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Analysing the controls over DOM quality in two contrasting subpolar marine environments

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Analys av variabler som styr över DOM-kvaliteten i två kontrasterande subpolära marina miljöer

Bachelor degree thesis, 15 credits in *Physical Geography and Ecosystem Science*

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Bachelor thesis, 15 credits, in *Physical Geography and Ecosystem Science*

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Abstract

In this study, Dissolved Organic Matter (DOM) quality was analysed through its optical properties. Samples from the estuarine waters of the Beagle Channel and oceanic ones of the Burdwood Bank were examined in order to understand how DOM quality was changing. The focus of the study was to determine whether the environmental variables or the microbial community were the main driver in DOM composition in the two study areas. The DOM composition was different between the two locations. The majority of DOM in the ocean was composed of protein-like, autochthonous material microbially produced while the contribution from the humic-like peaks was very low. A different pattern was observed in the Beagle Channel, where the contribution from the different peaks seemed to be more equally distributed with significant amounts of humic material of terrestrial origin and high amounts of protein material as well. The organic matter in the Beagle Channel was characterised by higher amounts of chromophoric DOM, high molecular weight material and more recalcitrant DOM while in the Burdwood Bank, DOM was more labile and bioavailable. Statistical analysis showed that both the physical conditions of the water column as well as the composition of the microbial community were influencing the quality of DOM. The variable importance in projection (VIP) scores revealed that in the Burdwood Bank the microbial community had greater influence on the DOM composition while the environmental variables were the main driver in the Beagle Channel. This study allowed the characterisation of DOM in these two environments and gave better understanding of the different controls.

Keywords: DOM optical properties; Absorbance; Fluorescence, EEMs; Burdwood Bank; Beagle Channel

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Abbreviations

BC: Beagle Channel

BP: Before Present

BIX: Biological index

CDOM: Chromophoric or coloured DOM

BCP: Biological Carbon Pump

DOC: Dissolved Organic Carbon

DOM: Dissolved Organic Matter

EEM: Excitation-Emission matrix

EEMs: Excitation-Emission matrixes

FDOM: Fluorescent DOM

LNA: Low nucleic acid content bacteria

HNA: High nucleic acid content bacteria

MCP: Microbial Carbon Pump

ML: Microbial Loop

NMPA: Namuncurà Marine Protected Area

PCA: Principal Component Analysis

PLSR: Partial Least Squared Regression

VIP: Variable Importance in Projection

1. Introduction

Dissolved organic matter (DOM) contains many different classes of compounds, some of which are based on carbon, i.e. Dissolved Organic Carbon (DOC) (Hansell 2001). In marine environments, DOM is the largest reservoir of reduced carbon (Hansell et al. 2009), and plays a key role in these ecosystems and in the global carbon cycle (Osburn and Bianchi 2016).

Both coastal and riverine inputs, as well as surface primary production, act as contributors to the marine DOM pool. The DOM in marine environments is produced either within the system (autochthonous) or outside the system (allochthonous). Autochthonous organic matter is usually fixed by phytoplankton, and then processed by plankton and various organisms in the food web. Allochthonous material is formed outside the system, and it is usually terrestrial material transported to coastal waters (Stedmon and Nelson 2015). Once in water, DOM undergoes biotic and abiotic transformation and degradation, altering its chemical structure and determining its fate in the water (Bauer and Bianchi 2011). Photodegradation and microbial activity are considered the two most important processes involved in both modification and removal of DOM from marine environments (Miller and Moran 1997). DOM, depending on its chemical properties, can be used and transformed in the water column by the microbial community or can accumulate and sink into the deep ocean, in this way acting as a carbon sink (Carlson and Hansell 2015).

The optical properties of DOM reflect the different chemical composition of allochthonous and autochthonous material. The fraction of light absorbing DOM, called chromophoric or coloured DOM (CDOM) and the DOM component emitting light as fluorescence (FDOM), can be used to study the optical properties (Hansen et al. 2016). Knowledge of the chemical properties through spectroscopic analysis can be used to determine the source and the type of DOM (Coble 1996, 2007). It is important to understand the source of DOM as well as the mechanisms of transformation to gain a better knowledge on the fate of organic matter in specific marine ecosystems.

Coastal or estuarine waters receive high amounts of allochthonous DOM (McKnight et al. 2001). The Beagle Channel in Tierra del Fuego (Southern Argentina) is an interoceanic passage connecting the Pacific Ocean to the Atlantic. The channel receives high contribution of freshwater from the surrounding rivers and glaciers (Hernando et al. 2012). In estuarine or coastal waters as in the Beagle Channel, high concentrations of CDOM can have important ecological impacts. CDOM can control the amount of light penetration in the water and can influence water colour. Furthermore, as suggested by Arrigo and Brown (1996), as CDOM absorbs light at the same wavebands as chlorophyll, high amounts of CDOM can limit light availability to photosynthesis and in this way can potentially lead to hypoxia (D'Sa and Dimarco 2009). Despite the negative effects of high concentrations of CDOM in waters, as also stated by Arrigo and Brown (1996), this part of the DOM pool can also absorb potentially harmful UVB and UVA, in this way protecting the planktonic community from potential damages. Moreover, allochthonous sources of organic carbon from river inputs might constitute an important fraction of organic carbon supply for bacteria in estuarine and coastal systems. River-borne DOC, although accounting for only 0.03% of the global

marine DOC pool (Cauwet 2002), is rapidly remineralised once in seawater (Hedges 2002) and seems to sustain high prokaryotic activity in coastal systems (Hopkinson and Vallino 1995). Glacial runoff is a quantitatively important source of bioavailable DOM to subpolar marine ecosystems (Hood et al. 2009). In the context of climatically driven changes in glacier volume, this has important implications for the quality of DOM entering coastal oceans at high latitudes, such as the Beagle Channel.

On the other hand, the Burdwood Bank, located in the Southern Ocean 200 km south of the Falkland Islands (Baldoni and Benavides 1999), is a submarine plateau and represents a purely oceanic environment. Its subpolar waters experience high seasonality, do not receive high contribution of allochthonous material and the DOM pool is mainly autochthonous. Data from these two contrasting ecosystems would allow an improved understanding about what the drivers of DOM transformation are.

There are very few studies regarding the transformations of DOM in these specific geographical areas. Subpolar environments are very sensitive to global warming and climate change, and the Southern Ocean plays a fundamental role in the global climate (Swart at al. 2018). In this context, it is necessary to gain better understanding of the dynamics controlling the fate of carbon in the water, and the controls on transformation and exportation of DOM.

An analysis of the composition and distribution of DOM through its optical properties was carried out, and their relationship with the different environmental parameters and microbial abundances in two contrasting subpolar environments was evaluated. Understanding the main drivers of DOM concentration and composition in oceanic and coastal environment was the main focus of this study. Part of the aim was also to compare the two sites and understand how DOM quality, source and bioavailability changed between an oceanic and coastal environment. The hypothesis was that the main drivers of DOM concentration and composition along the Beagle Channel were the environmental parameters, while the bacterio- and phytoplankton community were the main driver in the oceanic waters of Burdwood Bank.

Two dataset including data describing the environmental conditions, microbial abundances and DOM optical properties were used to test the hypothesis. Samples for both datasets were collected during austral spring. A first dataset from November 2018 included samples from the Burdwood Bank, and a second from November 2019 consisted of samples from the Beagle Channel.

2. Background

2.1 DOM role in marine ecosystems and carbon cycle

DOM is added to marine ecosystems by the atmosphere, terrestrial input coming mainly from rivers and by microbial activity (Bauer and Bianchi 2011). Once in seawater, DOM undergoes three main processes: respiration by marine microbes, oxidation via photodegradation, or burial in sediments (Repeta 2015).

The resistance of DOM to degradation is used to classify it into labile, semi-labile and recalcitrant (Hansell et al. 2009). DOM's role in the carbon cycle depends on its bioavailability and thus its resistance. Labile DOM is the most reactive DOM and is produced and consumed by microbes (Repeta 2015). Photochemical degradation also produces labile DOM which is consumed by microbes and connected to higher trophic levels and then converted to CO_2 and nutrients through the so-called Microbial Loop (Azam et al. 1991).

Semi-labile DOM is defined as organic matter with a long cycling time from months to decades (Repeta 2015). Semi-labile DOM is produced by marine algae, bacteria, zooplankton sloppy feeding and viral lysis (Jiao et al. 2010). Due to its cycling time, too long to be detected in experiments and too short to be analysed by radiocarbon measurements, understanding the sources and dynamics of semi-labile DOM is complicated (Repeta 2015).

Refractory DOM does not degrade and remains in the water column for thousands of years. This DOM thus constitutes a carbon sink in the sea defined by the Microbial Carbon Pump (Jiao et al. 2010), where microbes and their viruses play a fundamental role in the production of refractory organic matter (Weinbauer et al. 2011).

2.2 DOM optical properties

The optical properties of both chromophoric and fluorescent (CDOM and FDOM respectively) can be considered "signals" used as indices of quantitative and qualitative changes in DOM composition (Stedmon and Nelson 2015). All the production, removal or transformation processes characterise the signal of DOM (Hansell 2001). The optical properties are studied through its absorbance and fluorescence. A different DOM composition is reflected by a distinct Excitation-Emission matrix (EEM) and absorption curve, and as shown in Figure 1 and 2, depending on the location or depth of the samples, the absorption curves are different as well as the EEM.

The absorption curves give information about CDOM concentration. Specific absorption coefficients, slopes for wavelength range and ratio of slope values are considered to be correlated to the molecular weight and photochemical degradation of DOM (Helms et al. 2008). On the other hand, FDOM fluorescence usually occurs at excitation wavelengths of 245-500 nm and emissions of 300-600 nm (Stedmon and Nelson 2015). Excitation-Emission matrixes, known as EEMs, are plots used to show the fluorescence properties of FDOM. EEMs, according to Coble (2007), are

characterized by two main groups of signals corresponding to specific wavelength regions: protein-like and humic-like signals. Depending on the type of material, the distribution and intensity of those signals in the EEM will change. In section 3.4 below some spectroscopic indices are summarized.

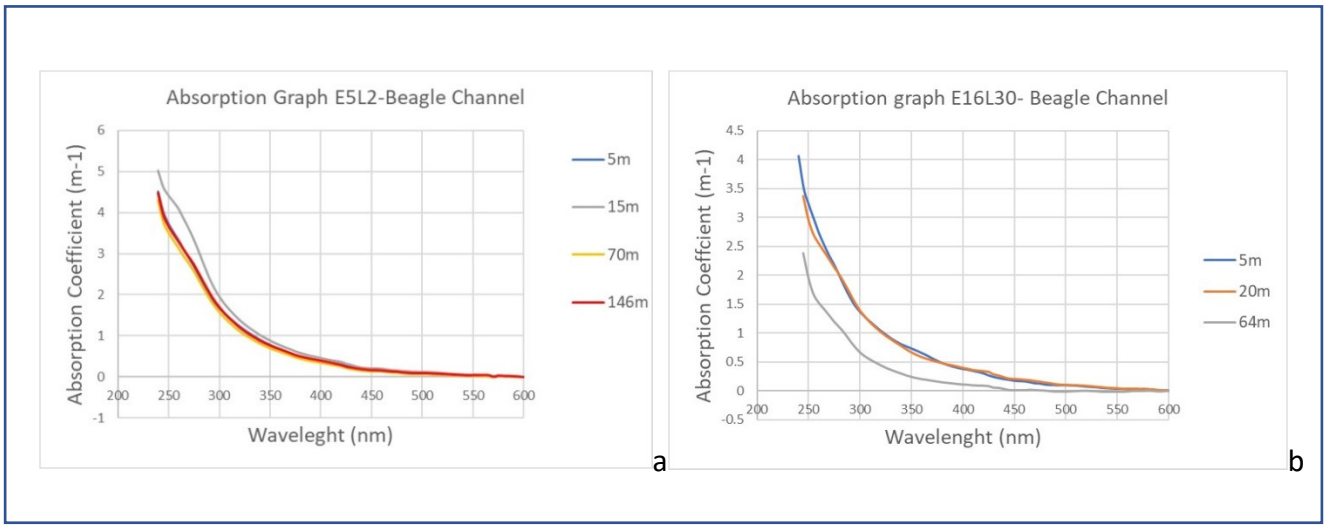

Figure 1: Absorption graphs for two samples in the Beagle Channel from the studied dataset. The plot to the right (E16L30) shows the absorption curves for samples at three depths from the area closer to the ocean of the Beagle Channel. On the left (E5L2), a sample from the waters close the city of Ushuaia is plotted.

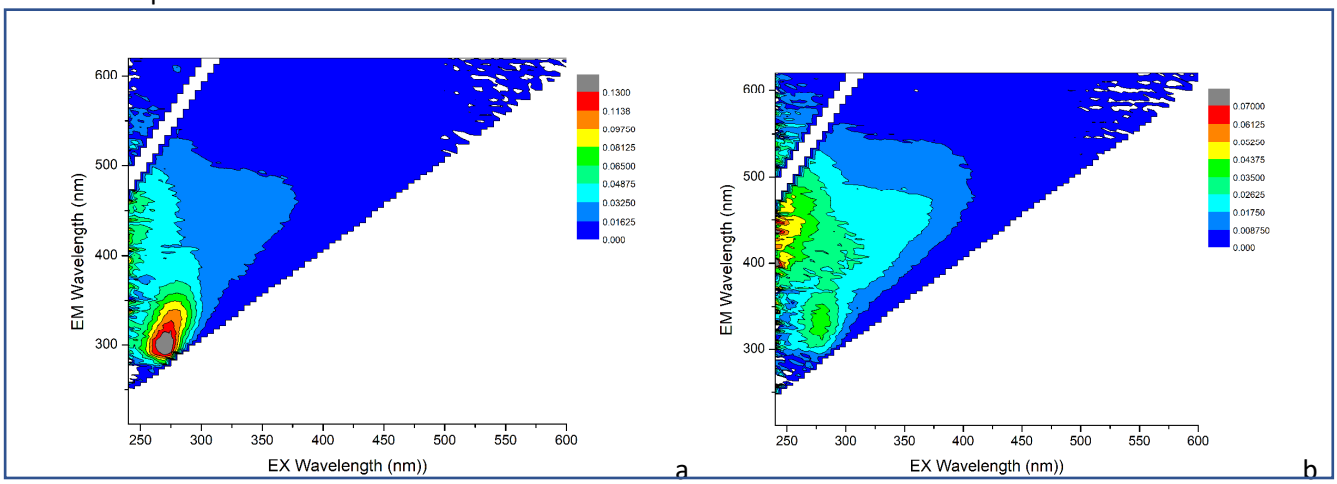

Figure 2: Excitation Emission Matrix (EEM) graphs of the dissolved organic matter fluorescence in two different samples from the studied dataset. On the left a sample from the Beagle Channel is shown and on the right a sample from the Burdwood Bank. The intensities, represented by the color gradient, are measured in Raman Units.

2.3 Microbial Carbon Pump, Microbial Loop and Biological Carbon Pump

The Microbial Carbon Pump (MCP), the Microbial Loop(ML) and the Biological Carbon Pump (BCP), play key roles in recycling, producing and transforming DOM in marine environments (Archer 2003; Jiao and Zheng 2011; McLachlan and Defeo 2018).

The ML in the ocean describes the link between the DOM and the classical grazing food chain through organisms at the very bottom of the food web (Azam et al. 1983). Dissolved Organic Carbon (DOC), introduced into the sea from exudation of photosyntetically fixed carbon, viral lysis at different trophic levels or the breakdown of allochtonous organic particles, is consumed by heterotophic bateria which themselves are consumed by protozoa. The ML is an important mechanism for carbon and nutrient cycling in the ocean and for the productvity of marine ecosystems (McLachlan and Defeo 2018).

The BCP is the most known mechanism of carbon sequestration in the ocean.The BCP is based on fixation of dissolved CO_2 by phytoplankton and its consequent transformation into organic carbon. Then, through sinking of organic particles or active transportation by zooplankton out of the mixed water column, carbon is exported from the atmosphere to the deep ocean (Zhang et al. 2018). The dissolved portion of organic carbon produced by phytoplankton can be remineralized by bacteria through the microbial loop and in this way it becomes available to organisms of higher trophic levels and can potentially be respired back to CO_2, or eventually sink into the deep ocean (Archer 2003). According to Legendre et al. (2015), between 0.6 and 1.3% of the annual primary production results in carbon exportation to the deep ocean through the BCP.

The MCP consists of a series of microbial activities transforming organic matter from labile into recalcitrant, thus not available for biodegradation (Jiao et al. 2010). The MCP acts as a carbon sequestration mechanicsm through biochemical transformation of the organic matter independently of depth. BCP on the contrary sequesters carbon by transferring it to the deep ocean (Legendre et al. 2015). As suggested by Jardillier at al. (2010), while BCP prevails in environments where the favourable conditions support large phytoplankton, the MCP is domianant in oligothrophic waters dominated by smaller phytoplankton species.

3. Methodology

3.1 Study areas

The two study areas analysed for this project were the interoceanic passage Beagle Channel (BC) and the Namuncurà Marine Protected Area (NMPA) at Burdwood Bank. Both areas are situated at the southern tip of South America, and politically belong to Argentina. Both sites are located at approximately latitude 55° S and stretch from longitude 68° to 58° W.

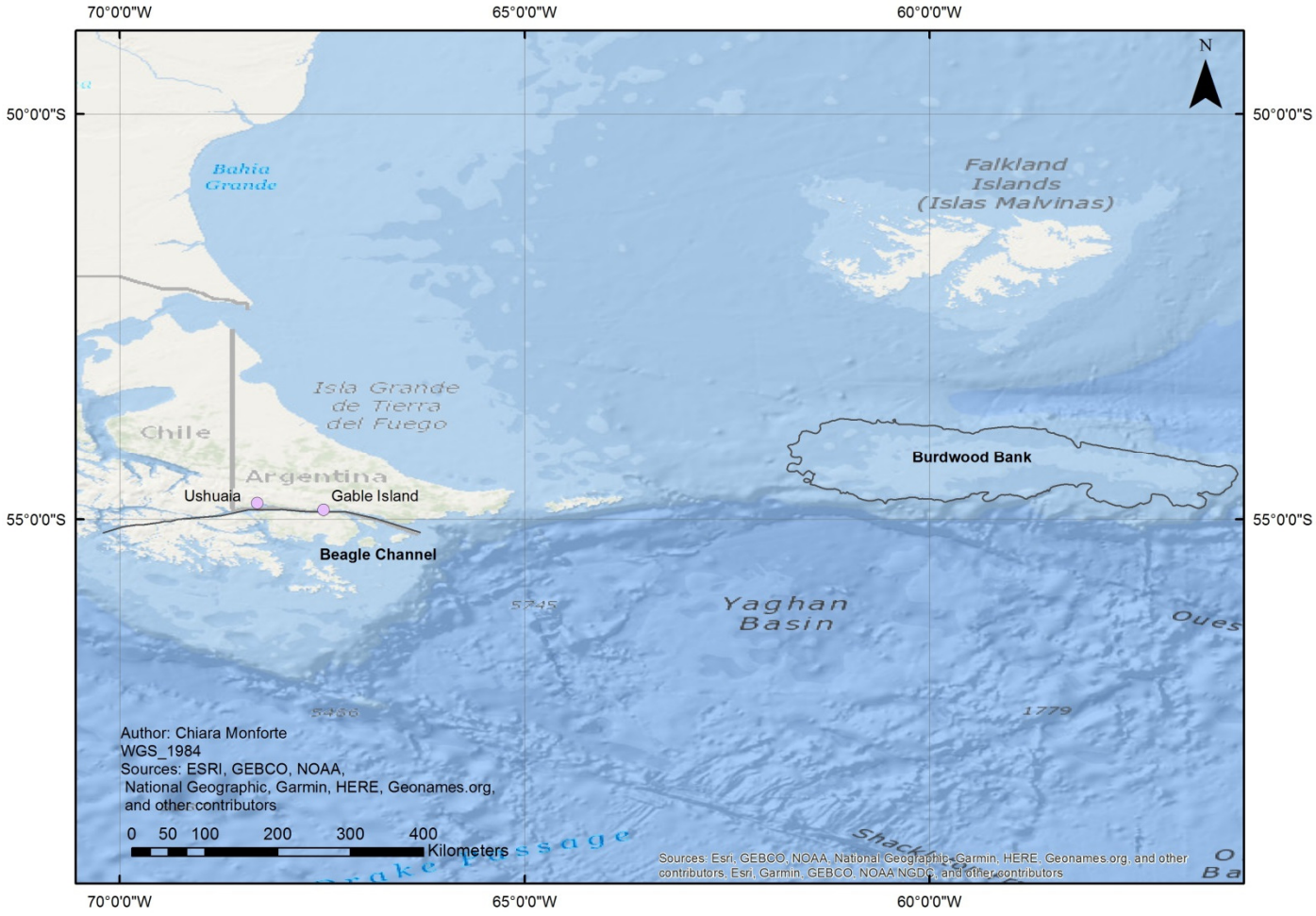

Figure 3: Map showing the location of the two study areas. The Beagle Channel is on the left side, delineated by the black line. The location of Gable Island and the city of Ushuaia is also shown. On the right side, shaped by the 200m isobath, the Burdwood Bank is plotted.

3.1.1 The Beagle Channel

The Beagle Channel is an interoceanic passage connecting the Pacific and Atlantic Ocean with a mean eastward circulation along the main channel. Located in the archipelago of Tierra del Fuego, this strait is roughly 180 km west-east long and between 4 and 13 km wide, depending on the location (Bujalesky 2007). The channel is a tectonic valley and during the Last Glaciation Period it

was completely covered by ice, while around 8000 years BP the channel experienced flooding and was thus transformed into a marine environment (Isla 1999). The tectonic and glacial past of Tierra del Fuego has imprinted a complex morphology and irregular bathymetry in the Beagle Channel that consists of of relatively deep (200-300m) basins alternated by shallow banks and islands. In fact, the openings of the Beagle Channel to the Pacific and Atlantic oceans are constrained by narrow sills as shallow as 15-40m depth (Bujalesky 2011). This situation imposes barriers to the free flow of the deeper waters inside the channel and hence likely limits the ventilation of deeper waters.

The channel divides the main island of Tierra del Fuego from smaller islands belonging to Chile located south. The western part of the channel entirely belongs to Chile. The rest of the strait is divided between Chile and Argentina in half, the north side is Argentinian, and the south is Chilean as show from Figure 3.

Considering the hydrological dynamics of the channel, it can be defined as an estuarine-like environment. It receives great contribution from the surrounding rivers and glaciers (Isla 1999) and tends to retain water due to the particular topographic situation. The eastern side of the channel can be divided by the narrowing of Gable Island where the channel is only about 4 km wide. The presence of this island limits the influence of the tidal flow from the Atlantic and marks the point from which the channel opens to the ocean and is thus considered outer channel (D'Onofrio 1989). Mean tidal range is of 1.1 m in the Ushuaia Bay and the tidal wave moves from west to east (Balestrini et al. 1998). Due to its location, the Beagle Channel's climate is mainly determined by the influence of the Andean Cordillera, the Westerlies winds and by the close Antarctic ice (Tuhkanen 1992). The average temperature is 5 to 6 °C, and annual rainfall of around 500 mm/yr according to the National Meteorological Institute (Servicio Metereologico Nacional 2020). The prevailing wind direction around the city of Ushuaia is southwest (Iturraspe et al. 1989).

3.1.2 Namuncurà Marine Protected Area at Burdwood Bank

The marine protected area Namuncurà Marine Protected Area (NMPA) at Burdwood Bank was created in 2013 in order to protect the marine biodiversity in the Southwest Atlantic Ocean and manage its resources in a sustainable way (Government of Argentina 2020b). The Burdwood Bank is located about 200 km south of the Malvinas Islands and about 150 km east of the coast of Isla de los Estados outside the coasts of Tierra del Fuego. It is a submerged plateau of an area of about 34.000 km² shaped by the 200 m isobath. It is located approximately between 54-55°S and 58-62° W, extending east-west for about 370 km and north-south width varies from 50 to 100 km. While the depth of the actual plateau varies from 50 to 200 m, the slopes of the bank can go as deep as 3000 m in the Yaghan basin (Schejter et al. 2016).

Its waters, located between the Drake Passage and the Scotia sea, are heavily influenced by the Circumpolar Antarctic current, Malvinas current and Cape Horn current (Piola and Gordon 1989) which induce upwelling of nutrinet rich waters when meeting the borders of the Bank (Matano et

al. 2019), potentially boosting primary production. The area is characterised by a sub Antarctic oceanic climate with low temperatures, annual precipitation of about 500 mm/yr and strong winds predominantly blowing from west (Governement of Argentina 2020a).

The Bank was formed as a result of the folding of the earth crust due to the movement of the Scotia plaque, which is located between the South American plaque and the Antarctic one. During the Last Glaciation, the sea level lowered, and the Bank probably resembled an island with an area of about 13.600 km² (Governement of Argentina 2020a). The Scotia arc is a submerged ridge between South America and Antarctica and the Burdwood Bank is part of this ridge together with island such as South Georgia, South Sandwich, South Orcades and South Shetland Island. The Scotia Arc according to Barnes (2005), is an area experiencing some of the highest rates of air, land and freshwater climate change.

The marine protected area is divided into 3 zones: the centrally located core where no activities apart from control and monitoring is allowed; the buffer zone sourrounding the core where authorized activities are permitted and finally a transitioning area which is protected but some activities are still allowed (Schejter et al. 2016). The location of this area is shown in Figure 3.

3.2 Data Collection

Two datasets were used for this study. The first one was composed of data collected in the 9th-25th November 2018 period, during the Oceanographic cruise “Namuncurà MPA Burdwood Bank: Understanding the Biological Carbon Pump” onboard the RV/ARA Austral. This oceanographic cruise falls in the framework of the project “Pampa Azul”, a strategic initiative of the Argentinian government aiming to protect and study this protected area. The dataset included 9 stations from the Burdwood Bank (Figure 4).

The second dataset included only data from the Beagle Channel. Data were collected in the 9th-15th November 2019 period, during the Binational Argentina-Chile Oceanographic cruise onboard the RV/ Victor Angelescu. This cruise aimed to study the effects of acidification and hypoxia in the Beagle Channel. The dataset consisted of a total of 15 samples from 8 different stations along the Argentinean part of the Beagle Channel (Figure 4).

Water samples were taken with Niskin bottles at three depths: surface, bottom and an intermediate depth (deep chlorophyll maximum) in order to approximate a vertical resolution of the biological data. For microbial abundances, water samples were fixed immediately and frozen until their analysis. The physicochemical parameters of the water column were obtained *in situ* by vertical profiling with a self-contained CTD (Conductivity, Temperature, Depth) probe "Rinko Profiler ASTD-102" (JFE, Japan) equipped with sensors for pressure (convertible to depth), temperature, conductivity (transformable in salinity), oxygen and fluorescence (convertible to chlorophyll).

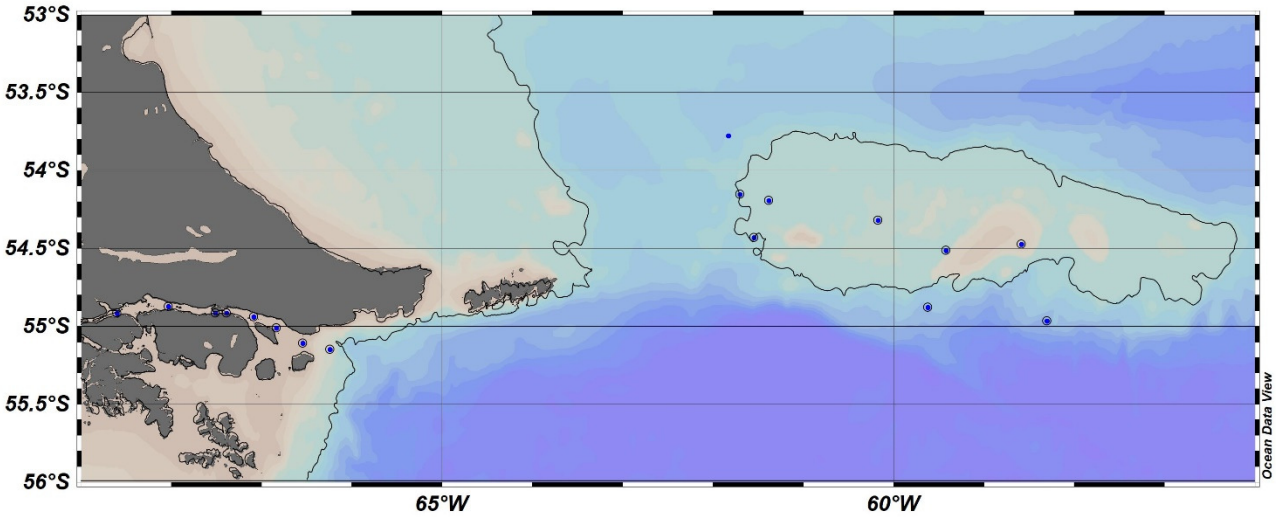

Figure 4: Map showing the location of the stations where samples have been collected. The black line shows the 200m isobath. The Burdwood bank shaped by this isobaths and is located on the right side of this map while the Beagle Channel is on the left side.

3.3 Sample processing and laboratory analysis

To determine the concentration of chlorophyll-a and to analyse CDOM/FDOM, 1-3 L of water were collected, filtered onto Whatman GF/F glass fiber filters, pre-combusted at 450°C for 4 hours. For chlorophyll-a analysis, filters were stored at -20 °C until processing. The chlorophyll extraction with acetone 90% for 24 h at 4 C in the dark was followed by the analysis with a GBC Cintra 10e spectrometer. Using the equations from Jeffrey and Humphrey (Jeffrey and Humphrey 1975) chlorophyll-a, b, c and total was quantified. For this study, only Chlorophyll-a was used.

For the analysis of microbial abundances by flow cytometry, water was prefiltered through a 115 µm net to eliminate the large organisms and material. Then, 1 ml of prefiltered water was transferred to a cryovial for bacteria and 4.5 ml more to a cryovial for pico- and nanophytoplankton. The three samples were fixed with glutaraldehyde, incubated at 4°C for 15-30 min and then stored in freezer at a -80 C temperature to be later analysed by flow cytometry. A Dickinson FACSCalibur flow cytometer was used and existing protocols were applied (Gasol and Giorgio 2000; Marie et al. 2001).

Using the spectrofluorometer Aqualog Horiba, the optical properties of DOM (CDOM, FDOM) were measured. Ultrapure water (MilliQ) was used to measure a blank daily before running samples. Samples from 2018 were run in a quartz cuvette with integration time of 2 seconds, gain equal to high and increment of 2 pixels. Samples from the 2019 cruise were analysed with the following settings: 2 seconds integration time, 4 pixels increment and a gain corresponding to medium. Corrections for Inner Filter Effect and Rayleigh Masking were performed with the Aqualog predefined tools. 3D Normalization with the Raman area graph was also performed with a program in the Aqualog software.

3.4 Data Analysis

Absorption graphs and EEMs were downloaded from the Aqualog software in ASCII files. Different parameters, indices and peaks were calculated from both the EEMs and absorption files. In Table 1, all the spectroscopic properties used for this study are summarised. Information about how those parameters were calculated and interpreted is included as well.

Table 1: Description of the spectroscopic parameters used in this study. Information on how the parameters were measured and whether the absorption data (Abs) or the fluorescence data (Fluo) from the EEM were used is included. The last column explains how to interpret these parameters.

Parameter	**Absorption or Fluorescence**	**Description**	**Interpretation**
S_R	Abs	Slope ratio of $S_{275-295}$ to $S_{350-400}$	Inversely correlated to molecular weight (Helms et al. 2008)
A_{350}	Abs	Absorption coefficient at 350 nm (Bricaud et al. 1981)	Indicator of the concentration of CDOM (Bricaud et al. 1981).
Freshness Index	Fluo	The ratio of emission at 380 nm and excitation at 310 nm divided by the maximum emission intensity between 420 nm and 435 nm at excitation of 310 nm (Parlanti et al. 2000).	This index can give information about the freshness of DOM. Higher values correspond to higher amount of recently produced DOM (Parlanti et al. 2000).
Biological Index (BIX)	Fluo	The ratio of emission intensity at 380 nm divided by 430nm at excitation 310 nm	An indicator of autotrophic productivity. High values (>1) correspond to recently produced DOM of autochthonous origin (Huguet et al. 2009).
Peak A	Fluo	250Ex- 450 Em (Coble 2007; Huguet et al. 2009)	Humic substances and recent material.
Peak C	Fluo	350Ex- 450Em (Coble 1996; Huguet et al. 2009)	Humic substances from terrestrial material.
Peak M	Fluo	310Ex-400Em (Coble 1996; Huguet et al. 2009)	Autochthonous production, marine humic-like material.
Peak T	Fluo	280Ex-330Em (Coble 1996; Huguet et al. 2009)	Protein-like material (resembling the aminoacid Tryptophan signal)
Peak B	Fluo	270Ex-300Em (Coble 1996; Huguet et al. 2009)	Protein-like material (resembling the aminoacid Tyrosine signal)
C:T ratio	Fluo	The ratio of Peak C and Peak T (Baker et al. 2008)	Amount of humic-like vs. protein-like fluorescence. Recacitrant vs. labile material

3.5 Statistical Analysis

Principal component analysis (PCA) was performed in RStudio with the function “prcomp” from the “stats” package. PCA is a multivariate statistical analysis used to reduce data dimension while preserving its variability (Jolliffe and Cadima 2016). The mathematical algorithm behind PCA calculates “principal components” which are eigenvectors. An eigenvector describes the direction along which the variability of the data is the highest. The first two principal components are the directions containing the most variation. To each variable is assigned an eigenvalue so its magnitude. PCA groups together individuals (samples) similar to one another and shows which variable make that specific group of individuals different from the others (Ringnér 2008). Before computing the PCA data must be normalized. This was done through the use of the arguments “scale” and “centre” included in the function “prcomp”. This statistical tool, in this study, was used to understand if differences existed between the two study sites and what were the variables potentially making the two sites different. The input for this calculation was a dataset including all the environmental variables, microbial variables and EEMs peaks together for both study sites.

Partial Least Squared Regression (PLSR) was performed to understand the relationship between the optical properties of DOM and the environment and microbial community. PLSR is a multivariate regression analysis used to find relationships between predictor variables (Huguet et al.) and a single or multiple response variables (Y). PLSR is based on latent variables which are new predicted variables computed as linear combinations between predictor and response to maximise the covariance between X and Y (Geladi and Kowalski 1986). It can be said that in some way PLSR is a combination of a PCA and multiple regression (Abdi 2010). The function “plsreg2” from the package “plsdepot” was used to compute the PLSR and correlation was calculated. The correlation was used to understand the relationships between the predictor and response variables (Riffenburgh 2012).

The Variable Importance in Projection (VIP) is a variable selection method commonly used. VIP scores can tell which of the predictor variable explains better the variability of the response variables (Farrés et al. 2015). A value of VIP higher than one expresses a significant influence of the variable (Tran et al. 2014). VIP was calculated through the “plsreg2” function separately for the two study sites. The microbial and environmental variables have been defined as the predictor variables and the EEMs peaks have been defined as the response variables.

3.6 Data Visualization

Ocean Data View was used to produce graphs and maps showing the different parameters variations between the different study areas as well as along the water column. The data points were interpolated with the weighted-average gridding tool provided by the software

Graphs to visualize the results of the performed statistical tests were produced in R. Biplot were produced using “Factoextra” and “ggbiplot” packages in R.

3.7 Description of the variables

In this section the variables used for this study will be described to allow the reader to get a better understanding.

A list of the variables describing the optical properties was presented in the section 3.3 above. For the statistical analysis only the FDOM peaks were used to describe the composition of DOM. The other variables were only plotted and used for visual interpretation.

The variables used to describe the environmental conditions were: (1) Temperature, (2) Salinity, (3) Oxygen and (4) Chlorophyll. In further sections all those variables will often be referred to as the "Environmental variables". While the first three variables simply describe the conditions of the water, the last is used to estimate phytoplankton biomass in the ocean. Phytoplankton biomass varies seasonally as it is influenced by climatic factors as well as by availability of nutrients in the water column, cloud cover and photosynthetically active radiation (PAR). Chlorophyll values are therefore very dependent on environmental conditions of the water. Phytoplankton also plays a key role in the Biological Carbon Pump and therefore it is and interesting variable to consider in this study (Chavez et al. 2010).

The variables referred to as "Microbial community" in this study were: Low and high nucleic acid content bacteria (LNA and HNA), autotrophic nano- and picoeukaryotes and Synechococcus. Synechococcus is a cyanobacterium contributing to the picophytoplankton. Autotrophic pico- and nanoeukaryotes are eukaryotic phytoplankton. Picophytoplankton can dominate primary production, but their production is considered regenerative and has a little contribution to the production of sinking material, thus does not represent an efficient contributor to the biological carbon pump (Carlson et al. 2001).

Bacteria are responsible for decomposition and respiration of organic matter and recycling of freshly produced DOM (Fuhrman et al. 1980; Azam and Malfatti 2007). The differentiation into the flowcytometric groups LNA and HNA provides some insight into the differences of the bacterial community between samples since these groups comprise different phylogenetic groups (Villa-Costa et al. 2012).

4. Results

4.1 Distribution of the FDOM peaks

The contribution of each peak to the FDOM pool from samples analysed at 5 to 10 m depth (surface waters) in different locations is shown in the map (Figure 5). It could be observed that Peak C in brown colour, representing humic-like peaks of DOM of terrestrial origin was present in the Beagle Channel, while its contribution was very low in the ocean. Peak T and B, representing protein-like material, made up most of the DOM in the ocean, except the most west point dominated with Peak A. Peak T and Peak B seemed to be very abundant in the Beagle Channel as well. Peak M, representing humic-like peaks of autochthonous production was present in both locations in relatively similar magnitude. Peak A, representing humic-like material in general was more abundant in the Beagle Channel.

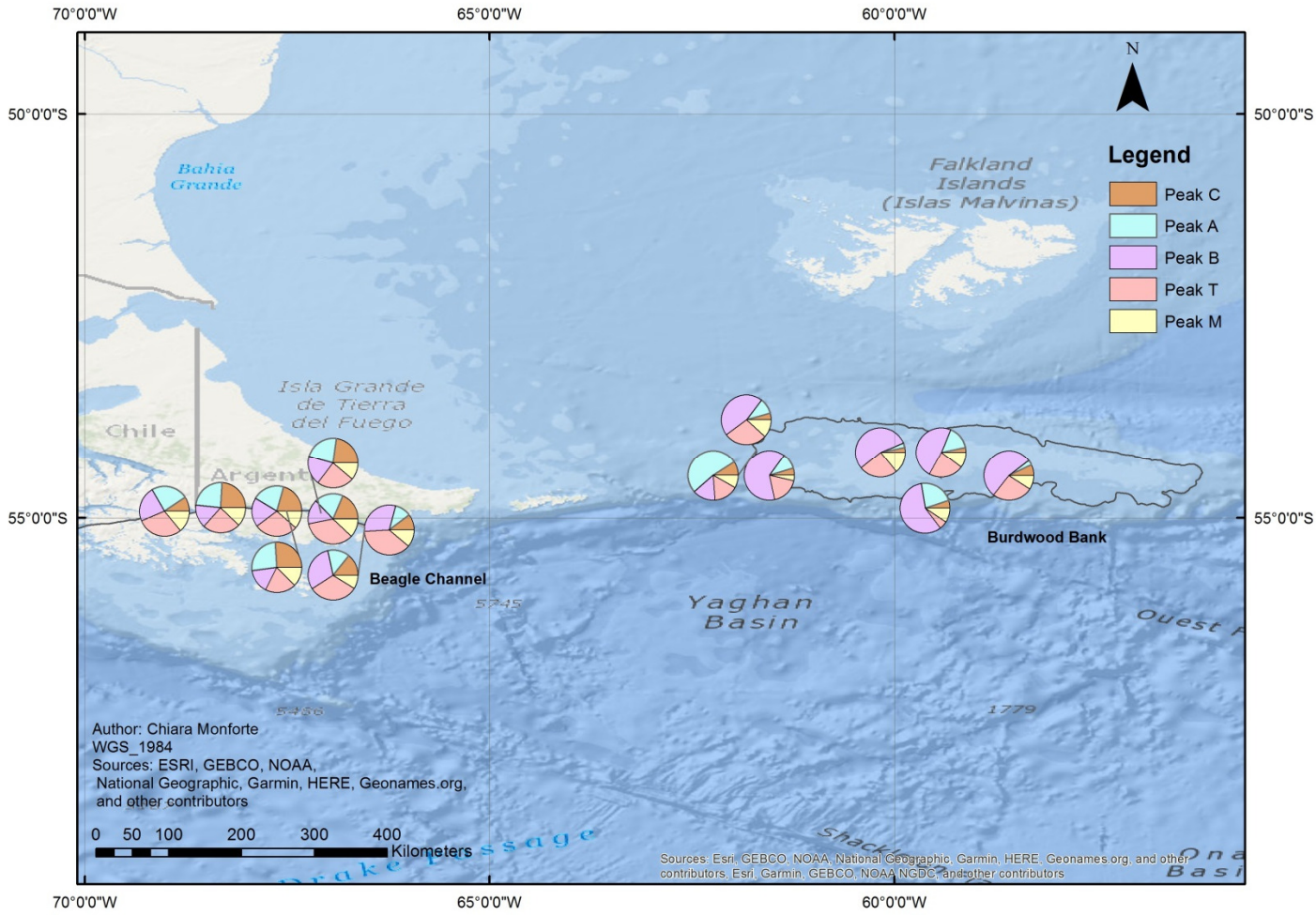

Figure 5: Map showing the relative contribution to FDOM pool at each station for samples from surface waters. The black line is the 200 m isobath shaping the Burdwood Bank.

Figure 6 can help further understanding the spatial distribution of the abundance of different types of DOM. Higher concentration of Peak C (material of terrestrial origin, Figure 6c) was

detected in the Beagle Channel (longitude 68-66°W), while values close to 0 were found in the Burdwood Bank (longitude 62-58°W).

Peak T (Figure 6e) had the highest values in the most eastern part of the channel, closer to the ocean. Lower values were observed in different areas of the Bank both at surface, deep chlorophyll maximum (around 50 m) and deep waters. Peak B (Figure 6b) on the other hand showed the highest values in the Burdwood Bank at different depths and locations. Relatively high concentration of Peak B could be noticed in the area of the Beagle Channel closer to the ocean while relatively very low values were measured in the other areas of the channel.

Peak A (Figure 6a) indicates the presence of humic-like material recently produced. A similar pattern to Peak C and M could be depicted. The highest values were registered in the most inner part of the channel, around the city of Ushuaia. In the Burdwood Bank, the values were very low, and the highest concentration was observed in the surface water of the west side of the Bank. A slightly higher value than average was observed in the surface waters of the centre and west part of the Bank. The values were very low in the rest of the Bank.

Figure 6d shows the distribution of Peak M which represents autochthonous humic-like material. The highest values were registered again in the area of Ushuaia Bay and centre of the Burdwood Bank in surface waters. From Ushuaia towards the ocean a gradient with values slowly decreasing could be noticed. Values close to zero were registered in the rest of the two study areas apart from relatively high values at 50-80 m in the waters around Ushuaia.

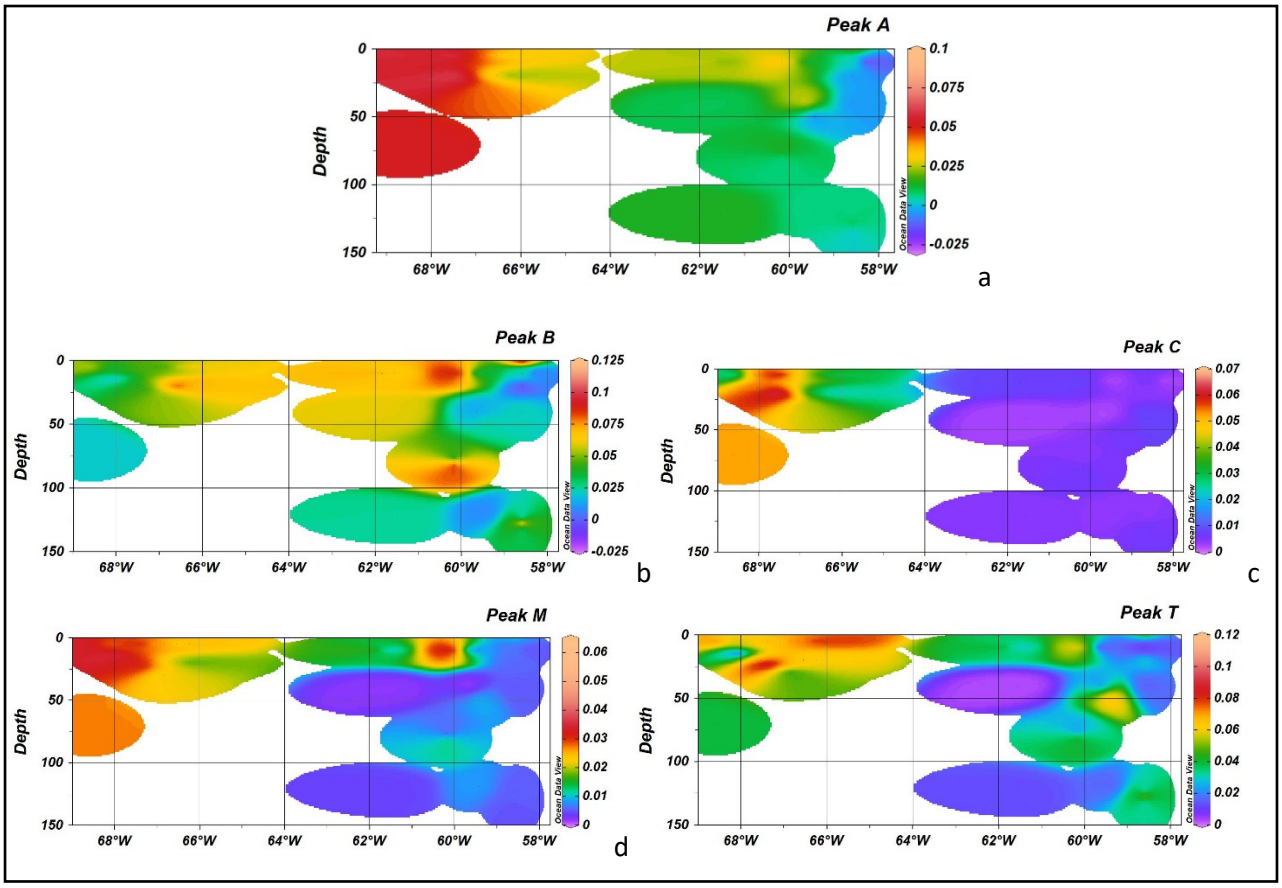

Figure 6: The distribution of the FDOM peaks in a gradient across the two study areas. The area between 68-66°W is corresponding to the Beagle Channel while 62-58°W corresponds to the Burdwood Bank. On the y -axis depth is expressed in metres. The intensities of the FDOM peaks are expressed in Raman units. The data points have been interpolated.

Lower values of peak C:T ratio (Figure 7) were measured in the ocean while higher values in the Beagle Channel meaning that DOM in the ocean was more labile while in the channel DOM resulted to be more recalcitrant. In the outer Channel samples a slow decease towards the ocean could be observed. One spot in the ocean, located in the west and about 50 m depth, had higher values.

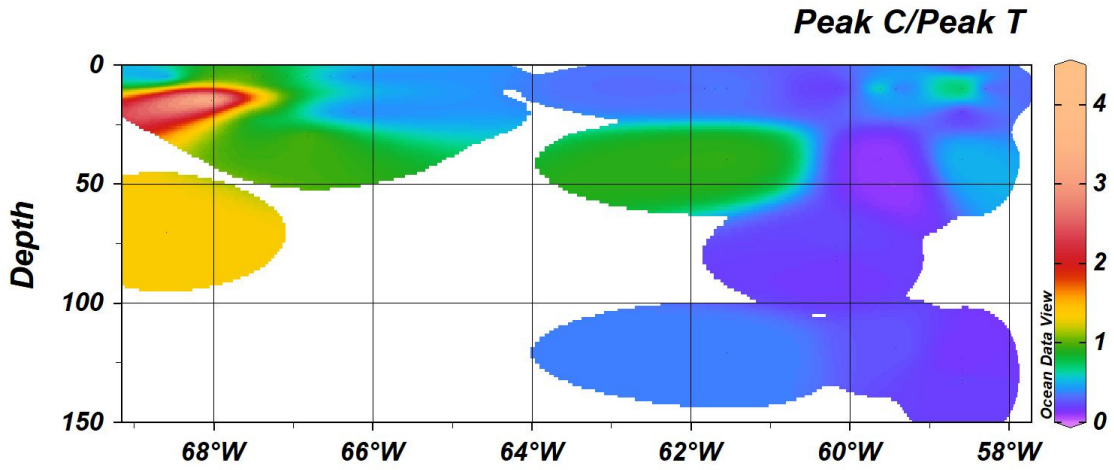

Figure 7: The value of C:T ratio in a gradient across the two study areas. The area between 68-66°W is corresponding to the Beagle Channel while 62-58°W corresponds to the Burdwood Bank. On the y -axis depth is expressed in metres. The intensities of the FDOM peaks are expressed in Raman units. The data points have been interpolated.

4.2 Microbial organism abundances

The abundance of nano and picoeukaryotes as well as Synechococcus were very low in the Beagle Channel, while higher values were depicted in the Burdwood Bank at various depths (Figure 8c, d and e). The highest values of Synechococcus (Figure 8d) were measured at surface to medium depth in the west part of the Bank. The central part of the Bank had a homogeneous distribution through the water column, while very low values were found in the east part of the Bank. For picoeukaryotes (Figure 8e) low values were registered in most of the Burdwood but in the centre of the Bank at 80-100 m depth the values were noticeably higher in comparison. As far as the nanoeukaryotes, the east area of the Bank seemed to be where the highest values could be found both at surface as well as at greater depth.

Figure 8a and b show the distribution of bacteria. Significantly lower values in LNA were registered in the Beagle Channel. The highest values of LNA could be found at about 50m in the west part of the Bank (longitude 62W). In the rest of the Bank the distribution was rather uniform. On the

other hand, HNA distribution varied a lot and did not show net differences between the two study sites. High values could be found in surface water all along the Beagle Channel with decreasing values at greater depths. Higher values were also registered in surface waters in the east part of the Bank as well as medium depth (50 m) both in the west and centre of the Burdwood.

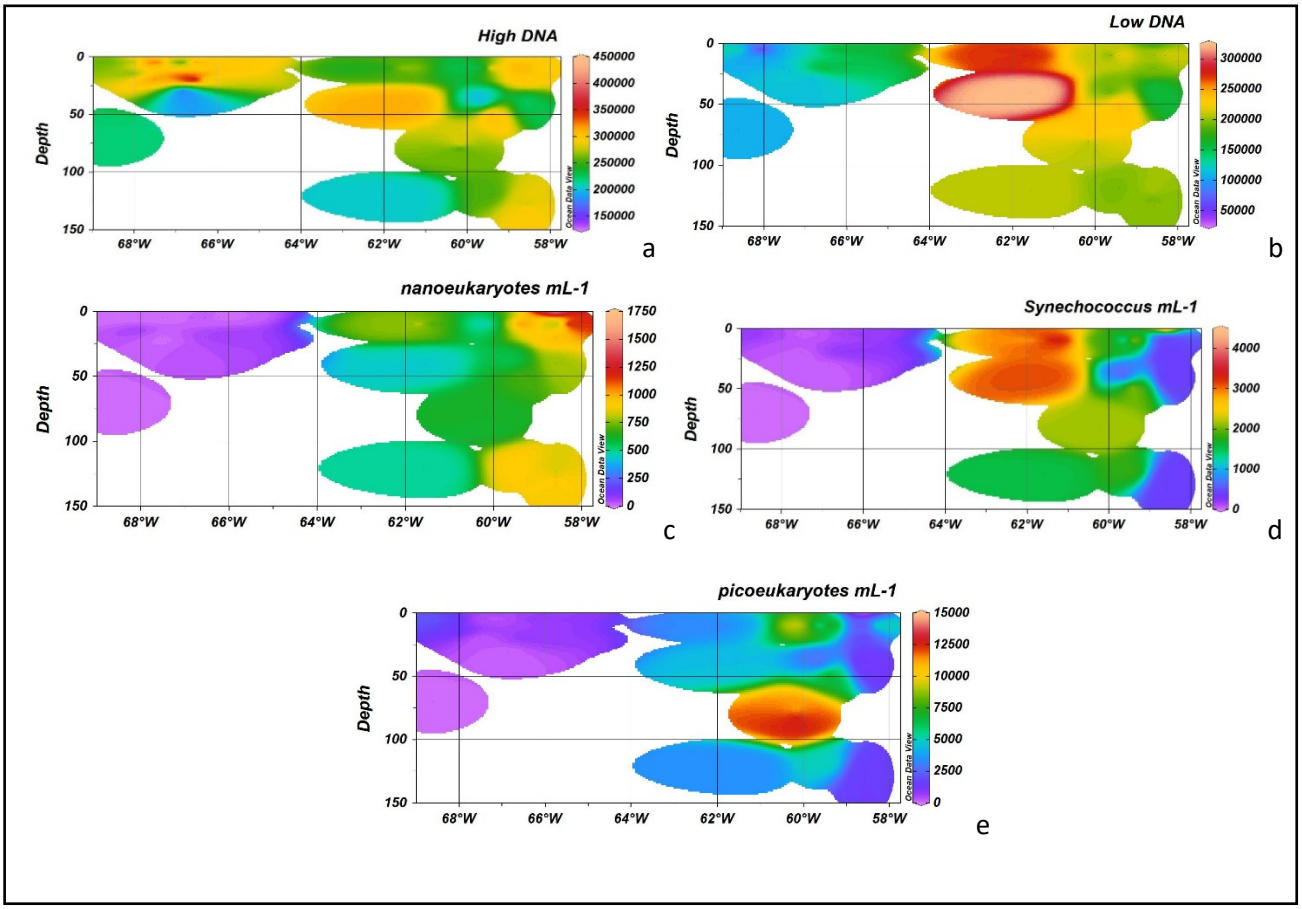

Figure 8: Distribution of the autotrophic nano and picoplankton and bacteria analysed in this study in a gradient across the two study areas. The area between 68-66°W is corresponding to the Beagle Channel while 62-58°W corresponds to the Burdwood Bank. On the y -axis depth is expressed in metres. The abundances of the different group are expressed in ml^{-1}. The data points have been interpolated.

4.3 Environmental conditions

The environmental conditions vary significantly between the two study areas. The Burdwood Bank seemed to experience more homogenous conditions, while big differences were experienced in the Beagle depending on the location. The Burdwood Bank waters had higher oxygen concentration and higher salinity (Figure 9a and d). Water in the Burdwood Bank was colder and its surface waters had higher temperature in the west than in the east. In both of the study areas water temperature decreased with depth (Figure 8b). In the Beagle Channel both salinity and oxygen increased gradually from the Ushuaia Bay towards the ocean (Figure 9a and d). In surface waters of the Beagle Channel, chlorophyll values showed a gradual increase eastward towards the Atlantic Ocean. On the other hand, in the Burdwood Bank, chlorophyll values were very low and

some areas with higher values could be found in surface waters both in the east as well as the west (Figure 9c).

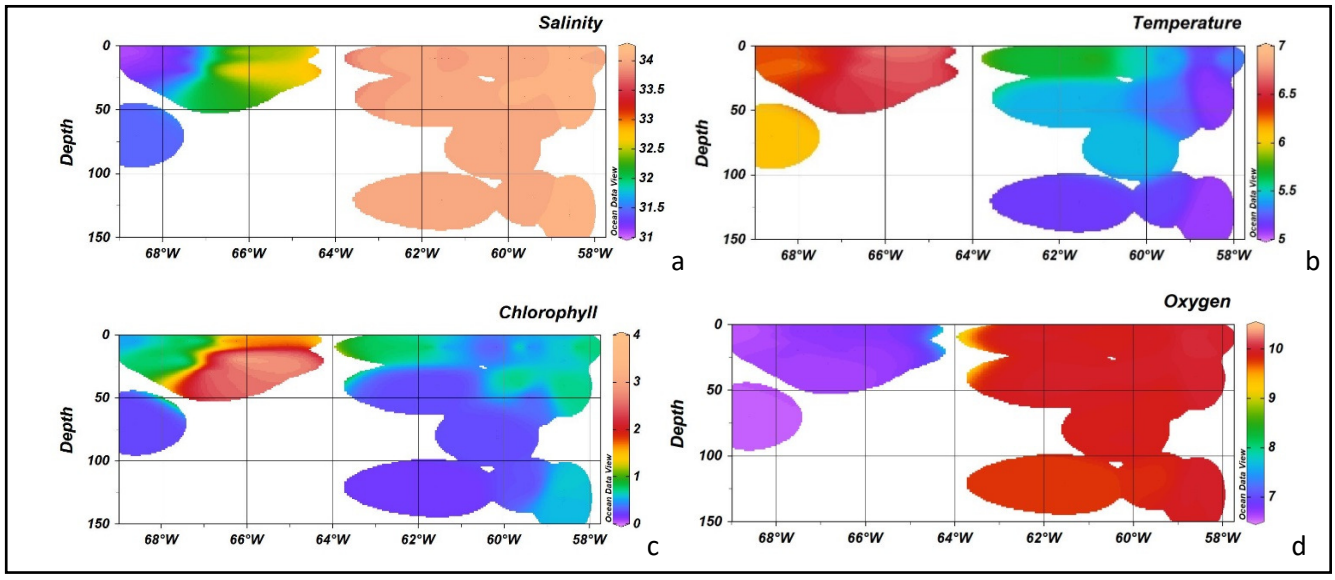

Figure 9: Environmental condition of the water measured with the CTD and laboratory analysis are shown in a gradient across the two study areas. The area between 68-66°W is corresponding to the Beagle Channel while 62-58°W corresponds to the Burdwood Bank. On the y-axis depth is expressed in metres. Salinity on the top left side is measured in ppt while temperature on the right is measured in degrees Celsius. On the bottom left, chlorophyll measured in µm/L and on the right oxygen measured in mg/L. The data points have been interpolated.

4.4 CDOM and FDOM indices

The absorption coefficient at 350 nm can be used to understand the concentration of CDOM. As shown from Figure 10a, there was high concentration of CDOM in the Beagle Channel, whereas it slowly decreased in intensity closer to the ocean. On the other hand, in the Burdwood Bank there was low concentration of CDOM with slightly higher concentration at greater depths.

The slope ratio is inversely correlated to the molecular weight of DOM. As shown in Figure 10d, higher values could be found in the eastern part of the Burdwood Bank. The values were quite constant along the water column with a slight decrease over 100 m depth. The lowest values of slope ratio were registered in the Beagle Channel, meaning that DOM had higher molecular weight in this area.

The Biological index (BIX) can be used to identify organic matter microbially produced. When BIX value is higher than one, the DOM is microbially produced. As shown in Figure 10b, in the Beagle Channel, there was microbially produced DOM at depth greater than 50 m as well as in the surface waters of the area closer to the ocean. The oceanic waters of the Burdwood had BIX value higher than 1 in surface waters and waters greater than 50 m. It could be noticed that at longitude 60°W at 80-100 m depth there was a hot spot of BIX where the highest values were registered. Two

patches of BIX lower than one located in the west area of the Bank at 50 and 100m depth could be observed.

Freshness Index plotted in Figure 10c gives indication on how recently produced the organic matter is. The highest values were registered in the Beagle Channel where the organic matter seemed to be very fresh while lower values were registered in the oceanic samples. In the centre of the Bank at medium to great depth high values were registered.

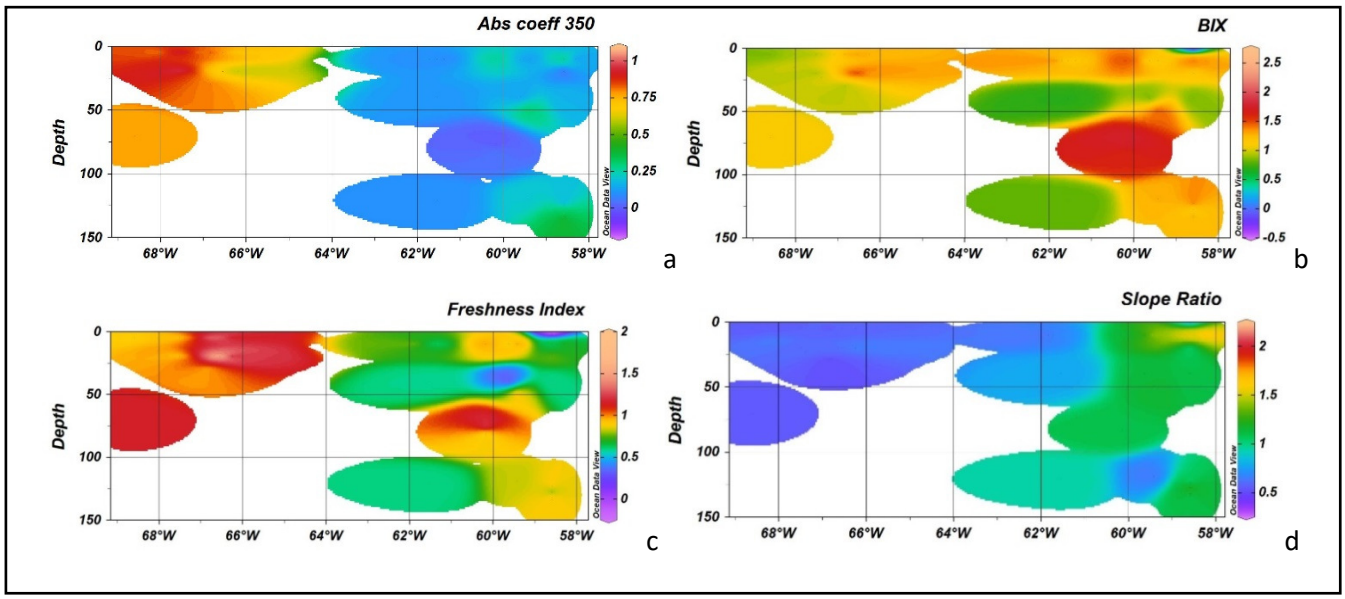

Figure 10: Intensities and distribution of indices measured both for CDOM and FDOM in a gradient across the two study areas. The area between 68-66°W is corresponding to the Beagle Channel while 62-58°W corresponds to the Burdwood Bank. On the y -axis depth is expressed in metres. The data points have been interpolated.

4.5 Results of the statistical analysis

The results of the PCA on a dataset including all the environmental and microbial variables for both study sites are plotted in Figure 11. PCA grouped similar samples together. The samples were identified by their location and it could be observed that the clusters resulting from the PCA were corresponding to specific locations. The Burdwood Bank samples were clearly different from the Beagle Channel samples and within the study areas sub distinctions could be also made.

In the case of the Beagle Channel, there were differences between the samples around Gable Island and the samples closer to Ushuaia, while the samples from the outer channel had mixed conditions. Different zones in the Burdwood Bank could also be found. The samples in the south slope of the bank were similar to the samples of the east side. The samples in the core were different from the ones in the east.

The arrows correspond to the variables and depending on their direction they tell which variables explain most of the variance in the study sites. Chlorophyll, and Temperature made the Beagle

Channel different from the Burdwood Bank. Salinity, Oxygen and most of the microbial variables explained most of the variance in the open ocean study area.

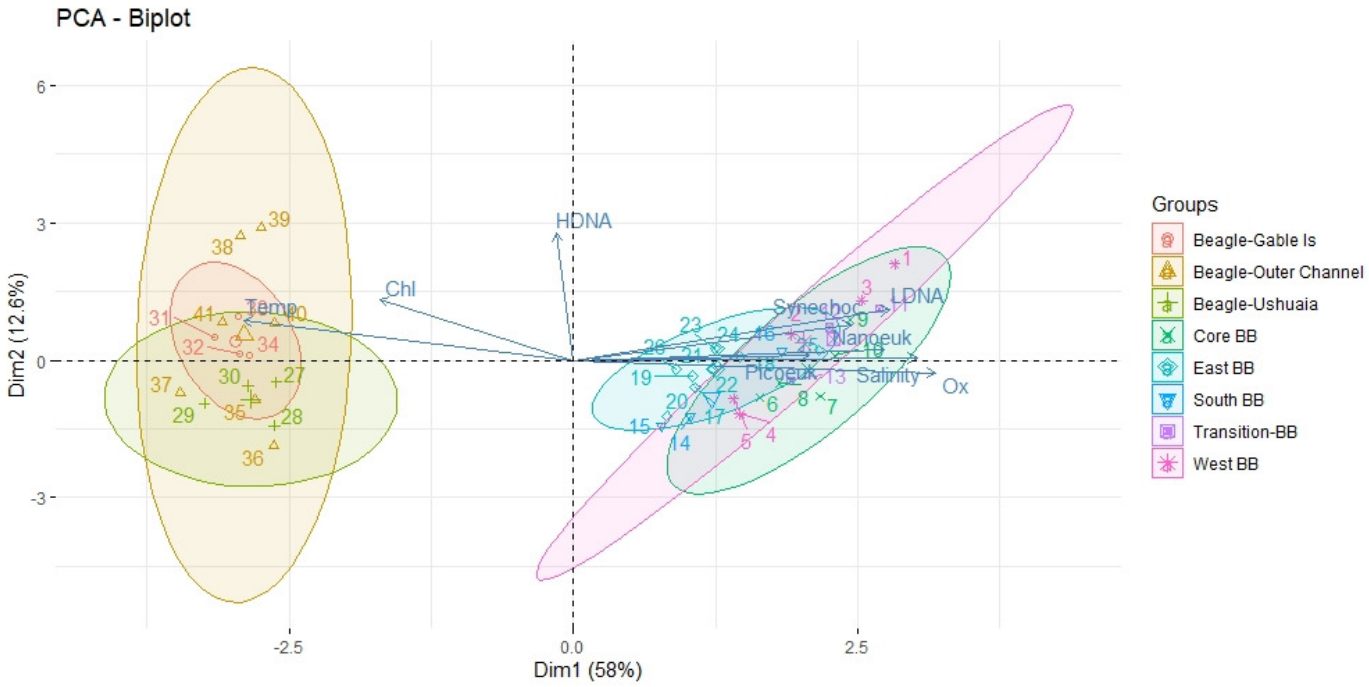

Figure 11: Biplot representing the results of the PCA for both observations and variables in the study sites. All the environmental and microbial variables have been included. The two axes represent the first two components which together explain 70.6% of the variability.

PCA on the FDOM peaks only was computed to understand if the DOM composition was different in the study areas (Figure 12). Most of the observations were spread along the x-axis corresponding to the first principal component of the PCA. This first principal component explained 70% of the variability alone. It could be observed from the biplot that the samples corresponding to the areas around Ushuaia and Gable Island were different from the oceanic samples. The observations from the outer channel were spread between the Beagle Channel and the Burdwood Bank observations as a sort of bridge between the two locations. The Burdwood Bank samples seemed to have similar DOM compositions as no evident distinction could be made among samples from the different areas.

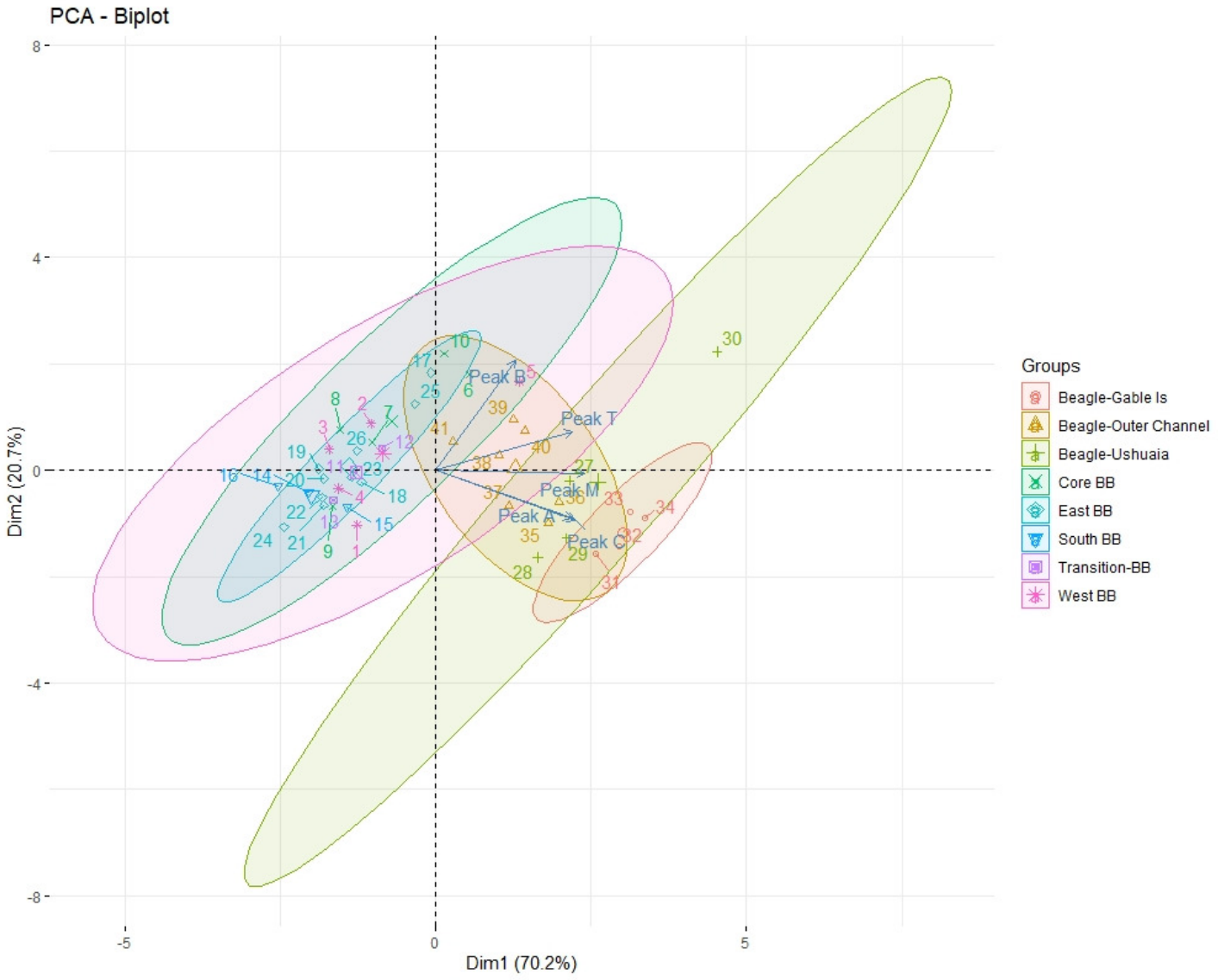

Figure 12: Biplot representing the results of the PCA for both observations and variables in the study sites. Only the FDOM have been used to run the PCA. The two axes represent the first two components which together explain 90.9% of the variability.

The correlation circle for the Burdwood Bank (Figure 13a) showed that Peak T, C, M and B were negatively correlated to Chlorophyll, Oxygen, Nanoeukaryotes and HNA. The two microbial variables mentioned before were closer to the correlation circle meaning that they influenced the peaks more than the environmental variables. A strong positive correlation between the peaks, especially peak A and picoeukaryotes, could also be observed.

In the case of the Beagle Channel (Figure 13b), it could be noticed that the peaks were not grouped together but each peak was explained by different variables. Peak T was strongly influenced by picoeukaryotes in respect to the second PLRS component. The environmental variables had negative correlation with humic-like peaks M and A. Salinity had the highest influence. Peak C had strong negative correlation with most of the microbial variables, especially synechococcus, HNA and nanoeukaryotes. Peak B, representing protein-like peaks (Tyrosine) had

strong correlation with microbial communities as well, especially with synechoccoccus. A weaker correlation between environement and Peak C could also be observed.

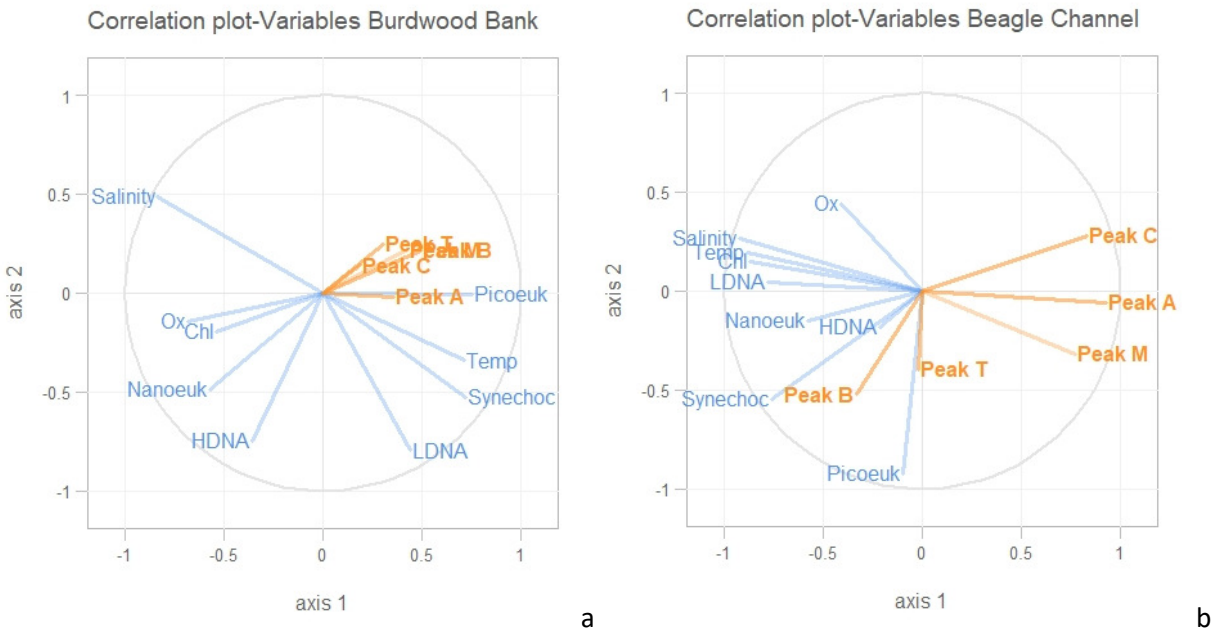

Figure 13: Correlation circle resulting from the PLSR analysis for the two study sites. The relationship between the predictor variables (in blue, environement and microbial abundances) and the response variables (in orange, the EEMs peaks) is shown. The angle between the variables indicates the type of correlation. The closer the variable to the circle of correlation 1, the higher is its influence.

As a result of the PLSR, the Variable Importance in Projection (VIP) was also computed. VIP estimates the importance of the variables in the PLSR model and in explaining the variance of the responses (Peaks). Two PLSR for the different study sites were run. The peaks were the response variable and the predictor were the environment and the microbes. As shown in Figure 14, for the Beagle Channel the significant variables with VIP score higher than 1 were Chlorophyll, Temperature, Salinity and Synechococcus. In the Burdwood Bank, the significant variables are Temperature, HNA, Nano and Picoeukaryotes and Synechococcus.

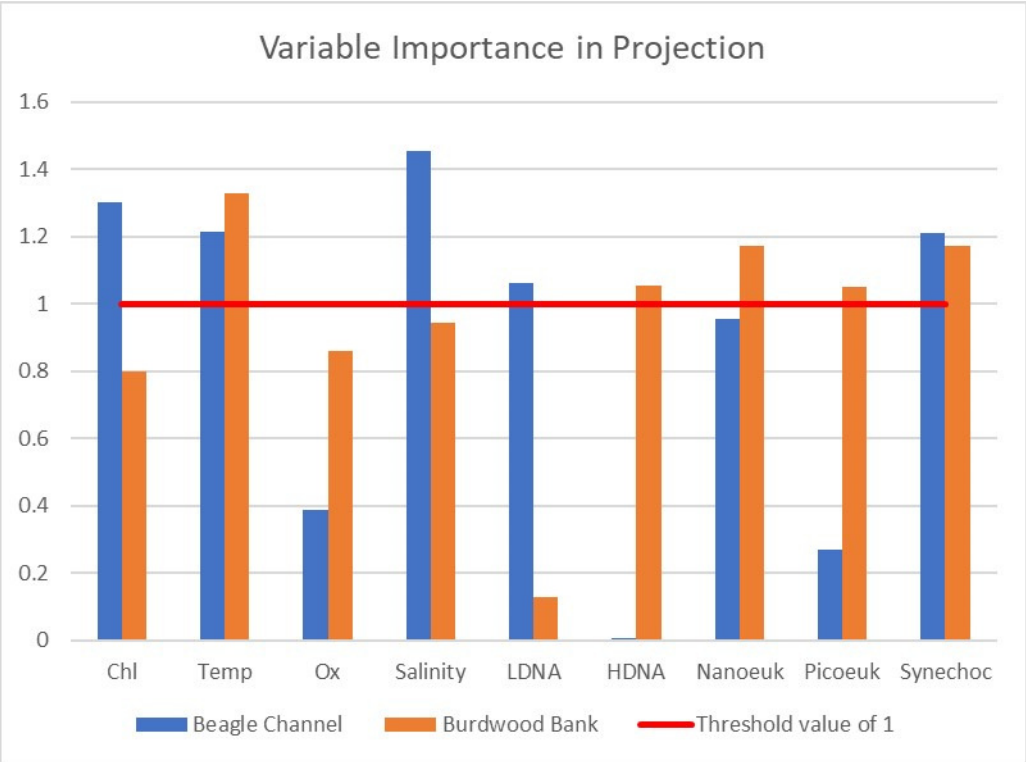

Figure 14: VIP scores resulting from the PLSR analysis for both study sites. The variable is considered to have an influence when the VIP score is higher than one.

5. Discussion

The aim of this study was to analyse the composition of DOM and its relation to the physical and chemical conditions of the water column as well as to the abundances of different bacterial, cyanobacterial and micro-algal fractions of the plankton community. The PCA results revealed that the two subpolar marine study locations were characterised by distinct microbial and environmental conditions. Previous studies (Mann et al. 2012; Jaffé et al. 2008) suggested such differences in abiotic and biotic conditions should be reflected in the quality and quantity of DOM. Thus, it could be expected that contrasting influence on DOM from those variables in the two study areas might be observed.

The spatial variation of DOM (Figure 5 and 6) revealed that there were some differences in DOM composition between the two study sites. As suggested by Asmala et al. (2016) concentration of autochthonous DOM is greater when the terrestrial influence is lower or when the conditions are favourable and allow high primary production. The low contribution of terrestrial material in the Burdwood Bank explains why the FDOM pool in this location was mainly composed of autochthonous material and protein-like material. On the other hand, the Beagle Channel is a productive environment and that is why the concentration of autochthonous DOM was high even if the terrestrial contribution was relevant. The results from the PCA performed on the FDOM peaks confirmed that differences in DOM composition between the two areas existed (Figure 12). The samples from the ocean and the inner part of the channel could clearly be distinguished, while the outer channel samples were spread between the two areas proving that this site had a mixed composition.

The distribution of synechococcus, autotrophic pico- and nanoeukaryotes varied a lot in the Burdwood Bank depending on location and depth. A study by Agawin et al. (2000) reveal that microbial communities are sensitive to changes in physical conditions of the water column, especially salinity and temperature. Considering that those variables were quite constant in the Burdwood Bank, no specific relationship linkage between microbial communities and physical conditions was observed in this study. However, it could be noticed that the highest values of nanoeukaryotes were registered in the coldest waters of the Bank and in these areas the lowest abundances of synechococcus and picoeukaryotes were observed. This suggests that those groups could be influenced by water temperature. As described by Li et al. (2009), with increasing temperatures nanoplankton abundance decreases and picoplankton concentration rises.

In the Beagle Channel relatively much lower abundances of the small size phytoplankton were observed. Despite this, the chlorophyll values measured in the area of the channel closer to the ocean were very high as well as high Freshness Index and Peak T and B suggesting the presence or start of a phytoplankton bloom. This could be due to very different species composition of the phytoplankton community in the two study areas. Larger phytoplankton such as diatoms might represent the biggest component of the population in a more nutrient rich environment like the Beagle Channel (Carlson et al. 2001). On the other hand, picoplankton fraction dominates phytoplankton production in more oligotrophic open ocean (Buitenhuis et al. 2012). Different environmental conditions and nutrient availability would support different populations.

To understand what influences the FDOM pool, the correlation circles from the PLSR could be used (Figure 13). In the Burdwood Bank the five peaks where grouped together suggesting that their origin was similar and their variability was influenced by the same environmental or microbial variables. On the contrary, in the Beagle Channel each peak had correlation with distinct variables. A study from Català et al. (2016) revealed that the two environmental variables controlling the composition of FDOM in the ocean were chlorophyll-a and oxygen. The correlation plot for the Burdwood Bank shows a similar situation as the two environmental variables influencing the peaks are the same.

The three humic peaks (Peak C-A-M) showed similar spatial distribution and in the correlation circle of the Beagle Channel they seemed to be negatively correlated to salinity, temperature, chlorophyll-a and LNA. Salinity indicates the amount of freshwater input, i.e. the lower the input of freshwater from rivers and glacier meltwater to the Channel, the higher the salinity. The lower the freshwater input, the lower the terrestrial material and by consequence decreasing values of Peak C and Peak A, both humic-like DOM of terrestrial origin, from the inner to the outer Beagle Channel. High abundance of refractory DOM of marine origin (peak M) in the inner Beagle Channel indicates microbial alteration of DOM (Helms et al. 2008). This suggests that DOM is retained in the deep basins of the inner Channel, recycled through bacterial activity, and made more refractory, i.e. unavailable for biodegradation (MCP, Jiao et al. 2010).

As a result of the PLSR, VIP scores were also calculated. This was helpful to explain what influences DOM composition the most. The environment seemed to have the highest influence on FDOM in the Beagle Channel while the microbial communities guided the composition or organic matter in the ocean. Considering that the composition of DOM in the Beagle Channel is highly influenced by rivers and glacier runoff, a strong influence from salinity was expected. The high chlorophyll values suggested high concentration of larger phytoplankton in the Beagle Channel. Considering that phytoplankton contributes to the production of autochthonous DOM (Archer 2003), a VIP score higher than one could be expected. In the Southern Ocean the primary production is mainly supported by small sized phytoplankton (Weber and El- Sayed 1987) and by consequence production of autochthonous DOM. Significant VIP scores for nano and picoeukaryotes as well synechococcus were therefore predicted.

The optical properties could be used to understand the source, age and bioavailability of DOM. In the Burdwood Bank high amounts of microbially produced and relatively recently produced material was detected. In addition, Peak T and B had similar patterns to the nano and picoeukaryotes and synechococcus, confirming that those microbes were responsible for DOM production. A recent study from Berggren at al. (2020) demonstrated that bacterioplankton[1] is responsible for the production of protein-like fluorescence. Lower molecular weight is usually corresponding to fresher material and more reactive (McKnight et al. 2001). The lower values of C:T ratio and the higher values of slope ratio revealed that DOM is more labile and bioavailable in this area.

[1] Synechococcus is considered bacterioplankton

On the contrary, in the Beagle Channel higher amounts of CDOM due to the greater freshwater inputs (Santos et al. 2016) and higher molecular weight material than the ocean were observed. A study from Cronin and Morris (1982) revealed that humic substances freshly produced are characterized by high molecular weight material. The presence of freshly produced material and high amounts of humic DOM would then explain the high molecular weight material in the channel.

No visible relationships were observed between the fluorescence peaks and the bacterial abundances. As suggested by Amaral et al. (2016), different species and clades of bacteria are correlated to different variables. Some have strong linkage with higher molecular weight material, some with higher DOC concentration or in areas of higher terrestrial humic material. Considering that no differentiation in clades was made but only a general distinction among groups of bacteria was applied in this study (LNA and HNA) such relations could not be observed. It is interesting though to notice some patterns: a very intense concentration of bacteria, especially LNA, could be observed at longitude 62°W and depth around 50 m. In the same area very low Freshness index could be observed. In Figure 7 it could be noticed that in that same area higher values of C:T ratio were registered suggesting the presence of relative higher amounts of humic material. This suggests that DOM is being recycled by bacteria and more recalcitrant material is being produced boosting the MCP (Jiao et al. 2010). Different studies showed that bacteria produce refractory DOM (Brophy and Carlson 1987; Ogawa et al. 2001; Gruber et al. 2006) and its optical signals corresponded to humic-like material (Català at al. 2015). Furthermore, a study from Amon and Benner (1996) suggested that bacterial growth and respiration was higher in high molecular weight (HMW) DOM. It could be noted that there was no evident pattern between HMW DOM and bacteria was registered in this study but the highest values of both LNA and HNA were observed in the areas of lower slope ratio which corresponded to higher molecular weight.

In general, from the results it could be noticed that variables were very dependent on each other therefore understanding the exact mechanisms was challenging. As a matter of fact, microbes and the environment were influencing the quality of DOM but the environment was in turn influencing the microbial communities. Furthermore, when many variables are correlating to each other, understanding what the actual relationships are becomes complicated. For example, two variables strongly correlated with a third variable might not have a direct causal link but will eventually show correlation. As clearly explained by Detto et al. (2012), in complex systems distinguishing a direct causality from the influence of external factors becomes difficult.

The hypothesis therefore has to be rejected because the complexity of ecosystem dynamics and the intricate relations between different variables did not allow determining the direct controls of DOM. Nevertheless, in the Beagle Channel the influence of the environment on DOM composition was strong. The composition of the microbial community could be influenced by the environment conditions, so an indirect effect of the environment on the autochthonous DOM was experienced. On the contrary, in the Burdwood Bank the environmental conditions are more homogeneous and their influence was less notable while a greater influence from the microbial communities could be observed, therefore fulfilling this aim.

5.1 Limitations of the study

The number of data points used for this study can be considered as a limitation to this project. A total of 15 samples from the Beagle Channel and 27 from the Burdwood Bank were available. Statistical results might have been influenced by the low amount of data points and thus caused misinterpretation. A small size sample may not be representative for the actual conditions of the water, microbial populations and DOM composition. This way, it could introduce under or overestimations of the influence of the variables (Cao et al. 2002).

Furthermore, the samples were collected in two different years which could have caused some errors due to interannual variability. However, samples from both study areas were collected in late austral spring so the conditions should not differ drastically and the potential errors should not be substantial.

When performing the PCA and PLSR, all the samples have been used without consideration of their depth. DOM composition can vary a lot along the water column especially at greater depths thus samples from different depths might have influenced the statistical results. Considering that in this study no samples from waters deeper than 150m were included, the comparison can still be considered relevant.

The high values of chlorophyll in the outer channel corresponding to a phytoplankton bloom can be considered as an outlier and thus create potential errors in the analysis. The samples from the inner part of the Channel were collected before the bloom and the ones closer to the ocean in the outer channel during the bloom. The microbial community abundances, the environmental conditions, as well as the DOM quality, changes substantially during a bloom (Cloern 1996). The difference between pre-bloom and bloom conditions might have influenced the analysis as the conditions were not similar among sampling sites. In this regard, it is important to highlight that the time lag in the sampling between different stations introduces a bias for comparative analysis.

5.2 Suggestions for further studies

A powerful statistical tool which would have been useful for this study is variance partitioning. This method reveals how much of the variation of a Y matrix (Peaks) is explained by X matrix (in this case, the environment, and the microbial community). This analysis was performed on the dataset, but the limited number of samples and variables did not allow the algorithm to work properly. In future studies, it would be a helpful tool to explain the variability of the peaks and its controls (Smith and Lundholm 2010).

The methodology used to analyse the FDOM peaks could have been improved by the use of PARAFAC (Parallel Factor Analysis). The “peak picking” technique used in this study might have led to new peaks not being detected or actual intensities not being observed, as not matching with the emission-excitation combinations suggested from literature (Bieroza et al. 2009). PARAFAC is a multivariate statistical model which decomposes the EEM into its distinctive fluorescent components (Stedmon and Bro 2008). In this way, the composition of DOM in the study area can be analysed and specific fluorophores could be detected.

The variables explaining the environment were not fully explicative. Due to time limitations, the samples for inorganic and organic nutrients had not yet been analysed. Including information about DOC and inorganic nutrients (Nitrite, Nitrate, Ammonium, Phosphorus and Silicate) would have been beneficial to gain better understanding about the environmental conditions of the water column. A Master's thesis from Ehnvall (2017) showed that in freshwater ecosystems nutrients, especially phosphorus have an important influence on DOM. In addition, DOC values would have allowed the calculations of interesting parameters, such as $SUVA_{254}$. Therefore, it would have been beneficial to include this type of data in this study.

As suggested by Asmala et al. (2014) flocculation can have significant influences of DOM removal or transformation in estuarine environments, it would therefore have been interesting to study this phenomenon and its effects in the Beagle Channel.

6. Conclusion

To conclude, the DOM composition between the two study sites features some differences. Higher amounts of microbially produced autochthonous DOM characterise the oceanic waters of the Burdwood Bank. A relevant contribution of humic DOM and terrestrial material is added to significant amounts of autochthonous material in the Beagle Channel. This last site has greater amounts of recalcitrant DOM while in the ocean DOM is represented by lower molecular weight material and more bioavailable DOM.

Finally, it can be said that it was difficult to determine what are the actual drivers of DOM composition were. In the two study areas the FDOM peaks were influenced by both the environmental variable and the microbial community. Nevertheless, it could be observed that the environmental variables had a greater influence the FDOM peaks in the Beagle Channel, while the microbes had the strongest influence on the Burdwood Bank.

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8.Appendix

Table 2: The table shows the information about the samples used in this study. Information about the location, depth and cruise are included for each sample

Station	Latitude S	Longitude W	Cruise	Cast	Depth (m)
30	-54.153	-61.703	BOANOV18	146	10
28	-54.430	-61.545	BOANOV18	84	10
28	-54.430	-61.545	BOANOV18	84	40
28	-54.430	-61.545	BOANOV18	85	120
34	-53.778	-61.829	BOANOV18	186	70
24	-54.321	-60.171	BOANOV18	50	10
24	-54.321	-60.171	BOANOV18	50	90
24	-54.321	-60.171	BOANOV18	59	10
24	-54.321	-60.171	BOANOV18	59	80
24	-54.321	-60.171	BOANOV18	66	10
24	-54.321	-60.171	BOANOV18	66	80
21	-54.512	-59.421	BOANOV18	43	10
21	-54.512	-59.421	BOANOV18	43	50
21	-54.512	-59.421	BOANOV18	43	120
16	-54.879	-59.621	BOANOV18	34	10
16	-54.879	-59.621	BOANOV18	34	40
18	-54.967	-58.302	BOANOV18	30	10
2	-54.474	-58.587	BOANOV18	2	10
2	-54.474	-58.587	BOANOV18	2	20
2	-54.474	-58.587	BOANOV18	2	132
2	-54.474	-58.587	BOANOV18	15	10
2	-54.474	-58.587	BOANOV18	15	40
2	-54.474	-58.587	BOANOV18	15	125
2	-54.474	-58.587	BOANOV18	18	10
2	-54.474	-58.587	BOANOV18	18	136
2	-54.474	-58.587	BOANOV18	24	1
2	-54.474	-58.587	BOANOV18	24	135
1	-54.920	-68.600	VA201911	1	5
1	-54.920	-68.600	VA201911	1	70
5	-54.870	-68.030	VA201911	7	5
5	-54.870	-68.030	VA201911	7	15
8	-54.920	-67.510	VA201911	12	5
8	-54.920	-67.510	VA201911	12	20
9	-54.910	-67.390	VA201911	14	5
9	-54.910	-67.390	VA201911	14	20
11	-54.940	-67.080	VA201911	16	5
13	-55.010	-66.830	VA201911	21	5
13	-55.010	-66.830	VA201911	21	30
15	-55.110	-66.540	VA201911	25	5
15	-55.110	-66.540	VA201911	25	20
16	-55.150	-66.240	VA201911	30	5
16	-55.150	-66.240	VA201911	30	20

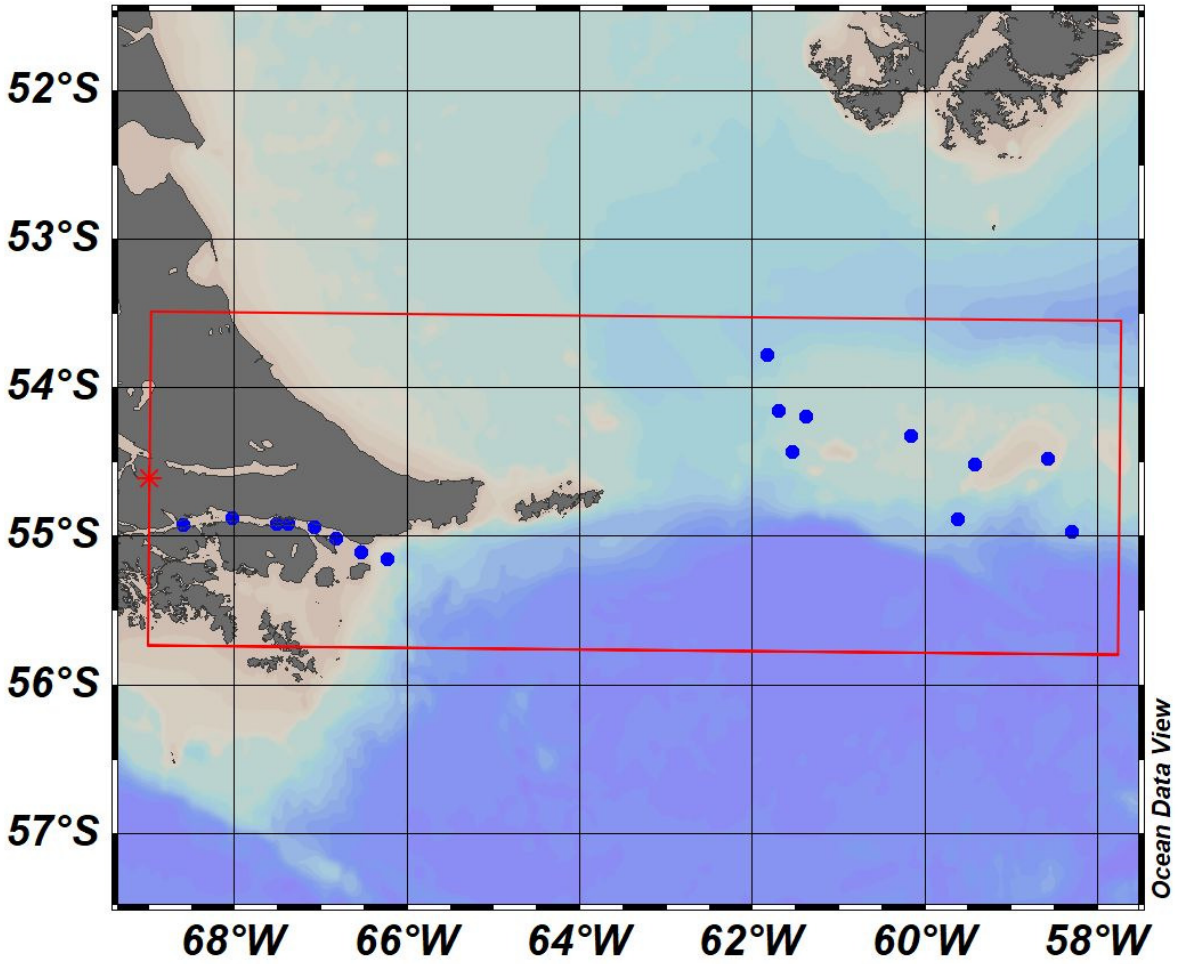

Figure 14: Section used to create the plots where the vertical distribution of the variables is shown. The blue dots represent the station where the samples have been collected