# Spatio-temporal variability of CO2 fluxes in the Atlantic sector of the Southern Ocean

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### Abstract

The Southern Ocean (SO) plays a fundamental role in the planet's climate system, due to its ability to absorb and redistribute heat and CO2 (an important greenhouse gas). Besides, the SO interconnects three large oceanic basins the Pacific, the Atlantic, and the Indian Oceans, and it has an important role in the nutrient distribution into these oceans. However, the SO is poorly sampled with most measurements made in austral spring and summer. The variability of the air-sea CO2 flux is estimated, as well as the role of atmospheric and oceanic variables in this variability. The CO2 fluxes are calculated by the bulk parameterization method, in the Atlantic sector of the Southern Ocean, from 2003 to 2022, using in situ measurements, satellites and reanalysis data set. A neural network model is built to produce maps of the partial pressure of CO2 in seawater (pCO2sea). The CO2 flux varies from -0.05 to 0.05 gC m-<sup>2</sup> month-1. The Atlantic sector of the SO is a sink of CO2 in summer and spring and becomes a source in austral winter and autumn. The CO2 absorption intensifies from 2003 to 2022 by 7.6 mmol m-<sup>2</sup>month-1, due stronger westerly winds, related to the trend of the positive phase of the Antarctic Oscillation and the extreme events of El Niño and La Niña.













Estimated pCOsea 350 300 250





# Spatio-temporal variability of CO<sub>2</sub> fluxes in the Atlantic sector of the Southern Ocean

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#### **Key Points:**

The CO<sub>2</sub> flux varies from -0.05 to 0.05 gC m<sup>-2</sup>month<sup>-1</sup> in the Atlantic sector of the Southern Ocean, depending on the seasons, from 2003 to 2022. 

The formation and melting of the sea ice cover has a strong influence on the variation in CO<sub>2</sub> absorption. 

The intensification of westerly winds on circumpolar oceanic fronts has intensified the absorption of CO<sub>2</sub>. 

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### 35 Abstract

The Southern Ocean (SO) plays a fundamental role in the planet's climate system, due to its ability 36 to absorb and redistribute heat and CO<sub>2</sub> (an important greenhouse gas). Besides, the SO 37 38 interconnects three large oceanic basins the Pacific, the Atlantic, and the Indian Oceans, and it has an important role in the nutrient distribution into these oceans. However, the SO is poorly sampled 39 with most measurements made in austral spring and summer. The variability of the air-sea CO<sub>2</sub> 40 flux is estimated, as well as the role of atmospheric and oceanic variables in this variability. The 41 CO<sub>2</sub> fluxes are calculated by the bulk parameterization method, in the Atlantic sector of the 42 Southern Ocean, from 2003 to 2022, using *in situ* measurements, satellites and reanalysis data set. 43 A neural network model is built to produce maps of the partial pressure of CO<sub>2</sub> in seawater 44 (pCO<sub>2sea</sub>). The CO<sub>2</sub> flux varies from -0.05 to 0.05 gC m<sup>-2</sup> month<sup>-1</sup>. The Atlantic sector of the SO is 45 a sink of CO<sub>2</sub> in summer and spring and becomes a source in austral winter and autumn. The CO<sub>2</sub> 46 absorption intensifies from 2003 to 2022 by 7.6 mmol m<sup>-2</sup>month<sup>-1</sup>, due stronger westerly winds, 47 related to the trend of the positive phase of the Antarctic Oscillation and the extreme events of El 48 Niño and La Niña. 49

50

### 51 Plain Language Summary

The Southern Ocean (SO) plays a fundamental role in the planet's climate, due to its strong 52 circulation of ocean waters, thus regulating heat and carbon reservoirs. The SO is an important 53 CO<sub>2</sub> sink for the atmosphere. However, the amount of absorbed CO<sub>2</sub> varies over time, which is 54 still poorly understood. The SO is not well sampled, due to difficulties in accessing the region and 55 inhospitable climate. Most cruises are carried out in the austral spring and summer. Here we use 56 in situ data, satellites, and modeled data to estimate the variability of the air-sea CO<sub>2</sub> flux, and the 57 role of atmospheric and oceanic variables, in the Atlantic sector of the SO from 2003 to 2022. The 58 CO<sub>2</sub> flux is calculated using the difference of partial pressure between the ocean and the 59 atmosphere (bulk method). The CO<sub>2</sub> flux varies from -0.05 to 0.05 gC m<sup>-2</sup> month<sup>-1</sup>, with the 60 strongest absorption occurring mainly in summer and spring. The absorption of CO<sub>2</sub> from 2003 to 61 2022 has intensified, due to the increase in wind speed in the region, related to atmospheric and 62 oceanic climate conditions. 63

64

# 65 **1 Introduction**

The Southern Ocean (SO) is considered an important  $CO_2$  sink area, with an absorption of -1.0 Pg C/year (Landschützer et al., 2013). The main cause is the cold waters of the region, which results in greater  $CO_2$  solubility (Silva et al., 2017, Rodrigues et al., 2023). In the SO, there is an intense

transformation and formation of water masses, with a strong seasonality (Santini et al., 2018) which helps to control oceanic carbon reservoirs (Goldemberg et al., 2011).

The  $CO_2$  flux (FCO<sub>2</sub>) exchange between the ocean and the atmosphere varies in time and space (Landschützer et al., 2015; Sutton et al., 2021). The oceanic mesoscale may play a crucial role in

these flux exchanges. For example, Pezzi et al. (2021) showed that sea surface temperature (SST) 73 74 anomalies caused by a warm core eddy (WCE) in the Southwestern Atlantic Ocean (SWA) near the SO, exerted a crucial influence on modifying the marine atmospheric boundary layer (MABL) 75 76 by transferring heat and CO<sub>2</sub> from the ocean to the atmosphere. The WCE presence in midlatitudes, surrounded by predominantly cold waters, caused the ocean to act locally as a CO<sub>2</sub> source. 77 Rodrigues et al. (2024) found that the intense horizontal gradient of SST combined with moderate 78 79 wind and turbulence, in the Brazil Malvinas Confluence, modulates FCO<sub>2</sub>, and leading to a CO<sub>2</sub> 80 sink. Seasonal variations are explained by SST variations and biological activity (Landschützer et al., 2015; Sutton et al., 2021). Interannual and decadal variations may be related to changes in deep 81 82 water formation and are associated with the Antarctic Oscillation (AO) and the El Niño-Southern Oscillation (ENSO) (Heinze et al., 2015; Brown et al., 2019; Avelina et al., 2020). Nevertheless, 83 the magnitude of the influence of ENSO and AO on FCO2 variability is still not understood (Sutton 84 et al., 2021). 85

The ENSO, despite occurring in equatorial regions, influences the SST variability and the wind 86 field in some regions of the SO, due to Rossby waves propagation. These waves are generated 87 through vorticity from adiabatic heating, which, when moving south, induce teleconnections 88 between ENSO and the SO climate (Parkinson and Cavalieri, 2012; Parkinson, 2019). ENSO has 89 a La Niña phase (cold phase) and an El Niño phase (warm phase) (Lovenduski et al., 2008). AO 90 is represented by an oscillation in surface pressure systems between medium and high latitudes in 91 the Southern Hemisphere, having positive and negative phases (Thompson and Wallace, 2000) 92 The Antarctic Oscillation is usually defined as the difference in the zonal mean sea level pressure 93 at 40°S (mid-latitudes) and 65°S (Antarctica) (Fogt and Marshall, 2020). 94

The positive AO phase is defined by negative anomalies of geopotential height and temperature, 95 in addition to the increase in the strength of the westerlies that lead to a greater upwelling of carbon 96 97 from the ocean depths to the surface, which reduces the absorption of CO<sub>2</sub>. The opposite occurs in the negative AO phase (Scholfield et al., 2018; Keppler and Landschützer, 2019; Nevison et al., 98 99 2020). During El Niño, there is an increase in the mixing of Circumpolar Deep Water (CDW) with Dense Shelf Water (DSW) advected from the Weddell Sea, leading to greater absorption of CO<sub>2</sub>. 100 The opposite occurs during La Niña (Keppler and landschützer, 2019; Brown et al., 2019; Nevison 101 et al., 2020; Costa et al., 2020; Avelina et al., 2020). 102

The SO location, the high seasonality and ice cover, make it difficult to carry out oceanographic cruises, generating a lack of spatio-temporal information from the existing data set (Takahashi et al., 2009; Sabine et al., 2013; Bakker et al., 2016). There are few measurements in autumn and winter, most of them are made in austral summer and spring (Parkinson et al., 2012; Meijers et al., 2014; Monteiro et al. 2020). This makes it necessary to use tools that interpolate available measurements.

Here we use *in situ* data from the unprecedented collections of the Antarctic Modeling and Observation System (ATMOS) project, the Surface Ocean CO<sub>2</sub> Atlas (SOCAT) (https://www.socat.info), satellite and reanalysis datasets to estimate the air-sea CO<sub>2</sub> flux and its variability from 2003 to 2022. As pCO<sub>2sea</sub> is not available from satellite, we build an Artificial Neural Network (ANN) model to produce maps of pCO<sub>2sea</sub>. The ANN has become an increasingly efficient tool in the field of CO<sub>2</sub> studies and has been applied in estimations of pCO<sub>2sea</sub> and CO<sub>2</sub>

- fugacity (Landshutzer et al., 2013; Zeng et al., 2014; Hadjer et al., 2016). In addition, it performs hetter than linear regressions (Hadjer et al., 2016)
- better than linear regressions (Hadjer et al., 2016).

117 Thus, this study contributes to increase our knowledge of the spatio-temporal variability of the

118 FCO<sub>2</sub> in the Atlantic sector of the Southern Ocean, as well as the role of atmospheric and oceanic

119 variables in explaining this variability. From this, it becomes possible to understand the causes of

120 the intensification of the  $CO_2$  absorption, as well as the consequences for the studied region.

121 Section 2 describes the methodology and the data. Section 3 brings the main results found in this

- study. Section 4 discusses the analysis carried out and, finally, Section 5 presents the conclusions
- 123 of this work.

### 124 **2 Materials and Methods**

125 The study area is presented in section 2.1, followed by in situ data (section 2.2) related to the

ATMOS Project, satellite and reanalysis data set (section 2.3). Direct measurements of  $CO_2$  fluxes

obtained from the ATMOS oceanographic cruise are described in Section 2.4. The training of the neural network based on ATMOS and SOCAT data set is described in Section 2.5. The  $CO_2$  flux

neural network based on ATMOS and SOCAT data set is described in Section 2.5. The  $CO_2$  flux data estimated from the bulk parameterization is described in section 2.6. Finally, the FCO<sub>2</sub>

- 129 data estimated from the bulk parameterization is described in section 2.6. Fina
- 130 variability analysis technique is described in section 2.7.

# 131 **2.1 Study area**

The SO has the largest and fastest ocean current on the globe, the Antarctic Circumpolar Current 132 (ACC), driven by the strong easterly winds characteristic of southern polar latitudes (Orsi et al. 133 1995; Klinck and Nowlin, 2001; Barkek et al., 2007). The oceanic circulation of the SO occurs as 134 follows: the upper cell of the meridional circulation is driven by wind, which causes upwelling of 135 the CDW along inclined isopycnals, due to divergent Ekman transport, which upwell in the ACC 136 (Marshall et al., 2012). At the surface, CDWs become Subantarctic Modal Waters (SMW) and 137 Antarctic Intermediate Waters (AIWs), which makes the upper part of the Southern Overturning 138 Circulation (Sallée et al., 2010). Surface buoyancy flows, ocean-atmosphere interactions, ice 139 shelves, and sea ice produce cold, salty Dense Shelf Water (DSW). DSW becomes the dense 140 141 Antarctic Bottom Water (ABW), formed in seas such as the Ross and Weddell seas, and along the east coast of Antarctic (Ohshima et al., 2013). 142

143 When the ACC reaches the Drake Passage, the narrowing between Antarctica Peninsula and southern end of South America causes an increase in the ACC speed, and results in the 144 strengthening of the main circumpolar oceanic fronts present in the region (Figure 1, Sprintall, 145 2003). These fronts, from south to north, are: 1) the Southern Boundary (BF), which is the northern 146 limit of the cold water mass; 2) the Southern Antarctic Circumpolar Current Front (SACCF), which 147 extends approximately along the Antarctic slope and deviates slightly northwards at 56° W; 3) the 148 149 Polar Front (PF), formed by the convergence of Antarctic and subantarctic waters, and 4) the Subantarctic Front (SAF) which defines the northern boundary of the ACC. To the north of the 150 SAF is the Subtropical Front (STF), which marks the northernmost extent of subantarctic waters 151 (Orsi et al. 1995). 152

Around Antarctica there is a cover of sea ice, which varies seasonally. During the warm season it reduces, due to melting (minimum in February), and during the cold season it expands, due to 155 freezing (maximum in September) (Parkinson and Cavalieri, 2012; Parkinson, 2019). In addition

to the aforementioned factors that can affect the  $FCO_2$ , there is also the passage of atmospheric

157 cold fronts. Indeed, the fronts cause changes in the surface wind field, pressure, temperature, and

other atmospheric variables during their trajectory, in addition to their interactions with the sea

surface (Wallace and Hobbs, 2006).



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**Figure 1** - Study area location in the Atlantic sector of the Southern Ocean. The isolines illustrate the circumpolar oceanic fronts from south to north, and they are the Southern Boundary (SB), the Southern Antarctic Circumpolar Current Front (SACCF), the Polar Front (PF), and the Subantarctic Front (SAF). To the north of the SAF is the Subtropical Front (STF) (Orsi et al. 1995).

### 165 **2.2** *In situ* data

*In situ* data were obtained from the ATMOS project (Table 1). The oceanographic cruise occurred

167 during OPERANTAR XL, aboard Brazilian Navy Polar Vessel (Po/V) Almirante Maximiano (H-

168 41), between November 2021 and February 2022 (Pezzi et al. 2021; Voermans et al, 2021). The

data was collected by sensors installed in the meteorological tower at the bow of the ship (available

in Carvalho, G. T., & Pezzi, L. P., 2024), and data measured by LI-COR (LI-850) installed in the laboratory aft of the ship (available in Carvalho, G. T., & Pezzi, L. P., 2024) (Table 1).

The Sea Surface Salinity (SSS) data were interpolated from reprocessing systems that combine 172 data from NASA's Soil Moisture Active Passive (SMAP) and European Space Agency's (ESA) 173 174 Soil Moisture Ocean Salinity (SMOS) satellites and in situ measurements (https://doi.org/10.48670/moi-00051). The Sea Surface Temperature (SST) data are from the 175 reprocessing of Along Track Scanning Radiometer (ATSR), Sea and Land Surface Temperature 176 Radiometer (SLSTR) and Advanced Very High Resolution Radiometer (AVHRR) satellite data 177 by the ESA SST Climate Change Initiative (CCI) and Climate Change Service (C3S) projects, they 178 were produced from the Operational Sea Surface Temperature and Sea Ice Analysis system 179 (OSTIA) (https://doi.org/10.48670/moi-00169). 180

SSS, SST, sea level pressure (SLP), H<sub>2</sub>O and partial pressure of CO<sub>2</sub> gas in sea (pCO<sub>2sea</sub>) were obtained from SOCAT. Interpolated Air temperature (Tair) and wind speed were obtained from the MERRA-2 satellite (https://disc.gsfc.nasa.gov/datasets/M2I1NXLFO\_5.12.4). Interpolated concentrations of CO<sub>2</sub> ( $xCO_{2air}$ ) were downloaded from Global View (https://gml.noaa.gov/). pCO<sub>2air</sub> can be considered as the pressure that the gas is in equilibrium in the air, which it would

exert on a surface of water containing dissolved  $CO_2$ . The p $CO_{2air}$  was obtained from  $xCO_{2air}$ , Patm

187 and  $pH_2O$  (Landshutzer et al., 2013).

Sensor	Model	Manufacturer	Variables sampled
Integrated CO <sub>2</sub> /H <sub>2</sub> O Open-path gas analyzer and 3D sonic anemometer	IRGASON	Campbell Scientific	CO <sub>2</sub> density, H <sub>2</sub> O density 3D wind components air temperature, air pressure
Multi axis inertial sensing system	Motion Pack II	Systron Donner Inertial	3D accelerations and 3D angular velocities
GPS	GPS16X-HVS	Garmin	Position

Infrared gas analyzer	LI-850	Li-cor	CO <sub>2</sub> concentrations in
		Biogeosciences	water

Table 1. Meteorological and oceanic sensors installed on the micrometeorological tower and ship
 hull during the ATMOS cruise.

### 190 2.3 Satellite and reanalysis data set

191 A collection of satellites and reanalysis data set were used for the study of the Atlantic sector of

the SO and for the  $FCO_2$  estimation. The  $FCO_2$  estimation was made using data set from satellite multi-sources to complete the time series for the period from 2003 to February 2022.

The satellite data used in this study were: The  $CO_2$  estimates used are from the Atmospheric 194 Infrared Sounder (AIRS) sensor, on board the Aqua satellite, with a spatial resolution of  $2.5^{\circ} \times 2^{\circ}$ , 195 from 2003 to 2014 (https://disc.gsfc.nasa.gov/datasets/AIRX3C2M\_005). The 2015 to 2022 CO2 196 estimates are from the Orbiting Carbon Observatory - 2 (OCO-2) satellite, which provides 197 estimations with spatial resolution of 1.29 km 2.25 198 а × km (https://disc.gsfc.nasa.gov/datasets?keywords=oco2). The SLP, Tair and wind speed were 199 obtained from the Modern-Era Retrospective analysis for Research and Applications, Version 2 200 (MERRA-2) satellite. With spatial resolution of 0.5° x 0.625°, from 2003 to 2022. 201

Monthly reanalysis SST and SSS were obtained from Multi Observation Global Ocean 202 ARMOR3D (https://doi.org/10.48670/moi-00052). These analyses combine satellite data from 203 Advanced Very High Resolution Radiometer (AVHRR) and Advanced Microwave Scanning 204 205 Radiometer-2 (AMSR-2), and in situ observations distributed by NOAA's National Climatic Data Center, with a spatial resolution of  $0.25^{\circ} \times 0.25^{\circ}$ , from 2003 to 2022. The Chlorophyll products 206 used in this work are from Global Ocean Color (https://doi.org/10.48670/moi-00052), with spatial 207 208 resolution of 4 km. This product uses data from several satellites, such as Sea-viewing Wide Fieldof-view Sensor (SeaWiFS), Moderate-Resolution Imaging Spectroradiometer (MODIS), Medium 209 Resolution Imaging Spectrometer (MERIS), Visible Infrared Imaging Radiometer Suite sensor 210 (VIIRS) aboard the Suomi-National Polar-orbiting Partnership (SNPP), Joint Polar Satellite 211 System-1 (JPSS1), Ocean Land Color Imager (OLCI) aboard the Sentinel-3A (S3A) and Sentinel-212 3B (S3B). 213

### 214 2.4 Eddy Covariance Method

Eddy Covariance (EC) is the method used to obtain direct measurements of turbulent fluxes from 215 the covariance between the fluctuations in the mean CO<sub>2</sub> density and the vertical component of 216 the wind, thus providing the flux of CO<sub>2</sub> between the ocean surface and the atmosphere as indicated 217 in the Equation 1 (Miller et al., 2010; Pezzi et al 2016; Santini et al., 2020). These measurements 218 are made at high temporal frequencies and are performed in the surface layer of the Marine 219 Atmospheric Boundary Layer (MABL) (Mcgillis et al., 2001, Pezzi et al., 2021). The MABL is 220 the layer nearest to the ocean surface, which is where momentum, heat and gas exchange take 221 222 place (Foken et al., 2008). The EC has already been used in previous studies in the Southwestern Atlantic such as Pezzi et al. (2016), Santini et al., (2020) and Pezzi et al, (2021) to study the MABL 223

stability. The role of roughness and stability on momentum fluxes at Brazil-Malvinas Confluence was studied in Hackerott et al. (2018). Recently Pezzi et al. (2021) studied the turbulence and instability of the MABL caused by an oceanic WCE and consequent modification in the behavior of CO<sub>2</sub>, heat and momentum fluxes in the BMC. Additional information about EC can be found in these cited articles, as the methodology employed here is the same.

The FCO<sub>2</sub> is given in  $\mu$ mol m-<sup>2</sup>s-1, by the fluctuations of the vertical wind component (w' in m/s) and the CO<sub>2</sub> mixing ratio (c' in mg/m<sup>3</sup>), in relation to their averages, and the average dry air density (a in  $\mu$ mol.m-<sup>3</sup>):

 $FCO_2 = \rho_a \, \underline{w'c'} \tag{1}$ 

The calculation of the FCO<sub>2</sub> was performed using the free open-source software EddyPro®v7.0.9, offered by LI-COR Biosciences Inc. (EddyPro v7.0.9). Fluxes are calculated using 30-minute averages of high-frequency (20 Hz) data. Before the FCO<sub>2</sub> estimation, the wind data were corrected due to the ship's movement (Miller et al. 2008; Rodrigues et al., 2023).

### 237 2.5 Artificial neural network to estimate pCO<sub>2sea</sub>

The ocean  $CO_2$  partial pressure (p $CO_{2sea}$ ) data are very sparse in the study area. Therefore, an Artificial Neural Network (ANN) was used to fill spatial and temporal gaps in p $CO_{2sea}$  (Nakaoka et al., 2013; Landshutzer et. al., 2013). In this study, 279.480 observations from SOCAT and ATMOS over the 2003-2022 period, are used to reconstruct the p $CO_{2sea}$  for the study region. The dataset is split into two distinct groups (Géron et al., 2017):

1) 85% of the data are randomly selected for utilization during the training phase. This will beidentified as the Train set.

245 2) The remaining 15% are allocated for the neural network diagnosis phase. Called Test set.

The standard procedure of data normalization (scaling) is implemented on every input and output 246 variable, aiming to achieve a mean of zero and a standard deviation of 1 for each of them. The 247 network consists of an input layer composed of 3 neurons, 3 hidden layers with 10, 8 and 5 nodes 248 respectively and an output layer, that is, the estimate of pCO<sub>2sea</sub>, as shown in Figure 2. For the 249 precision analysis of the pCO<sub>2sea</sub> estimate, the mean squared error and Pearson's coefficient were 250 defined (Géron et al., 2017). Previous studies that applied this methodology over the Atlantic 251 Ocean used SST, SSS and chlorophyll in data input (Landshutzer et. al., 2013). However, in this 252 study, during the initial tests to produce the model, the set of variables SST, SSS and pCO<sub>2air</sub> 253 (Figure 2a) proved to be more efficient in estimating  $pCO_{2sea}$  than the input data used by 254 Landshutzer et. al., (2013). The Pearson correlation (r) showed that the variables SSS, SST and 255 chlorophyll (Figure 2a) as input data for the ANN model, have r = 0.59 with the observed pCO<sub>2sea</sub> 256 data. While with SSS, SST and pCO<sub>2air</sub> data (Figure 2b) the correlation is greater (r = 0.69). 257 Furthermore, the root mean-square (RMS) error calculated based on the two sets of input data for 258 the ANN was lower with the SSS, SST and pCO2air data (RMS = 33.47) (Figure 2c), from than 259 in relation to the set of SSS, SST and chlorophyll variables (RMS = 40.41) (Figure 2b). The model 260

- was produced in the Python 3 programming language, available at Carvalho, G. T & Mejia, C.,
   2024. Two platforms were also installed: TensorFlow and Keras (Chollet et al., 2018).
- The ANN estimates  $pCO_{2sea}$ . With  $pCO_{2sea}$ , it is then possible to calculate  $FCO_2$  on a large spatial and temporal scale.



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**Figure 2** - a) Scheme of the produced Deep Artificial Neural Network. The input data are salinity (SSS) (psu) and sea surface temperature (SST) (°C) and CO<sub>2</sub> partial pressure of air (pCO<sub>2air</sub>) ( $\mu$ atm). The ANN includes 3 hidden layers with 10, 8 and 5 nodes. The output layer gives the seawater partial pressure of CO<sub>2</sub> (pCO<sub>2sea</sub>) ( $\mu$ atm). b) Pearson correlation between pCO<sub>2sea</sub> estimates using SSS, SST and Chl as ANN input data. c) Pearson correlation between pCO<sub>2sea</sub> estimates using SSS, SST and pCO<sub>2air</sub> as ANN input data. Scatterplots and regression lines were

- calculated from Test data (with 15% of the data set).
- 273 2.6 Bulk parameterization

FCO<sub>2</sub> was determined by the bulk parameterization (FCO<sub>2BK</sub>) shown in Equation 2, where FCO<sub>2BK</sub> is defined by the product of the ocean-atmosphere CO<sub>2</sub> partial pressure gradient  $\Delta pCO_2$  ( $\Delta pCO_2$ = pCO<sub>2sea</sub> - pCO<sub>2air</sub>), the solubility (s) and the wind-dependent air-sea gas transfer velocity (K) (Farias et al., 2013; Ito et al., 2016):

$$FCO_{2BK} = s.k. \Delta pCO_2(sea-air)$$
(2)

The solubility (s)  $CO_2$  in seawater was defined with the relationship used by Weiss, 1974. K was calculated according to Sweeney et al. (2007). The direction and part of the magnitude of FCO<sub>2</sub> are defined by  $\Delta pCO_2$ , whose variability is dominated by  $pCO_{2sea}$  in our observations.

are defined by  $\Delta p CO_2$ , whose variability is dominated by  $p CO_{2sea}$  in our observations.

The bulk parameterization was applied using satellite and reanalysis data, from 2003 to 2022. Due to each of the satellite and reanalysis data having different spatial resolutions, as can be seen in

Table 2, it was necessary to re-grid them. The interpolation was based on the spatial resolution of

 $CO_2$  observations from the AIRS and OCO-2 satellites. From 2003 to 2014 the data had a final

spatial resolution of  $2^{\circ} \times 2.5^{\circ}$ , and from 2015 to 2022 the final spatial resolution was  $0.5^{\circ} \times 0.625^{\circ}$ .

287 The interpolation was performed using the Cubic Convolution Interpolation tool applied using the

Python 3 tool. In this method, the 16 closest pixels (4x4 window) are considered and the

interpolation is performed by adjusting cubic polynomials to each column, to then interpolate a new cubic polynomial to these results. It is the most suitable method for studies that need to work

with data at different resolutions (Cunha et al., 2012; Dourado et al., 2014).

# 292 **2.7 CO**<sub>2</sub> flux variability analysis

The analysis of  $FCO_2$  in the Drake Passage covered the months of February of the years 2016 and 2019 based on bulk SOCAT data, and from 12/01/2021 to 02/15/2022 based on the ATMOS

project collections (Pezzi et al., 2021; Voermans et al, 2021; Rodrigues et al., 2023), obtained by

the Eddy Covariance (EC) method.

Afterwards, the bulk was applied again, but now with satellite data, reanalysis, and ANN, in the Atlantic sector of the Southern Ocean. Next, an analysis of the monthly FCO<sub>2</sub> series was carried out and the role of atmospheric and oceanic variables in FCO<sub>2</sub> variability was described. The influence of ENSO and AO on FCO<sub>2</sub> was also investigated. ENSO and AO information is available from the Climate Prediction Center (CPC), National Oceanic and Atmospheric Administration (NOAA) National Center for Environmental Prediction (NCEP) during the period 2003 to February 2022.

# 304 **3 Results**

In this section we present the results of this study, based on in situ data collection, estimated flows and reanalysis data, in addition to flow estimates resulting from the artificial neural network model.

# **307 3.1 CO<sub>2</sub> flux variability in February**

The monthly FCO<sub>2</sub> in the Drake Passage is presented for February of 2016, 2019 and 2022 (Figure

309 3). Using bulk parameterization with SOCAT data, it was -0.01 gC m<sup>-2</sup>month<sup>-1</sup> in 2016 and -0.005

 $gC m^{-2}month^{-1}$  in 2019. Using eddy covariance with ATMOS data in 2022, the flux was -0.04 gC

 $m^{-2}$ month<sup>-1</sup>. Similar results were observed by Takahashi et al. (2009), with a flux of -0.02 gC m<sup>-1</sup>

 $^{2}$ month<sup>-1</sup>. These values were due to the Southern Ocean acting as a CO<sub>2</sub> sink during the austral

summer (Dejong et al., 2017; Brown et al., 2019; Monteiro et al., 2020). This absorption in the

- summer occurs because it is a period of increased availability of light and nutrients. Nutrients are
- from upwelled Circumpolar Deep Waters, which leads to an increase phytoplankton blooms,
- decreasing  $pCO_{2sea}$ , and increasing  $CO_2$  uptake by the ocean (Ducklow et al., 2013; Heinze et al.,
- 2015; Viana et al., 2021). Despite the predominance of CO<sub>2</sub> absorption in the Drake Passage, there







### 323 **3.3 FCO<sub>2</sub> calculated with artificial neural network.**

The 2003–2022 average FCO<sub>2</sub>, calculated from the maps of pCO<sub>2sea</sub>, was -0.027 gC m<sup>-2</sup>month<sup>-1</sup>, 324 and from *in situ* data was -0.029 gC m<sup>-2</sup>month<sup>-1</sup>, but the average bias is small (-0.002 gC m<sup>-2</sup>month<sup>-1</sup> 325 <sup>1</sup>). FCO<sub>2</sub> from in situ data (SOCAT and ATMOS data) was determined by the bulk method from 326 2003-2022. The comparison between the two fluxes can be seen in the Taylor diagram, which 327 provides a simple graphical representation of what the next one will bring from the other (Figure 328 329 4). In relation to the standard deviation of the observed data, it was 2.4 and that of the model was 1.7 (Figure 4). The root mean square error (RMS) error between the two was 1.5. The FCO<sub>2</sub>, based 330 on the reconstruction of pCO<sub>2sea</sub>, may have overestimated the flow variability by 5.3%. However, 331 this underestimation is low, given what was observed by Gloege et al., (2021) for the Southern 332 Ocean, of 31%. The percentage overestimation is, by definition, inversely proportional to the 333 standard deviation of the model (GLOEGE et al., 2021). According to the dispersion of -0.013 gC 334 335  $m^{-2}$ month<sup>-1</sup>, obtained by the absolute error, it indicates that the amplitude of the monthly variability of the CO<sub>2</sub> flow produced may be close to the original. The correlation with the flow calculated 336 with *in situ* data was high (r = 0.76), being higher than that observed in Gloege et al., (2021) with 337 338 r = 0.54.



339

Figura 4 - Taylor diagram for comparison between the  $FCO_2$  calculated with *in situ* data (Reference) and from the ANN pCO<sub>2sea</sub> reconstruction (ANN). The blue lines are the root-meansquare (RMS) error.

To detect possible increase or decrease of  $CO_2$  absorption, we calculate the monthly  $CO_2$  flux anomalies over 2003-2022 using the maps produced by the ANN (Figure 5).

The area from 40°S to 45°S exhibits large seasonal changes with positive flux in the months of 345 December, January, February (austral summer) and in the months of September, October, and 346 November (austral spring), and negative values in the months of June, July and August (austral 347 winter) and in March, April and May (austral autumn). The region from 45°S to 55°S also exhibits 348 seasonal changes, ranging from being a strong sink of CO<sub>2</sub> in summer and spring, and having 349 reduced absorption in winter and autumn, indicating that it is a year-round sink. This zone is the 350 Antarctic Divergence area, located within the high wind speed zone ( $40-60^{\circ}$ S). The strong winds 351 cause a large vertical mixing of seawater, which increases the exchange of  $CO_2$  at the air-sea 352 interface, explaining the strong CO<sub>2</sub> sink (Arrigo et al., 2007; Le Queré et al., 2007). In this region, 353 the North Atlantic Deep Water resurfaces from 2000 m depth to 200 m, with higher temperatures 354 (Tomczak; Godfrey, 1994). South of  $55^{\circ}$ S is an area of year-round CO<sub>2</sub> absorption. However, 355 absorption is reduced in winter and autumn. During the southern spring-summer, phytoplankton 356 blooms occur near the ice and increase the CO<sub>2</sub> absorption. This indicates the effect of ice cover 357 on the FCO<sub>2</sub> in this region, as observed in Takahashi et al. (2009), Shetye et al. (2017) and 358 Monteiro et al. (2020). 359

In summer, absorption is more intense than in other seasons (Figure 5), absorbing 72% more than 360 in autumn and winter, and 51% more than in the southern spring. The absorption peak occurs 361 mainly in February, and the lowest absorption values are mainly in August, in the study region. 362 This is due to the expansion of sea ice cover that occurs in autumn and winter, with maximum 363 expansion in August and September (Parkinson and Cavalieri, 2012; Parkinson, 2019). The ice 364 cover can extend from the Antarctic continent to 55°S in the Atlantic sector in some years, 365 however, on average it can extend up to 62°S in winter (Takahashi et al., 2009). As winter 366 progresses, ice formation increases, releasing salts, which can contribute to the release of CO<sub>2</sub> into 367 the water. The layer of mixed water under the ice is rich in CO<sub>2</sub>, mainly due to the vertical mixing 368

of deep waters (Nomura et al., 2006; Takahashi et al., 2009). However, in the summer and spring the ice cover melts, and reaches its minimum size in February, which is why this is the month in which the greatest absorption of  $CO_2$  occurs (Wadhams, 2000). Furthermore, in the southern summer and spring there is an increase in light availability and stable stratification of surface water, which allows an increase in primary biological productivity, which leads to an increase in  $CO_2$ absorption during these seasons (Ducklow et al., 2013; Heinze et al., 2015; Viana et al., 2021).

The FCO<sub>2</sub> varies from -0.05 to 0.05 gC m<sup>-2</sup>month<sup>-1</sup> in the Atlantic sector of the SO, absorbed in 375 the summer and spring periods, and in the southern winter and autumn, absorption decreases. CO<sub>2</sub> 376 absorption has intensified in the study area, with an increase of 0.076 gC m<sup>-2</sup>month<sup>-1</sup> from 2003 to 377 2022. This behavior is shaped by wind speed and SST, but mainly by the intensification of winds 378 that increased during the studied period, which may be driven by climate variability (Marshall et 379 al., 2003; Stammerjohn et al., 2008; Brown et al., 2008, 2019). Furthermore, an increasing trend 380 in pCO<sub>2air</sub> was also observed, which has been increasingly higher than in water. The increase in 381 pCO<sub>2air</sub> is due to anthropogenic CO<sub>2</sub> emissions. The rate of increase of pCO<sub>2sea</sub> is slower in highly 382 mixed regions as deeper waters with a lower CO<sub>2</sub> content are brought to the surface. In high 383 stratified regions, the same rate of increase is observed in the ocean and in the atmosphere. 384 Previous studies that modeled future scenarios already expected this response from the Southern 385 Ocean to increased CO<sub>2</sub> emissions (Sabine; Cols., 2004; Friedlingstein et al., 2006; Roy et al., 386 2011; Arora et al., 2013; Steinacher et al., 2013; Zickfeld et al., 2013). These models predicted 387 that in scenarios with high greenhouse gas emissions, there would be a reduction in the efficiency 388 of absorption by the ocean. This occurs because the increase in atmospheric CO<sub>2</sub> concentration is 389 linked to the increase in anthropogenic emissions. Thus, although absorption by the ocean has 390 intensified, the ocean is not able to absorb all the excess CO<sub>2</sub> present in the atmosphere resulting 391 from anthropogenic emissions. 392

In the Drake Passage, the absorption in the summer and spring periods is of -0.01 gc/m<sup>2</sup>.month and -0.013 gC m<sup>-2</sup>month<sup>-1</sup>, respectively. In the autumn and winter periods, there is a reduction in absorption of -0.012 gC m<sup>-2</sup>month<sup>-1</sup>. Similar results were observed by Takahashi et al. (2009). In summer and spring, they observed strong CO<sub>2</sub> absorption, and in autumn and winter there is a reduction in absorption, being -0.09 gC m<sup>-2</sup>month<sup>-1</sup>, -0.02 gC m<sup>-2</sup>month<sup>-1</sup>, 0.01 gC m<sup>-2</sup>month<sup>-1</sup> and 0.013 gC m<sup>-2</sup>month<sup>-1</sup>, respectively.

399 SST anomaly maps produced by reanalysis data (Figure 6) illustrate that some regions of the study area are becoming increasingly warmer over time, which affects  $FCO_2$ . The waters coming from 400 the Pacific Ocean through the Drake Passage to the Atlantic sector of the Southern Ocean are 401 releasing more  $CO_2$  than the expected average (Figure 5). These waters are the waters of the PF. 402 The PF is located approximately at latitude 50°S in the Atlantic oceans and at latitude 60°S in the 403 Pacific, it is a region where CO<sub>2</sub> is released, due to its average surface temperature being higher 404 than that south of this region. This behavior was also observed with SOCAT and ATMOS data 405 (Figure 3). The surface water south of this region moves north and sinks when it reaches the PF, 406 thus causing convergence at the surface (Pickard and Emery, 1990). However, with the increase 407 in SST, the PF shows stronger CO<sub>2</sub> outgassing. To the north of the PF there is an increase in CO<sub>2</sub> 408 release, this region has higher temperatures, due to the dominant effect of seasonal SST changes 409 (Tomczak; Godfrey, 1994). However, to the south of the PF there is an increase in CO<sub>2</sub> absorption. 410 In this region the surface waters of the Antarctic Zone have very low temperatures, reaching values 411 412 close to the freezing point  $(-1,9^{\circ}C)$ , as a result of the summer melting of the sea ice and surface 413 cooling in winter (Tomczak; Godfrey, 1994). Below the surface in the Antarctic Zone, extending

414 up to 4000 m deep, is the Antarctic Circumpolar Water (AACW), with temperatures of 1.5 to  $2.5^{\circ}$ C

415 (Tomczak; Godfrey, 1994). Close to the coast of the Antarctic continent, some regions also

intensified the release of  $CO_2$ , despite being a region with a higher potential temperature than at the shelf break, the SST was also warmer. This region is where the Deep Circumpolar Water rises

417 the shell break, the SST was also warner. This region is where the Deep Cheunpolar Water rises 418 over the slope to enter the platform, it has warmer and saline waters (Baines, 2006). However, the

waters that are a source of  $CO_2$ , are expanding southward, and the waters that are sinks of  $CO_2$ 

420 become stronger sinks. This is due to the increase in strength and southward displacement of the

421 westerly winds, associated with the positive trend of the AO, which forced the migration of the FS

towards the Antarctic continent, thus migrating warm and saline waters, which cause the release

of CO<sub>2</sub>. This trend towards the positive phase of OA is due to the increase in greenhouse gases
(Thompson; Solomon, 2002; Marshall et al., 2003; Cai et al., 2005; Cai; Cowan, 2007).



425

426 **Figure 5** –Monthly anomalies of the  $CO_2$  flux (in gC m<sup>-2</sup>month<sup>-1</sup>) calculated from 2003 to 2022.



427

Figure 6 – Monthly sea surface temperature (°C) anomalies produced after reanalysis, from 2003
 to 2022.

### 430 **3.4 Variability of CO<sub>2</sub> flux**

In the region between  $-63^{\circ}$  to  $-54^{\circ}$ W and  $-59^{\circ}$  to  $-62^{\circ}$ S, in the Drake Passage, an analysis of the temporal variability of FCO<sub>2</sub> and atmospheric and oceanic variables was carried out, including the climate indices ENSO and OA, based on the historical series from 2003 to 2022.

434 There is a tendency towards negative  $CO_2$  values throughout the period studied (Figure 7a), with peaks and decreasing values, which follow the seasonality of the SST (Figure 7b). The SLP varies 435 inversely to the temperature, that is, when the temperature increases the SLP decreases and vice 436 versa (Figure 7e, 7b). Furthermore, the SLP appears to be inversely proportional to the FCO<sub>2</sub>, so 437 it is possible to observe that where there is a drop in the SLP, there is an increase in the values of 438  $FCO_2$ , which become more positive (Figure 7e). This relationship between SLP and  $FCO_2$ 439 indicates a decrease in the concentration of atmospheric CO<sub>2</sub> near the surface and, consequently, 440 there is a tendency to transfer  $CO_2$  from the ocean to the atmosphere. Wind speed is strongest in 441 the months of March to November, ranging from 11-13 (m/s), and reduces in the months of 442 December to February (southern summer), ranging from 9-10 (m/s) (Figure 7g). CHL varies 443 seasonally, CHL blooms occur during the austral spring-summer, and reduce in the austral autumn-444 winter (Figure 7c). The months of August and September have the lowest concentrations of CHL. 445

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It was observed from \Delta pCO_2 (Figure 7d), which defines the direction and part of the magnitude of FCO<sub>2</sub>, that pCO<sub>2air</sub> is what dominates the variability of FCO<sub>2</sub> in this study. \Delta pCO_2 has a decreasing
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trend, indicating that the direction of  $FCO_2$  is towards the atmosphere towards the ocean. An 448 449 increasing trend in pCO<sub>2air</sub> was also observed (Figure 7h), which has been increasingly higher than in pCO<sub>2sea</sub>. The increase in pCO<sub>2air</sub> may be caused by the high concentration of anthropogenic CO<sub>2</sub> 450 present in the air, which is not being captured by the ocean with the same efficiency as before. 451 Previous studies that modeled future scenarios already expected this response from the SO to 452 increased CO<sub>2</sub> emissions (Sabine and Cols., 2004; Friedlingstein et al., 2006; Roy et al., 2011; 453 Arora et al., 2013; Steinacher et al., 2013; Zickfeld et al., 2013). These models predicted that in 454 scenarios with high greenhouse gas emissions, there would be a reduction in the efficiency of 455 absorption by the ocean. The weakening of  $CO_2$  absorption by the SO is due to the existence of a 456 natural limit in gas exchange at the atmosphere-ocean interface, CO<sub>2</sub> dissociation, turbulent mixing 457 and ocean circulation, which causes only a certain percentage of excess  $CO_2$  atmospheric pressure 458 to be absorbed. Therefore, although oceanic absorption is increasing, there are still high 459

460 concentrations of CO<sub>2</sub> in the atmosphere (Le Quéré et al., 2013; IPCC, 2013; Heinze et al., 2015).

461 CO<sub>2</sub> absorption increased by 0.076 gC m<sup>-2</sup>month<sup>-1</sup>, from 2003 to 2022. Winds were intense, 462 averaging 11.1 m/s (Figure 7g). The SST was higher than the air temperature (SST >Tair) 463 throughout the studied period (Figure 7b), which indicates that the Marine Atmospheric Boundary 464 Layer (CLAM) in this region is unstable and that an intense exchange of CO<sub>2</sub> occurs, as suggested 465 by Pezzi et al. (2009).

The months 05/2005, 05/2007, 06/2009, 06/2011, 06/2015, 07/2019 and 07/2021 had absorption 466 anomalies (FCO<sub>2</sub> varying from 0.075 gC m<sup>-2</sup>month<sup>-1</sup>to 0.2 gC m<sup>-2</sup>month<sup>-1</sup>) (Figure 7a), that is, 467 absorption was more intense in these periods than the expected average. These periods showed 468 that the high negative values of FCO<sub>2</sub> were due to high values of SLP (ranging from 1008 hPa to 469 1013 hPa) and low values of SST (ranging from 8°C to 10°C) and Tar (ranging from 4.7 °C to 470 6.7°C), intense winds (ranging from 11 m/s to 12.3 m/s), which caused the exchange of CO<sub>2</sub> at the 471 472 ocean surface to be greater, with K varying from 18 to 33. However, on 02/2013 (FCO<sub>2</sub> 0.0134 gC m<sup>-2</sup>month<sup>-1</sup>) CO<sub>2</sub> absorption was lower than the expected average, due to low SLP values (1006 473 474 hPa) and wind speed, warmer SST and Tair, which caused gas transfer at the ocean-atmosphere interface to be lower, the K was 4.8. 475

Interannual variations are related to the phase variation of OA and ENSO, as observed by 476 Lovenduski et al., 2008, Lenton et al., 2009, Brown et al., 2019, Costa et al., 2020 and Avelina et 477 478 al., 2020. The months when intense reduction in  $CO_2$  absorption occurred, such as 02/2013, had the influence of positive OA (+OA). +OA is defined by negative geopotential height and 479 temperature anomalies. +OA increases the strength of westerly winds that lead to an increase in 480 the upwelling of natural carbon from the depths of the ocean to the surface, causing a reduction in 481  $CO_2$  absorption. However, the opposite occurred in the months 05/2005, 05/2007, 06/2009, 482 06/2011, 06/2015, 07/2019 and 07/2021, which had intense CO<sub>2</sub> absorption, a period of -OA 483 (Gupta and England, 2006; Scholfield et al., 2018; Meredith et al., 2017; Keppler and 484 Landschützer, 2019; Nevison et al., 2020). Furthermore, 06/2015, despite being a +OA month, 485 was the most extreme El Niño period since 1998 (Monteiro et al., 2020). In this case, the role of 486 El Niño was greater than that of OA. During El Niño, there is an increase in the mixing of Deep 487 Circumpolar Waters with Dense Shelf Water advected from the Weddell Sea, leading to greater 488 absorption of CO<sub>2</sub>. The opposite occurs in La Niña (Scholfield et al., 2018; Meredith et al., 2017; 489 Brown et al., 2019; Keppler and Landschützer, 2019; Nevison et al., 2020; Costa et al., 2020; 490 Avelina et al., 2020). The change in OA phase influences the flux variability, being able to increase 491

492 (negative phase) or reduce (positive phase) the absorption of  $CO_2$ . ENSO becomes the main 493 influence only in periods of strong intensity, as occurred in 06/2015. Therefore, most of the time

494 the main modulator of  $FCO_2$  is OA.



495

**Figure 7** – Time series of atmospheric and oceanographic variables in the Drake Passage, from 2003 to 2022.  $CO_2$  flux (FCO<sub>2</sub>) (a), sea surface temperature (SST) and air temperature (Tair) (b), chlorophyll-a concentration (CHL) (c), difference of CO<sub>2</sub> partial pressure between the ocean and the atmosphere ( $\Delta pCO_2$ ) (d), atmospheric pressure at sea level (SLP) (e), salinity surface water (SSS) (f), wind speed (u) (g), seawater partial pressure of CO<sub>2</sub> (pCO<sub>2sea</sub>), atmospheric partial pressure of CO<sub>2</sub> (pCO<sub>2air</sub>) (h).

### 502 **4 Final remarks and conclusions**

This study showed the spatio-temporal variability on the sea-air  $FCO_2$  caused by the ocean and atmosphere conditions, in the Atlantic sector of the Southern Ocean. The  $FCO_2$  calculated through EC method using in situ data collected by ATMOS project (Pezzi et al. 2021; Voermans et al., 2021, Rodirgues, et al., 2023) offered a new source of atmospheric and oceanic data for  $CO_2$ , heat and momentum in the Atlantic Sector of the Southern Ocean.

508 Monthly maps of FCO<sub>2</sub> were produced using an ANN for estimating pCO<sub>2sea</sub> with satellite and 509 reanalysis data from 2003 to 2022. The absolute error between the FCO<sub>2</sub> produced from ANN and 510 that produced with *in situ* data was -1.3  $\mu$ mol/m<sup>2</sup>/month and the correlation was high (r = 0.9). 511 This corresponds to a slight overestimation of 5.3% compared to the 31% obtained by Gloege et

512 al., (2021) in the SO.

- The FCO<sub>2</sub> varies from -0.05 to 0.05 gC m<sup>-2</sup>month<sup>-1</sup> in the Atlantic sector of the SO, with the strongest CO<sub>2</sub> sink occurring in the summer and spring periods, and a lower sink in the austral winter and autumn. The seasonal variation of FCO<sub>2</sub> is modulated by changes in SST, in the Atlantic sector of the SO. In summer absorption is more intense than in other seasons, the peak occurs mainly in February. Summer absorption is 72% greater than in autumn and winter, and 51% greater than in the southern spring. The lowest absorption values occur mainly in August (winter). This is due to the expansion of sea ice cover that occurs in autumn and winter, with maximum expansion
- 520 in August and September.
- From 2003 to 2022, CO<sub>2</sub> absorption has intensified by 0.076 gC m<sup>-2</sup>month<sup>-1</sup>. In summer, absorption
- increased by 0.093 gC m<sup>-2</sup>month<sup>-1</sup> compared to 2003 to 2022. In autumn, winter and spring the increase was 0.11 gC m<sup>-2</sup>month<sup>-1</sup>, 0.14 gC m<sup>-2</sup>month<sup>-1</sup> and 0.1 gC m<sup>-2</sup>month<sup>-1</sup>, respectively, from
- 524 2003 to 2021.
- 525 During the study period, FCO<sub>2</sub> varied spatially, shaped by the characteristics of ocean fronts. The
- areas of the SF, because they have warm and saline waters, act as a source. Areas between the SF and the SAF, characterized by moderate SST and SSS, and intense winds, have strong absorption.
- 528 Finally, there are areas with moderate absorption, located in the regions of the SB, in the SACCF
- 529 and in the PF, which have colder and less saline waters.
- 530 The waters, which act as a source of  $CO_2$ , are expanding southwards, and the waters, which act as
- sinks, have been intensifying the absorption of  $CO_2$ . This is due to the increased strength and
- southward displacement of the westerly winds, associated with the positive trend of the AO, which

forced the migration of the SF towards the Antarctic continent. Thus, warm and saline waters

migrate and cause the release of  $CO_2$ . In addition, the intensification of westerly winds on the circumpolar oceanic fronts intensifies the absorption of  $CO_2$  in this region. The influence of ENSO

- only overlaps with the influence of the OA phase in periods of extreme ENSO, such as what
- 537 occurred in 2015.
- 538 The results of this study show that  $FCO_2$  in the SO are highly dependent on oceanographic and meteorological conditions. The spatial variation of FCO<sub>2</sub> is affected by the displacement of water 539 masses. In addition, the intensification of westerly winds in the SAF, which increases gas exchange 540 at the ocean-atmosphere interface, intensifies the absorption of  $CO_2$  in this region. It also supports 541 previous studies that modeled future scenarios on the reduction in the efficiency of CO<sub>2</sub> absorption 542 by the ocean as a response by the Southern Ocean to the increase in greenhouse gas emissions. 543 544 The ANN model for pCO<sub>2sea</sub> estimates is a very important tool to fill data gaps of pCO<sub>2sea</sub> in difficult-to-access areas, such as the SO, mainly in winter and southern autumn periods. It is also 545 evident that the continuity of *in situ* sampling in this region with high quality data will allow us to 546 improve the models produced and the understanding of the role of dynamic and thermodynamic 547 processes that act as modulating mechanisms of CO<sub>2</sub> fluxes at the ocean-atmosphere interface of 548 the Atlantic sector of the Southern Ocean. 549

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561

# 562 **Open Research**

The Artificial Neural Network (ANN) software was designed to estimate pCO2sea. The ANN used 563 in the article can be found at https://doi.org/10.5281/zenodo.10854860, and can be developed 564 openly in Python 3. Data from the meteorological tower installed on the bow of the Brazilian Navy 565 Polar Ship (Po/V) Almirante Maximiano (H-41) were used to calculate the CO2 flux (FCO2) in 566 567 the EddyPro®v7.0.9 software. These available data are in Carvalho, G. T., & Pezzi, L. P., 2024 (https://doi.org/10.5281/zenodo.10871385). LI-COR (LI-850) data installed in the laboratory aft 568 of the Brazilian Navy Polar Ship (Po/V) Almirante Maximiano (H-41) were used to calculate 569 pCO2sea, available in Carvalho, G. Т., & Pezzi. L. P., 2024 570 (https://doi.org/10.5281/zenodo.10887055). 571

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# 573 **References**

- 574
- Arrigo, k. R., and g. L. Van dijken (2007), Interannual variation in air-sea CO2 flux in the Ross
  Sea, Antarctica: A model analysis, J. Geophys. Res., 112, C03020,
  doi:10.1029/2006JC003492
- Avelina R, da Cunha Lc, Farias Co, Hamacher C, Kerr R & Mata Mm. 2020. Contrasting dissolved 578 organic carbon concentrations in the Bransfield Strait, northern Antarctic Peninsula: insights 579 into **ENOS** and SAM effects. J Mar Syst 212: 1-51. 580 https://doi.org/10.1016/j.jmarsys.2020.103457. 581
- Bakker, Dce, Pfeil, B., Landa, Cs, Metzl, N., O'brien, Km, Olsen, A., et al. (2016) A multi-decade
  record of high quality fCO<sub>2</sub> data in version 3 of the Surface Ocean CO<sub>2</sub> Atlas (SOCAT). *Earth System Science Data*, 8: 383-413. doi:10.5194/essd-8-383-2016
- Benallal, M.A.; Moussa, H.; Lencina-Avila, J.M.; Touratier, F.; Goyet, C.; JAI, M.C. El; 585 POISSON, N.; POISSON, A.. Satellite-derived CO2 flux in the surface seawater of the 586 Austral Ocean south of Australia. International Journal Of Remote Sensing, [S.L.], v. 38, n. 587 UK 1600-1625, 6 fev. 2017. Informa Limited. 588 6, p. http://dx.doi.org/10.1080/01431161.2017.1286054. 589
- Brown, Michael S.; Munro, David R.; Feehan, Colette J.; Sweeney, Colm; Ducklow, Hugh W.;
  Schofield, Oscar M.. Enhanced oceanic CO2 uptake along the rapidly changing West
  Antarctic Peninsula. Nature Climate Change, [S.L.], v. 9, n. 9, p. 678-683, 26 ago. 2019.
  Springer Science and Business Media LLC. http://dx.doi.org/10.1038/s41558-019-0552-3.
- Cai, W.J., Cowan, T. (2007). Trends in Southern Hemisphere circulation in IPCC AR4 models
   over 1950-99: Ozone-depletion vs. greenhouse forcing, *Journal of Climate*, 20(4), 681–693.

Carvalho, G. T. and Mejia, C. (2024). Artificial Neural Network (ANN) to estimate pCO2sea.
 (Version 1.1.0) [Software]. (RNApCO2sea-Carvalho). Zenodo.
 https://doi.org/10.5281/zenodo.10854860

- Carvalho, G. T., & Pezzi, L. P. (2024). Data from the micrometeorological tower of the Antarctic
   Modeling Observation System (ATMOS) project of the 40th Brazilian Antarctic Operation
   (OPERANTAR XL) to calculate the CO2 flux (FCO2) [Data set]. Zenodo.
   https://doi.org/10.5281/zenodo.10871385
- Carvalho, G. T., & Pezzi, L. P. (2024). LI-COR (LI-850) sensor data obtained by the Antarctic
   Modeling Observation System (ATMOS) project during the 40th Brazilian Antarctic
   Operation (OPERANTAR XL) and were used to calculate the partial pressure of CO2
   (pCO2) [Data set]. Zenodo. https://doi.org/10.5281/zenodo.10887055
- Chahine, M., Barnet, C., Olsen, E.T., Chen, L., Maddy, E., 2005. On the determination of
  atmospheric minor gases by the method of vanishing partial derivatives with application to
  CO2: DETERMINATION OF MINOR GASES BY VPD. Geophys. *Res. Lett.* 32
  https://doi.org/10.1029/2005gl024165.
- Chatterjee A., Gierach MM, Sutton AJ, Feely RA, Crisp D., Eldering A., Gunson MR, O'Dell CW,
  Stephens BB, Schimel DS. Influence of El Nino on atmospheric CO<sub>2</sub> over tropical Pacific
  Ocean: Findings from NASA's OCO-2 mission, *Science* 13 out 2017, Vol. 358, Issue 6360,
  eaam5776 DOI: 10.1126/science.aam5776.
- 615 Chollet, f. (2018). Deep Learning with Python (First). Manning Publications Co.
- Clowes, A.J. Influence of the Pacific on the circulation in the South-West Atlantic Ocean. Nature,
   v. 131, p. 189-191, 1933.
- Cook, A. J., FOX, A. J., VAUGHAN, D. G. & FERRIGNO, J. G. Retreating glacier fronts on the
   Antarctic Peninsula over the past half-century. Science 308, 541–544 (2005).
- Costa, R. R. et al. Dynamics of an intense diatom bloom in the Northern Antarctic Peninsula,
   February 2016. *Limnol. Oceanogr.* 66, 1–20 (2020).
- Dejong, Hb & Dunbar, Rb. Air-sea CO2 exchange in the Ross Sea, Antarctica. J. Geophys. Res.
   Oceano 122, 8167-8181 (2017).
- Ducklow, H. W. et al. West Antarctic Peninsula: an ice-dependent coastal marine ecosystem in
   transition. *Oceanography* 26, 190–203 (2013).
- Farias, E. G. G.; Nobre, P.; Lorenzzetti, J. A.; Almeida, R. A. F.; Junior, L. C. I. Variability of air sea CO2 fluxes and dissolved inorganic carbon distribution in the Atlantic basin: a coupled
   model analysis. *International Journal of Geosciences*, v. 2013, p. 249–258, 2013.
- Fogt, Ryan L.; Marshall, Gareth J.. The Southern Annular Mode: variability, trends, and climate
  impacts across the southern hemisphere. Wires Climate Change, [S.L.], v. 11, n. 4, p. 1-24,
  19 maio 2020. Wiley. http://dx.doi.org/10.1002/wcc.652.
- Géron, Aurélien. Hands-on machine learning with Scikit-Learn and TensorFlow: concepts, tools,
   and techniques to build intelligent systems. [S.l.]: "O'Reilly Media, Inc.", 2017.
- Goldemberg, José et al. Antarctica and global changes: a challenge for humanity. Publishing
   company Blucher, 2011.
- Hackerott, J. A. et al. The role of roughness and stability on the momentum flux in the marine
  atmospheric surface layer: A study on the southwestern Atlantic Ocean. J. Geophys. Res.
  Atmos. 123, 3914–3932.https:// doi. org/ 10. 1002/ 2017J D0279 94 (2018).
- Hadjer, M. & Benallal, Mohamed & Goyet, Catherine & Lefèvre, Nathalie. (2016). Satellitederived CO2 fugacity in surface seawater of the tropical Atlantic Ocean using a feedforward
  neural network. *International Journal of Remote Sensing*. 37. 580–598.
  10.1080/01431161.2015.1131872

- Heinze, C., Meyer, S., Goris, N., Anderson, L., Steinfeldt, R., Chang, N., Le Quéré, C., And
  Bakker, D. C. E.: The ocean carbon sink impacts, vulnerabilities and challenges, Earth
  Syst. Dynam., 6, 327–358, https://doi.org/10.5194/esd-6-327-2015, 2015.
- IPCC Intergovernmental Panel on Climate Change, Working Group I Contribution to the Fifth
   Assessment Report, Climate Change 2013 the Physical Science Basis.
- Ito, R. G.; Garcia, C. A. E.; Tavano, V. M.. Net sea-air CO2 fluxes and modelled pCO2 in the
  southwestern subtropical Atlantic continental shelf during spring 2010 and summer 2011. *Continental Shelf Research*, [S.L.], v. 119, p. 68-84, maio 2016. Elsevier BV.
  http://dx.doi.org/10.1016/j.csr.2016.03.013.
- Keppler & Landschützer P. 2019. Regional wind variability modulates the Southern Ocean carbon
   sink. Sci Rep 9(1): 1-10. https://doi.org/10.1038/s41598-019-43826-y.
- Klinck, J. M., and W. D. Nowlinx Jr. (2001), Antarctic Circumpolar Current, in *Encyclopedia of Ocean Science*, 1st ed., pp. 151–159, Academic, San Diego, Calif.
- Landschützer, P.; Gruber, N.; Bakker, D. C. E.; Schuster, U.; Nakaoka, S.; Payne, M. R.; Sasse,
  T. P.; Zeng, J.. A neural network-based estimate of the seasonal to inter-annual variability
  of the Atlantic Ocean carbon sink. *Biogeosciences*, [S.L.], v. 10, n. 11, p. 7793-7815, 29 nov.
  2013. Copernicus GmbH. http://dx.doi.org/10.5194/bg-10-7793-2013.
- Landschutzer, P., et al. (2015), The reinvigoration of the Southern Ocean carbon sink, Science, 349, 6253.
- Le Quéré, C., et al. Saturation of the Southern Ocean CO2 sink due to recent climate change,
   Science, 316, 1735–1738, 2007.
- Le Quéré, C., Andres, R. J., Boden, T., Conway, T., Houghton, R. A., House, J. I., Marland, G.,
  Peters, G. P., van der Werf, G. R., Ahlström, A., Andrew, R. M., Bopp, L., Canadell, J. G.,
  et al.: The global carbon budget 1959–2011, Earth Syst. Sci. Data, 5, 165–185,
  https://doi.org/10.5194/essd-5-165-2013, 2013.
- Lovenduski, N. S., N. Gruber, and S. C. Doney (2008), Toward a mechanistic understanding of
   the decadal trends in the Southern Ocean carbon sink, Global Biogeochem. Cycles, 22,
   GB3016, doi:10.1029/2007GB003139.
- Mcgillis, W.R., Edson, J.B., Fairall, C.W., 2001. Direct covariance air-sea CO2 fluxes. J. Geophys.
   Res. 106, 16,729–16,745.
- 673Meijers, Ajs (2014). The Southern Ocean in the Phase-5 Coupled Model Intercomparison Project.674Philosophical Transactions of the Royal Society of London, Series A: Mathematical,675Physical and Engineering Sciences, 372 (2019),67620130296.https://doi.org/10.1098/rsta.2013.0296
- Meredith et al. Changing distributions of sea ice melt and meteoric water west of the Antarctic
   Peninsula. *Deep Sea Res.* Pt II 139, 40–57 (2017).
- Miller, S. D. et al. Platform motion effects on measurements of turbulence and air-sea exchange
   over the open ocean. *Journal of Atmospheric and Oceanic Technology*, v. 25, n. 9, p. 1683–
   1694, 2008.
- Monteiro, T., Kerr, R. & Machado, E.D. Seasonal variability of net sea-air CO2 fluxes in a coastal
   region of the northern Antarctic Peninsula. Sci Rep 10, 14875 (2020).
   https://doi.org/10.1038/s41598-020-71814-0
- Moussa, H., M. A. Benallal, C. Goyet, And N. Lefèvre. 2016. Satellite-Derived CO2 Fugacity in
  Surface Seawater of the Tropical Atlantic Ocean Using a Feedforward Neural Network.
  International Journal of Remote Sensing 37 (3): 580–
  598.doi:10.1080/01431161.2015.1131872.

Nakaoka, S., Telszewski, M., Nojiri, Y., Yasunaka, S., Miyazaki, C., Mukai, H., and Usui, N.:
Estimating temporal and spatial variation of ocean surface pCO2 in the North Pacific using
a self-organizing map neural network technique, *Biogeosciences*, 10, 6093–6106,
https://doi.org/10.5194/bg-10-6093-2013, 2013.

Nevison, C. D.; Munro, D. R.; Lovenduski, N. S.; Keeling, R. F.; Manizza, M.; Morgan, E. J.;
Rödenbeck, C.. Southern Annular Mode Influence on Wintertime Ventilation of the
Southern Ocean Detected in Atmospheric O2 and CO2 Measurements. *Geophysical Research Letters*, [S.L.], v. 47, n. 4, p. 1-9, 17 fev. 2020. American Geophysical Union
(AGU). http://dx.doi.org/10.1029/2019gl085667.

- Nomura, D., Yoshikawa -Inoue, H., Toyota, T., 2006. The effect of sea-ice growth on air–sea CO2
   flux in a tank experiment. Tellus 58 B, 418–426.
- Parkinson, C. L. and Cavalieri, D. J.: Antarctic sea ice variability and trends, 1979–2010,
  The Cryosphere, 6, 871–880, https://doi.org/10.5194/tc-6-871-2012, 2012.
- Parkinson, C. L. 40–y record reveals gradual Antarctic sea ice increases followed by
  decreases at rates far exceeding the rates seen in the Arctic. Proceedings of the National
  Academy of Sciences 116(29): 14414-14423. https://doi.org/10.1073/pnas.190655611.
  2019.
- Pezzi, L. P.; Souza, R. B.; Acevedo, O.; Wainer, I.; Mata, M. M.; Garcia, C. A. E.; Camargo, R.
   Multiyear measurements of the oceanic and atmospheric boundary layers at the Brazil Malvinas confluence region. *Journal of Geophysical Research Atmospheres*, v. 114, n. 19,
   p. 1–19, 2009.
- Pezzi, L.P., de Souza, R.B., Santini, M.F. et al. Oceanic eddy-induced modifications to air–sea
  heat and CO2 fluxes in the Brazil-Malvinas Confluence. Sci Rep 11, 10648 (2021).
  https://doi.org/10.1038/s41598-021-89985-9
- Rodrigues, C. C. F., Santini, M. F., Lima, L. S., Sutil, U. A., Carvalho, J. T., Cabrera, M. J., Rosa,
  E. B., Burns, J. W., & Pezzi, L. P.. (2023). Ocean-atmosphere turbulent CO2 fluxes at Drake
  Passage and Bransfield Strait. Anais Da Academia Brasileira De Ciências, 95, e20220652.
  https://doi.org/10.1590/0001-3765202320220652
- Rodrigues C.C.F., Santini, M.F,Brunsell, N.A., Pezzi, L.P (2024). CO2 fluxes under different
  oceanic and atmospheric conditions in the Southwest Atlantic Ocean. Journal of Marine
  Systems 243, 2024,03949. https://doi.org/10.1016/j.jmarsys.2023.103949.
- Sabine, C. L.; Hankin, S.; Koyuk, H.; Bakker, D. C. E.; Pfeil, B.; Olsen, A.; Metzl, N.; Kozyr, A.;
  Fassbender, A.; Manke, A.. Surface Ocean CO2 Atlas (SOCAT) gridded data products, Earth
  System Science Data, [S.L.], v. 5, n. 1, p. 145-153, 4 abr. 2013. Copernicus GmbH.
  http://dx.doi.org/10.5194/essd-5-145-2013.
- Santini, M. F., Souza, R. B., Pezzi, L. P. & Swart, S. Observations of air-sea heat fluxes in the
   Southwestern Atlantic under highfrequency ocean and atmospheric perturbations. Q. J. R.
   Meteorol. Soc. https://doi.org/10.1002/qj.3905 (2020).
- Santini, M. F., Souza, R. B., Wayner, I. K. & Muelbert, M. Temporal analysis of water masses and
   sea ice formation rate west of the Antarctic Peninsula in 2008 estimated from southern
   elephant seals' SRDL–CTD data. Deep Sea Res. Part II Top. Stud. Oceanogr. (2018)
- Silva, L. A.; Andrade, J. B. D.; Lopes, W. A.; Carvalho, L. S.; Pereira, P. A. P.. Solubility and
  reactivity of gases. New Chemistry, [S.L.], p. 824-832, 24 mar. 2017. Sociedade Brasileira *de Química (SBQ)*. http://dx.doi.org/10.21577/0100-4042.20170034.
- Sutton, A. J.; Williams, N. L.; Tilbrook, B.. Constraining Southern Ocean CO2 Flux Uncertainty
   Using Uncrewed Surface Vehicle Observations. *Geophysical Research Letters*, [S.L.], v. 48,

 735
 n.
 3,
 p.
 1-9,
 9
 fev.
 2021.
 American
 Geophysical
 Union
 (AGU).

 736
 http://dx.doi.org/10.1029/2020gl091748.

 <

- Takahashi, T.; Sutherland, S. C.; Wanninkhof, R.; Sweeney, C.; Feely, R. A.; Chipman, D.W.;
  Hales, B.; Friederich, G.; Chavez, F.; Sabine, C.. Climatological mean and decadal change
  in surface ocean pCO2, and net sea–air CO2 flux over the global oceans. Deep Sea Research
  Part II: Topical Studies in Oceanography, [S.L.], v. 56, n. 8-10, p. 554-577, abr. 2009.
  Elsevier BV. http://dx.doi.org/10.1016/j.dsr2.2008.12.009.
- Talley, L. D., Reid, J. L. & Robbins, P. E. 2003. Data-based meridional overturning streamfunctions for the global ocean. J. Clim. 16, 3213–3226.
- Taylor, K. E. Summarizing multiple aspects of model performance in a single diagram. Journal of
   Geophysical Research, v.106, n.7, p.7183-7192, 2001.
- Thompson, D. W. J.; Wallace, J. M.. Annular Modes in the Extratropical Circulation. Part I:
  month-to-month variability\*. Journal Of Climate, [S.L.], v. 13, n. 5, p. 1000-1016, mar.
  2000. American Meteorological Society. http://dx.doi.org/10.1175/15200442(2000)0132.0.co;2.
- Turner, J. et al. Antarctic climate change and the environment: an update. *Polar Rec.* 50, 237–259 (2014).
- Viana, D. De L.; Oliveira, J. E. L.; Hazin, F. H. V.; Souza, M. A. C.; Marine sciences: from the
   world's oceans to northeast Brazil. Olinda (PE): Via Design Publicações, 2021. 512 p.
- Voermans, J. J., Babanin, A., Kirezci, C., Carvalho, J. T., Santini, M. F., Pavani, B. F. And Pezzi,
  L. P. Wave Anomaly Detection in Wave Measurements. J. Atmos. Ocean. Technol. 38, 525–
  536 (2021).. DOI: https://doi.org/10.1175/JTECH-D-20-0090.1
- Wadhams, P. Ice in the ocean. Amsterdam: Gordon and Breach Science Publishers. 351 p. 2000.
- Wallace, J.M.; Hobbs, P.V. Atmospheric Science: An Introductory Survey 2 ed., London
   Academic Press, 2006, 483 p.
- Wanninkhof, R. Relationship between wind speed and gas exchange over the ocean revisited. *Limnology and Oceanography*: Methods, v. 12, p. 351– 362, 2014.Weiss, A.; Kuss, J.;
  Peters, G.; Schneider, B. Evaluating transfer velocity wind speed relationship using a long-term series of direct eddy correlation CO2 flux measurements. *Journal of Marine Systems*, v. 66, n. 1/4, p. 130-139, 2007.
- Weiss, R. F. Carbon dioxide in water and seawater: the solubitity of a non-ideal gas. *Marine Chemistry*, Amsterdam, v. 2, p. 203-215, 1974.
- Zeng, J.; Nojiri, Y.; Landschützer, P.; Telszewski, M.; Nakaoka, S.. A Global Surface Ocean fCO2
  Climatology Based on a Feed-Forward Neural Network. Journal Of Atmospheric And
  Oceanic Technology, [S.L.], v. 31, n. 8, p. 1838-1849, 1 ago. 2014. American
  Meteorological Society. http://dx.doi.org/10.1175/jtech-d-13-00137.1.

Figure 1.





Figure 2.



Figure 3.



Figure 4.



Figure 5.





![](_page_39_Figure_2.jpeg)

![](_page_39_Figure_3.jpeg)

Figure 6.

![](_page_41_Figure_0.jpeg)

![](_page_41_Figure_1.jpeg)

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Figure 7.

![](_page_43_Figure_0.jpeg)

# Spatio-temporal variability of CO<sub>2</sub> fluxes in the Atlantic sector of the Southern Ocean

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#### **Key Points:**

The CO<sub>2</sub> flux varies from -0.05 to 0.05 gC m<sup>-2</sup>month<sup>-1</sup> in the Atlantic sector of the Southern Ocean, depending on the seasons, from 2003 to 2022. 

The formation and melting of the sea ice cover has a strong influence on the variation in CO<sub>2</sub> absorption. 

The intensification of westerly winds on circumpolar oceanic fronts has intensified the absorption of CO<sub>2</sub>. 

34

### 35 Abstract

The Southern Ocean (SO) plays a fundamental role in the planet's climate system, due to its ability 36 to absorb and redistribute heat and CO<sub>2</sub> (an important greenhouse gas). Besides, the SO 37 38 interconnects three large oceanic basins the Pacific, the Atlantic, and the Indian Oceans, and it has an important role in the nutrient distribution into these oceans. However, the SO is poorly sampled 39 with most measurements made in austral spring and summer. The variability of the air-sea CO<sub>2</sub> 40 flux is estimated, as well as the role of atmospheric and oceanic variables in this variability. The 41 CO<sub>2</sub> fluxes are calculated by the bulk parameterization method, in the Atlantic sector of the 42 Southern Ocean, from 2003 to 2022, using *in situ* measurements, satellites and reanalysis data set. 43 A neural network model is built to produce maps of the partial pressure of CO<sub>2</sub> in seawater 44 (pCO<sub>2sea</sub>). The CO<sub>2</sub> flux varies from -0.05 to 0.05 gC m<sup>-2</sup> month<sup>-1</sup>. The Atlantic sector of the SO is 45 a sink of CO<sub>2</sub> in summer and spring and becomes a source in austral winter and autumn. The CO<sub>2</sub> 46 absorption intensifies from 2003 to 2022 by 7.6 mmol m<sup>-2</sup>month<sup>-1</sup>, due stronger westerly winds, 47 related to the trend of the positive phase of the Antarctic Oscillation and the extreme events of El 48 Niño and La Niña. 49

50

### 51 Plain Language Summary

The Southern Ocean (SO) plays a fundamental role in the planet's climate, due to its strong 52 circulation of ocean waters, thus regulating heat and carbon reservoirs. The SO is an important 53 CO<sub>2</sub> sink for the atmosphere. However, the amount of absorbed CO<sub>2</sub> varies over time, which is 54 still poorly understood. The SO is not well sampled, due to difficulties in accessing the region and 55 inhospitable climate. Most cruises are carried out in the austral spring and summer. Here we use 56 in situ data, satellites, and modeled data to estimate the variability of the air-sea CO<sub>2</sub> flux, and the 57 role of atmospheric and oceanic variables, in the Atlantic sector of the SO from 2003 to 2022. The 58 CO<sub>2</sub> flux is calculated using the difference of partial pressure between the ocean and the 59 atmosphere (bulk method). The CO<sub>2</sub> flux varies from -0.05 to 0.05 gC m<sup>-2</sup> month<sup>-1</sup>, with the 60 strongest absorption occurring mainly in summer and spring. The absorption of CO<sub>2</sub> from 2003 to 61 2022 has intensified, due to the increase in wind speed in the region, related to atmospheric and 62 oceanic climate conditions. 63

64

# 65 **1 Introduction**

The Southern Ocean (SO) is considered an important  $CO_2$  sink area, with an absorption of -1.0 Pg C/year (Landschützer et al., 2013). The main cause is the cold waters of the region, which results in greater  $CO_2$  solubility (Silva et al., 2017, Rodrigues et al., 2023). In the SO, there is an intense

transformation and formation of water masses, with a strong seasonality (Santini et al., 2018) which helps to control oceanic carbon reservoirs (Goldemberg et al., 2011).

The  $CO_2$  flux (FCO<sub>2</sub>) exchange between the ocean and the atmosphere varies in time and space (Landschützer et al., 2015; Sutton et al., 2021). The oceanic mesoscale may play a crucial role in

these flux exchanges. For example, Pezzi et al. (2021) showed that sea surface temperature (SST) 73 74 anomalies caused by a warm core eddy (WCE) in the Southwestern Atlantic Ocean (SWA) near the SO, exerted a crucial influence on modifying the marine atmospheric boundary layer (MABL) 75 76 by transferring heat and CO<sub>2</sub> from the ocean to the atmosphere. The WCE presence in midlatitudes, surrounded by predominantly cold waters, caused the ocean to act locally as a CO<sub>2</sub> source. 77 Rodrigues et al. (2024) found that the intense horizontal gradient of SST combined with moderate 78 79 wind and turbulence, in the Brazil Malvinas Confluence, modulates FCO<sub>2</sub>, and leading to a CO<sub>2</sub> 80 sink. Seasonal variations are explained by SST variations and biological activity (Landschützer et al., 2015; Sutton et al., 2021). Interannual and decadal variations may be related to changes in deep 81 82 water formation and are associated with the Antarctic Oscillation (AO) and the El Niño-Southern Oscillation (ENSO) (Heinze et al., 2015; Brown et al., 2019; Avelina et al., 2020). Nevertheless, 83 the magnitude of the influence of ENSO and AO on FCO2 variability is still not understood (Sutton 84 et al., 2021). 85

The ENSO, despite occurring in equatorial regions, influences the SST variability and the wind 86 field in some regions of the SO, due to Rossby waves propagation. These waves are generated 87 through vorticity from adiabatic heating, which, when moving south, induce teleconnections 88 between ENSO and the SO climate (Parkinson and Cavalieri, 2012; Parkinson, 2019). ENSO has 89 a La Niña phase (cold phase) and an El Niño phase (warm phase) (Lovenduski et al., 2008). AO 90 is represented by an oscillation in surface pressure systems between medium and high latitudes in 91 the Southern Hemisphere, having positive and negative phases (Thompson and Wallace, 2000) 92 The Antarctic Oscillation is usually defined as the difference in the zonal mean sea level pressure 93 at 40°S (mid-latitudes) and 65°S (Antarctica) (Fogt and Marshall, 2020). 94

The positive AO phase is defined by negative anomalies of geopotential height and temperature, 95 in addition to the increase in the strength of the westerlies that lead to a greater upwelling of carbon 96 97 from the ocean depths to the surface, which reduces the absorption of CO<sub>2</sub>. The opposite occurs in the negative AO phase (Scholfield et al., 2018; Keppler and Landschützer, 2019; Nevison et al., 98 99 2020). During El Niño, there is an increase in the mixing of Circumpolar Deep Water (CDW) with Dense Shelf Water (DSW) advected from the Weddell Sea, leading to greater absorption of CO<sub>2</sub>. 100 The opposite occurs during La Niña (Keppler and landschützer, 2019; Brown et al., 2019; Nevison 101 et al., 2020; Costa et al., 2020; Avelina et al., 2020). 102

The SO location, the high seasonality and ice cover, make it difficult to carry out oceanographic cruises, generating a lack of spatio-temporal information from the existing data set (Takahashi et al., 2009; Sabine et al., 2013; Bakker et al., 2016). There are few measurements in autumn and winter, most of them are made in austral summer and spring (Parkinson et al., 2012; Meijers et al., 2014; Monteiro et al. 2020). This makes it necessary to use tools that interpolate available measurements.

Here we use *in situ* data from the unprecedented collections of the Antarctic Modeling and Observation System (ATMOS) project, the Surface Ocean CO<sub>2</sub> Atlas (SOCAT) (https://www.socat.info), satellite and reanalysis datasets to estimate the air-sea CO<sub>2</sub> flux and its variability from 2003 to 2022. As pCO<sub>2sea</sub> is not available from satellite, we build an Artificial Neural Network (ANN) model to produce maps of pCO<sub>2sea</sub>. The ANN has become an increasingly efficient tool in the field of CO<sub>2</sub> studies and has been applied in estimations of pCO<sub>2sea</sub> and CO<sub>2</sub>

- fugacity (Landshutzer et al., 2013; Zeng et al., 2014; Hadjer et al., 2016). In addition, it performs
- better than linear regressions (Hadjer et al., 2016).

117 Thus, this study contributes to increase our knowledge of the spatio-temporal variability of the

118 FCO<sub>2</sub> in the Atlantic sector of the Southern Ocean, as well as the role of atmospheric and oceanic

119 variables in explaining this variability. From this, it becomes possible to understand the causes of

120 the intensification of the  $CO_2$  absorption, as well as the consequences for the studied region.

121 Section 2 describes the methodology and the data. Section 3 brings the main results found in this

- study. Section 4 discusses the analysis carried out and, finally, Section 5 presents the conclusions
- 123 of this work.

### 124 **2 Materials and Methods**

125 The study area is presented in section 2.1, followed by in situ data (section 2.2) related to the

ATMOS Project, satellite and reanalysis data set (section 2.3). Direct measurements of  $CO_2$  fluxes

obtained from the ATMOS oceanographic cruise are described in Section 2.4. The training of the neural network based on ATMOS and SOCAT data set is described in Section 2.5. The  $CO_2$  flux

neural network based on ATMOS and SOCAT data set is described in Section 2.5. The  $CO_2$  flux data estimated from the bulk parameterization is described in section 2.6. Finally, the FCO<sub>2</sub>

- 129 data estimated from the bulk parameterization is described in section 2.6. Fina
- 130 variability analysis technique is described in section 2.7.

# 131 **2.1 Study area**

The SO has the largest and fastest ocean current on the globe, the Antarctic Circumpolar Current 132 (ACC), driven by the strong easterly winds characteristic of southern polar latitudes (Orsi et al. 133 1995; Klinck and Nowlin, 2001; Barkek et al., 2007). The oceanic circulation of the SO occurs as 134 follows: the upper cell of the meridional circulation is driven by wind, which causes upwelling of 135 the CDW along inclined isopycnals, due to divergent Ekman transport, which upwell in the ACC 136 (Marshall et al., 2012). At the surface, CDWs become Subantarctic Modal Waters (SMW) and 137 Antarctic Intermediate Waters (AIWs), which makes the upper part of the Southern Overturning 138 Circulation (Sallée et al., 2010). Surface buoyancy flows, ocean-atmosphere interactions, ice 139 shelves, and sea ice produce cold, salty Dense Shelf Water (DSW). DSW becomes the dense 140 141 Antarctic Bottom Water (ABW), formed in seas such as the Ross and Weddell seas, and along the east coast of Antarctic (Ohshima et al., 2013). 142

143 When the ACC reaches the Drake Passage, the narrowing between Antarctica Peninsula and southern end of South America causes an increase in the ACC speed, and results in the 144 strengthening of the main circumpolar oceanic fronts present in the region (Figure 1, Sprintall, 145 2003). These fronts, from south to north, are: 1) the Southern Boundary (BF), which is the northern 146 limit of the cold water mass; 2) the Southern Antarctic Circumpolar Current Front (SACCF), which 147 extends approximately along the Antarctic slope and deviates slightly northwards at 56° W; 3) the 148 149 Polar Front (PF), formed by the convergence of Antarctic and subantarctic waters, and 4) the Subantarctic Front (SAF) which defines the northern boundary of the ACC. To the north of the 150 SAF is the Subtropical Front (STF), which marks the northernmost extent of subantarctic waters 151 (Orsi et al. 1995). 152

Around Antarctica there is a cover of sea ice, which varies seasonally. During the warm season it reduces, due to melting (minimum in February), and during the cold season it expands, due to 155 freezing (maximum in September) (Parkinson and Cavalieri, 2012; Parkinson, 2019). In addition

to the aforementioned factors that can affect the  $FCO_2$ , there is also the passage of atmospheric

157 cold fronts. Indeed, the fronts cause changes in the surface wind field, pressure, temperature, and

other atmospheric variables during their trajectory, in addition to their interactions with the sea

surface (Wallace and Hobbs, 2006).

![](_page_48_Figure_6.jpeg)

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**Figure 1** - Study area location in the Atlantic sector of the Southern Ocean. The isolines illustrate the circumpolar oceanic fronts from south to north, and they are the Southern Boundary (SB), the Southern Antarctic Circumpolar Current Front (SACCF), the Polar Front (PF), and the Subantarctic Front (SAF). To the north of the SAF is the Subtropical Front (STF) (Orsi et al. 1995).

### 165 **2.2** *In situ* data

*In situ* data were obtained from the ATMOS project (Table 1). The oceanographic cruise occurred

167 during OPERANTAR XL, aboard Brazilian Navy Polar Vessel (Po/V) Almirante Maximiano (H-

168 41), between November 2021 and February 2022 (Pezzi et al. 2021; Voermans et al, 2021). The

data was collected by sensors installed in the meteorological tower at the bow of the ship (available

in Carvalho, G. T., & Pezzi, L. P., 2024), and data measured by LI-COR (LI-850) installed in the laboratory aft of the ship (available in Carvalho, G. T., & Pezzi, L. P., 2024) (Table 1).

The Sea Surface Salinity (SSS) data were interpolated from reprocessing systems that combine 172 data from NASA's Soil Moisture Active Passive (SMAP) and European Space Agency's (ESA) 173 174 Soil Moisture Ocean Salinity (SMOS) satellites and in situ measurements (https://doi.org/10.48670/moi-00051). The Sea Surface Temperature (SST) data are from the 175 reprocessing of Along Track Scanning Radiometer (ATSR), Sea and Land Surface Temperature 176 Radiometer (SLSTR) and Advanced Very High Resolution Radiometer (AVHRR) satellite data 177 by the ESA SST Climate Change Initiative (CCI) and Climate Change Service (C3S) projects, they 178 were produced from the Operational Sea Surface Temperature and Sea Ice Analysis system 179 (OSTIA) (https://doi.org/10.48670/moi-00169). 180

SSS, SST, sea level pressure (SLP), H<sub>2</sub>O and partial pressure of CO<sub>2</sub> gas in sea (pCO<sub>2sea</sub>) were obtained from SOCAT. Interpolated Air temperature (Tair) and wind speed were obtained from the MERRA-2 satellite (https://disc.gsfc.nasa.gov/datasets/M2I1NXLFO\_5.12.4). Interpolated concentrations of CO<sub>2</sub> ( $xCO_{2air}$ ) were downloaded from Global View (https://gml.noaa.gov/). pCO<sub>2air</sub> can be considered as the pressure that the gas is in equilibrium in the air, which it would

exert on a surface of water containing dissolved  $CO_2$ . The p $CO_{2air}$  was obtained from  $xCO_{2air}$ , Patm

187 and  $pH_2O$  (Landshutzer et al., 2013).

Sensor	Model	Manufacturer	Variables sampled
Integrated CO <sub>2</sub> /H <sub>2</sub> O Open-path gas analyzer and 3D sonic anemometer	IRGASON	Campbell Scientific	CO <sub>2</sub> density, H <sub>2</sub> O density 3D wind components air temperature, air pressure
Multi axis inertial sensing system	Motion Pack II	Systron Donner Inertial	3D accelerations and 3D angular velocities
GPS	GPS16X-HVS	Garmin	Position

Infrared gas analyzer	LI-850	Li-cor	CO <sub>2</sub> concentrations in
		Biogeosciences	water

Table 1. Meteorological and oceanic sensors installed on the micrometeorological tower and ship
 hull during the ATMOS cruise.

### 190 2.3 Satellite and reanalysis data set

191 A collection of satellites and reanalysis data set were used for the study of the Atlantic sector of

the SO and for the  $FCO_2$  estimation. The  $FCO_2$  estimation was made using data set from satellite multi-sources to complete the time series for the period from 2003 to February 2022.

The satellite data used in this study were: The  $CO_2$  estimates used are from the Atmospheric 194 Infrared Sounder (AIRS) sensor, on board the Aqua satellite, with a spatial resolution of  $2.5^{\circ} \times 2^{\circ}$ , 195 from 2003 to 2014 (https://disc.gsfc.nasa.gov/datasets/AIRX3C2M\_005). The 2015 to 2022 CO2 196 estimates are from the Orbiting Carbon Observatory - 2 (OCO-2) satellite, which provides 197 estimations with spatial resolution of 1.29 km 2.25 198 а × km (https://disc.gsfc.nasa.gov/datasets?keywords=oco2). The SLP, Tair and wind speed were 199 obtained from the Modern-Era Retrospective analysis for Research and Applications, Version 2 200 (MERRA-2) satellite. With spatial resolution of 0.5° x 0.625°, from 2003 to 2022. 201

Monthly reanalysis SST and SSS were obtained from Multi Observation Global Ocean 202 ARMOR3D (https://doi.org/10.48670/moi-00052). These analyses combine satellite data from 203 Advanced Very High Resolution Radiometer (AVHRR) and Advanced Microwave Scanning 204 205 Radiometer-2 (AMSR-2), and in situ observations distributed by NOAA's National Climatic Data Center, with a spatial resolution of  $0.25^{\circ} \times 0.25^{\circ}$ , from 2003 to 2022. The Chlorophyll products 206 used in this work are from Global Ocean Color (https://doi.org/10.48670/moi-00052), with spatial 207 208 resolution of 4 km. This product uses data from several satellites, such as Sea-viewing Wide Fieldof-view Sensor (SeaWiFS), Moderate-Resolution Imaging Spectroradiometer (MODIS), Medium 209 Resolution Imaging Spectrometer (MERIS), Visible Infrared Imaging Radiometer Suite sensor 210 (VIIRS) aboard the Suomi-National Polar-orbiting Partnership (SNPP), Joint Polar Satellite 211 System-1 (JPSS1), Ocean Land Color Imager (OLCI) aboard the Sentinel-3A (S3A) and Sentinel-212 3B (S3B). 213

### 214 2.4 Eddy Covariance Method

Eddy Covariance (EC) is the method used to obtain direct measurements of turbulent fluxes from 215 the covariance between the fluctuations in the mean CO<sub>2</sub> density and the vertical component of 216 the wind, thus providing the flux of CO<sub>2</sub> between the ocean surface and the atmosphere as indicated 217 in the Equation 1 (Miller et al., 2010; Pezzi et al 2016; Santini et al., 2020). These measurements 218 are made at high temporal frequencies and are performed in the surface layer of the Marine 219 Atmospheric Boundary Layer (MABL) (Mcgillis et al., 2001, Pezzi et al., 2021). The MABL is 220 the layer nearest to the ocean surface, which is where momentum, heat and gas exchange take 221 222 place (Foken et al., 2008). The EC has already been used in previous studies in the Southwestern Atlantic such as Pezzi et al. (2016), Santini et al., (2020) and Pezzi et al, (2021) to study the MABL 223

stability. The role of roughness and stability on momentum fluxes at Brazil-Malvinas Confluence was studied in Hackerott et al. (2018). Recently Pezzi et al. (2021) studied the turbulence and instability of the MABL caused by an oceanic WCE and consequent modification in the behavior of CO<sub>2</sub>, heat and momentum fluxes in the BMC. Additional information about EC can be found in these cited articles, as the methodology employed here is the same.

The FCO<sub>2</sub> is given in  $\mu$ mol m-<sup>2</sup>s-1, by the fluctuations of the vertical wind component (w' in m/s) and the CO<sub>2</sub> mixing ratio (c' in mg/m<sup>3</sup>), in relation to their averages, and the average dry air density (a in  $\mu$ mol.m-<sup>3</sup>):

 $FCO_2 = \rho_a \, \underline{w'c'} \tag{1}$ 

The calculation of the FCO<sub>2</sub> was performed using the free open-source software EddyPro®v7.0.9, offered by LI-COR Biosciences Inc. (EddyPro v7.0.9). Fluxes are calculated using 30-minute averages of high-frequency (20 Hz) data. Before the FCO<sub>2</sub> estimation, the wind data were corrected due to the ship's movement (Miller et al. 2008; Rodrigues et al., 2023).

### 237 2.5 Artificial neural network to estimate pCO<sub>2sea</sub>

The ocean  $CO_2$  partial pressure (p $CO_{2sea}$ ) data are very sparse in the study area. Therefore, an Artificial Neural Network (ANN) was used to fill spatial and temporal gaps in p $CO_{2sea}$  (Nakaoka et al., 2013; Landshutzer et. al., 2013). In this study, 279.480 observations from SOCAT and ATMOS over the 2003-2022 period, are used to reconstruct the p $CO_{2sea}$  for the study region. The dataset is split into two distinct groups (Géron et al., 2017):

1) 85% of the data are randomly selected for utilization during the training phase. This will beidentified as the Train set.

245 2) The remaining 15% are allocated for the neural network diagnosis phase. Called Test set.

The standard procedure of data normalization (scaling) is implemented on every input and output 246 variable, aiming to achieve a mean of zero and a standard deviation of 1 for each of them. The 247 network consists of an input layer composed of 3 neurons, 3 hidden layers with 10, 8 and 5 nodes 248 respectively and an output layer, that is, the estimate of pCO<sub>2sea</sub>, as shown in Figure 2. For the 249 precision analysis of the pCO<sub>2sea</sub> estimate, the mean squared error and Pearson's coefficient were 250 defined (Géron et al., 2017). Previous studies that applied this methodology over the Atlantic 251 Ocean used SST, SSS and chlorophyll in data input (Landshutzer et. al., 2013). However, in this 252 study, during the initial tests to produce the model, the set of variables SST, SSS and pCO<sub>2air</sub> 253 (Figure 2a) proved to be more efficient in estimating  $pCO_{2sea}$  than the input data used by 254 Landshutzer et. al., (2013). The Pearson correlation (r) showed that the variables SSS, SST and 255 chlorophyll (Figure 2a) as input data for the ANN model, have r = 0.59 with the observed pCO<sub>2sea</sub> 256 data. While with SSS, SST and pCO<sub>2air</sub> data (Figure 2b) the correlation is greater (r = 0.69). 257 Furthermore, the root mean-square (RMS) error calculated based on the two sets of input data for 258 the ANN was lower with the SSS, SST and pCO2air data (RMS = 33.47) (Figure 2c), from than 259 in relation to the set of SSS, SST and chlorophyll variables (RMS = 40.41) (Figure 2b). The model 260

- was produced in the Python 3 programming language, available at Carvalho, G. T & Mejia, C.,
   2024. Two platforms were also installed: TensorFlow and Keras (Chollet et al., 2018).
- The ANN estimates  $pCO_{2sea}$ . With  $pCO_{2sea}$ , it is then possible to calculate  $FCO_2$  on a large spatial and temporal scale.

![](_page_52_Figure_3.jpeg)

265

**Figure 2** - a) Scheme of the produced Deep Artificial Neural Network. The input data are salinity (SSS) (psu) and sea surface temperature (SST) (°C) and CO<sub>2</sub> partial pressure of air (pCO<sub>2air</sub>) ( $\mu$ atm). The ANN includes 3 hidden layers with 10, 8 and 5 nodes. The output layer gives the seawater partial pressure of CO<sub>2</sub> (pCO<sub>2sea</sub>) ( $\mu$ atm). b) Pearson correlation between pCO<sub>2sea</sub> estimates using SSS, SST and Chl as ANN input data. c) Pearson correlation between pCO<sub>2sea</sub> estimates using SSS, SST and pCO<sub>2air</sub> as ANN input data. Scatterplots and regression lines were

- calculated from Test data (with 15% of the data set).
- 273 2.6 Bulk parameterization

FCO<sub>2</sub> was determined by the bulk parameterization (FCO<sub>2BK</sub>) shown in Equation 2, where FCO<sub>2BK</sub> is defined by the product of the ocean-atmosphere CO<sub>2</sub> partial pressure gradient  $\Delta pCO_2$  ( $\Delta pCO_2$ = pCO<sub>2sea</sub> - pCO<sub>2air</sub>), the solubility (s) and the wind-dependent air-sea gas transfer velocity (K) (Farias et al., 2013; Ito et al., 2016):

$$FCO_{2BK} = s.k. \Delta pCO_2(sea-air)$$
(2)

The solubility (s)  $CO_2$  in seawater was defined with the relationship used by Weiss, 1974. K was calculated according to Sweeney et al. (2007). The direction and part of the magnitude of FCO<sub>2</sub> are defined by  $\Delta pCO_2$ , whose variability is dominated by  $pCO_{2sea}$  in our observations.

are defined by  $\Delta p CO_2$ , whose variability is dominated by  $p CO_{2sea}$  in our observations.

The bulk parameterization was applied using satellite and reanalysis data, from 2003 to 2022. Due to each of the satellite and reanalysis data having different spatial resolutions, as can be seen in

Table 2, it was necessary to re-grid them. The interpolation was based on the spatial resolution of

 $CO_2$  observations from the AIRS and OCO-2 satellites. From 2003 to 2014 the data had a final

spatial resolution of  $2^{\circ} \times 2.5^{\circ}$ , and from 2015 to 2022 the final spatial resolution was  $0.5^{\circ} \times 0.625^{\circ}$ .

287 The interpolation was performed using the Cubic Convolution Interpolation tool applied using the

Python 3 tool. In this method, the 16 closest pixels (4x4 window) are considered and the

interpolation is performed by adjusting cubic polynomials to each column, to then interpolate a new cubic polynomial to these results. It is the most suitable method for studies that need to work

with data at different resolutions (Cunha et al., 2012; Dourado et al., 2014).

# 292 **2.7 CO**<sub>2</sub> flux variability analysis

The analysis of  $FCO_2$  in the Drake Passage covered the months of February of the years 2016 and 2019 based on bulk SOCAT data, and from 12/01/2021 to 02/15/2022 based on the ATMOS

project collections (Pezzi et al., 2021; Voermans et al, 2021; Rodrigues et al., 2023), obtained by

the Eddy Covariance (EC) method.

Afterwards, the bulk was applied again, but now with satellite data, reanalysis, and ANN, in the Atlantic sector of the Southern Ocean. Next, an analysis of the monthly FCO<sub>2</sub> series was carried out and the role of atmospheric and oceanic variables in FCO<sub>2</sub> variability was described. The influence of ENSO and AO on FCO<sub>2</sub> was also investigated. ENSO and AO information is available from the Climate Prediction Center (CPC), National Oceanic and Atmospheric Administration (NOAA) National Center for Environmental Prediction (NCEP) during the period 2003 to February 2022.

# 304 **3 Results**

In this section we present the results of this study, based on in situ data collection, estimated flows and reanalysis data, in addition to flow estimates resulting from the artificial neural network model.

# **307 3.1 CO<sub>2</sub> flux variability in February**

The monthly FCO<sub>2</sub> in the Drake Passage is presented for February of 2016, 2019 and 2022 (Figure

309 3). Using bulk parameterization with SOCAT data, it was -0.01 gC m<sup>-2</sup>month<sup>-1</sup> in 2016 and -0.005

 $gC m^{-2}month^{-1}$  in 2019. Using eddy covariance with ATMOS data in 2022, the flux was -0.04 gC

 $m^{-2}$ month<sup>-1</sup>. Similar results were observed by Takahashi et al. (2009), with a flux of -0.02 gC m<sup>-1</sup>

 $^{2}$ month<sup>-1</sup>. These values were due to the Southern Ocean acting as a CO<sub>2</sub> sink during the austral

summer (Dejong et al., 2017; Brown et al., 2019; Monteiro et al., 2020). This absorption in the

- summer occurs because it is a period of increased availability of light and nutrients. Nutrients are
- from upwelled Circumpolar Deep Waters, which leads to an increase phytoplankton blooms,
- decreasing  $pCO_{2sea}$ , and increasing  $CO_2$  uptake by the ocean (Ducklow et al., 2013; Heinze et al.,
- 2015; Viana et al., 2021). Despite the predominance of CO<sub>2</sub> absorption in the Drake Passage, there

![](_page_55_Figure_1.jpeg)

![](_page_55_Figure_2.jpeg)

![](_page_55_Figure_3.jpeg)

### 323 **3.3 FCO<sub>2</sub> calculated with artificial neural network.**

The 2003–2022 average FCO<sub>2</sub>, calculated from the maps of pCO<sub>2sea</sub>, was -0.027 gC m<sup>-2</sup>month<sup>-1</sup>, 324 and from *in situ* data was -0.029 gC m<sup>-2</sup>month<sup>-1</sup>, but the average bias is small (-0.002 gC m<sup>-2</sup>month<sup>-1</sup> 325 <sup>1</sup>). FCO<sub>2</sub> from in situ data (SOCAT and ATMOS data) was determined by the bulk method from 326 2003-2022. The comparison between the two fluxes can be seen in the Taylor diagram, which 327 provides a simple graphical representation of what the next one will bring from the other (Figure 328 329 4). In relation to the standard deviation of the observed data, it was 2.4 and that of the model was 1.7 (Figure 4). The root mean square error (RMS) error between the two was 1.5. The FCO<sub>2</sub>, based 330 on the reconstruction of pCO<sub>2sea</sub>, may have overestimated the flow variability by 5.3%. However, 331 this underestimation is low, given what was observed by Gloege et al., (2021) for the Southern 332 Ocean, of 31%. The percentage overestimation is, by definition, inversely proportional to the 333 standard deviation of the model (GLOEGE et al., 2021). According to the dispersion of -0.013 gC 334 335  $m^{-2}$ month<sup>-1</sup>, obtained by the absolute error, it indicates that the amplitude of the monthly variability of the CO<sub>2</sub> flow produced may be close to the original. The correlation with the flow calculated 336 with *in situ* data was high (r = 0.76), being higher than that observed in Gloege et al., (2021) with 337 338 r = 0.54.

![](_page_56_Figure_1.jpeg)

339

Figura 4 - Taylor diagram for comparison between the  $FCO_2$  calculated with *in situ* data (Reference) and from the ANN pCO<sub>2sea</sub> reconstruction (ANN). The blue lines are the root-meansquare (RMS) error.

To detect possible increase or decrease of  $CO_2$  absorption, we calculate the monthly  $CO_2$  flux anomalies over 2003-2022 using the maps produced by the ANN (Figure 5).

The area from 40°S to 45°S exhibits large seasonal changes with positive flux in the months of 345 December, January, February (austral summer) and in the months of September, October, and 346 November (austral spring), and negative values in the months of June, July and August (austral 347 winter) and in March, April and May (austral autumn). The region from 45°S to 55°S also exhibits 348 seasonal changes, ranging from being a strong sink of CO<sub>2</sub> in summer and spring, and having 349 reduced absorption in winter and autumn, indicating that it is a year-round sink. This zone is the 350 Antarctic Divergence area, located within the high wind speed zone ( $40-60^{\circ}$ S). The strong winds 351 cause a large vertical mixing of seawater, which increases the exchange of  $CO_2$  at the air-sea 352 interface, explaining the strong CO<sub>2</sub> sink (Arrigo et al., 2007; Le Queré et al., 2007). In this region, 353 the North Atlantic Deep Water resurfaces from 2000 m depth to 200 m, with higher temperatures 354 (Tomczak; Godfrey, 1994). South of  $55^{\circ}$ S is an area of year-round CO<sub>2</sub> absorption. However, 355 absorption is reduced in winter and autumn. During the southern spring-summer, phytoplankton 356 blooms occur near the ice and increase the CO<sub>2</sub> absorption. This indicates the effect of ice cover 357 on the FCO<sub>2</sub> in this region, as observed in Takahashi et al. (2009), Shetye et al. (2017) and 358 Monteiro et al. (2020). 359

In summer, absorption is more intense than in other seasons (Figure 5), absorbing 72% more than 360 in autumn and winter, and 51% more than in the southern spring. The absorption peak occurs 361 mainly in February, and the lowest absorption values are mainly in August, in the study region. 362 This is due to the expansion of sea ice cover that occurs in autumn and winter, with maximum 363 expansion in August and September (Parkinson and Cavalieri, 2012; Parkinson, 2019). The ice 364 cover can extend from the Antarctic continent to 55°S in the Atlantic sector in some years, 365 however, on average it can extend up to 62°S in winter (Takahashi et al., 2009). As winter 366 progresses, ice formation increases, releasing salts, which can contribute to the release of CO<sub>2</sub> into 367 the water. The layer of mixed water under the ice is rich in CO<sub>2</sub>, mainly due to the vertical mixing 368

of deep waters (Nomura et al., 2006; Takahashi et al., 2009). However, in the summer and spring the ice cover melts, and reaches its minimum size in February, which is why this is the month in which the greatest absorption of  $CO_2$  occurs (Wadhams, 2000). Furthermore, in the southern summer and spring there is an increase in light availability and stable stratification of surface water, which allows an increase in primary biological productivity, which leads to an increase in  $CO_2$ absorption during these seasons (Ducklow et al., 2013; Heinze et al., 2015; Viana et al., 2021).

The FCO<sub>2</sub> varies from -0.05 to 0.05 gC m<sup>-2</sup>month<sup>-1</sup> in the Atlantic sector of the SO, absorbed in 375 the summer and spring periods, and in the southern winter and autumn, absorption decreases. CO<sub>2</sub> 376 absorption has intensified in the study area, with an increase of 0.076 gC m<sup>-2</sup>month<sup>-1</sup> from 2003 to 377 2022. This behavior is shaped by wind speed and SST, but mainly by the intensification of winds 378 that increased during the studied period, which may be driven by climate variability (Marshall et 379 al., 2003; Stammerjohn et al., 2008; Brown et al., 2008, 2019). Furthermore, an increasing trend 380 in pCO<sub>2air</sub> was also observed, which has been increasingly higher than in water. The increase in 381 pCO<sub>2air</sub> is due to anthropogenic CO<sub>2</sub> emissions. The rate of increase of pCO<sub>2sea</sub> is slower in highly 382 mixed regions as deeper waters with a lower CO<sub>2</sub> content are brought to the surface. In high 383 stratified regions, the same rate of increase is observed in the ocean and in the atmosphere. 384 Previous studies that modeled future scenarios already expected this response from the Southern 385 Ocean to increased CO<sub>2</sub> emissions (Sabine; Cols., 2004; Friedlingstein et al., 2006; Roy et al., 386 2011; Arora et al., 2013; Steinacher et al., 2013; Zickfeld et al., 2013). These models predicted 387 that in scenarios with high greenhouse gas emissions, there would be a reduction in the efficiency 388 of absorption by the ocean. This occurs because the increase in atmospheric CO<sub>2</sub> concentration is 389 linked to the increase in anthropogenic emissions. Thus, although absorption by the ocean has 390 intensified, the ocean is not able to absorb all the excess CO<sub>2</sub> present in the atmosphere resulting 391 from anthropogenic emissions. 392

In the Drake Passage, the absorption in the summer and spring periods is of -0.01 gc/m<sup>2</sup>.month and -0.013 gC m<sup>-2</sup>month<sup>-1</sup>, respectively. In the autumn and winter periods, there is a reduction in absorption of -0.012 gC m<sup>-2</sup>month<sup>-1</sup>. Similar results were observed by Takahashi et al. (2009). In summer and spring, they observed strong CO<sub>2</sub> absorption, and in autumn and winter there is a reduction in absorption, being -0.09 gC m<sup>-2</sup>month<sup>-1</sup>, -0.02 gC m<sup>-2</sup>month<sup>-1</sup>, 0.01 gC m<sup>-2</sup>month<sup>-1</sup> and 0.013 gC m<sup>-2</sup>month<sup>-1</sup>, respectively.

399 SST anomaly maps produced by reanalysis data (Figure 6) illustrate that some regions of the study area are becoming increasingly warmer over time, which affects  $FCO_2$ . The waters coming from 400 the Pacific Ocean through the Drake Passage to the Atlantic sector of the Southern Ocean are 401 releasing more  $CO_2$  than the expected average (Figure 5). These waters are the waters of the PF. 402 The PF is located approximately at latitude 50°S in the Atlantic oceans and at latitude 60°S in the 403 Pacific, it is a region where CO<sub>2</sub> is released, due to its average surface temperature being higher 404 than that south of this region. This behavior was also observed with SOCAT and ATMOS data 405 (Figure 3). The surface water south of this region moves north and sinks when it reaches the PF, 406 thus causing convergence at the surface (Pickard and Emery, 1990). However, with the increase 407 in SST, the PF shows stronger CO<sub>2</sub> outgassing. To the north of the PF there is an increase in CO<sub>2</sub> 408 release, this region has higher temperatures, due to the dominant effect of seasonal SST changes 409 (Tomczak; Godfrey, 1994). However, to the south of the PF there is an increase in CO<sub>2</sub> absorption. 410 In this region the surface waters of the Antarctic Zone have very low temperatures, reaching values 411 412 close to the freezing point  $(-1,9^{\circ}C)$ , as a result of the summer melting of the sea ice and surface 413 cooling in winter (Tomczak; Godfrey, 1994). Below the surface in the Antarctic Zone, extending

414 up to 4000 m deep, is the Antarctic Circumpolar Water (AACW), with temperatures of 1.5 to  $2.5^{\circ}$ C

415 (Tomczak; Godfrey, 1994). Close to the coast of the Antarctic continent, some regions also

intensified the release of  $CO_2$ , despite being a region with a higher potential temperature than at the shelf break, the SST was also warmer. This region is where the Deep Circumpolar Water rises

417 the shell break, the SST was also warner. This region is where the Deep Cheunpolar Water rises 418 over the slope to enter the platform, it has warmer and saline waters (Baines, 2006). However, the

waters that are a source of  $CO_2$ , are expanding southward, and the waters that are sinks of  $CO_2$ 

420 become stronger sinks. This is due to the increase in strength and southward displacement of the

421 westerly winds, associated with the positive trend of the AO, which forced the migration of the FS

towards the Antarctic continent, thus migrating warm and saline waters, which cause the release

of CO<sub>2</sub>. This trend towards the positive phase of OA is due to the increase in greenhouse gases
(Thompson; Solomon, 2002; Marshall et al., 2003; Cai et al., 2005; Cai; Cowan, 2007).

![](_page_59_Figure_2.jpeg)

425

426 **Figure 5** –Monthly anomalies of the  $CO_2$  flux (in gC m<sup>-2</sup>month<sup>-1</sup>) calculated from 2003 to 2022.

![](_page_60_Figure_1.jpeg)

427

Figure 6 – Monthly sea surface temperature (°C) anomalies produced after reanalysis, from 2003
 to 2022.

### 430 **3.4 Variability of CO<sub>2</sub> flux**

In the region between  $-63^{\circ}$  to  $-54^{\circ}$ W and  $-59^{\circ}$  to  $-62^{\circ}$ S, in the Drake Passage, an analysis of the temporal variability of FCO<sub>2</sub> and atmospheric and oceanic variables was carried out, including the climate indices ENSO and OA, based on the historical series from 2003 to 2022.

434 There is a tendency towards negative  $CO_2$  values throughout the period studied (Figure 7a), with peaks and decreasing values, which follow the seasonality of the SST (Figure 7b). The SLP varies 435 inversely to the temperature, that is, when the temperature increases the SLP decreases and vice 436 versa (Figure 7e, 7b). Furthermore, the SLP appears to be inversely proportional to the FCO<sub>2</sub>, so 437 it is possible to observe that where there is a drop in the SLP, there is an increase in the values of 438  $FCO_2$ , which become more positive (Figure 7e). This relationship between SLP and  $FCO_2$ 439 indicates a decrease in the concentration of atmospheric CO<sub>2</sub> near the surface and, consequently, 440 there is a tendency to transfer  $CO_2$  from the ocean to the atmosphere. Wind speed is strongest in 441 the months of March to November, ranging from 11-13 (m/s), and reduces in the months of 442 December to February (southern summer), ranging from 9-10 (m/s) (Figure 7g). CHL varies 443 seasonally, CHL blooms occur during the austral spring-summer, and reduce in the austral autumn-444 winter (Figure 7c). The months of August and September have the lowest concentrations of CHL. 445

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It was observed from \Delta pCO_2 (Figure 7d), which defines the direction and part of the magnitude of FCO<sub>2</sub>, that pCO<sub>2air</sub> is what dominates the variability of FCO<sub>2</sub> in this study. \Delta pCO_2 has a decreasing
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trend, indicating that the direction of  $FCO_2$  is towards the atmosphere towards the ocean. An 448 449 increasing trend in pCO<sub>2air</sub> was also observed (Figure 7h), which has been increasingly higher than in pCO<sub>2sea</sub>. The increase in pCO<sub>2air</sub> may be caused by the high concentration of anthropogenic CO<sub>2</sub> 450 present in the air, which is not being captured by the ocean with the same efficiency as before. 451 Previous studies that modeled future scenarios already expected this response from the SO to 452 increased CO<sub>2</sub> emissions (Sabine and Cols., 2004; Friedlingstein et al., 2006; Roy et al., 2011; 453 Arora et al., 2013; Steinacher et al., 2013; Zickfeld et al., 2013). These models predicted that in 454 scenarios with high greenhouse gas emissions, there would be a reduction in the efficiency of 455 absorption by the ocean. The weakening of  $CO_2$  absorption by the SO is due to the existence of a 456 natural limit in gas exchange at the atmosphere-ocean interface, CO<sub>2</sub> dissociation, turbulent mixing 457 and ocean circulation, which causes only a certain percentage of excess  $CO_2$  atmospheric pressure 458 to be absorbed. Therefore, although oceanic absorption is increasing, there are still high 459

460 concentrations of CO<sub>2</sub> in the atmosphere (Le Quéré et al., 2013; IPCC, 2013; Heinze et al., 2015).

461 CO<sub>2</sub> absorption increased by 0.076 gC m<sup>-2</sup>month<sup>-1</sup>, from 2003 to 2022. Winds were intense, 462 averaging 11.1 m/s (Figure 7g). The SST was higher than the air temperature (SST >Tair) 463 throughout the studied period (Figure 7b), which indicates that the Marine Atmospheric Boundary 464 Layer (CLAM) in this region is unstable and that an intense exchange of CO<sub>2</sub> occurs, as suggested 465 by Pezzi et al. (2009).

The months 05/2005, 05/2007, 06/2009, 06/2011, 06/2015, 07/2019 and 07/2021 had absorption 466 anomalies (FCO<sub>2</sub> varying from 0.075 gC m<sup>-2</sup>month<sup>-1</sup>to 0.2 gC m<sup>-2</sup>month<sup>-1</sup>) (Figure 7a), that is, 467 absorption was more intense in these periods than the expected average. These periods showed 468 that the high negative values of FCO<sub>2</sub> were due to high values of SLP (ranging from 1008 hPa to 469 1013 hPa) and low values of SST (ranging from 8°C to 10°C) and Tar (ranging from 4.7 °C to 470 6.7°C), intense winds (ranging from 11 m/s to 12.3 m/s), which caused the exchange of CO<sub>2</sub> at the 471 472 ocean surface to be greater, with K varying from 18 to 33. However, on 02/2013 (FCO<sub>2</sub> 0.0134 gC m<sup>-2</sup>month<sup>-1</sup>) CO<sub>2</sub> absorption was lower than the expected average, due to low SLP values (1006 473 474 hPa) and wind speed, warmer SST and Tair, which caused gas transfer at the ocean-atmosphere interface to be lower, the K was 4.8. 475

Interannual variations are related to the phase variation of OA and ENSO, as observed by 476 Lovenduski et al., 2008, Lenton et al., 2009, Brown et al., 2019, Costa et al., 2020 and Avelina et 477 478 al., 2020. The months when intense reduction in  $CO_2$  absorption occurred, such as 02/2013, had the influence of positive OA (+OA). +OA is defined by negative geopotential height and 479 temperature anomalies. +OA increases the strength of westerly winds that lead to an increase in 480 the upwelling of natural carbon from the depths of the ocean to the surface, causing a reduction in 481  $CO_2$  absorption. However, the opposite occurred in the months 05/2005, 05/2007, 06/2009, 482 06/2011, 06/2015, 07/2019 and 07/2021, which had intense CO<sub>2</sub> absorption, a period of -OA 483 (Gupta and England, 2006; Scholfield et al., 2018; Meredith et al., 2017; Keppler and 484 Landschützer, 2019; Nevison et al., 2020). Furthermore, 06/2015, despite being a +OA month, 485 was the most extreme El Niño period since 1998 (Monteiro et al., 2020). In this case, the role of 486 El Niño was greater than that of OA. During El Niño, there is an increase in the mixing of Deep 487 Circumpolar Waters with Dense Shelf Water advected from the Weddell Sea, leading to greater 488 absorption of CO<sub>2</sub>. The opposite occurs in La Niña (Scholfield et al., 2018; Meredith et al., 2017; 489 Brown et al., 2019; Keppler and Landschützer, 2019; Nevison et al., 2020; Costa et al., 2020; 490 Avelina et al., 2020). The change in OA phase influences the flux variability, being able to increase 491

492 (negative phase) or reduce (positive phase) the absorption of  $CO_2$ . ENSO becomes the main 493 influence only in periods of strong intensity, as occurred in 06/2015. Therefore, most of the time

494 the main modulator of  $FCO_2$  is OA.

![](_page_62_Figure_3.jpeg)

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**Figure 7** – Time series of atmospheric and oceanographic variables in the Drake Passage, from 2003 to 2022.  $CO_2$  flux (FCO<sub>2</sub>) (a), sea surface temperature (SST) and air temperature (Tair) (b), chlorophyll-a concentration (CHL) (c), difference of CO<sub>2</sub> partial pressure between the ocean and the atmosphere ( $\Delta pCO_2$ ) (d), atmospheric pressure at sea level (SLP) (e), salinity surface water (SSS) (f), wind speed (u) (g), seawater partial pressure of CO<sub>2</sub> (pCO<sub>2sea</sub>), atmospheric partial pressure of CO<sub>2</sub> (pCO<sub>2air</sub>) (h).

### 502 **4 Final remarks and conclusions**

This study showed the spatio-temporal variability on the sea-air FCO<sub>2</sub> caused by the ocean and atmosphere conditions, in the Atlantic sector of the Southern Ocean. The FCO<sub>2</sub> calculated through EC method using in situ data collected by ATMOS project (Pezzi et al. 2021; Voermans et al., 2021, Rodirgues, et al., 2023) offered a new source of atmospheric and oceanic data for CO<sub>2</sub>, heat and momentum in the Atlantic Sector of the Southern Ocean.

508 Monthly maps of FCO<sub>2</sub> were produced using an ANN for estimating pCO<sub>2sea</sub> with satellite and 509 reanalysis data from 2003 to 2022. The absolute error between the FCO<sub>2</sub> produced from ANN and 510 that produced with *in situ* data was -1.3  $\mu$ mol/m<sup>2</sup>/month and the correlation was high (r = 0.9). 511 This corresponds to a slight overestimation of 5.3% compared to the 31% obtained by Gloege et

512 al., (2021) in the SO.

- The FCO<sub>2</sub> varies from -0.05 to 0.05 gC m<sup>-2</sup>month<sup>-1</sup> in the Atlantic sector of the SO, with the strongest CO<sub>2</sub> sink occurring in the summer and spring periods, and a lower sink in the austral winter and autumn. The seasonal variation of FCO<sub>2</sub> is modulated by changes in SST, in the Atlantic sector of the SO. In summer absorption is more intense than in other seasons, the peak occurs mainly in February. Summer absorption is 72% greater than in autumn and winter, and 51% greater than in the southern spring. The lowest absorption values occur mainly in August (winter). This is due to the expansion of sea ice cover that occurs in autumn and winter, with maximum expansion
- 520 in August and September.
- From 2003 to 2022, CO<sub>2</sub> absorption has intensified by 0.076 gC m<sup>-2</sup>month<sup>-1</sup>. In summer, absorption
- increased by 0.093 gC m<sup>-2</sup>month<sup>-1</sup> compared to 2003 to 2022. In autumn, winter and spring the increase was 0.11 gC m<sup>-2</sup>month<sup>-1</sup>, 0.14 gC m<sup>-2</sup>month<sup>-1</sup> and 0.1 gC m<sup>-2</sup>month<sup>-1</sup>, respectively, from
- 524 2003 to 2021.
- 525 During the study period, FCO<sub>2</sub> varied spatially, shaped by the characteristics of ocean fronts. The
- areas of the SF, because they have warm and saline waters, act as a source. Areas between the SF and the SAF, characterized by moderate SST and SSS, and intense winds, have strong absorption.
- 528 Finally, there are areas with moderate absorption, located in the regions of the SB, in the SACCF
- 529 and in the PF, which have colder and less saline waters.
- 530 The waters, which act as a source of  $CO_2$ , are expanding southwards, and the waters, which act as
- sinks, have been intensifying the absorption of  $CO_2$ . This is due to the increased strength and
- southward displacement of the westerly winds, associated with the positive trend of the AO, which

forced the migration of the SF towards the Antarctic continent. Thus, warm and saline waters

migrate and cause the release of  $CO_2$ . In addition, the intensification of westerly winds on the circumpolar oceanic fronts intensifies the absorption of  $CO_2$  in this region. The influence of ENSO

- only overlaps with the influence of the OA phase in periods of extreme ENSO, such as what
- 537 occurred in 2015.
- 538 The results of this study show that  $FCO_2$  in the SO are highly dependent on oceanographic and meteorological conditions. The spatial variation of FCO<sub>2</sub> is affected by the displacement of water 539 masses. In addition, the intensification of westerly winds in the SAF, which increases gas exchange 540 at the ocean-atmosphere interface, intensifies the absorption of  $CO_2$  in this region. It also supports 541 previous studies that modeled future scenarios on the reduction in the efficiency of CO<sub>2</sub> absorption 542 by the ocean as a response by the Southern Ocean to the increase in greenhouse gas emissions. 543 544 The ANN model for pCO<sub>2sea</sub> estimates is a very important tool to fill data gaps of pCO<sub>2sea</sub> in difficult-to-access areas, such as the SO, mainly in winter and southern autumn periods. It is also 545 evident that the continuity of *in situ* sampling in this region with high quality data will allow us to 546 improve the models produced and the understanding of the role of dynamic and thermodynamic 547 processes that act as modulating mechanisms of CO<sub>2</sub> fluxes at the ocean-atmosphere interface of 548 the Atlantic sector of the Southern Ocean. 549

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# 562 **Open Research**

The Artificial Neural Network (ANN) software was designed to estimate pCO2sea. The ANN used 563 in the article can be found at https://doi.org/10.5281/zenodo.10854860, and can be developed 564 openly in Python 3. Data from the meteorological tower installed on the bow of the Brazilian Navy 565 Polar Ship (Po/V) Almirante Maximiano (H-41) were used to calculate the CO2 flux (FCO2) in 566 567 the EddyPro®v7.0.9 software. These available data are in Carvalho, G. T., & Pezzi, L. P., 2024 (https://doi.org/10.5281/zenodo.10871385). LI-COR (LI-850) data installed in the laboratory aft 568 of the Brazilian Navy Polar Ship (Po/V) Almirante Maximiano (H-41) were used to calculate 569 pCO2sea, available in Carvalho, G. Т., & Pezzi. L. P., 2024 570 (https://doi.org/10.5281/zenodo.10887055). 571

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# 573 **References**

- 574
- Arrigo, k. R., and g. L. Van dijken (2007), Interannual variation in air-sea CO2 flux in the Ross
  Sea, Antarctica: A model analysis, J. Geophys. Res., 112, C03020,
  doi:10.1029/2006JC003492
- Avelina R, da Cunha Lc, Farias Co, Hamacher C, Kerr R & Mata Mm. 2020. Contrasting dissolved 578 organic carbon concentrations in the Bransfield Strait, northern Antarctic Peninsula: insights 579 into **ENOS** and SAM effects. J Mar Syst 212: 1-51. 580 https://doi.org/10.1016/j.jmarsys.2020.103457. 581
- Bakker, Dce, Pfeil, B., Landa, Cs, Metzl, N., O'brien, Km, Olsen, A., et al. (2016) A multi-decade
  record of high quality fCO<sub>2</sub> data in version 3 of the Surface Ocean CO<sub>2</sub> Atlas (SOCAT). *Earth System Science Data*, 8: 383-413. doi:10.5194/essd-8-383-2016
- Benallal, M.A.; Moussa, H.; Lencina-Avila, J.M.; Touratier, F.; Goyet, C.; JAI, M.C. El; 585 POISSON, N.; POISSON, A.. Satellite-derived CO2 flux in the surface seawater of the 586 Austral Ocean south of Australia. International Journal Of Remote Sensing, [S.L.], v. 38, n. 587 UK 1600-1625, 6 fev. 2017. Informa Limited. 588 6, p. http://dx.doi.org/10.1080/01431161.2017.1286054. 589
- Brown, Michael S.; Munro, David R.; Feehan, Colette J.; Sweeney, Colm; Ducklow, Hugh W.;
  Schofield, Oscar M.. Enhanced oceanic CO2 uptake along the rapidly changing West
  Antarctic Peninsula. Nature Climate Change, [S.L.], v. 9, n. 9, p. 678-683, 26 ago. 2019.
  Springer Science and Business Media LLC. http://dx.doi.org/10.1038/s41558-019-0552-3.
- Cai, W.J., Cowan, T. (2007). Trends in Southern Hemisphere circulation in IPCC AR4 models
   over 1950-99: Ozone-depletion vs. greenhouse forcing, *Journal of Climate*, 20(4), 681–693.

Carvalho, G. T. and Mejia, C. (2024). Artificial Neural Network (ANN) to estimate pCO2sea.
 (Version 1.1.0) [Software]. (RNApCO2sea-Carvalho). Zenodo.
 https://doi.org/10.5281/zenodo.10854860

- Carvalho, G. T., & Pezzi, L. P. (2024). Data from the micrometeorological tower of the Antarctic
   Modeling Observation System (ATMOS) project of the 40th Brazilian Antarctic Operation
   (OPERANTAR XL) to calculate the CO2 flux (FCO2) [Data set]. Zenodo.
   https://doi.org/10.5281/zenodo.10871385
- Carvalho, G. T., & Pezzi, L. P. (2024). LI-COR (LI-850) sensor data obtained by the Antarctic
   Modeling Observation System (ATMOS) project during the 40th Brazilian Antarctic
   Operation (OPERANTAR XL) and were used to calculate the partial pressure of CO2
   (pCO2) [Data set]. Zenodo. https://doi.org/10.5281/zenodo.10887055
- Chahine, M., Barnet, C., Olsen, E.T., Chen, L., Maddy, E., 2005. On the determination of
  atmospheric minor gases by the method of vanishing partial derivatives with application to
  CO2: DETERMINATION OF MINOR GASES BY VPD. Geophys. *Res. Lett.* 32
  https://doi.org/10.1029/2005gl024165.
- Chatterjee A., Gierach MM, Sutton AJ, Feely RA, Crisp D., Eldering A., Gunson MR, O'Dell CW,
  Stephens BB, Schimel DS. Influence of El Nino on atmospheric CO<sub>2</sub> over tropical Pacific
  Ocean: Findings from NASA's OCO-2 mission, *Science* 13 out 2017, Vol. 358, Issue 6360,
  eaam5776 DOI: 10.1126/science.aam5776.
- 615 Chollet, f. (2018). Deep Learning with Python (First). Manning Publications Co.
- Clowes, A.J. Influence of the Pacific on the circulation in the South-West Atlantic Ocean. Nature,
   v. 131, p. 189-191, 1933.
- Cook, A. J., FOX, A. J., VAUGHAN, D. G. & FERRIGNO, J. G. Retreating glacier fronts on the
   Antarctic Peninsula over the past half-century. Science 308, 541–544 (2005).
- Costa, R. R. et al. Dynamics of an intense diatom bloom in the Northern Antarctic Peninsula,
   February 2016. *Limnol. Oceanogr.* 66, 1–20 (2020).
- Dejong, Hb & Dunbar, Rb. Air-sea CO2 exchange in the Ross Sea, Antarctica. J. Geophys. Res.
   Oceano 122, 8167-8181 (2017).
- Ducklow, H. W. et al. West Antarctic Peninsula: an ice-dependent coastal marine ecosystem in
   transition. *Oceanography* 26, 190–203 (2013).
- Farias, E. G. G.; Nobre, P.; Lorenzzetti, J. A.; Almeida, R. A. F.; Junior, L. C. I. Variability of air sea CO2 fluxes and dissolved inorganic carbon distribution in the Atlantic basin: a coupled
   model analysis. *International Journal of Geosciences*, v. 2013, p. 249–258, 2013.
- Fogt, Ryan L.; Marshall, Gareth J.. The Southern Annular Mode: variability, trends, and climate
  impacts across the southern hemisphere. Wires Climate Change, [S.L.], v. 11, n. 4, p. 1-24,
  19 maio 2020. Wiley. http://dx.doi.org/10.1002/wcc.652.
- Géron, Aurélien. Hands-on machine learning with Scikit-Learn and TensorFlow: concepts, tools,
   and techniques to build intelligent systems. [S.l.]: "O'Reilly Media, Inc.", 2017.
- Goldemberg, José et al. Antarctica and global changes: a challenge for humanity. Publishing
   company Blucher, 2011.
- Hackerott, J. A. et al. The role of roughness and stability on the momentum flux in the marine
   atmospheric surface layer: A study on the southwestern Atlantic Ocean. J. Geophys. Res.
   Atmos. 123, 3914–3932.https:// doi. org/ 10. 1002/ 2017J D0279 94 (2018).
- Hadjer, M. & Benallal, Mohamed & Goyet, Catherine & Lefèvre, Nathalie. (2016). Satellitederived CO2 fugacity in surface seawater of the tropical Atlantic Ocean using a feedforward
  neural network. *International Journal of Remote Sensing*. 37. 580–598.
  10.1080/01431161.2015.1131872

- Heinze, C., Meyer, S., Goris, N., Anderson, L., Steinfeldt, R., Chang, N., Le Quéré, C., And
  Bakker, D. C. E.: The ocean carbon sink impacts, vulnerabilities and challenges, Earth
  Syst. Dynam., 6, 327–358, https://doi.org/10.5194/esd-6-327-2015, 2015.
- IPCC Intergovernmental Panel on Climate Change, Working Group I Contribution to the Fifth
   Assessment Report, Climate Change 2013 the Physical Science Basis.
- Ito, R. G.; Garcia, C. A. E.; Tavano, V. M.. Net sea-air CO2 fluxes and modelled pCO2 in the
  southwestern subtropical Atlantic continental shelf during spring 2010 and summer 2011. *Continental Shelf Research*, [S.L.], v. 119, p. 68-84, maio 2016. Elsevier BV.
  http://dx.doi.org/10.1016/j.csr.2016.03.013.
- Keppler & Landschützer P. 2019. Regional wind variability modulates the Southern Ocean carbon
   sink. Sci Rep 9(1): 1-10. https://doi.org/10.1038/s41598-019-43826-y.
- Klinck, J. M., and W. D. Nowlinx Jr. (2001), Antarctic Circumpolar Current, in *Encyclopedia of Ocean Science*, 1st ed., pp. 151–159, Academic, San Diego, Calif.
- Landschützer, P.; Gruber, N.; Bakker, D. C. E.; Schuster, U.; Nakaoka, S.; Payne, M. R.; Sasse,
  T. P.; Zeng, J.. A neural network-based estimate of the seasonal to inter-annual variability
  of the Atlantic Ocean carbon sink. *Biogeosciences*, [S.L.], v. 10, n. 11, p. 7793-7815, 29 nov.
  2013. Copernicus GmbH. http://dx.doi.org/10.5194/bg-10-7793-2013.
- Landschutzer, P., et al. (2015), The reinvigoration of the Southern Ocean carbon sink, Science, 349, 6253.
- Le Quéré, C., et al. Saturation of the Southern Ocean CO2 sink due to recent climate change,
   Science, 316, 1735–1738, 2007.
- Le Quéré, C., Andres, R. J., Boden, T., Conway, T., Houghton, R. A., House, J. I., Marland, G.,
  Peters, G. P., van der Werf, G. R., Ahlström, A., Andrew, R. M., Bopp, L., Canadell, J. G.,
  et al.: The global carbon budget 1959–2011, Earth Syst. Sci. Data, 5, 165–185,
  https://doi.org/10.5194/essd-5-165-2013, 2013.
- Lovenduski, N. S., N. Gruber, and S. C. Doney (2008), Toward a mechanistic understanding of
   the decadal trends in the Southern Ocean carbon sink, Global Biogeochem. Cycles, 22,
   GB3016, doi:10.1029/2007GB003139.
- Mcgillis, W.R., Edson, J.B., Fairall, C.W., 2001. Direct covariance air-sea CO2 fluxes. J. Geophys.
   Res. 106, 16,729–16,745.
- 673Meijers, Ajs (2014). The Southern Ocean in the Phase-5 Coupled Model Intercomparison Project.674Philosophical Transactions of the Royal Society of London, Series A: Mathematical,675Physical and Engineering Sciences, 372 (2019),67620130296.https://doi.org/10.1098/rsta.2013.0296
- Meredith et al. Changing distributions of sea ice melt and meteoric water west of the Antarctic
   Peninsula. *Deep Sea Res.* Pt II 139, 40–57 (2017).
- Miller, S. D. et al. Platform motion effects on measurements of turbulence and air-sea exchange
   over the open ocean. *Journal of Atmospheric and Oceanic Technology*, v. 25, n. 9, p. 1683–
   1694, 2008.
- Monteiro, T., Kerr, R. & Machado, E.D. Seasonal variability of net sea-air CO2 fluxes in a coastal
   region of the northern Antarctic Peninsula. Sci Rep 10, 14875 (2020).
   https://doi.org/10.1038/s41598-020-71814-0
- Moussa, H., M. A. Benallal, C. Goyet, And N. Lefèvre. 2016. Satellite-Derived CO2 Fugacity in
  Surface Seawater of the Tropical Atlantic Ocean Using a Feedforward Neural Network.
  International Journal of Remote Sensing 37 (3): 580–
  598.doi:10.1080/01431161.2015.1131872.

Nakaoka, S., Telszewski, M., Nojiri, Y., Yasunaka, S., Miyazaki, C., Mukai, H., and Usui, N.:
Estimating temporal and spatial variation of ocean surface pCO2 in the North Pacific using
a self-organizing map neural network technique, *Biogeosciences*, 10, 6093–6106,
https://doi.org/10.5194/bg-10-6093-2013, 2013.

Nevison, C. D.; Munro, D. R.; Lovenduski, N. S.; Keeling, R. F.; Manizza, M.; Morgan, E. J.;
Rödenbeck, C.. Southern Annular Mode Influence on Wintertime Ventilation of the
Southern Ocean Detected in Atmospheric O2 and CO2 Measurements. *Geophysical Research Letters*, [S.L.], v. 47, n. 4, p. 1-9, 17 fev. 2020. American Geophysical Union
(AGU). http://dx.doi.org/10.1029/2019gl085667.

- Nomura, D., Yoshikawa -Inoue, H., Toyota, T., 2006. The effect of sea-ice growth on air–sea CO2
   flux in a tank experiment. Tellus 58 B, 418–426.
- Parkinson, C. L. and Cavalieri, D. J.: Antarctic sea ice variability and trends, 1979–2010,
  The Cryosphere, 6, 871–880, https://doi.org/10.5194/tc-6-871-2012, 2012.
- Parkinson, C. L. 40–y record reveals gradual Antarctic sea ice increases followed by
  decreases at rates far exceeding the rates seen in the Arctic. Proceedings of the National
  Academy of Sciences 116(29): 14414-14423. https://doi.org/10.1073/pnas.190655611.
  2019.
- Pezzi, L. P.; Souza, R. B.; Acevedo, O.; Wainer, I.; Mata, M. M.; Garcia, C. A. E.; Camargo, R.
   Multiyear measurements of the oceanic and atmospheric boundary layers at the Brazil Malvinas confluence region. *Journal of Geophysical Research Atmospheres*, v. 114, n. 19,
   p. 1–19, 2009.
- Pezzi, L.P., de Souza, R.B., Santini, M.F. et al. Oceanic eddy-induced modifications to air–sea
  heat and CO2 fluxes in the Brazil-Malvinas Confluence. Sci Rep 11, 10648 (2021).
  https://doi.org/10.1038/s41598-021-89985-9
- Rodrigues, C. C. F., Santini, M. F., Lima, L. S., Sutil, U. A., Carvalho, J. T., Cabrera, M. J., Rosa,
  E. B., Burns, J. W., & Pezzi, L. P.. (2023). Ocean-atmosphere turbulent CO2 fluxes at Drake
  Passage and Bransfield Strait. Anais Da Academia Brasileira De Ciências, 95, e20220652.
  https://doi.org/10.1590/0001-3765202320220652
- Rodrigues C.C.F., Santini, M.F,Brunsell, N.A., Pezzi, L.P (2024). CO2 fluxes under different
  oceanic and atmospheric conditions in the Southwest Atlantic Ocean. Journal of Marine
  Systems 243, 2024,03949. https://doi.org/10.1016/j.jmarsys.2023.103949.
- Sabine, C. L.; Hankin, S.; Koyuk, H.; Bakker, D. C. E.; Pfeil, B.; Olsen, A.; Metzl, N.; Kozyr, A.;
  Fassbender, A.; Manke, A.. Surface Ocean CO2 Atlas (SOCAT) gridded data products, Earth
  System Science Data, [S.L.], v. 5, n. 1, p. 145-153, 4 abr. 2013. Copernicus GmbH.
  http://dx.doi.org/10.5194/essd-5-145-2013.
- Santini, M. F., Souza, R. B., Pezzi, L. P. & Swart, S. Observations of air-sea heat fluxes in the
   Southwestern Atlantic under highfrequency ocean and atmospheric perturbations. Q. J. R.
   Meteorol. Soc. https://doi.org/10.1002/qj.3905 (2020).
- Santini, M. F., Souza, R. B., Wayner, I. K. & Muelbert, M. Temporal analysis of water masses and
   sea ice formation rate west of the Antarctic Peninsula in 2008 estimated from southern
   elephant seals' SRDL–CTD data. Deep Sea Res. Part II Top. Stud. Oceanogr. (2018)
- Silva, L. A.; Andrade, J. B. D.; Lopes, W. A.; Carvalho, L. S.; Pereira, P. A. P.. Solubility and
  reactivity of gases. New Chemistry, [S.L.], p. 824-832, 24 mar. 2017. Sociedade Brasileira *de Química (SBQ)*. http://dx.doi.org/10.21577/0100-4042.20170034.
- Sutton, A. J.; Williams, N. L.; Tilbrook, B.. Constraining Southern Ocean CO2 Flux Uncertainty
   Using Uncrewed Surface Vehicle Observations. *Geophysical Research Letters*, [S.L.], v. 48,

 735
 n.
 3,
 p.
 1-9,
 9
 fev.
 2021.
 American
 Geophysical
 Union
 (AGU).

 736
 http://dx.doi.org/10.1029/2020gl091748.

- Takahashi, T.; Sutherland, S. C.; Wanninkhof, R.; Sweeney, C.; Feely, R. A.; Chipman, D.W.;
  Hales, B.; Friederich, G.; Chavez, F.; Sabine, C.. Climatological mean and decadal change
  in surface ocean pCO2, and net sea–air CO2 flux over the global oceans. Deep Sea Research
  Part II: Topical Studies in Oceanography, [S.L.], v. 56, n. 8-10, p. 554-577, abr. 2009.
  Elsevier BV. http://dx.doi.org/10.1016/j.dsr2.2008.12.009.
- Talley, L. D., Reid, J. L. & Robbins, P. E. 2003. Data-based meridional overturning streamfunctions for the global ocean. J. Clim. 16, 3213–3226.
- Taylor, K. E. Summarizing multiple aspects of model performance in a single diagram. Journal of
   Geophysical Research, v.106, n.7, p.7183-7192, 2001.
- Thompson, D. W. J.; Wallace, J. M.. Annular Modes in the Extratropical Circulation. Part I:
  month-to-month variability\*. Journal Of Climate, [S.L.], v. 13, n. 5, p. 1000-1016, mar.
  2000. American Meteorological Society. http://dx.doi.org/10.1175/15200442(2000)0132.0.co;2.
- Turner, J. et al. Antarctic climate change and the environment: an update. *Polar Rec.* 50, 237–259 (2014).
- Viana, D. De L.; Oliveira, J. E. L.; Hazin, F. H. V.; Souza, M. A. C.; Marine sciences: from the
   world's oceans to northeast Brazil. Olinda (PE): Via Design Publicações, 2021. 512 p.
- Voermans, J. J., Babanin, A., Kirezci, C., Carvalho, J. T., Santini, M. F., Pavani, B. F. And Pezzi,
  L. P. Wave Anomaly Detection in Wave Measurements. J. Atmos. Ocean. Technol. 38, 525–
  536 (2021).. DOI: https://doi.org/10.1175/JTECH-D-20-0090.1
- Wadhams, P. Ice in the ocean. Amsterdam: Gordon and Breach Science Publishers. 351 p. 2000.
- Wallace, J.M.; Hobbs, P.V. Atmospheric Science: An Introductory Survey 2 ed., London
   Academic Press, 2006, 483 p.
- Wanninkhof, R. Relationship between wind speed and gas exchange over the ocean revisited. *Limnology and Oceanography*: Methods, v. 12, p. 351– 362, 2014.Weiss, A.; Kuss, J.;
  Peters, G.; Schneider, B. Evaluating transfer velocity wind speed relationship using a long-term series of direct eddy correlation CO2 flux measurements. *Journal of Marine Systems*, v. 66, n. 1/4, p. 130-139, 2007.
- Weiss, R. F. Carbon dioxide in water and seawater: the solubitity of a non-ideal gas. *Marine Chemistry*, Amsterdam, v. 2, p. 203-215, 1974.
- Zeng, J.; Nojiri, Y.; Landschützer, P.; Telszewski, M.; Nakaoka, S.. A Global Surface Ocean fCO2
  Climatology Based on a Feed-Forward Neural Network. Journal Of Atmospheric And
  Oceanic Technology, [S.L.], v. 31, n. 8, p. 1838-1849, 1 ago. 2014. American
  Meteorological Society. http://dx.doi.org/10.1175/jtech-d-13-00137.1.