



## GEOSCIENCES

# Ocean-atmosphere turbulent CO<sub>2</sub> fluxes at Drake Passage and Bransfield Strait

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**Abstract:** The oceans play an important role in mitigating climate change by acting as large carbon sinks, especially at high latitude regions. The Southern Ocean plays a major role in the global carbon dioxide (CO<sub>2</sub>) budget. This work aims to investigate the behavior of turbulent CO<sub>2</sub> fluxes and quantify it under different atmospheric and oceanic conditions in the Drake Passage and Bransfield Strait regions on high spatiotemporal resolutions when compared with traditional CO<sub>2</sub> fluxes estimations. The atmospheric stability condition was used to corroborate the description of CO<sub>2</sub> fluxes. *In situ*, satellite, and reanalysis data from 08 to 22 November 2018, were used in this work. The Bransfield Strait uptaked 38.59% more CO<sub>2</sub> than the Drake Passage due to the cold and fresh waters, allied to the influence of glacial meltwater dilution. Which increased the CO<sub>2</sub> solubility, directing the CO<sub>2</sub> fluxes to the ocean. The Bransfield Strait had predominantly stable atmospheric conditions, which contributed to this region acting as a CO<sub>2</sub> sink. The Drake Passage, on average, behaved as a CO<sub>2</sub> sink, mainly due to physical characteristics. This research contributes to a better understanding of the Southern Ocean's role in the global carbon balance on scales that are very difficult to monitor.

**Key words:** carbon flux, sea-air interaction, carbon sinks, Antarctic Peninsula.

## INTRODUCTION

The main cause of global warming, according to the Intergovernmental Panel on Climate Change (IPCC) (IPCC 2021), is the increase of greenhouse gases (GHG) emissions in the atmosphere since the pre-industrial period. Carbon dioxide (CO<sub>2</sub>), one of the most important GHG, has increased by over 40% since the pre-industrial period. These values increased from 278 ppm in 1750 to 411.97 ppm in 2019, and the average global air temperature increased 0.89 °C between the years 1880 and 2019 (NOAA 2019).

Relevant scientific questions about global climate involve the understanding of the interaction between the ocean and atmosphere (Pezzi et al. 2009, 2016, 2021, Hackerott et al. 2018, Santini et al. 2020, Souza et al. 2021). According to Canadell et al. (2007), the oceans are responsible for sequestering approximately 1/3 of anthropogenic carbon emissions per year. The CO<sub>2</sub> partial pressure in the ocean (pCO<sub>2sw</sub>) has great spatial and temporal variability, being middle and high latitude regions considered CO<sub>2</sub> sinks (Takahashi et al. 2009). The high latitudes have an important role in CO<sub>2</sub> exchange between ocean-atmosphere, which in turn are controlled by physical, chemical, and biogeochemical processes (Ito et al. 2018, Monteiro et al. 2020, Jiang et al. 2014).

Recent studies show that the Southern Ocean (SO) plays a major role in the global CO<sub>2</sub> cycle, accounting for 43% (42 Pg C) of the global anthropogenic CO<sub>2</sub> uptake from the atmosphere from 1870

to 1995 (Takahashi et al. 2009, Frölicher et al. 2015, Le Quéré et al. 2016, 2018). The SO sinks more CO<sub>2</sub> during the spring-summer than the autumn-winter due mainly to the sea-ice cover retreats and biologically driven (Roden et al. 2016, Ito et al. 2018, Ogundare et al. 2021).

Several modelling and observational studies suggest a reduction in the efficiency of SO CO<sub>2</sub> uptake over the past few decades (Lovenduski et al. 2013, 2015, Le Quéré et al. 2010, Metzl 2009). Nevertheless, other studies suggest that global ocean uptake of CO<sub>2</sub> has increased over the past decade, largely due to the SO (Landschützer et al. 2014, Majkut et al. 2014, Munro et al. 2015, Xue et al. 2015). There is a need for studies that allow a better understanding of the processes involved in the exchange between the ocean and the atmosphere, at different spatiotemporal scales. Understanding how CO<sub>2</sub> turbulent flux behaves in different oceanic regions is very important for global carbon budget studies. The Atlantic Carbon and Fluxes Experiment (ACEx) project (Pezzi et al. 2016), the Ocean-Atmosphere Interaction Program in the Brazil-Malvinas Confluence Region (INTERCONF) (Pezzi et al. 2005, 2009), Southern Ocean Studies for Understanding Global Climate Issues (SOS-CLIMATE; Orselli et al. 2017, Ito et al. 2018, Monteiro et al. 2020), Programme de Coopération avec l'Argentine pour l'étude de l'océan Atlantique Austral (ARGAU cruises; Bianchi et al. 2009) and more recently the Antarctic Modeling Observation System (ATMOS) project (Pezzi et al. 2021), are some of the South America research programs dedicated to study the exchange of ocean-atmosphere turbulent fluxes in the Southwest Atlantic Ocean (SAO) and the SO.

The observations in the Drake Passage (DP) show higher pCO<sub>2sw</sub> values located in the north of the Antarctic Polar Front (PF) than to the south (Munro et al. 2015). Additionally, the seasonal cycle amplitude north of the front is much larger and well defined than south of the front. In the south of the PF has been a persistent CO<sub>2</sub> sink, due to the pCO<sub>2sw</sub> being lower than the CO<sub>2</sub> partial pressure in the atmosphere (pCO<sub>2atm</sub>) (Caetano et al. 2020), influenced by the cold sea surface temperature (SST) during the summer and the presence of the upwelling of waters with low anthropogenic CO<sub>2</sub> content (Pardo et al. 2014) and mixed layer depths greater in winter (Stephenson et al. 2012). The upwelling of old and CO<sub>2</sub> rich waters around Antarctica influences the carbonate system in the NAP environments (Lencina-Avila et al. 2018, Monteiro et al. 2020). It increases the macronutrients and CO<sub>2</sub> and decrease the carbonate concentration; however, those changes vary depending on mixing processes in response to sea ice, eddies formation, topography, and atmospheric forces (Henley et al. 2019). At the Northern Antarctic Peninsula, the coastal waters of the straits and bays are considered the most productive areas in the SO (Costa et al. 2020). However, according to Caetano et al. (2020), the Bransfield Strait (BS) in late spring indicates a near-neutral air-sea CO<sub>2</sub> flux with a slight source to the atmosphere. Those authors suggest the temperature-sensitive metabolic and physical-chemical process cause significant impact on the spatial distribution of pCO<sub>2sw</sub> at the BS.

Due to the major role in understanding climate, the biogeochemical cycles, the global energy balance, mass and energy fluxes are important study fields (Trenberth et al. 2009, Takahashi et al. 2009, Le Quéré et al. 2018, Fay et al. 2018). Changes in energy and mass fluxes between the ocean and atmosphere are controlled mainly by wind speed, air and sea temperature, humidity, radiation and evaporation (Sato 2005). The SO provides major contributions to maintaining our planet's climate and plays an important role in the nutrient distribution to other oceans basins (Fay et al. 2018). However, due to its distance and hostility and adverse nature, it is difficult to collect *in situ* data (Pezzi et al. 2021, Monteiro et al. 2020). *In situ* data is typically collected in the summer because

the complex environment for experimentation. Therefore, the utilization of satellite data have been complement the in situ data, which help to improve our knowledge of the role of the SO in the global climate (Shutler et al. 2016, Benallal et al. 2017, Wannikhoff & Triñanes 2017, Lohrenz et al. 2018).

The main objective of this work is to investigate the behavior of CO<sub>2</sub> fluxes at the Drake Passage and the Bransfield Strait west coastal areas under different atmospheric and oceanic conditions, during the Spring of 2018 on high spatiotemporal resolutions when compared with traditional CO<sub>2</sub> fluxes estimations. This article is outlined as follows: the section Materials and Methods presents the study area and the experimental design. The Results and Discussion section brings the results and discussion. We finish this article by presenting the conclusions.

## **MATERIALS AND METHODS**

### **Study area**

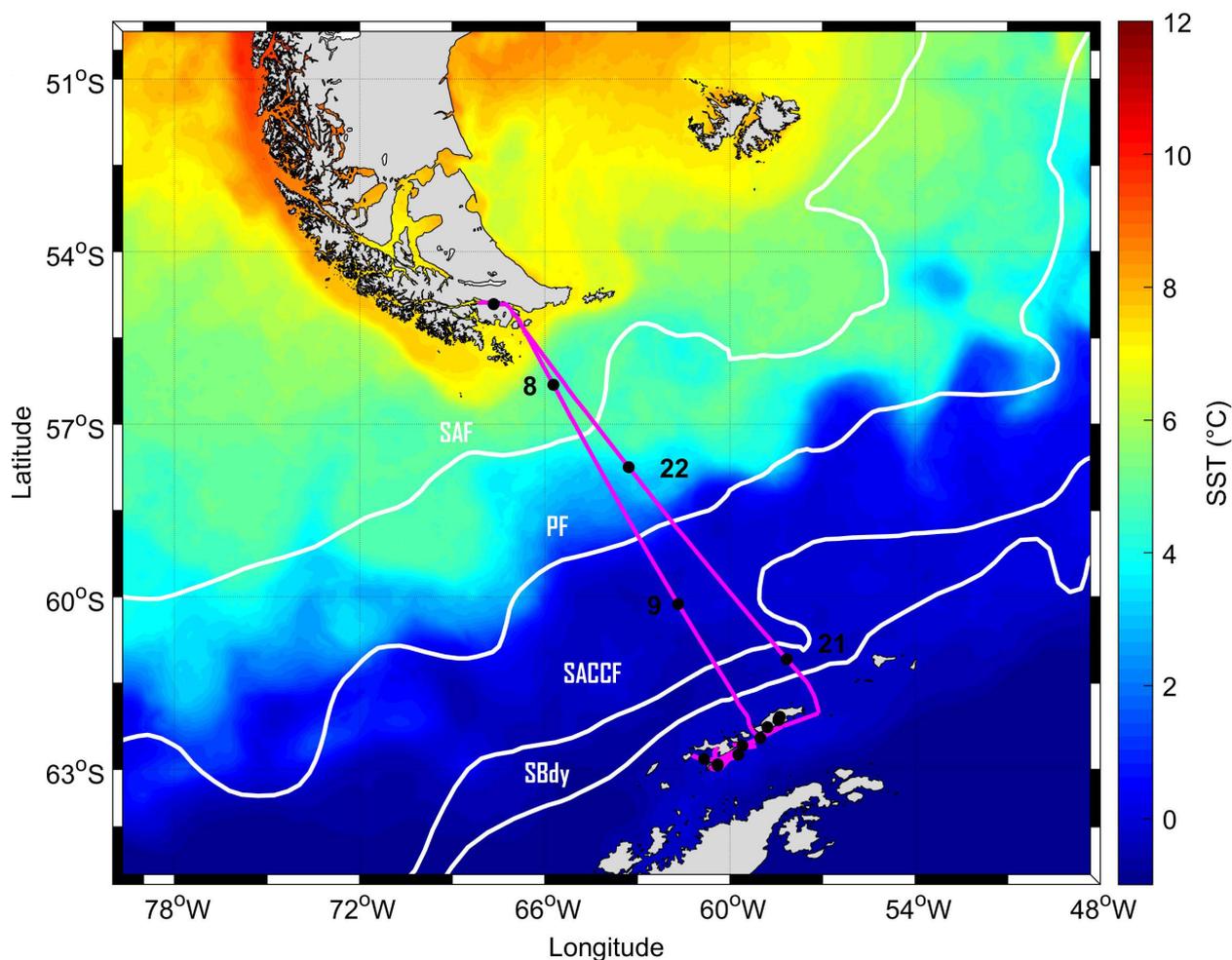
The main oceanic structure in the SO is the Antarctic Circumpolar Current. It is characterized by strong flows eastward that connect all ocean basins and is responsible for distributing physical and biogeochemical properties around the world (Orsi et al. 1995, Rintoul et al. 2001, Ito et al. 2018). The SO is characterized by extreme winds, strong meridional temperature gradients, and high variability of seasonal climate (e.g. sea ice cover; Swart et al. 2019).

The study region analyzed here is the Atlantic sector of the SO, comprising DP and BS at the east coastal region of the South Shetland Islands. They are in the northwest region of the Antarctic Peninsula and are influenced by waters coming from the southeast sector of DP, BS and the Weddell Sea (WS). The DP comprises the Subantarctic front (SAF), Polar Front (PF), South Antarctic circumpolar front (SACCF), and southern boundary (SBdy, Figure 1). The region that goes from the Antarctic continent to the PF is the Antarctic Zone, and the region between the PF and the Subtropical Front is the Subantarctic Zone (Orsi et al. 1995).

The BS encompasses a transition zone between the Bellingshausen Sea and the WS. According to Lopez et al. (1999) this strait is mainly controlled by the interaction of two different fluxes: (i) the warmer and less saline waters from the Bellingshausen Sea (which enters on passages further west at South Shetland Islands) and (ii) the colder and more saline waters from the WS (which enters near the Joinville island). The frontal structure results from the meeting of these two currents, named the Bransfield Front. The BS also is influenced by Antarctic Circumpolar Current that promotes intrusions of Circumpolar Deep Water associated to climatic modes (Barllet et al. 2018). The DP waters also enter at BS, but stay near to the South Shetland Islands, and their interference at BS is negligible (Zhou et al. 2002). Our study area includes the DP and BS as seen in Figure 1.

### **Observed data**

The data sets used here were collected by a micrometeorological tower installed on the bow of the Brazilian Navy Polar Vessel (Po/V) Almirante Maximiano (H41) during the Antarctic Operation 37 (OP37) between 08 to 22 November 2018. This oceanographic cruise is part of the activities planned and developed by the Studies Center of Ocean-Atmosphere-Cryosphere Interaction (CIInt) supported by the National Institute for Cryosphere Technology Science that meets the objectives of the ATMOS Project. Those projects surged as a response to a Brazilian Antarctic Program (PROANTAR) scientific call.



**Figure 1.** Route of the Brazilian Navy Polar Vessel (Po/V) Almirante Maximiano (H41) and study area. Composite for the period between November 08 to 22 November 2018, Sea surface temperature (°C) derived from Multi-scale Ultra-high Resolution (MUR). White lines: Subantarctic front (SAF), polar front (PF), South Antarctic circumpolar front (SACCF), and southern boundary (SBdy) are frontal positions as defined by Orsi et al. (1995)

The ship tracks are illustrated in Figure 1 and are overlaid on the sea surface temperature (SST) field, which highlights the intense along track SST gradients, characteristic of the Antarctic Circumpolar Current (Orsi et al. 1995). The H41 and micrometeorological tower used in the campaign are shown in Figure 2. The micrometeorological tower was installed approximately 16 m above sea level with a similar setup used in previous cruises in the Southwestern Atlantic (Pezzi et al. 2016, Oliveira et al. 2019, Santini et al. 2020, Souza et al. 2021). More recently this same setup was used in an oceanic mesoscale eddy turbulent flux study at Brazil-Malvinas Confluence (BMC) by Pezzi et al. (2021).

For direct CO<sub>2</sub> turbulent fluxes measurements, in the ocean-atmosphere interface, were used micrometeorological sensors sampling in high-frequency rate (20 Hz; Table I). The sensors included a three-dimensional Sonic Anemometer with an integrated CO<sub>2</sub>/H<sub>2</sub>O Gas Analyzer (IRGASON, Campbell Scientific, Inc., Logan, UT, USA), a 3-axis IMU (MotionPak 2, Systron Donner), a magnetic compass



**Figure 2. Brazilian Navy Polar Vessel (Po/V) Almirante Maximiano (H41) with its micrometeorological tower during the OP37, between 08 to 22 November 2018.**

(KVH C100) and a Garmin GPS (GPS16X). The three-dimensional (3-D) linear accelerations, angular rates and geographical position of the ships were measured at the same frequency as the primary measurements used for computing the CO<sub>2</sub> fluxes. The sonic anemometer was fixed in a 1 m long metal bar installed perpendicularly to the vertical mechanical structure of the micrometeorological towers and forward to the ship's bows. This configuration allowed measurements to avoid the flow distortions of the ships' structure on the vertical component of the wind vector (Santini et al. 2020). The tower sensors were tested and calibrated by the Meteorological Instrumentation Laboratory of INPE before and after the experiment. The Infrared Gas Analyzer (IRGA) is calibrated following the manual instructions (Campbell Scientific 2016) using two different gas concentrations of CO<sub>2</sub>, and zero humidity concentration and dew point temperature for the H<sub>2</sub>O. The first part of the procedure simply measures the CO<sub>2</sub> and H<sub>2</sub>O zero and span, without making adjustments. This allows the CO<sub>2</sub> and H<sub>2</sub>O gain factors to be calculated. These gain factors quantify the state of the analyzer before the zero-and-span procedure and were used to correct recent measurements for drift. The last part of the zero-and-span procedure adjusts internal processing parameters to correct subsequent measurements. For zero we used the Analytical Nitrogen 5.0 with minimum purity of the 99.999% to CO<sub>2</sub> and H<sub>2</sub>O. The

**Table I. Description of the sensors installed in the micrometeorological tower, during the OP37, between 08 to 22 November 2018.**

Data Source (sampling frequency)	Sensor / Manufacturer	Meteorological Variable
Micrometeorological Tower (20 Hz)	3D Sonic Anemometer and Gas Analyzer (IRGASON/CAMPBELL)	CO <sub>2</sub> concentration (mg m <sup>-3</sup> ); H <sub>2</sub> O concentration (g m <sup>-3</sup> ); u, v e w (m/s);
	Motion Pack II/ Systron Donner	Angular velocity (deg s <sup>-2</sup> ); Acceleration (m s <sup>-2</sup> )
Micrometeorological Tower (0.06 Hz)	PT101/CAMPBELL	Atmospheric pressure (hPa)
	HC2S3/VAISALA	Air temperature (°C); Relative humidity (%)
Micrometeorological Tower (20 Hz)	GPS/Garmin	Ship heading (°) Ship velocity (m/s)

CO<sub>2</sub> SPAN was obtained using N<sub>2</sub> balanced CO<sub>2</sub> at a concentration of 396.45 +/- 0.05ppm. The H<sub>2</sub>O SPAN was obtained using a Li-Cor LI-610, with the accuracy of ± 0.2 °C dew point.

Unlike traditional measurements performed for oceanic and atmospheric pCO<sub>2</sub> monitoring, where a closed path IRGA (i.e. LI7000 Licor Biogeosciences) was used, we used an open path sensor (IRGASON, Campbell Scientific), where its optical cells were exposed. Closed path sensors require more frequent calibration and quality control than open path sensors. In addition, because the gas needs to travel a path to reach the optical cell, it loses turbulent frequencies compromising the quality of the CO<sub>2</sub> and H<sub>2</sub>O fluxes (Fratini et al. 2012). The IRGASON, according to the manufacturer’s manual (Campbell Scientific 2016), has a monthly calibration recommendation, a period shorter than the duration of our experiment. The calibration before and after the field campaign was sufficient to maintain the quality of the sampled data. In order to reduce the influence of salt and dust accumulation on the IRGASON optical cells, periodic cleaning of its cells was performed at least weekly. During the processing of the high frequency data, we followed the quality check proposed by Foken et al. (2005).

**Eddy Covariance method**

The Eddy Covariance (EC) method is based on the covariance between vertical wind components and the gas concentration in the near surface of the atmosphere, which was used to determine turbulent fluxes of mass and heat (Arya 2001, Stull 1988). The EC method measures the covariance between the turbulent fluctuations around their mean and to the dry air density mean during a determined sample interval. The CO<sub>2</sub> flux ( $F_{CO_2}$ ) is mathematically defined by Equation 1.

$$F_{CO_2} = \overline{\rho a w'c'}$$
(1)

where  $F_{CO_2}$  is the CO<sub>2</sub> flux in μmol m<sup>-2</sup> s<sup>-1</sup>, the bars correspond to the means and the apostrophes indicate the turbulent fluctuations around the mean;  $\rho a$  is the dry air density (kg m<sup>-3</sup>),  $w'$  is the vertical wind component (m s<sup>-1</sup>),  $c'$  is the ratio of CO<sub>2</sub> to dry air density (μmol mol<sup>-1</sup>).

Wind data sampled by mobile platforms need corrections to remove the influence of ship movements. The spurious fluctuations caused by these movements must be removed, with the methodology applied by Edson et al. (1998) and Miller et al. (2008) originally based on Fujitani (1981). A detailed description of the wind data correction to remove ship's movement influence can be found in Hackerott et al. (2018) and Santini et al. (2020). The wind speed sampled on a mobile platform can be corrected using Equation 2.

$$\vec{V}_{real} = T_{ae} \vec{V}_{obs} + T_{ae} (\vec{V}_t + \vec{W} \vec{r}) + \vec{V}_n \quad (2)$$

Where  $\vec{V}_{real}$  is the real wind speed vector at the moment of measurement;  $\vec{V}_{obs}$  is the speed measured by the anemometer;  $\vec{V}_t$  and  $\vec{W}$  are the angular and linear velocities of the measuring equipment itself, respectively;  $\vec{V}_n$  is the ship's travel speed;  $\vec{r}$  is the anemometer position vector in relation to the motion sensor and  $T_{ae}$  is the coordinate transformation matrix from the anemometer reference system to the earth coordinate system (x-axis, y-axis and z-axis).

According to Dong et al. (2021), the flux uncertainty from the motion correction procedure is less than 6%. There are a potential flux bias resulting from instrument calibration (gas analyzer, anemometer and meteorological sensors required to calculate air density: air temperature, relative humidity and pressure) is up to 4 %. The propagation bias for the imperfection calibration of each sensor can be up to 7%.

After the wind data correction, the turbulent flux calculations were performed by using the EddyPro - version 6.0<sup>®</sup> software (<https://www.licor.com/eddypro>) developed by LI-COR Environmental. We used the Webb Correction (Webb 1982) in order to minimize the moisture environmental interference in CO<sub>2</sub> data samples. In addition, this software was set to remove spurious values and to calculate the average flux in a 30-min window. Similar calculations based on EC were used in SW Atlantic for heat fluxes (Pezzi et al. 2016, Santini et al. 2020), momentum fluxes (Hackerott et al. 2018) and CO<sub>2</sub> fluxes (Oliveira et al. 2019, Pezzi et al. 2021). Recently Pezzi et al. (2021) showed these calculations for both heat and CO<sub>2</sub> fluxes over a warm core eddy in the SW Atlantic. A complementary variable used in this study is the friction velocity ( $u^*$ ). This variable gives us information about how turbulent the environment is (Arya 2001).

### Satellite and reanalysis data

The satellite and reanalysis data set were used as auxiliary data to complement the understanding of the surface characteristics of the ocean's mesoscale and synoptic atmospheric conditions in the study region. The satellite data used in this study were: SST from the Multi-scale Ultra-high Resolution (MUR) with a spatial resolution of 1 km and daily temporal resolution. This study also used the Sea Surface Salinity (SSS) from the Soil Moisture – Ocean Salinity (SMOS) with daily temporal resolution and 0.25° spatial resolution and Chlorophyll (Chl) from Visible Infrared Imaging Radiometer Suite (VIIRS) sensor aboard the Suomi-NPP satellite (SNPP) with daily and 4 km of temporal and spatial resolutions. The Reanalysis derived data were the Sea Level Pressure (SLP), Air Temperature ( $T_{air}$ ), and wind speed and direction were obtained from the European Centre for Medium-Range Weather Forecast (ECMWF) ERA5 (Hersbach et al. 2018). The ERA5 has the hourly temporal resolution with a 0.25° spatial resolution. More details are presented in Table II.

**Table II. Satellite and reanalysis data used in this project, during the OP37, between 08 to 22 November 2018.**

Variable	Data Source	Spatial resolution	Temporal resolution
Chlorophyll	VIIRS	4 km	Daily
Salinity	SMOS	0.25°	Daily
Sea Surface Temperature	MUR	1 km	Daily
Wind speed and direction	ERA 5	0.25°	Hourly
Sea Level Pressure	ERA 5	0.25°	Hourly

## RESULTS AND DISCUSSION

The study region was split into two areas during H41 cruise, the DP and the BS, due to the different oceanic and atmospheric characteristics found between them. The CO<sub>2</sub> fluxes varied along the ship's route. Table III summarizes all data for the study region (DP, BS and total area). The CO<sub>2</sub> fluxes data were discarded under atmospheric stable conditions when the Monion-Obukhov stability parameter was greater than 0.2 (here,  $\zeta > 0.2$ ). This is due to the inaccuracy in measuring turbulent fluxes when the turbulence is very small or intermittent (Sun et al. 2018, Yusup & Liu 2016, Pattey et al. 2002).

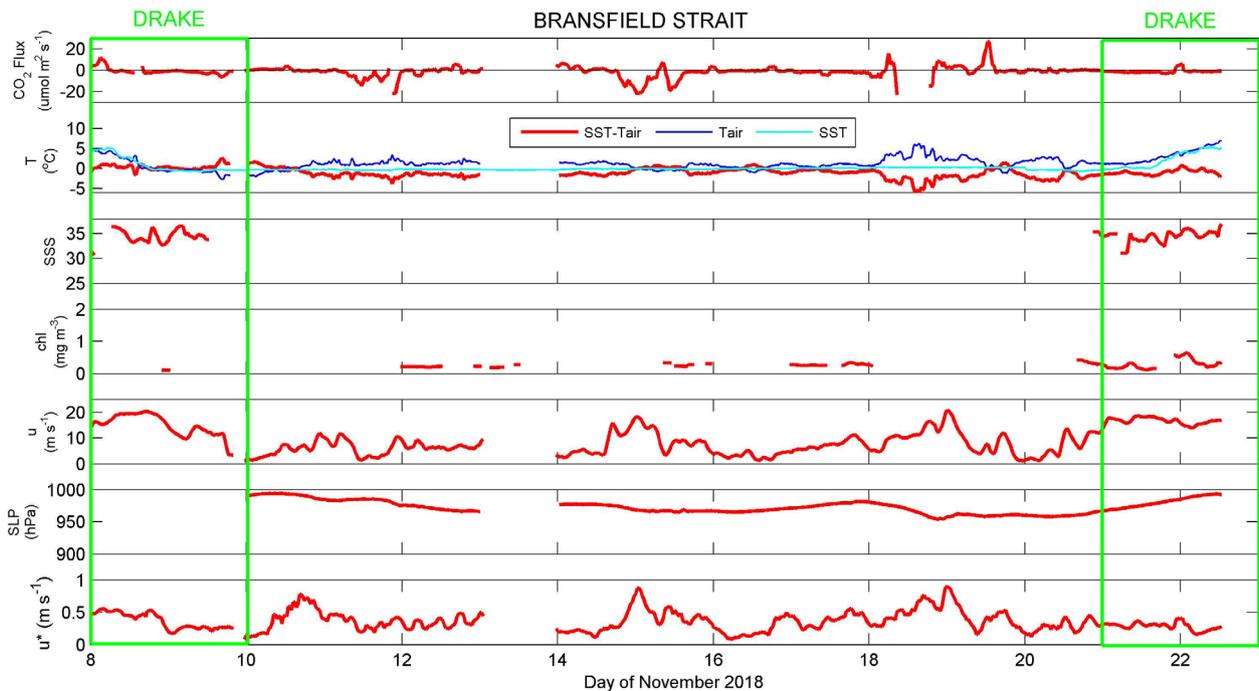
Our experiment was conducted during the Spring of 2018 (08 to 22 November 2018), which may have impacted on fluxes direction, and as a result both areas, DP and BS, acted on average as CO<sub>2</sub> sink. Those results agree the mean behavior for those areas for the entire season (Munro et al. 2015, Monteiro et al. 2020). However, the variability of the pCO<sub>2sw</sub> may affect the flux results during the season. The pCO<sub>2sw</sub> at DP changes during the spring, as seen by Fay et al. (2018), where their values were higher at the beginning of the season. Munro found at DP, at the south of the PF, that the increasing pCO<sub>2sw</sub> is slower than pCO<sub>2atm</sub>, making this area a persistent CO<sub>2</sub> sink. The phytoplankton blooms typically occur at south of DP during spring (Carranza & Gille 2015). At the BS for late spring, photosynthesis decreases the CO<sub>2</sub> partial pressure in the surface seawater, enhancing ocean CO<sub>2</sub> uptake (Caetano et al. 2020).

The BS uptaked on average 38.59% more CO<sub>2</sub> than DP, as shown in Table III. This difference is attributed to the variability of both atmospheric and oceanic conditions along the H41's route. During the study period, the mean SST decreased from the DP towards BS (Figure 1 and Table III). The SSS data did not cover the entire area, there was just some data especially for the BS region. The Chl data also has gaps, due to clouds cover in this area during cruise period. These gaps are a result of how Chl is obtained, which is through a passive sensor that suffers interference from the clouds on its quality measurements. The BS presented more turbulence in the atmosphere boundary layer, with a maximum u\* value of 0.9, allied to that the wind speed reached maximum value, 20.7 m s<sup>-1</sup>.

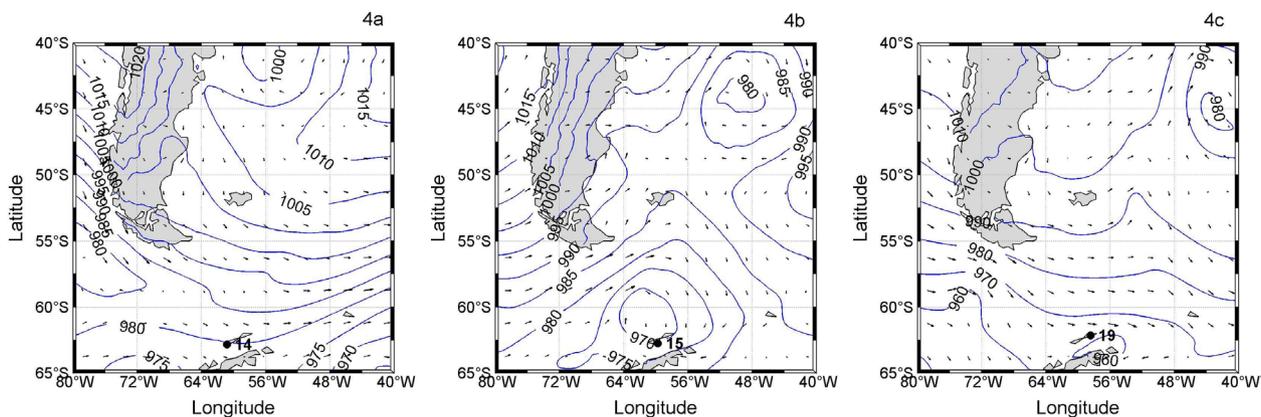
The BS is characterized by colder waters than DP, which increases the CO<sub>2</sub> solubility and due the difference of partial pressure of carbon dioxide ( $\Delta p\text{CO}_2$ ) between ocean and atmosphere, that may direct the fluxes to the ocean. In addition, during the sampled period, the BS had a predominance of stable atmospheric conditions contributing to the region act as a CO<sub>2</sub> sink. The stability condition is observed in the marine atmospheric boundary layer (MABL), it is due to the difference between SST - T<sub>air</sub> (Figure 3). The SST-T<sub>air</sub> at the near-surface interface is an atmospheric stability parameter

**Table III.** Mean, maximum, and minimum values of the Ocean-atmosphere CO<sub>2</sub> fluxes (CO<sub>2</sub> Flux) (mmol m<sup>-2</sup>d<sup>-1</sup>); Sea Level Pressure (SLP) (hPa) (Air Pressure), Wind speed (m s<sup>-1</sup>); and Friction velocity (u\*) (m s<sup>-1</sup>), Sea Surface Salinity (SSS); Sea Surface Temperature (SST) (°C); Chlorophyll-a concentration (chl) (mg m<sup>-3</sup>); for the Drake Passage, Bransfield Strait and Total area. Values obtained along the ship track and the data were collected in the OP37 during the period of 08 to 22 November 2018.

		CO <sub>2</sub> flux	SLP	Wind speed	u*	SST-Tar	SSS	SST	chl
Drake Passage	mean	-1.70	980.94	15.48	0.33	-0.24	34.44	1.45	0.27
	max	21.38	993.40	20.29	0.56	2.47	36.98	5.31	0.64
	min	-11.46	967.35	1.30	0.08	-1.99	30.70	-0.76	0.10
Bransfield Strait	mean	-2.77	972.04	7.17	0.37	-1.21	35.11	-0.13	0.26
	max	47.84	994.35	20.73	0.90	1.70	35.38	0.32	0.41
	min	-41.05	953.08	1.00	0.08	-5.92	34.35	-0.76	0.19
Total area	mean	-2.49	973.22	9.27	0.36	-0.97	34.48	0.26	0.26
	max	47.84	994.35	20.73	0.90	2.47	36.98	5.31	0.64
	min	-41.05	953.08	1.00	0.08	-5.92	30.70	-0.76	0.10



**Figure 3.** Time series of oceanographic and meteorological variables taken along the Po/V H41 route, from 08 to 22 November 2018. Ocean-atmosphere CO<sub>2</sub> fluxes (CO<sub>2</sub> Flux) (μmolm<sup>-2</sup>s<sup>-1</sup>); Sea Surface Temperature - air temperature (TSM-Tar) (°C), Sea Surface Temperature (SST), and Air temperature (Tair) (°C); Sea Surface Salinity (SSS); Chlorophyll-a concentration (chl) (mg m<sup>-3</sup>); Wind speed (m s<sup>-1</sup>); Sea Level Pressure (hPa) (SLP) and Friction velocity (u\*) (m s<sup>-1</sup>) The green rectangle separates the 2 areas: Drake Passage and Bransfield Strait.



**Figure 4.** Sea mean level pressure (blue lines), wind direction (arrows) and Po/V H41 location (black point) during the days 14, 15 e 19 November 2018, 00h for each day. Data from Era5.

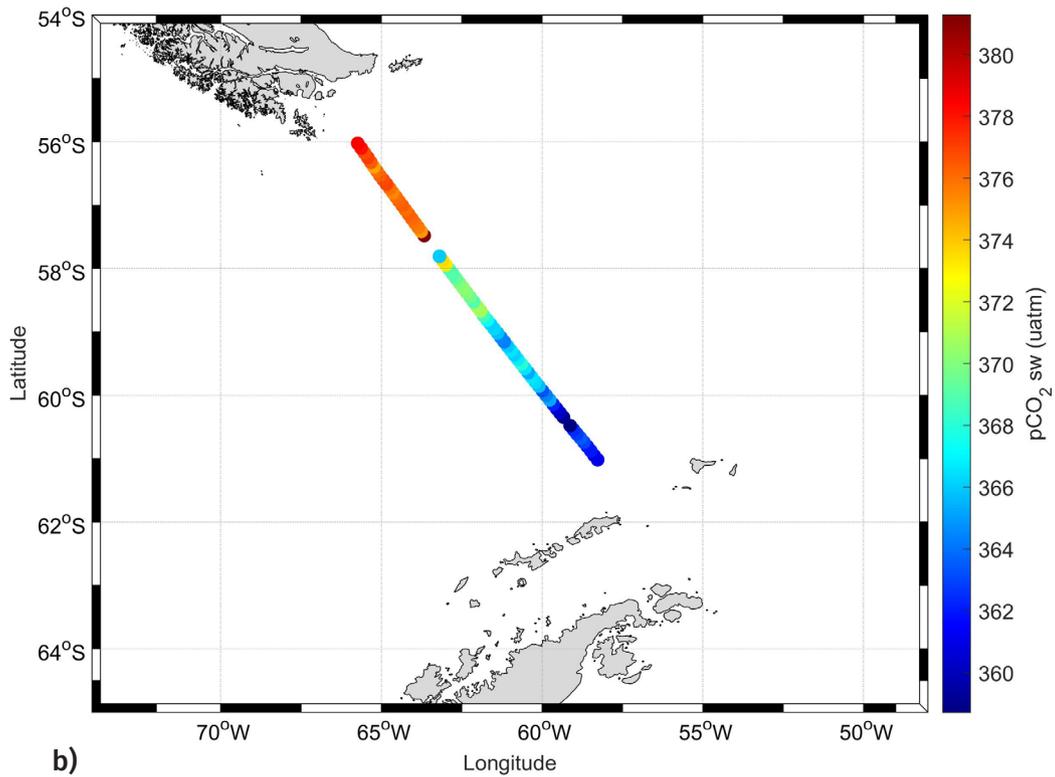
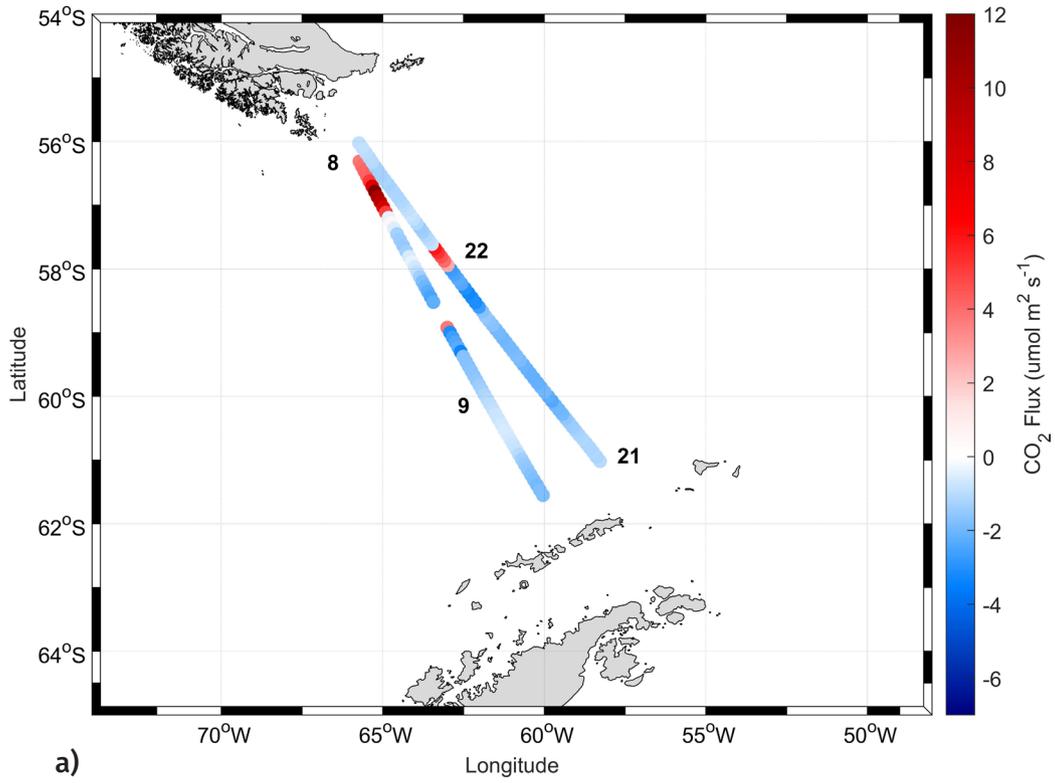
that indicates the preferential surface flux direction. When  $SST - T_{air} > 0$ , MABL is unstable, and when  $SST - T_{air} < 0$ , MABL is stable (Pezzi et al. 2005, 2009, 2016, De Camargo et al. 2013). Besides, during the ship's route, light to moderate rain occurred on some days. This rainfall allied to the influence of glacial meltwater dilution could reduce the salinity concentration in the ocean, also could induce the upwelling of nutrient-rich water supporting declines in  $pCO_{2sw}$  if light is not limiting for primary producers. The glacial meltwater inputs could influence in carbonate chemistry, by the dilution of carbonated ion concentration, so with a reduction of  $pCO_{2sw}$ . This condition, combined with colder waters that increase the ocean CO<sub>2</sub> solubility, could favors the CO<sub>2</sub> fluxes to be directed to the ocean. This result suggests the complexity of the factors controlling the spatial distribution of  $pCO_{2sw}$  in BS. Similar results were found by Ito et al. (2018), for this region. The authors also investigated the role played by surface waters in controlling the  $pCO_{2sw}$  and sea-air CO<sub>2</sub> fluxes in the Northern Antarctic Peninsula region. For the BS, during the Summer of 2009, the physical effects such as glacial meltwater discharges, oceanic fronts and eddies, thermodynamic effects and stratification of the mixing layer also modified the  $pCO_{2sw}$  variability. When considering the BS, the biological processes were responsible for the CO<sub>2</sub> sink in this area, but during 2009, the physical processes dominated, and the area was a weak source of CO<sub>2</sub>. Caetano et al. (2020) suggested the temperature might cause significant variability in the ocean surface distribution of CO<sub>2</sub> over short shoreline distances in the Northern Antarctic Peninsula. During the period from 14 to 15 November 2018, the ship was near to a low pressure atmospheric system as seen in Figure 4a e 4b and produced strong winds at the surface ( $\sim 17 \text{ m s}^{-1}$ ) as well as high-friction velocities ( $\sim 0.8 \text{ m s}^{-1}$ ; Figure 3). These factors favored the vertical mass movement and the ocean surface mixing that driving the fluxes to the ocean. According to Wanninkhof & Triñanes (2017), the increase in wind speed affects the absorption of CO<sub>2</sub> by the oceans regardless of the direction of flow.

However, changes in  $pCO_{2sw}$  under the influence of glacial meltwater input in the BS region, could influence the CO<sub>2</sub> flux behavior. The glacial meltwater and sea-ice melting input modify the surface layer stability and favors the development of phytoplankton blooms (Varela et al. 2002). Changes in the salinity, derived from freshwater input, may cause the nitrate (NO<sub>3</sub><sup>-</sup>) reduction caused by biological utilization reducing seawater alkalinity that has as consequence the increase of the  $pCO_{2sw}$  becoming sources of CO<sub>2</sub> (Takahashi et al. 2014) as observed some peaks on days of November 15, 18

and 19. Monteiro et al. (2020) found the Northern Antarctic Peninsula absorbed more CO<sub>2</sub> in the Spring and Summer than Autumn and Winter. Those authors showed in the Northern Antarctic Peninsula, in autumn and winter, upwelling events that increased the remineralized carbon in the sea surface, leading the region to act as a CO<sub>2</sub> source to the atmosphere. Furthermore, the peak on 19 November 2018, where the ocean acted as a source of CO<sub>2</sub>, was due to a combination of some other factors: proximity of a low atmospheric pressure system, with approximately 950 ha (Figure 4c) and light to moderates surface winds (less than 10 m s<sup>-1</sup>). Those factors contributed to the vertical movement in the MABL, thus decreasing CO<sub>2</sub> concentrations in the atmosphere near the ocean surface. As a result, the CO<sub>2</sub> fluxes were directed from ocean to atmosphere, with a mean value of 20 μmol m<sup>-2</sup> s<sup>-1</sup> (Figure 3). On the other days 10, 12, 16, 17 and 20 of November 2018, the CO<sub>2</sub> fluxes were near the neutrality, with a stable MABL and low turbulence, thus inhibiting the mass exchange at the ocean-atmosphere interface

The DP on average behaved as a sink of CO<sub>2</sub> as seen in Table III and Figure 5a. The main causes were associated with the colder SST (1.45 °C), and fresher (34.44) waters as seen in Table III. Thereby, the water properties such as SST and SSS had more impact on CO<sub>2</sub> fluxes compared to the presence of Chl, which had low concentration at DP. The Figure 5a shows in the south of the PF has acted as a CO<sub>2</sub> sink, due to the pCO<sub>2sw</sub> being lower than the pCO<sub>2atm</sub> (Munro et al. 2015), influenced by the cold and fresh water. However, the CO<sub>2</sub> fluxes at DP are less intense than at BS, due to the presence of the intense upwelling process around 60 – 65 °S, which increases remineralized carbon to the surface (Takahashi et al. 2012, Henley et al. 2020). The mean pCO<sub>2sw</sub> for the DP was 368 μatm, value higher than as found by Fay et al. (2018), it was approximately 355 uatm in November of the period between 2002 and 2016, in DP. Similar results were found for Ito et al. (2018) in this region, for summer 2008. In their study which took place in the Northern Antarctic Peninsula and observed the role of surface water on controlling pCO<sub>2sw</sub> and air CO<sub>2</sub> flux, the DP also presented a low concentration of Chl. However, in this study in the summer of 2008, DP acted as a source of CO<sub>2</sub>. The surface Chl concentration is a proxy for the presence of primary production which has a role in the air-sea CO<sub>2</sub> fluxes as they may have a significant control on the gas partial pressure in the seawater (Monteiro et al. 2020, Henley et al. 2020). Song et al. (2015) discovered in their investigation the role of mesoscale eddies in modulating air-sea CO<sub>2</sub> flux in DP. In this study, the mesoscale eddies SST had a negative correlation with pCO<sub>2sw</sub> in the ocean during the summer. Moreover, they highlighted that the dissolved inorganic carbon has more impact on CO<sub>2</sub> modulation than it does on temperature. However, Munro et al. (2015) reported the importance of the DP in the CO<sub>2</sub> sink for the SO during winter, especially in the south of the PF. Previous studies had reported the impacts of the SST and SSS on CO<sub>2</sub> fluxes, e.g., Woolf et al. (2016). And, found that SST has more considerable effects on the CO<sub>2</sub> ocean solubility (Woolf et al. 2016). This can may the main cause that led to less CO<sub>2</sub> assimilation by the ocean, at DP, where the warmer waters in this region produced less solubility of CO<sub>2</sub> in the ocean when compared to the BS.

At DP the ocean acted as a source of CO<sub>2</sub> to the atmosphere as seen in the CO<sub>2</sub> flux peaks during 8 and 22 of November 2018 (Figure 3 and 5a). Those days the ship was located at the north of the PF, that region has similar pCO<sub>2sw</sub> and pCO<sub>2atm</sub>, indicating near-neutral air-sea CO<sub>2</sub> flux or slight source to the atmosphere, those results are similar to the Munro et al. (2015) and Caetano et al. (2020). The pCO<sub>2sw</sub> on the PF north was higher than to the south (Figure 5b), with mean values of 375 uatm, similar values found Ito et al. 2018. Moreover, this fact is also related to the unstable condition observed in



**Figure 5.** a) Ocean-atmosphere CO<sub>2</sub> fluxes (CO<sub>2</sub> Flux) (μmolm<sup>-2</sup>s<sup>-1</sup>), and b) pCO<sub>2sw</sub> (μatm) with Po/V H41 route at Drake Passage during the days 8, 9, 21 e 22 November 2018.

the MABL observed during those days produced an intensification of the wind speed at surface and above it within MABL vertical extension. Consequently, more turbulence was produced and shown by the  $u^*$ , which favored the transfer of mass between the sea surface and the atmosphere (Wanninkhof & Triñanes, 2017). On the following days, 9 and 21 November 2018, when the ship was surveying over DP, the CO<sub>2</sub> fluxes were near to zero as seen in Figure 3 and 5a. In other words, there was no mass exchange between the ocean and the atmosphere. In this period, there was a predominance of low turbulence of less than 0.5 m s<sup>-1</sup> (Figure 3), which inhibited the CO<sub>2</sub> fluxes.

The climate modes of variability, such as El Niño-Southern Oscillation (ENSO) and Southern Annular Mode (SAM), impact the variability of the surface carbonate system especially on interannual scale. During the November of 2018 the El Niño was active and SAM was in a positive phase, in this case, some studies indicate more CO<sub>2</sub> uptake in the Northern Antarctic Peninsula (Brown et al. 2019, Costa et al. 2020). However, other studies have opposite results, they found that in the positive SAM phase the ocean acted as a CO<sub>2</sub> source due to the reduction in biological activities (Lovenduski et al. 2007; Leung et al. 2015). Another study did not find any effect of the SAM on the CO<sub>2</sub> carbon sink variability for 35 years (Keppler & Landschützer 2019). Our study period (8 to 22 November 2018) was conducted during a positive and active phase of the SAM and El Niño, and the area was a sink of CO<sub>2</sub>. The results could have some influence of those climate modes of variability. However, it is difficult to address the sink CO<sub>2</sub> behavior in the area due to the climate modes of variability. The influence of ENSO and SAM changing the carbonate system parameters still not well understood in the scientific community.

## CONCLUSIONS

This study showed the impacts of different atmospheric and oceanic conditions on the ocean-atmosphere CO<sub>2</sub> fluxes based on a combination of *in situ*, satellite, and reanalysis data sets. The *in situ* CO<sub>2</sub> fluxes data were collected in the DP and the BS in the second phase of OP37, covering the period from 8 to 22, November 2018. The CO<sub>2</sub> fluxes were obtained with the Eddy Covariance method (Miller et al. 2008, Pezzi et al. 2021). The synoptic oceanic conditions were analyzed with chlorophyll, SSS and SST from satellites. The atmospheric synoptic conditions were obtained through ERA5 reanalysis data set analyzing  $T_{air}$ , SLP, wind speed and direction.

The BS and DP behaved as CO<sub>2</sub> sinks on average, where the main cause was attributed to the colder water that intensified the CO<sub>2</sub> solubility in the ocean. Comparing the mean value of CO<sub>2</sub> fluxes, the BS uptaked on average 38.59% more CO<sub>2</sub> than DP. The DP, on average, behaved as a sink of CO<sub>2</sub> mainly due to physical characteristics. The south of the PF, DP has acted as a persistent CO<sub>2</sub> sink, due to the  $pCO_{2sw}$  being lower than the  $pCO_{2atm}$ , influenced by the cold and fresh water. However, the CO<sub>2</sub> fluxes at DP are less intense than at BS, due to the presence of the intense upwelling process around 60 – 65 °S, which increases remineralized carbon to the surface. There were some peaks of source of CO<sub>2</sub> in the north of the PF at DP, due to the unstable conditions of the atmosphere.

The BS was characterized by its colder waters compared to the DP, that contributes to the ocean act as sink. Furthermore, during the ship route, light to moderate rainfall was recorded in some days. This rainfall may have contributed to the reduction of salinity concentration in the ocean, thus decreasing  $pCO_{2sw}$  directing the fluxes toward the ocean, or minimizing the CO<sub>2</sub> outgassing. In addition, during the sampled period, the BS had a predominance of stable atmospheric conditions

contributing to the region act as a CO<sub>2</sub> sink. However, during the period there were some peaks of CO<sub>2</sub> source at BS, due to the reduction of seawater alkalinity by the glacial meltwater and sea-ice melting inputs, as consequence the increase of the pCO<sub>2sw</sub>. Allied to that, the proximity of a low atmospheric pressure system and light to moderate turbulence and wind at the surface, thus it contributed to the vertical movement in the MABL.

This study supports the hypothesis that ocean-atmosphere CO<sub>2</sub> fluxes are highly dependent on oceanographic and meteorological conditions. This study also contributes to an improved understanding of the importance of the SO in the global carbon balance. The provided evidence shows that it is necessary to continue with observational campaigns in this region, to expand the knowledge about the SO's role in the global carbon dioxide cycle.

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## Author contributions

CCFR, LPP and MFS conceived this study. CCFR conducted the data process, data analysis and wrote most of the manuscript.; LPP and MFS, corrected the manuscript. MSF, MJC, EBR and UAS were on board and collected the data during OP37. LSL, MJC, EBR, UAS, JTC AND JWB participated in the discussion and provided suggestions on the study format.

