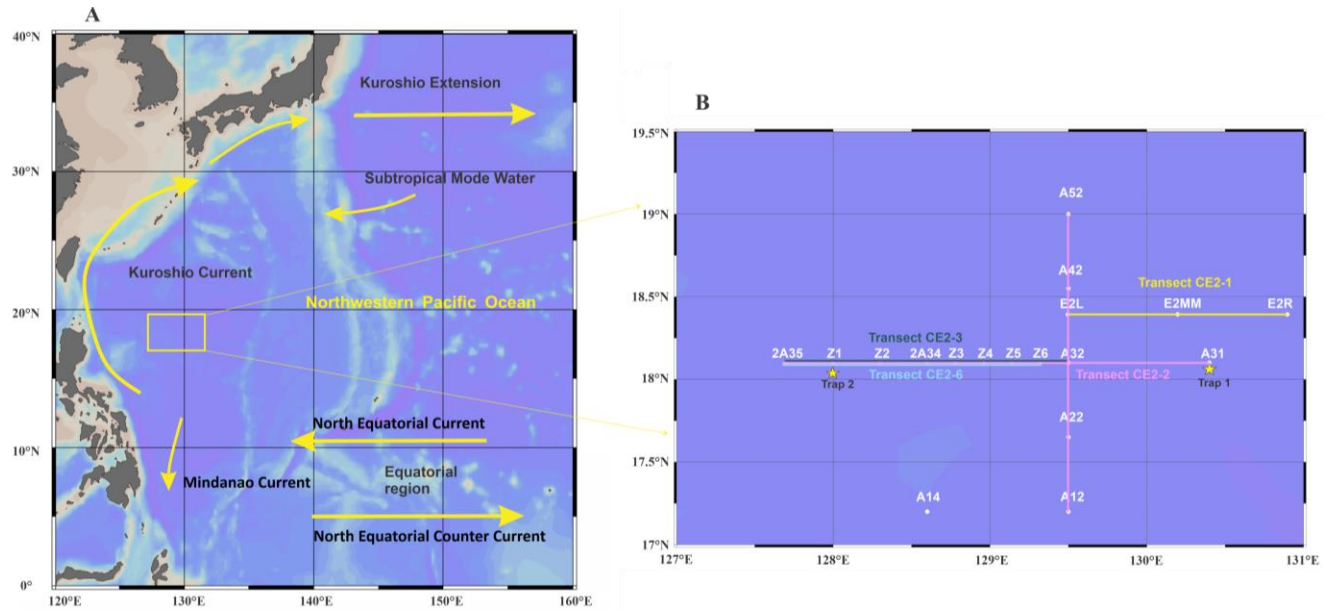

Figure 17: (A) Geographical location of studied area with major ocean circulation patterns in NPSG (Modified after Ujii *et al.*, 2016); (B) Location of the stations and traps inside cyclonic eddy CE2.

ambient water column. To better understand the statistical view of the vertical dynamics of mesoscale scale cyclonic eddies, we analysed bottle samples (continuous measurements for four consecutive weeks CE2-1, CE2-2, CE2-3, and CE2-6) along with two sediment traps in the western NPSG. A month-long intensive hydrographic survey was also conducted (Figure 17B). The results are discussed in relation to potential mechanisms that control the magnitude of large phytoplankton bloom and particle fluxes related to BSi production.

An observable doming of isothermal and isohaline surfaces, indicated the upwelling of deep nutrient-rich water at least in the first weeks of investigation where deep chlorophyll-a maximum (DCM) shoaled from a depth of about 130 m in the outer regions of the eddy to about 90 m in the EC (Figure 18). The average concentration of BSi from

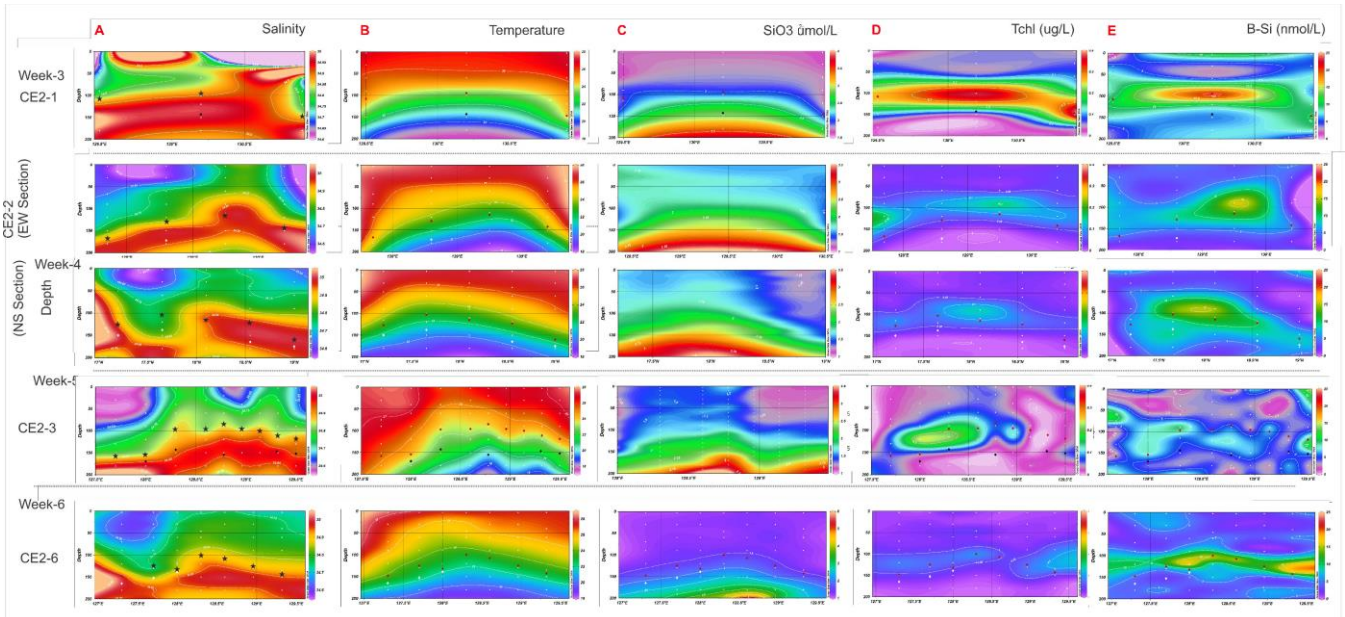

Figure 18: Distributions of (A) Salinity (B) Temperature- °C (C) Silicate- µmol/L (D) TChl a -µg/L (E) Biogenic silica-nmol/L, in CE2-1, CE2-2, CE2-3 and CE2-4 in 3rd, 4th,5th and 6th weeks respectively. Black stars mark the depth of NDL.

surface to 200 m in CE2 was 5.39 ± 3.75 nmol/L (0.49-22.52 nmol/L), generally amplified at DCM (90-150 m). Concentrations and inventories showed substantial spatial variability within the eddy system, but the enhancement of BSi signals was not necessarily reflected in its corresponding fluxes.

Our investigations confirmed that the eddy CE2 is productive and large phytoplankton such as diatoms enhanced significantly. Additionally, during the course of this study, siliceous diatoms contributed more towards the BSi inventory rather than picophytoplankton. New insights related to the influence of mesoscale processes associated with BSi distribution endorses the enhancement of diatoms through complicated dynamics of cyclonic eddies in the oligotrophic ecosystem of NPSG.

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Emma de Jong began her Masters of Science majoring in Environmental Studies in 2021 at Victoria University of Wellington in New Zealand after finishing her Bachelor of Science majoring in Environmental Studies and Psychology. Emma is currently completing her one-year thesis looking at a present-day distribution of organic lipids in snow, seawater, and sediment samples representing primary production and marine microbes.

The unknown future of Ross Sea, Antarctic phytoplankton: A multi-archive biomarker approach to the recent past

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The Ross Sea, in the Southern Ocean, is one of the most productive areas in the world supporting a unique ecosystem and contributing to the oceanic carbon sink (Bolinesi *et al.*, 2020). Our understanding of how phytoplankton in the Ross Sea may respond to future climate change is limited by short observational records. Satellite imagery provides global coverage of continuous chlorophyll-a data over the past 25 years. Yet, this satellite record is too short to understand the drivers of phytoplankton change (Pinkerton *et al.*, 2021). Molecular fossils (lipid biomarkers) of phytoplankton may be able to extend observational records of primary production (Ashley *et al.*, 2021; King *et al.*, 2019). Fatty acids (acidic biomarkers) have been measured in Antarctic sediment cores and have recently been measured in Antarctic ice cores for the first time (King *et al.*, 2019).

The overall aim of this MSc project is to investigate the present-day spatial distributions of phytoplankton biomarkers in the Southwestern Ross Sea to help interpret longer paleoclimate records of phytoplankton. Trends in the concentration of phytoplankton biomarkers will be compared across different environmental archives: sediment, snow, and seawater samples (refer to Figure 19 for locations of samples).

Biomarkers are extracted using ultrasonic extraction with solvents, resulting in a total lipid extract. The total lipid extract is then saponified, which allows the neutral compounds to be separated from the fatty acids. The fatty acids are derivatised into methyl ester groups to make interpretation easier and the neutral compounds are separated over silica columns into apolar and polar fractions. Samples are then measured via gas chromatography-mass spectrometry. The concentration of peaks is interpreted using total ion current and concentration is calculated relative to an internal standard.

Preliminary results of snow on sea ice samples from around McMurdo Sound demonstrate the presence of multiple compounds, notably C16:0, and C18:0, which are algae and bacteria biomarkers (Figure 19). Figure 20 shows that compounds are present in similar concentrations across the sea ice in front of McMurdo Sound, demonstrating samples are undergoing similar

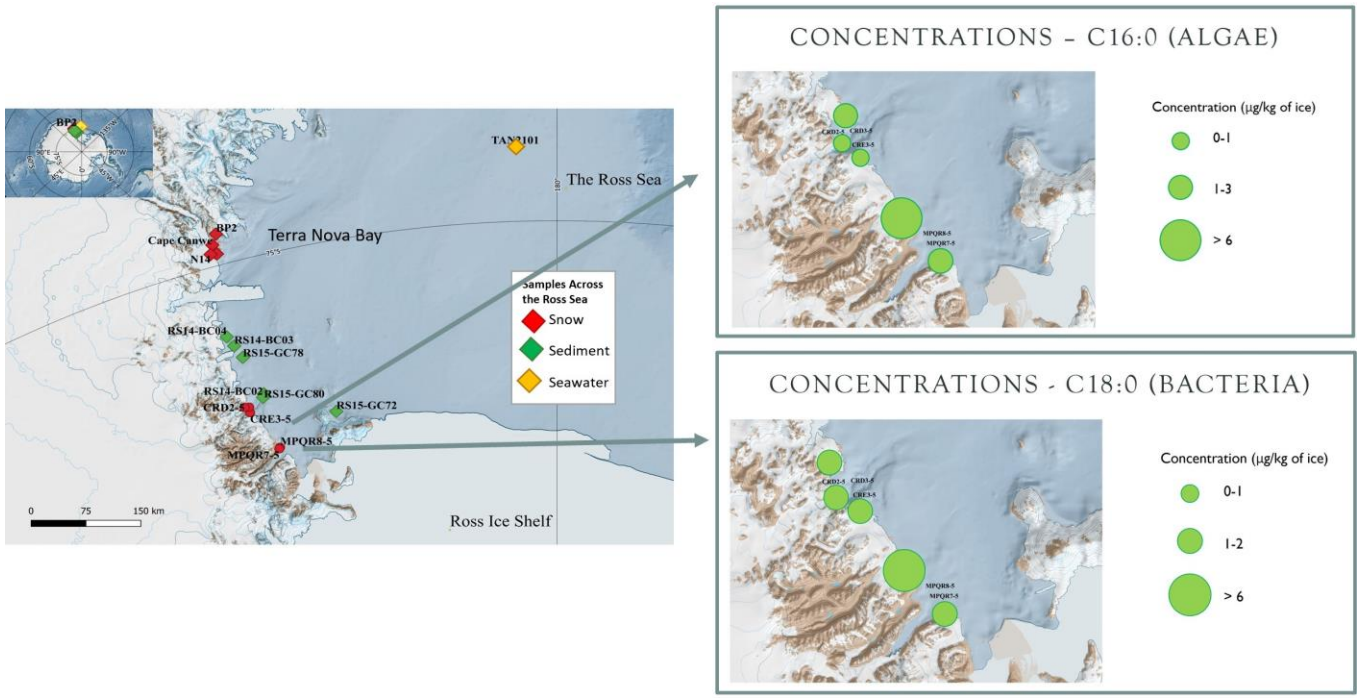

Figure 19: Left: map of the Southwestern Ross Sea with an inlay of Antarctica. Location of samples are indicated using squares (still to measure) and circles (already measured). Right: zoomed in map of the Southwestern Ross Sea with concentrations of fatty acid compounds represented by green circles. Base map from Quantarctica GIS package, Norwegian Polar Institute.

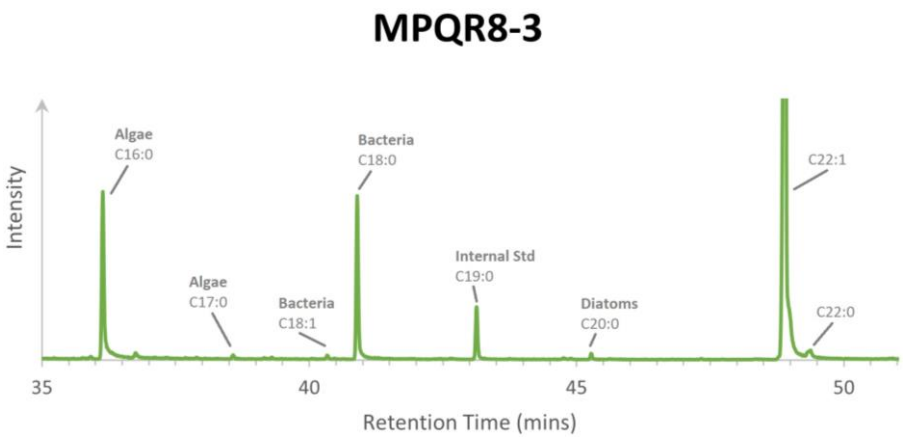

Figure 20: Fatty acids present in a snow sample.

depositional processes. The sample MPQR8-5 has concentrations over four times higher than other samples in the area, potentially caused by the abundance of dust in this sample that lipids could attach to.

The preliminary results demonstrate the presence of fatty acids in snow samples from the Ross Sea for the first time, providing an exciting opportunity to compare with sediment samples from underneath the sea ice. Sediment samples and seawater samples from the Ross Sea have been collated and the results from these archives will be able to better inform us about how biogenic emissions are incorporated into ice cores.

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Charles Izuma Addey is studying Marine Geology and Geochemistry at the University of Hawai'i at Mānoa, USA. His doctorate research focuses on air-sea carbon and oxygen uptake in the Kuroshio Extension region. Charles holds a B.Tech in Marine Science from FUTA, Nigeria, and an M.Sc in Marine Chemistry from Zhejiang University, China.

Regional wind variability modulates carbon sink in the northwest Pacific Ocean

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About 30% of the world's carbon dioxide (CO_2) emissions are absorbed by the oceans, making them a significant sink for CO_2 (Gruber *et al.*, 2009). The northwest Pacific Ocean is the major CO_2 uptake area in the Pacific Ocean (Bushinsky and Emerson, 2018). The change in sea surface temperature (SST) has a profound influence on the seasonal variation in pCO_2 and CO_2 flux. The thermodynamics relationship of seawater pCO_2 has shown it to be higher in the summer and lower in the winter (Takahashi et al., 2009). However, during the winter, intense vertical mixing in the subarctic region raises the pCO_2 concentration by bringing subsurface water with a high dissolved inorganic carbon (DIC) content to the surface (Jiang *et al.*, 2013).The spatial variability between the subtropics and subarctic regions of the northwest Pacific Ocean necessitates a deep understanding of the controlling mechanism, as the regional variability might be attributed to physical, chemical, and biological processes that vary seasonally and can drive a region to shift from a sink to a source over time (Takahashi *et al.*, 2009).

In the study conducted, the study area was divided into three sub-regions based on latitudinal differences due to the unique SST - pCO_2 relationship that cut across the subarctic to the subtropical region (Figure 21): subtropics = 25-40°N, transition = 40-45°N, and subarctic = 45-55°N. In the

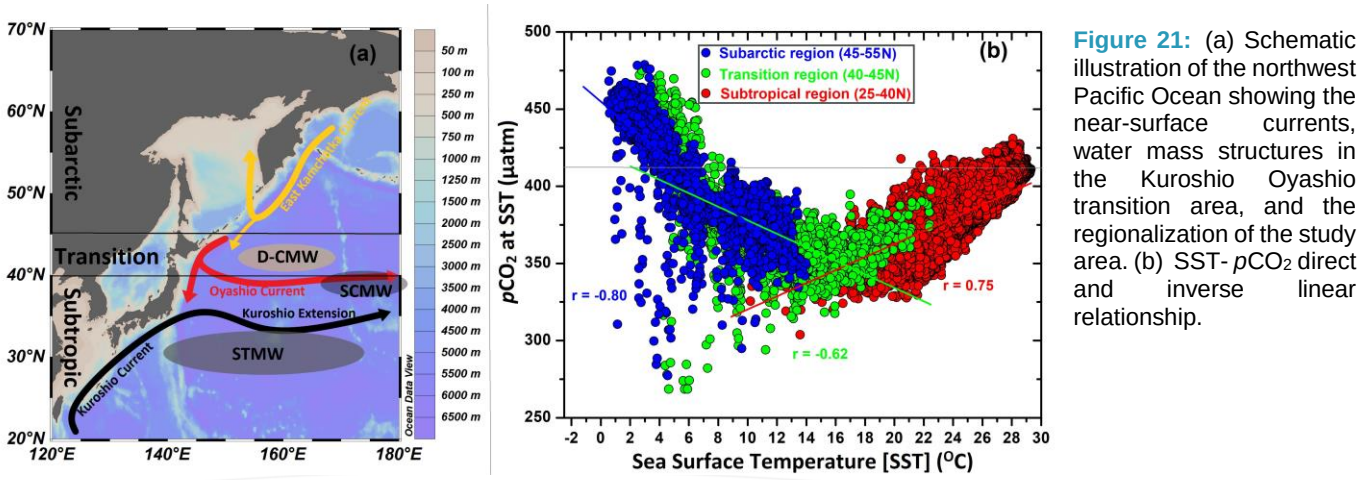

Figure 21: (a) Schematic illustration of the northwest Pacific Ocean showing the near-surface currents, water mass structures in the Kuroshio Oyashio transition area, and the regionalization of the study area. (b) SST- pCO_2 direct and inverse linear relationship.

subtropics, the temperature changes dominate seasonal pCO_2 variability (strong positive correlation), making the region a sink for atmospheric CO_2 in winter and a weak source of CO_2 to the atmosphere in summer (Figure 21b). Seasonal pCO_2 variability in the transition and subarctic zones showed a substantial negative connection with SST (Figure 21b). The subarctic region saw winter-spring pCO_2 peak due to subsurface water entrainment and summer-autumn minima due to biological drawdown.

Sea surface temperature, vertical and lateral mixing, and biological activity played key roles in surface seawater pCO_2 variability. Regional wind variability had a considerable influence on the carbon sink, making it stronger as the wind speed increased (Figure 22; correlation coefficient; r > -0.75). This result demonstrates the global relevance of the northwest Pacific Ocean as a hotspot for ocean carbon uptake and thus advances our understanding of the governing processes there.
My future research project in the area aims to overcome the spatial and temporal constraints of

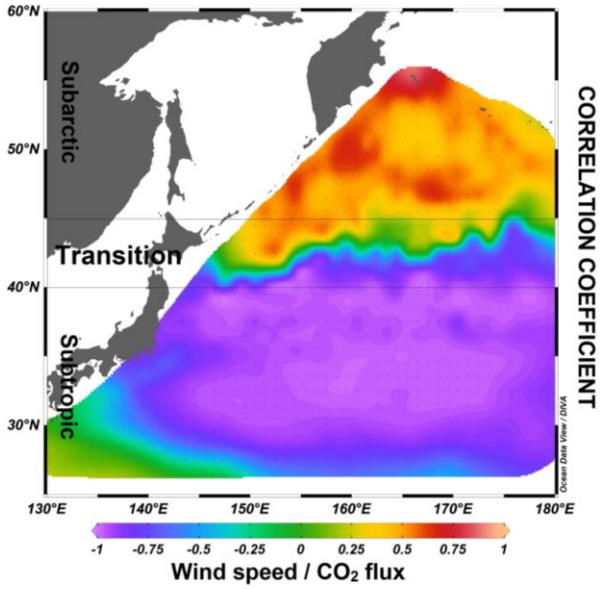

Figure 22: Net annual CO_2 flux versus wind speed and their correlation coefficient.

ship observations by utilising BioGeoChemical Argo float data to unravel the physical and biological controls on air-sea carbon and oxygen uptake (Addey, 2022) in the mode-water formation region. In general, the findings of the study will have a significant impact on the scientific community by addressing present knowledge gaps concerning air-sea carbon and oxygen exchange in response to climate change throughout the Kuroshio extension region.

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Mahendar Chand Rajwar works as a research scholar in the atmospheric science division of the Aryabhatta Research Institute of Observational Science (ARIES), Nainital, India. Mahendar's PhD research is mainly focused on assessing the role of Non-methane hydrocarbons (NMHCs) in tropospheric ozone chemistry in various environments, including central Himalayan sites and the Indo Gangetic Plain region. The work involves air-sample collection and their analysis using gas chromatography (for NMHCs). Apart from this, Mahendar also interested in box modelling and satellite data utilization.

Studies of Non-Methane Hydrocarbons (NMHCs) in the Ambient Air Over the Central Himalayan and Associated Regions

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Non-methane hydrocarbons (NMHCs) are important precursors of tropospheric ozone and secondary organic aerosols (SOAs). The air quality in South Asia is rapidly deteriorating due to increasing pollution levels, and transporting these pollutants to pristine regions in the Himalayas also exacerbates the problem. Despite this, air quality studies are very limited in South Asia, particularly in remote Himalayan regions. This study presents first time, a comprehensive analysis of light NMHCs (C2-C5) at the central Himalayas mountain site (Nainital; 29.37°N, 79.45°E, 1958 m, above mean sea level) and an Indo Gangetic Plain (IGP) site (Haldwani; 29.22°N 79.51°E, 554 m, above mean sea level). Observations were made from January 2017 to December 2020 using a Thermal Desorption Gas Chromatograph equipped with Flame Ionization Detectors (TD-GC-FID).

The continuous online observations showed diurnal variation in light-NMHCs with higher values in the daytime throughout the year except for the summer/monsoon months. The mixing levels of alkanes, alkenes and alkynes vary from the lowest level of 1.96 ± 0.77 ppbv, 0.29 ± 0.06 ppbv, and 0.22 ± 0.20 ppbv respectively, to the highest levels of 4.43±0.84 ppbv, 1.03 ± 0.39 ppbv, and 0.75 ± 0.40ppbv in November, respectively (Figure 23). However, an IGP site showed much higher levels at nighttime than in the daytime, where alkanes, alkenes and alkyne showed 19.24 ± 0.24 ppbv, 2.88 ± 1.76 ppbv, 1.41 ± 1.21 ppbv levels during winter and 13.41±9.33 ppbv,1.88 ± 1.65 ppbv, 0.67 ± 0.59 ppbv. Among eight light-NMHCs, the observed levels of ethane, ethylene, propane, n-butane and acetylene were highest during winter and spring and minimum in summer/monsoon at both sites. Ethane is most dominant at the Himalayan site, while propane is at the IGP site.

The investigation of the natural logarithmic ratio between two different pairs (ln([n-butane] / [ethane]) to ln([i-butane] / [ethane]) and ln([Propane]/[ethane]) to ln([n-butane]/[ethane]) suggested the role of oxidation of OH mechanism for light-NMHCs removal in the atmosphere at

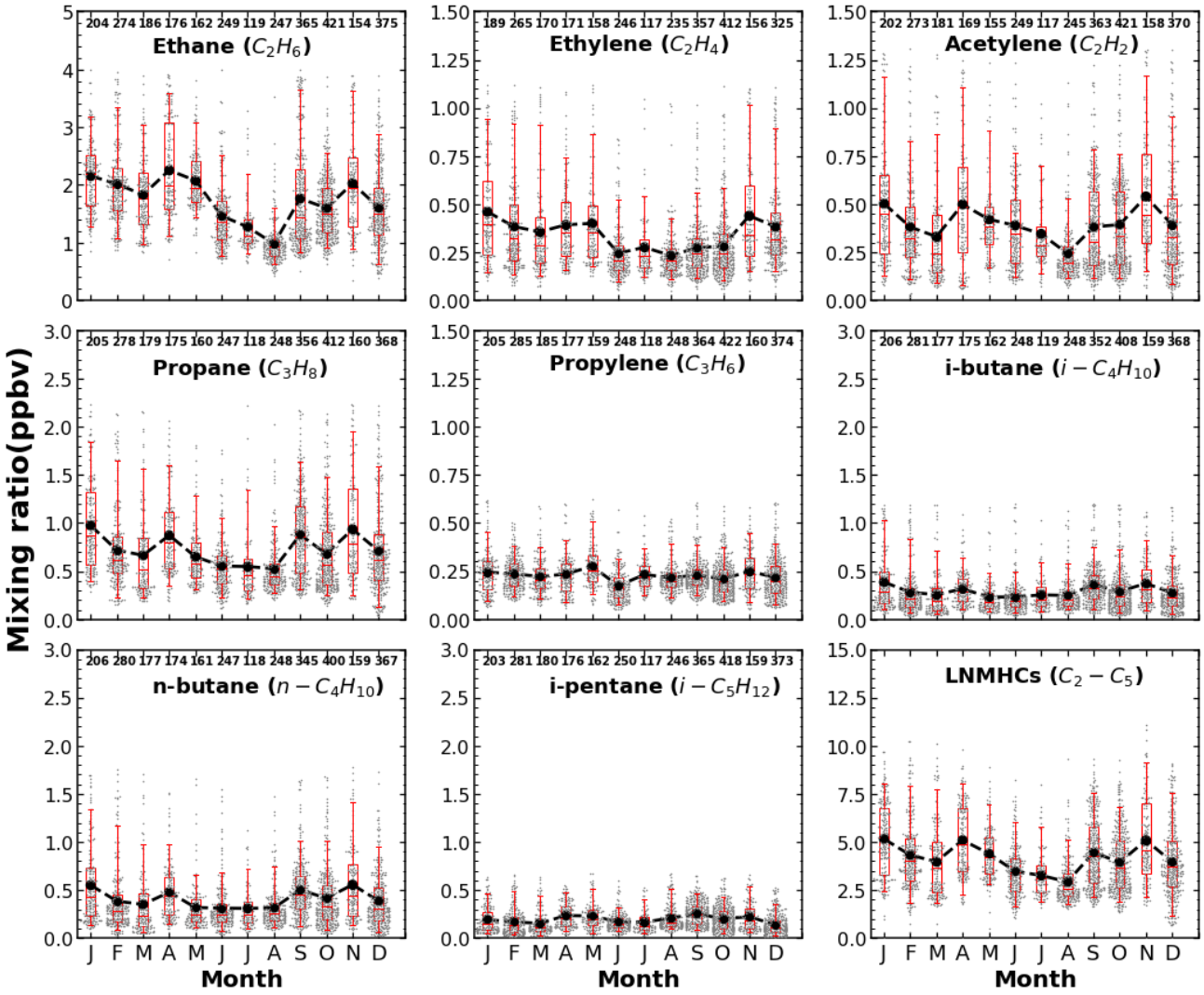

Figure 23: The box plots represent the monthly variation in observed light- Non-methane hydrocarbons (NMHCs, C2-C5) mixing ratios for January 2017 to December 2020 at a mountain site in the Central Himalayas. The swarm plots complement the box plots and show the distribution of mixing ratios of observed light-NMHCs. In box plots, the upper and lower edges of the boxes represent the third quartile (75th percentile) and first quartile (25th percentile), respectively. The whiskers below and above are the minimum (10th percentiles) and maximum (90th percentiles), and the outliers in the box plot indicate the 5th and 95th percentiles. The black circle and the solid horizontal line inside the box represent the monthly mean and the median of the observed data, respectively.

both the sites and globally compared results showed a heterogeneous nature of these light NMHCs in the atmosphere. There is a strong inter-correlation among ethane, i-butane, propane, and n-butane acetylene, which supports the influence of natural gas, LPG leakage and biomass burning. Additionally, a good correlation of combustion tracer carbon monoxide (CO) with ethane, propane, and acetylene reconfirmed that biomass burning is the source of these light-NMHCs at the central Himalayas site, especially during spring. The OH reactivity, ozone formation potential (OFP) and secondary organic aerosol potential (SOAP) is also studied. The OH-reactivity is minimal at a mountain site compared to an IGP site. Propylene (25%-30) and ethylene (10-25%) strongly contributed to OH-reactivity. Both sites have maximum OFP during the winter and a minimum. The OFP during the summer/monsoon for all the seasons. Propylene (23%-35%) and ethylene (18-22%) are species dominated by OFP throughout the year at both sites. SOAP showed wintertime maxima and springtime minima with the dominance of propylene (35%-45%) and i-

butane (15%-38%) at the Himalayan site, whereas propylene (25-40%) and n-butane (20-35%) dominance at the IGP site. Further, these datasets can be used to develop emission inventories and validate various chemical transport models.

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