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# Relação do metabolismo ecossistêmico com a dinâmica oceanográfica na Plataforma Continental do Sul do Brasil

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Gabriela Souza Gomes

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O presente trabalho em nível de mestrado foi avaliado e aprovado por banca examinadora composta pelos seguintes membros:

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# RESUMO

O objetivo deste estudo foi estimar o metabolismo do ecossistema em uma região da plataforma subtropical brasileira, relacionando-o com a sazonalidade oceanográfica e meteorológica através de séries temporais de alta frequência de variáveis meteo-oceanográficas. Processos de mesoescala, como a Água Subtropical de Plataforma influenciada pela Água da Pluma do Plata, e processos pontuais, como o aumento da precipitação, foram determinantes para estimativa do metabolismo do ecossistema. O sistema foi heterotrófico em 99% do período amostrado/avaliado, sugerindo que a região é uma fonte de $CO_2$ para a atmosfera. Durante eventos de chuvas, as entradas de água costeira (ricas em matéria orgânica e nutrientes) influenciaram os máximos das estimativas da produção primária bruta (PPB). De acordo com o índice trófico TRIX, o sistema foi caracterizado como mesotrófico, enquanto que pelas estimativas da PPB o sistema foi oligotrófico, podendo ser aumentado para meso ou eutrófico durante os eventos de chuva. Essas diferenças podem estar associadas à limitação da produção primária fitoplanctônica pelo nitrogênio como observada nas águas da região Os resultados aqui encontrados (N=389) corroboram as poucas estimativas de produção primária e de metabolismos feitos para a Plataforma Subtropical Brasileira, podendo servir de referência para a compreensão da dinâmica desse processo em maior detalhamento temporal.

**Palavras-chave:** Metabolismo Ecossistêmico. Eventos de Precipitação. Sistema Heterotrófico.

# ABSTRACT

The objective of this study was to estimate ecosystem metabolism in a region of the Brazilian subtropical platform, relating it to the oceanographic and meteorological seasonality through high frequency time series of meteo-oceanographic variables. Mesoscale processes, such as Subtropical Platform Water influenced by Plata Plume Water, and punctual processes, such as increased precipitation, were determinant for ecosystem metabolism. The system was heterotrophic in 99% of the measurements, suggesting that the region is a source of CO2 to the atmosphere. During rainfall events, coastal water inflows (rich in organic matter and nutrients) influenced maximum gross primary production (PPB). According to the trophic index (TRIX), the system was characterized as mesotrophic, while by PPB measurement the system was oligotrophic and could be increased to meso or eutrophic during rain events. This difference may be associated with the limitation of phytoplankton primary production by N observed in waters of region. The results found here corroborate the few estimates of primary production and metabolism made in the Brazilian Subtropical Platform, and may serve as a reference for understanding the dynamics of this process in greater temporal detail (N = 389).

**Keywords:** Ecosystem metabolism. Precipitation events. Heterotrophic system.

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# LISTA DE ABREVIATURAS E SIGLAS

ASTP Água Subtropical de Plataforma

APP Água da Pluma do Plata

AT Água Tropical

C Carbono

$CO_2$ Dióxido de carbono

F Fluxo interface oceano- atmosfera

GPP Gross Primary Production

K Coeficiente de troca gasosa

MO Matéria orgânica

NEP Net Primary Production

%OD Oxigênio saturado

PPB Produção Primária Bruta

PPL Produção Primária Líquida

PPW Plata Plume Water

R Respiração

SBB South Brazilian Bight

Sc Coeficiente de Scmidt

STSW Subtropical Shelf Water

TW Tropical Water

$U_{10}$ Vento a 10 m de altura

# SUMÁRIO

# 1 INTRODUÇÃO

As plataformas continentais têm alta importância ecológica e econômica devido ao aumento da produtividade e da biomassa pesqueira (Braga et al., 2008). A produção primária nessa região baseia-se na dinâmica da interface continente-oceano, que envolve a sazonalidade da estrutura física da coluna de água, entradas fluviais e a disponibilidade de luz e nutrientes (Cloern et al., 2014; Hall et al., 2016; Basterretxea et al., 2017). O fitoplâncton marinho é a principal fonte de matéria orgânica (MO) nas plataformas continentais (Libes, 2009). O carbono (C) total fixado em um determinado ecossistema representa a Produção Primária Bruta (PPB), definida pela soma da Produção Primária Líquida (PPL) e da Respiração (R) de organismos autotróficos. A diferença entre PPB e R é o metabolismo do ecossistema (Brandini e Gaeta, 2006). Se o PPB for maior que R, o sistema será chamado de autotrófico, considerado um sumidouro de dióxido de carbono ($CO_2$) e fonte de $O_2$ para a atmosfera. O oposto ocorre em sistemas heterotróficos, onde R domina o PPB (Tonetta et al., 2016). Através do estudo entre esse equilíbrio da produção e respiração (consumo de MO) é possível descrever o estado trófico do ecossistema, e segundo alguns autores, a grande maioria das medições realizadas sugere predominância de heterotrófia nos ambientes marinhos por receberem grandes insumos de carbono orgânico de regiões adjacentes (Del Giorgio et al. 2002; Duarte et al., 2013; Lutz et al 2018).

As águas tropicais e subtropicais da plataforma continental do sudoeste do Atlântico (costa brasileira) são fonte de $CO_2$ para a atmosfera, porém estudos que abordam a relação do ciclo C com o metabolismo do ecossistema são escassos nessa região (Ito et al., 2005; Padin et al., 2010). Além disso, no contexto das mudanças climáticas globais, a dinâmica meteo-oceanográfica pode favorecer o desenvolvimento do fitoplâncton e, consequentemente, a produtividade do sistema. Eventos de precipitação aumentam o escoamento de nutrientes continentais e MO para a costa, interrompendo as condições de equilíbrio e influenciando o metabolismo do ecossistema, podendo desencadear com isso um processo de eutrofização nas regiões mais costeiras, incluindo também o *bloom* de algas que pode afetar na concentração de oxigênio na água (Basterretxea et al., 2017; Tonetta et al., 2016). Além disso, diferentes condições de vento favorecem a intrusão de massas de água ricas em nutrientes, como as observadas na região Sueste do Brasil, alterando as condições biogeoquímicas do sistema (Bordin et al., 2018). Portanto, é necessário entender como as condições ambientais afetam o metabolismo do ecossistema para avaliar o potencial da plataforma continental como fonte ou sumidouro de C (Ito et al., 2016; Lovett et al., 2006; Cole et al., 2007).

As medições de alta frequência de OD, clorofila-a e radiação fotossinteticamente ativa são capazes de capturar variações metabólicas que podem ser perdidas em abordagens de amostras discretas e o monitoramento dessas medições pode detectar a variabilidade sazonal da plataforma continental em resposta a diferentes condições climáticas, cobrindo eventos de curto e longo prazo (Staehr e Sand-Jensen, 2007; Jennings et al., 2012; Klug et al., 2012). Houve uma melhoria no entendimento das propriedades metabólicas dos ecossistemas devido ao desenvolvimento de instrumentos de baixo custo, como sondas ópticas de oxigênio, que ajudaram a aumentar a quantidade de dados que podem ser coletados *in situ* de maneira eficiente.

Concomitantemente, novas abordagens de modelagem têm sido desenvolvidas para estimar os diferentes processos biológicos e físicos através dessas séries temporais medindo a variabilidade espacial e temporal com alta precisão e entre as metodologias utilizadas, o método "água livre" mede o metabolismo do ecossistema a partir da variação do oxigênio dissolvido na água, desconsiderando os fluxos do gás com a atmosfera promovido pela mistura física e difusão em sistemas abertos (Venkiteswaran et al., 2007; Hanson et al., 2008; Holtgrieve et al. , 2010; Brighenti et al., 2015). De acordo com Staehr et al. (2010), o método da "água livre" considera que a produção líquida de OD ocorre apenas durante o dia pela atividade fotossintética, enquanto a respiração é o único processo metabólico que demanda oxigênio e é exclusivo durante a noite (Figura 1).

Assim, a PPB, R e PPL podem ser estimados medindo as alterações na concentração de OD durante um período de 24 horas (nictemeral), levando em consideração o desconto das trocas físicas e de difusão de OD na interface oceano-atmosfera O fluxograma a seguir indica as etapas dos cálculos utilizados para estimar a PPB, R e PPL diários, seguindo as etapas propostas por Staerh et al. (2010), adaptado com modificações para regiões marinhas de plataforma costeira (Figura 2).

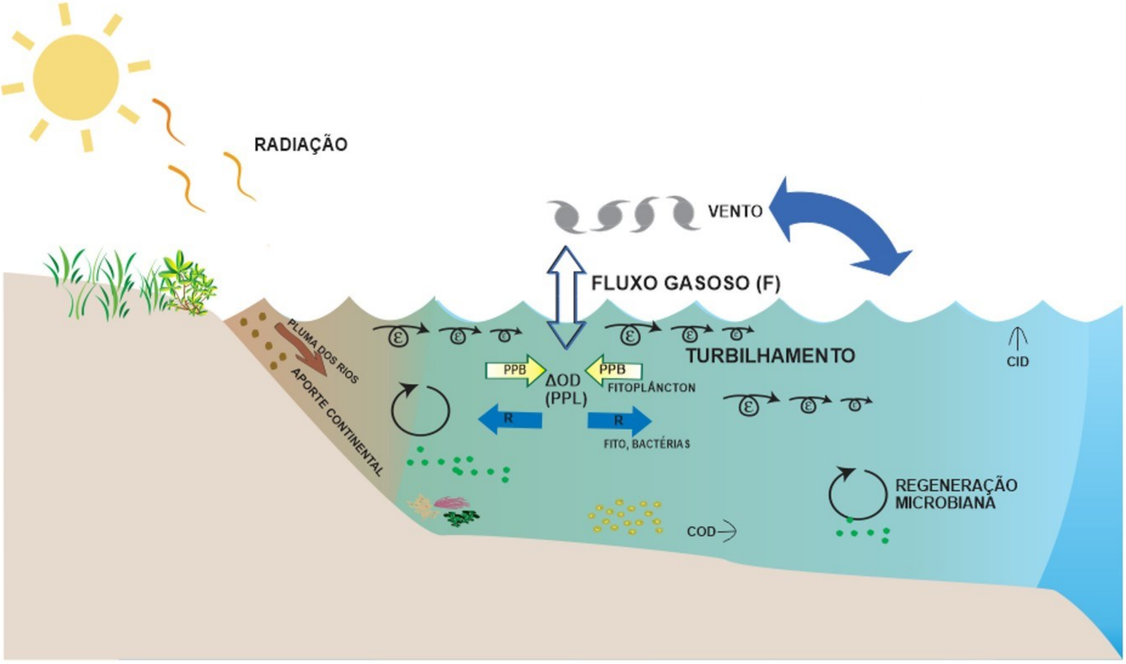

Figura 1: Modelo conceitual de medidas de metabolismo estimadas pela variação do OD, usando o método da água-livre. A troca de OD entre a interface oceano-atmosfera é descontada, e a produção menos a respiração é o metabolismo líquido do sistema, que é influenciado por fatores como aporte continental, vento, radiação e processos regenerativos, em região de Plataforma Continental. Adaptado para região costeira de Staehr et al. (2010).

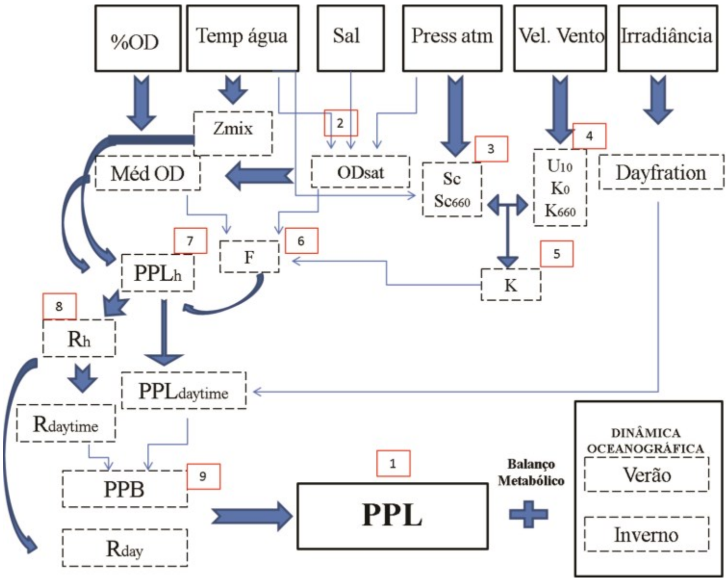

Figura 2: Fluxograma de equações utilizadas para o cálculo dos processos metabólicos: 1. Produção Primária Liquida diária (PPL); 2. Determinação de oxigênio saturado (%OD), a partir da temperatura e salinidade; 3. Cálculo do coeficiente de Scmidt a partir da temperatura da água; 4. Cálculo do vento a 10 m de altura da superfície; 5. Cálculo do coeficiente de troca gasosa; 6. Cálculo do fluxo interface oceano- atmosfera; 7. Cálculo da PPL horário; 8. Cálculo da R; 9. Cálculo da PPB; O balanço metabólico é o PPL associado com a dinâmica oceanográfica que apresenta principais diferenças nas estações do verão e inverno. OBS: os números indicados estão descritos em ordem na tabela 2.

A quantificação das taxas primárias de produção e respiração e sua dominância relativa (o metabolismo) são cruciais para a compreensão do fluxo de MO, ciclagem de nutrientes, estado trófico e sua relação com a dinâmica oceanográfica (Brandini et al. 2014; Ito et al. 2016). Estudos que abordam séries temporais ainda são incipientes na plataforma continental brasileira (Gonzalez-Silvera et al., 2004, Brandini et al., 2000, Garcia et al., 2004). A área de estudo está situada na região Sul da Plataforma Brasileira, onde as porções média e interna são dominadas pela Água Subtropical de Plataforma (ASTP), que é influenciada pela Água Tropical (AT) (no verão) e Água da Pluma do Plata (APP) (no inverno), na porção interna e mediana (Moller et al 2008). Esses processos de mesoescala de misturas de massas de água de diferentes temperaturas e salinidade, aliados as mudanças nas trocas gasosas da interface oceano-atmosfera, são os fatores necessários para que se tenha um monitoramento adequado do metabolismo ecossistêmico (Freire et al. 2017).

Para este estudo, os dados de alta frequência utilizados para os cálculos do PPL, PPB e R foram retirados de da boia do projeto SimCosta (Figura 3) fundeada na Reserva Biológica Marinha do Arvoredo (16 metros de profundidade), uma unidade de conservação (UC) federal (a uma distância de 12 km do continente e a 11 km da Ilha de Florianópolis). Ainda mais escassos são os estudos que relacionam a variabilidade dos processos físicos e o metabolismo do ecossistema. Segundo Lutz et al. (2018), no hemisfério sul e no sudoeste do Atlântico, as estimativas de PPB são poucas e as estimativas globais são geralmente feitas usando métodos indiretos (por modelos de satélite ou biogeoquímicos), que devem ser validados e ajustados com dados de campo para produzir resultados confiáveis.

Figura 3: Boia meteo-oceanográfica do Sistema de Monitoramento Costeiro do Brasil (SIMCosta) SC-01, fundeada no litoral de Santa Catarina, dentro da Reserva Biológica Marinha do Arvoredo.

## 2 HIPÓTESES

1) As taxas metabólicas dependem sazonalmente dos eventos meteorológicos e oceanográficos;

2) O pico de PPB ocorre durante o inverno, associado à maior disponibilidade de biomassa e nutrientes fitoplanctônicos;

3) A precipitação favorece o aumento das taxas de respiração devido à entrada de nutrientes e águas continentais ricas em MO.

## 3 OBJETIVO

O objetivo deste estudo é avaliar a variabilidade do metabolismo do ecossistema da superfície do oceano, em um local interno da região Sueste do Brasil, de alta dinâmica, dentro de uma área de proteção marinha, a Reserva Marinha de Arvoredo (Brasil Subtropical) sob diferentes condições meteo-oceanográficas.

# 4 RESULTADOS

Os resultados dessa dissertação serão apresentados na forma de um artigo científico submetido na revista Jornal of Marine Systems, conforme permitido pelo regulamento da PPGOceano.

# High-frequency ecosystem metabolism in a site on the continental shelf of the South Brazil Bight

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# ABSTRACT

The objective of this study was to estimate the ecosystem metabolism of the sea surface in a region of the Brazilian subtropical shelf, relating it to the oceanographic and biogeochemical seasonality. The metabolism was calculated by the high-frequency oxygen daily variation, recorded by a meteo-oceanographic buoy, between April 2017 and June 2018. We hypothesized that 1) metabolic rates depends on the seasonally of meteorological and oceanographic events; 2) GPP peak occurs during the winter, associated with higher availability of phytoplankton biomass and nutrients; and 3) precipitation favors the increase of respiration rates due to the input of nutrient and OM-rich continental waters. High-frequency time series of solar radiation, water temperature, salinity, dissolved oxygen, chlorophyll, precipitation and wind were compiled and separated by seasons. Monthly discrete data of salinity, temperature, nutrients, chlorophyll and inorganic carbon were also used to correlated with the ecosystem metabolism. The summer and winter seasons were influenced by several meteo-oceanographic processes. In our study, respiration dominated NEP in 99% of the samples, suggesting that the region is a source of $CO_2$ to the atmosphere. During rainy events, coastal water inputs (rich in OM and nutrients) directly influence the metabolism, which showed heterotrophic conditions associated with nutrient regeneration, and the trophic state that according to TRIX showed average values indicating an oligotrophic system (0.16 $gC.m^{-2}.d^{-1}$) can be increased to meso or eutrophic during these rain events, harming local biodiversity causing environmental problems such as algae blooms.

KEYWORDS: Ecosystem metabolism, Arvoredo Marine Reserve, Precipitation events, Trophic potential, Heterotrophic system.

## INTRODUCTION

The continental shelves have high ecological and economic importance due to the elevate productivity and fishing biomass (Braga et al., 2008). Primary production in this region rely on the continent-ocean interface dynamics, which involves the seasonality of the physical structure of the water column, riverine inputs and the availability of light and nutrients (Cloern et al., 2014; Hall et al., 2016; Basterretxea et al., 2017). Marine phytoplankton are the main sources of organic matter (OM) in the continental shelves (Libes, 2009). The total carbon fixed in a given ecosystem represents the Gross Primary Production (GPP), defined by the sum of Net Primary Production (NEP) and Respiration (R) of autotrophic organisms. The difference between GPP and R is the ecosystem metabolism (NEP) (Brandini and Gaeta, 2006). If the GPP is higher than R, the system is called autotrophic, considered a $CO_2$ sink and source of $O_2$ to the atmosphere. The opposite occurs in heterotrophic systems, where R dominates the GPP (Tonetta et al., 2016).

The tropical and subtropical waters of the southwest Atlantic continental shelf (Brazilian coast) are source of $CO_2$ to the atmosphere, however studies that address the relation of the C cycle to the ecosystem metabolism are scarce in this region (Ito et al., 2005; Padin et al., 2010). Also, in the context of global climate changes, meteo-oceanographic dynamics may favor phytoplankton development and, consequently, the system`s productivity. Precipitation events boost continental nutrient and OM runoff to the coast, disrupting the equilibrium conditions and influencing the ecosystem metabolism (Basterretxea et al., 2017; Tonetta et al., 2016). Moreover, different wind conditions favor the intrusion of nutrient-rich water masses, such as observed in the South Brazilian Bight (SBB), changing the biogeochemical conditions of the system (Bordin et al., 2019). Therefore, understand how environmental conditions affect the ecosystem metabolism is necessary in order to assess the continental shelf potential to be a source or sink of C (Ito et al., 2016; Lovett et al., 2006; Cole et al., 2007).

There has been an improvement in the understanding of the metabolic properties of ecosystems, due to the development of low-cost instruments, such as optical oxygen probes, which have helped to increase the amount of data that can be efficiently collected *in situ*. In parallel, new modeling approaches have been developing to estimate the different biological and physical processes of oxygen time series data, measuring spatial and temporal variability with high accuracy (Venkiteswaran et al., 2007; Hanson et al., 2008; Holtgrieve et al., 2010;

Grace et al., 2015). Among the methodologies used the "free water" method measure gas fluxes in open systems (Brighenti et al., 2014). According to Staehr et al. (2010), the "free water" method estimated the NEP through the dissolved oxygen (DO) variation (diel), considering that the net photosynthetic DO production occurs only during the day, while respiration is the only metabolic process that demands oxygen and predominates during the night. Thus, GPP, R and NEP can be estimated by measuring changes in DO concentration over a 24-hour period, taking into account the physical DO exchanges in the ocean-atmosphere interface. High-frequency measurements of DO, chlorophyll-*a* and photosynthetically active radiation are able to capture metabolic variations that might be missed in discrete sample approaches. Therefore, high-frequency monitoring can detect the daily, monthly and seasonal variability of the continental shelf in response to different weather conditions, covering both short and long-term events (Staehr and Sand-Jensen, 2007; Jennings et al., 2012; Klug et al., 2012).

The quantification of primary production and respiration rates, and their relative dominance, is, therefore, crucial for the understanding of OM flow, nutrient cycling, trophic status and their relation to the oceanographic dynamics (Brandini et al., 2014; Ito et al., 2016). Studies that address time series are still incipient in the Brazilian continental shelf (Gonzalez-Silvera et al., 2004, Brandini et al., 2000, Garcia et al., 2004). Even more scarce are the studies that relate the variability of the physical processes and the ecosystem metabolism. Thus, the objective of this study is to evaluate the ecosystem metabolism variability of the ocean surface under different meteo-oceanographic conditions. Our study was made in an internal site of the high dynamic SBB, within a marine protect area, the Arvoredo Marine Reserve (Subtropical Brazil) (at a distance of 12 km from the mainland and 11 km from Florianopolis Island). We tested the hypothesis that (1) metabolic rates depends on the seasonally of meteorological and oceanographic events; 2) GPP peak occurs during the winter, associated with higher availability of phytoplankton biomass and nutrients; and 3) precipitation favors the increase of respiration rates due to the input of nutrient and OM-rich continental waters.

## MATERIALS AND METHODS

### *Study area*

The South Brazil Bight (SBB) extends between 22ºS and 28ºS (Piola et al., 2000) it is a transitional region between the tropical and temperate systems, where water fertilization in the euphotic zone is influenced by meteo-oceanographic processes (Loder, 1998; Castro, et al., 2006). In the summer, the surface water is dominated by the Tropical Water (TW), which is warm and oligotrophic (Brandini et al., 2018).

Due to the intensification of northeast winds during the summer, the intrusion of South Atlantic Central Water (SACW) is observed associated to Ekman Transport (Moller et al., 2008). The SACW brings nutrient-rich waters to the euphotic zone, promoting chlorophyll maxima in pycnocline (Braga et al., 2008; Brandini et al., 2014). In the winter, southerly winds bring the Plata Plume Water (PPW) to the, in addition to the water of other estuaries (e.g. Patos lagoon), which are rich in particulate organic matter (POM) and nutrients, favoring chlorophyll maxima in surface waters (Freire et al., 2017; Bordin et al., 2018). The Subtropical Shelf Water (STSW) dominates the internal and median (Moller et al 2008) portion of SSB when associated to high precipitation events.

The present study was carried out in Arvoredo Marine Reserve (AMR) located in the southern region of SBB (Fig. 4). The AMR is a Conservation Federal Unit (UCs) covering an area of 17,000 ha. In Brazil there are only two Marine Reserves, Rocas atoll and Arvoredo archipelago, but because the Arvoredo is closer to the coast, it is more subject to coastal influences, port activities, tourism and diving (Freire et al., 2017). This site (AMR) is also influenced by the Tijucas Plume Water (TPW) and Florianopolis North Bay Water (NBW), which are the main sources of nutrients and suspended particulate matter, which has surface organic origin (intense biological activity) and this continental contribution increases especially during intense precipitation events (Freire, et al., 2017).

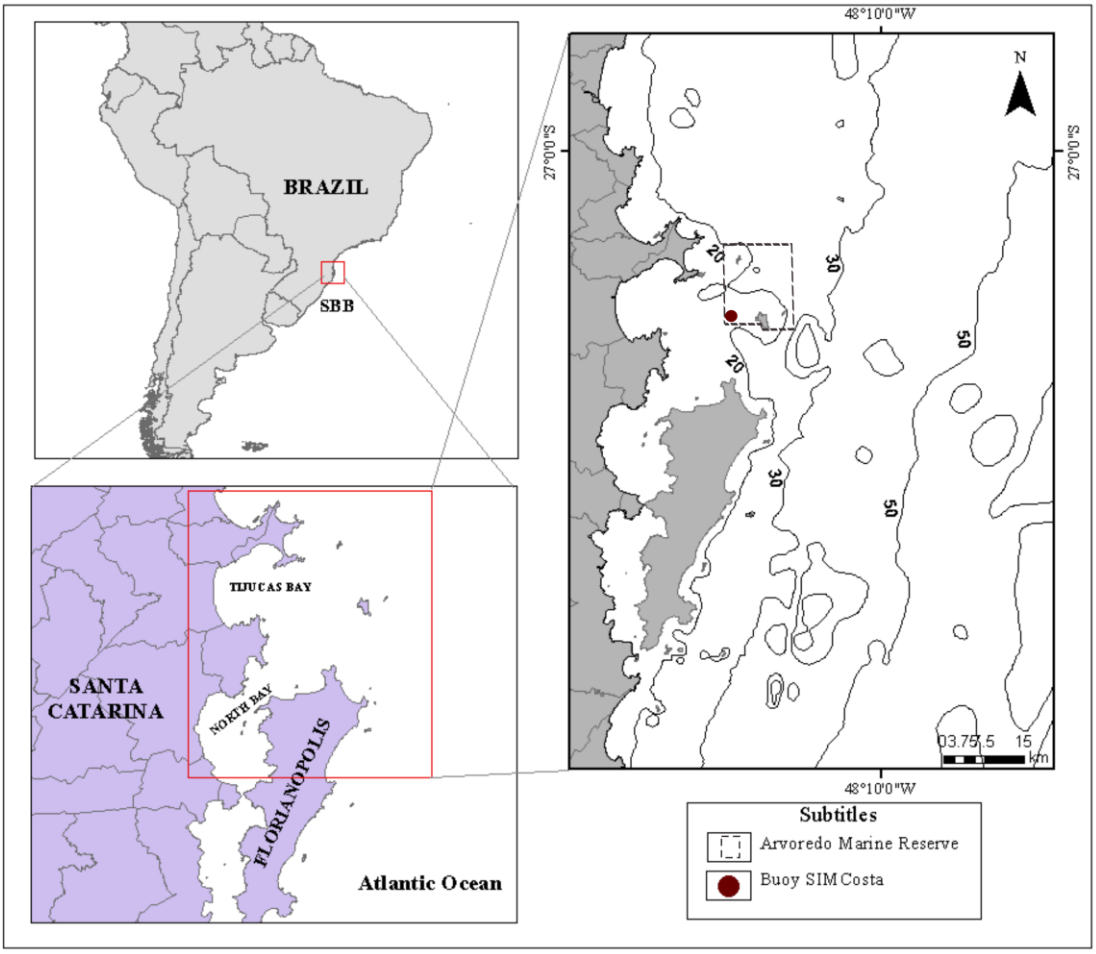


Figure 4. Location of the study area, in the southern portion of SBB, identifying where the Arvoredo Marine Reserve and the SIMCosta buoy are located.

### *Data sampling*

In order to improve the monitoring in the region, in February of 2017, the SIMCosta SC-01 meteo-oceanographic buoy (http://www.simcosta.furg.br) was moored at 48°25'15.7"W and 27°16'28.1"S in a water column of 16 m depth. The buoy is equipped with several meteorological sensors at 1m from the water surface and oceanographic sensors installed at 0.8 m of depth in the water column (Table 1). High-frequency data was recorded every at hour by the data logger (Sea Bird, Mod. STOR-X) from the *in situ* sensors, as described in Table 1.

Table 1. Description of the instruments and parameters measured by SIMCosta buoy, with measurement record every one hour.

| Frequency of measurement | Parameters and units | Sensor and model | Manufacturer |
|---|---|---|---|
| Time (one in an hour)<br>**Oceanographic Data** | Dissolved oxygen - DO(mg.L$^{-1}$)<br>Chlorophyll (µg.L$^{-1}$)<br>Salinity<br>Water temperature (°C) | WQM$_x$ | SeaBird (Satlantic) |
| Time (one in an hour)<br>**Meteorological Data** | Air temperature (°C) | Ultrasonic Probe | Rotronics MP 101A |
| | Radiation (W.m$^{-2}$) | Pyranometer | Licor 200SA-50 |

Monthly (April 2017 to June-2018), where the buoy is moored, water was collected in three depths (0.8, 7 and 13 m), using a Van Dorn bottle. The water was used to measure DO, alkalinity, dissolved inorganic nutrients (orthophosphate, nitrate + nitrite and ammonium) and phytoplankton biomass. Temperature and salinity vertical profiles of the water column were measured *in situ* by a CTD (YSI, Mod. CastAway). The depth of the euphotic zone was estimated by the Secchi disk depth (Kratzer et al., 2014). Water samples for DO and alkalinity analysis, collected in duplicate, were sampled and preserved followed the Winkler (Labasque et al., 2004) and Gran methodology (Carmouze, 1994), respectively. Water samples for phytoplankton biomass (chlorophyll-a) and nutrient analyses were stored in high density polyethylene bottles, previously washed with 10 % HCl, kept in the dark and refrigerated until laboratory filtration. pH was measured with a calibrated ION PH-500 pHmeter (0.01±0.01 pH), equipped with a temperature sensor.

*Laboratory analyses*

Water samples were vacuum filtered with fiberglass micro filters (47mm diameter and 0.7µm porosity Whatman GF/F). The filtered water was used for nutrients quantification by colorimetric analysis (Grasshoff et al., 1999), using a spectrophotometer Hitachi UV-2900. The filter was used to chlorophyll-*a* quantification (Strickland and Parsons, 1972). Oxygen analysis was performed according to Labasque et al. (2004), also by spectrophotometry. Total alkalinity was determined by the potentiometric Gran titration (Gran, 1952), using the analytical procedures described by the United States Geological Survey for water samples (Rounds, 2012). Dissolved Inorganic Carbon (CID) and Carbon Dioxide ($CO_2$) concentration were estimated using the CO2calc® 1.2.9 program, following the methodology described in Robbins et al. (2010).

*Trophic Index (TRIX)*

Oxygen, chlorophyll-a, dissolved inorganic phosphorus (DIP as phosphate) and dissolved inorganic nitrogen (DIN as the sum of nitrate, nitrite and ammonium) were used to calculate the trophic state of each water sample, according to equation 1 (Vollenweider et al., 1998). The values of m and k were standardized for this study data, where m=0.53 and k=0.67. The TRIX ranges from 0 to 10, covering a spectrum of ultra-oligotrophic (0-2), oligotrophic (2-4), mesotrophic (4-6), eutrophic (6-8), and hypertrophic (8-10) conditions.

(1) $TRIX = [Log10\ (Chlorophyll*DIN*DIP*|aD\%DO|-(k=0.67)/(m=0.53)]$

*High-frequency data*

In this study, we used data from the buoy with Flag 3 (generated from quality control and data used in QARTOD manuals - Oceanographic Data on Air and Water Temperature, Salinity, Radiation, Dissolved Oxygen in Real-Time Quality Assurance Chlorophyll, 2017), it is, there is no exclusion of extreme values, since it may be associated with our hypothesis (e.g. precipitation events). The wind (velocity and direction) and precipitation data were obtained from the ERA-Interim data base (https://www.ecmwf.int/en/forecasts/datasets/reanalysis-datasets/era-interim). Data were extracted for a region between 27.25ºW and 27.5ºW and -48°S and -48.5°S, with a spatial grid of 0.125 ° x 0.125 ° (~ 1 km). Adjustment was made to the DO and chlorophyll data measured by the analytical values obtained by discrete sampling (see the Table 1 in Appendix).

*Metabolism estimates*

The governing equation (Eq. 1) for estimating the metabolism by the free water technique from DO measurements was first established by Odum (1956). It considers the variation in oxygen concentration as a result of gross primary production (GPP), discounting the respiration (R) and the fluxes (F) with the atmosphere (Tab. 2).

The oxygen exchange in the ocean-atmosphere interface considers the DO concentration in the water and its saturation concentration in relation to the gas pressure in the atmosphere, which depends on physical water parameters, and the wind intensity in the sea surface (Wanninkhof, 1992; Staerh et al., 2010). The concentration of oxygen in water in equilibrium with the atmosphere (oxygen saturation) can be estimated based on water temperature and salinity (Eq 2), correcting for atmospheric pressure (Eq. 2.1).

Table 2. Description of the equations used for the calculations of the ecosystem metabolism, adaptated of Staerh et al. 2010, with their respective references (see routine used for the calculations in Appendix).

| NAME (REFERENCE) | EQUATION | DESCRIPTION | RELEVANCE |
|---|---|---|---|
| 1.Basic Conceptual Equation<br>**(Odum 1956)** | $\Delta OD_2/\Delta t = GPP - R + F$ | **$\Delta DO_2$** (g $m^{-3}$ $hr^{1}$) = Oxygen variation<br>**$\Delta t$** = Time variation<br>**GPP** = Gross primary production<br>**R**= Respiration<br>**F** = Physical exchanges | Dissolved oxygen is produced and consumed by metabolic processes (GPP and R**)** |
| 2.Determination of saturated OD concentration<br>**(Weiss 1970 )** | $O_{2sat} = (e^{C})\ 1\ .423\ O_2$<br>$C = (-1\ 73.4292 + 249.6339 - 21\ .8492 \times (T / 1\ 00) + S \times [-0.033096 + 0.01\ 4259 \times (T / 1\ 00) - 0.001\ 7000 \times (T / 1\ 00)^2]$ | **$O_{2sat}$** = Saturated saturated OD concentration (mg $L^{-1}$)<br>**C**= $O_{2sat}$ as a function of temperature (T, kelvin) and salinity (ml.$L^{-1}$) | It is necessary to know the solubility of the gas at sea and what may influence this solubility (barometric pressure). |
| 2.1Correction made for barometric pressure<br>**(USGS memo #81 .1 1 1 981)**<br>**(USGS memo #81 .1 5 1 981)** | #ml.L for mg.L = x 1.42<br>$O_{2sat} = O_{2sat}$ x correct fator<br>Correction fator = (BP x 0.0987 - 0.01 1 2)/1 00 | **BP** = Barometric press | |
| 3.Schmidt coefficient calculation from water temperature (T, Celsius) | $Sc = 1920.4 + (-135.6 \times T) + (5.2122 \times T^2) + (-0.10939 \times T^{\wedge 3}) + (0.00093777 \times T^{\wedge 4})$ | **Sc**= Scmidt number | Necessary coefficients that provide energy to mix water and promote gas exchange between water and the atmosphere. Data from nearby stations may be used if it cannot be measured on site. |
| 3.1Relation between Schimidt number and 660<br>**(Wanninkhof 1992)** | Sc660 = (660/Sc).^0.5 | **Sc660**= Relation between two numbers for calculation $k_{660}$ | |
| 4.Wind speed calculation at 1 0 m height<br>**(Smith 1985)** | $(U_{1\ 0})\ U_{10} = U_Z \times \alpha$<br>$\alpha = 1\ .4125\ z^{-0.1\ 5}$ | **$U_{10}$ =** Wind speed at 10 height (m $s^{-1}$)<br>$U_Z$<br>**α =** Conversion factor for a given height *z* | |

| | | | |
|---|---|---|---|
| 5.Piston velocity<br>**(Cole and Caraco 1998)**<br>**(Jahne et al 1987)** | $K_0$ = 2.718281^(–58.3877+ 85.8079 (1 00/T) + 23.8439 x ln (T/1 00) + S x [(–0.034892+ 0.01 5568 x (T/1 00) +(–0.001 9387) x (T/1 00)2])) (–0.001 9387) x (T/1 00)2]))<br>$K_{660} = (0.251 \times U_{10}^{1.7})/100$<br>$K = k_{660} \times ([660/Sc]^{0.5})$ | **$K_0$** = Gas solubility coefficient<br>**K660**= Wind speed function at 10 m (m $h^{-1}$)<br>**K**= Coefficient exchange gas OD (m $h^{-1}$) | Gas exchange and solubility constants used in salt water for subsequent flow calculation between water-atmosphere interface |
| 6.Physical gas flux<br>**(Staehr et al 2010)** | $F = K \times (O_2 - O_{sat})$ | **F**= Gas exchange ocean atmosphere flux | |
| 7.NEP calculation<br>**(Cole et al 2000)** | $NEP_h = \Delta DO_2 - F/Zmix$<br>$NEP_{daytime}$= mean $NEP_h$ during daylight x dayfraction<br>NEP= GPP – Rday<br>#dayfration = light_hours in 24h | **$NEP_h$** = Hourly Net (g $O_2$ $m^{-3}$ $hr^{-1}$)<br>**NEPdaytime**=Net integrated daylight hours (g O2 $m^{-3}$ daylight $period^{-1}$)<br>**Zmix**= Deph of blend (m)<br>**NEP**= Daily Net metabolism (g$O_2$ $m^{-3}$ $d^{-1}$) | In the ocean several processes influence metabolic rates, it is necessary to calculate the turbulent flows caused by the wind, and remove from the calculation of metabolism to find the values of what was produced and breathed, calculating the hours of the day by irradiation (dayfration). |
| 8.Respiration calculation<br>**(Staehr 2010)** | $R_h$= mean $NEP_h$ during darkness<br>$R_{daytime} = R_h \times$ dayfraction<br>$R_{day} = R_h \times 24$ h # sunset extrapolated | **$R_h$** =Hourly respirations rates<br>**$R_{daytime}$** = Respiration between sunrise and over day length (g$O_2$ $m^{-3}$ daylight $period^{-1}$)<br>**$R_{day}$**= Extrapolated respiratory rates to 24h (g$O_2$ $m^{-3}$ $d^{-1}$) | |
| 9.GPP calculation<br>**(Staehr 2010)** | $GPP = NEP_{daytime} + R_{daytime}$ | **GPP** = Gross Primary Production (g$O_2$ $m^{-3}$ $d^{-1}$) | |

The gas exchange with the atmosphere was estimated at each time interval (1 h) using gas exchange coefficient (k) calculated from $k_0$, $k_{660}$ and the Schmidt number ratio (Sc, Eq. 3), which indicates the stability of the water column. $K_0$ is the gaseous solubility constant and $k_{660}$ is estimated as a function of wind velocity at 10 m above the ocean surface (Eq 4). As the wind sensor was below 10m, a value adjustment was made based on equation 4 (Table 2). These parameters (Sc, $U_{10}$, $k_0$, k) were used to estimate the gas flux between sea-air interface (Eq. 5).

Because net production (NEP) indicates oxygen gains from photosynthesis and oxygen depletion during respiration, Net primary production (NEPh, $gO_2.m^{-3}.h^{-1}$) was calculated from the DO concentration (converted to $g.m^{-3}$) budget estimated for each time interval (by hourly), discounting the air-sea DO exchange (F) in the mixing zone (Zmix) by physical and diffusion processes, according equation 7 (Tab.1). NEPdaytime ($gO_2.m^{-3}$daylight period$^{-1}$) is the portion of NEP occurring while photosynthesis is taking place. Thus, NEPdaytime is the mean NEPhr rate occurring between sunrise and sunset extrapolated over Day Length (dayfraction). The depth of the mixing zone (Zmix) was calculated from the sea surface to the top of thermocline, using the CTD discrete samples (N = 10) and the TS profiles of Freire et al. (2017) (N = 6). We found an average Zmix of 9 ± 4.7 m.

The opposite is done with the calculation of respiration (R), considering that this processes occurred exclusively at night period. Therefore, hourly respiration (Rhr, $gO_2.m^{-3}.h^{-1}$) was calculated from the DO concentration budget estimated for each time interval (hourly) at night. This R could be extrapolated to the respiration rates that occurred during the light period (Rdaytime, $gO_2.m^{-3}$ daylight period$^{-1}$), multiplying it by the number of daylight hours (dayfraction). Besides that, daily respiration (Rday, $gO_2.m^{-3}.d^{-1}$) was estimated by multiplying the Rhr by 24 hours.

Gross Primary Production (GPP, $gO_2.m^{-3}.d^{-1}$) is the sum between NEPdaytime and Rdaytime (Staehr et al., 2010). The metabolic balance is the difference between those values. GPP rates ($gO_2.m^{-3}.d^{-1}$) were integrated for the mixing zone ($gO_2.m^{-2}.d^{-1}$), multiplying it by the average Zmix depth (m). This measurement was converted to moles of oxygen ($molO_2.m^{-2}.d^{-1}$), dividing it by 32 (Lana et al., 2006). The photosynthetic quotient (PQ) of 1.2 was used to covert oxygen to carbon fixed (Asmus, 1982). The PQ establishes the relationship between the number of moles of $O_2$ released in the photosynthesis and the number of moles $CO_2$

assimilated, resulting in molC.m$^{-2}$.d$^{-1}$, converted to mass of C by multiplying by 12. GPP was converted from daily to annual by multiplying by 365 days (gC.m$^{-2}$.year$^{-1}$).

Photosynthetically active radiation (PAR) corresponds approximately to 47% of visible light (Vollenweider, 1974). The hourly average of sunlight (W.m$^{-2}$) was transformed into μmol.photon.m$^{-2}$.s$^{-1}$ by the conversion factor of 4.6 (Plant Growth Chamber Handbook, 1997). Radiation that reaches the water surface, recorded by the light sensor, was defined as atmospheric radiation (atmospheric PAR), being used in the analysis with the other meteorological variables. The PAR that reaches the depth of the water column where the oceanographic (water PAR) sensors are installed was estimated from the light incident on the atmospheric sensor and the depth of the euphotic zone (Kirk, 1979).

### *Statistics analyses*

Spearman's correlation was used to evaluate the linear relationships ($p < 0.05$) among all variables. A distance-based redundancy analysis (dbRDA) was performed to verify the multivariate association between the physical, biological and chemical variables throughout the seasons. The data was normalized and standardized before the similarity analysis by Euclidean distance. Third-order polynomial regression analysis was used to assess the seasonal trend of meteo-oceanographic and metabolism variables. These regressions were plotted using the Matlab 2018a "polyfit" and "polyval" functions (Chen et al., 1999). The non-parametric Generalized Additive Model (GAM) was used to detect nonlinear trends between a dependent variable, the GPP, and independent variables (chlorophyll-*a*, water temperature, salinity, precipitation, wind speed and PAR). The tests that compose GAM are resistant to extreme value effects and robust against deviations from a normal distribution (Wood et al., 2016). The independent variables were tested by the Analysis of covariance (ANCOVA) to avoid data redundancy. The GAM was performed by the studio R package “mgcv”, using the simple Gaussian random effect and the GCV smothing parameter (Wood et al., 2016). The software RStudio 1.0 Open Source (R Core Team, 2013) and PRIMER-E were used to perform the other graphs and statistical analyses.

## RESULTS

### Meteorological variables

In general, winds from the north quadrant, followed by the southerly winds, predominated in the study area (Figure 5). Both NE and S winds reached maximum velocities (6 to 8 m.s$^{-1}$.d$^{-1}$), depending on the sampling period (Figure 5).

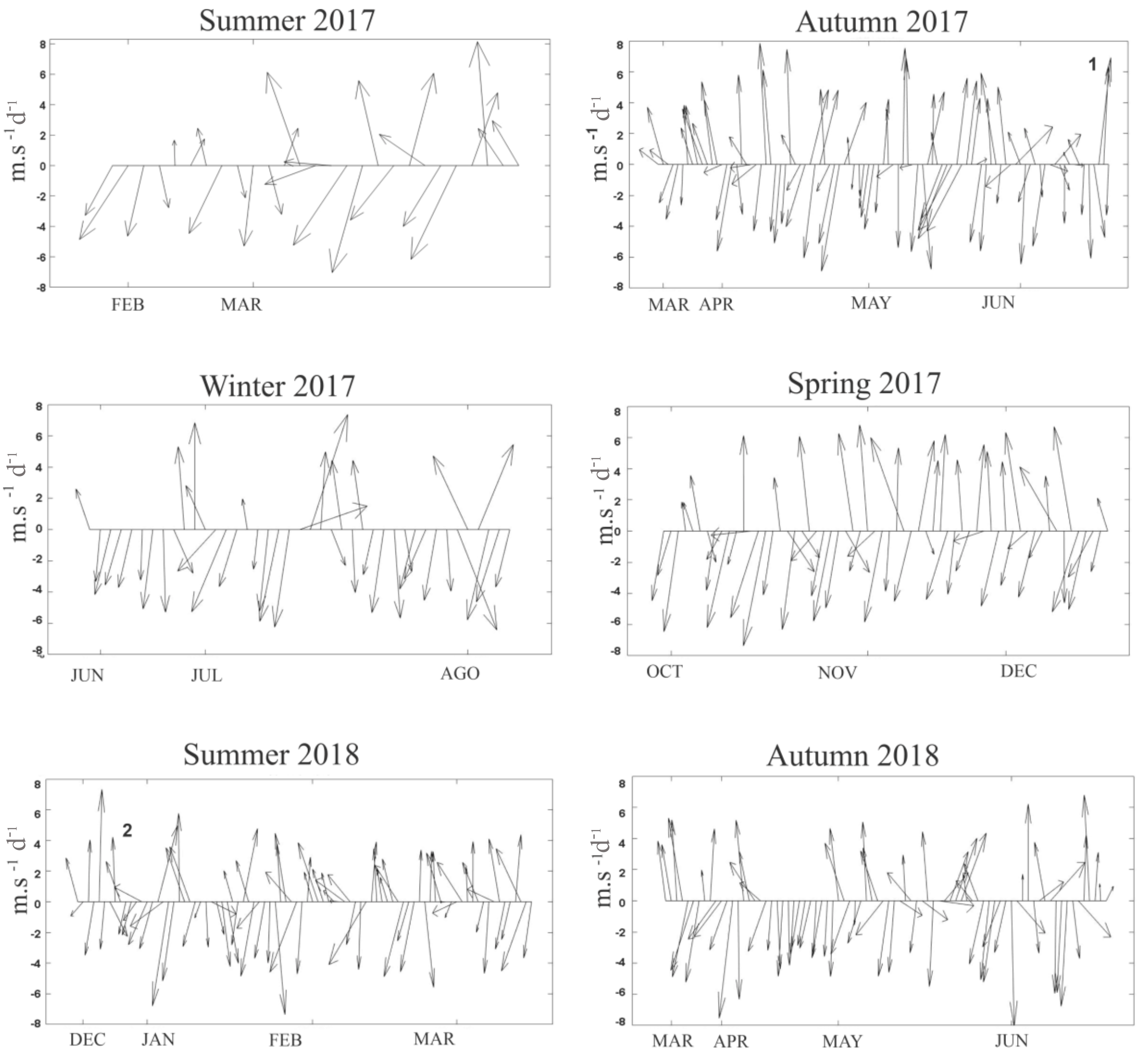


Figure 5. Wind direction (negative values indicated wind N and positive values wind S) and intensity (represented by vector length) in days (x axis) to all the seasons (2017 and 2018). Details 1 and 2 correspond to the GPP peaks.

Atmospheric temperature, ranging from 11 to 27 °C (Fig. 6a) and PAR, 0 to 4.10$^{-3}$ µmol.photons.m$^{-2}$.s$^{-1}$, showed typical values for the subtropical region of Brazil, which can be observed by the polynomial regression, $r^2 = 0.61$ and $r^2 = 0.33$, respectively (Fig. 6). Despite this trend, the lowest values were recorded in early spring 2017, when air temperature dropped to (11 °C), shortly after precipitation (8.5 mm).

Rainfall showed some periods of high accumulations, the highest values were recorded in the autumn 2017, up to 100 mm in 12 days between fall and winter. In winter 2017, the accumulate rainfall was 51.8 mm; and in summer 2018, 83.3 mm.

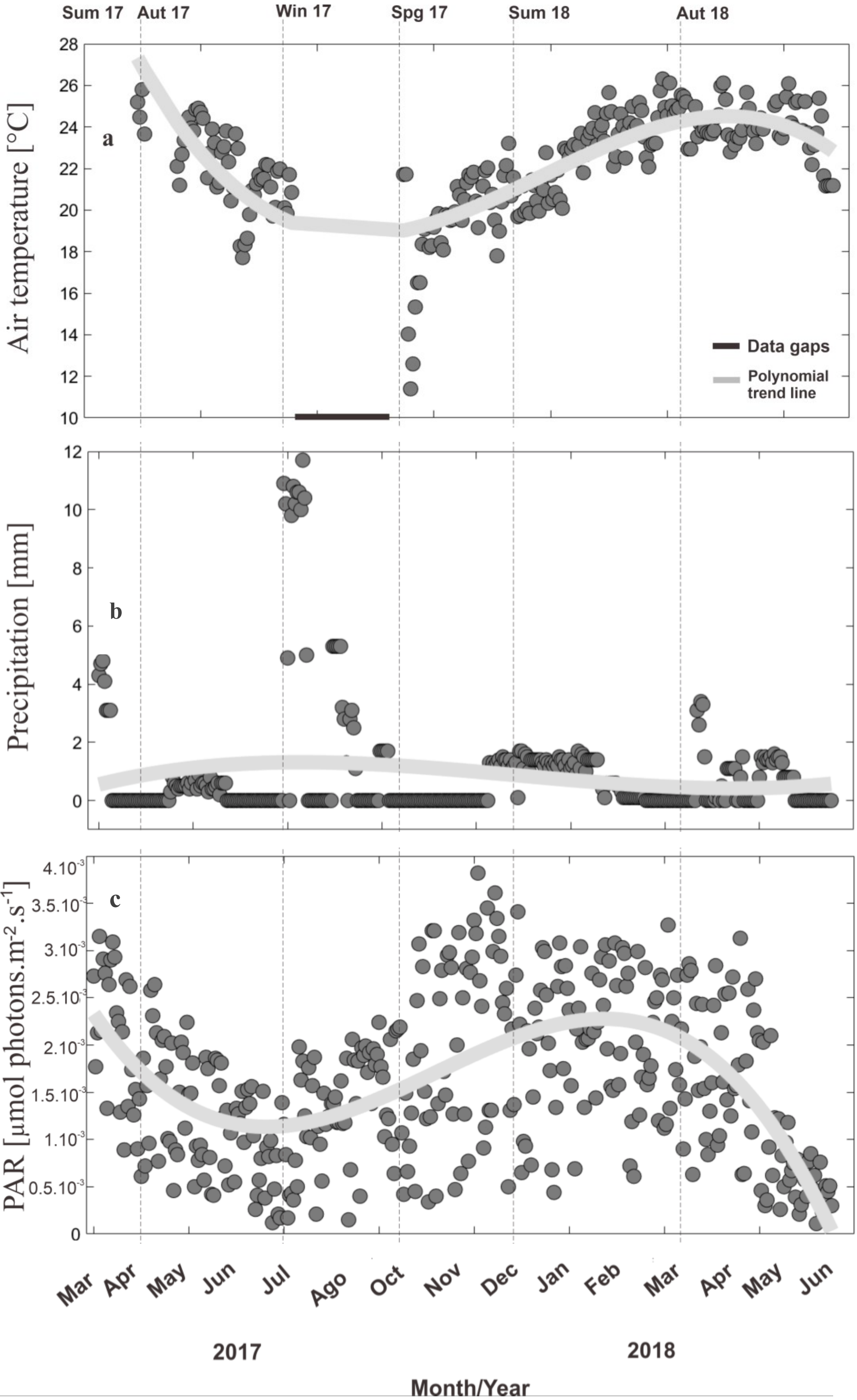


Figure 6. Time daily series of meteorological variables (Air temperature, a, Precipitation, b, and, PAR, c).

Oceanographic variables

The water temperature showed a seasonal trend ($r^2 = 0.77$, Fig. 7a), ranging between 18.0 to 27.0°C. Atmospheric and seawater surface temperatures were highly correlated ($r = 0.95$, $p < 0.05$). Salinity ranged from 28 to 36 (Fig. 7b), minimum values were observed during periods of heavy rainfall. DO also showed a seasonal tendency ($r^2 = 0.34$, Fig. 7c), ranging from 7.8 to 9.0 $mg.L^{-1}$. The lowest DO values were recorded in July 2017, after a period of heavy rainfall (> 10 $mm.d^{-1}$), when low salinities were also recorded. Rainfall was correlated ($p<0.05$) with DO ($r = 0.66$) and salinity ($r = -0.26$). In general, oxygen supersaturation conditions were observed in the water column (112 ± 15%) in all periods.

Chlorophyll-*a* ranged from 0.3 to 3.2 $\mu g.L^{-1}$ (Fig. 8a). High values occurred in late autumn (2.4 $\mu g.L^{-1}$), early winter (3.0 $\mu g.L^{-1}$) of 2017, and in the summer of 2018 (3.1 $\mu g.L^{-1}$), all during rainy periods. GPP ranged from 14 to 940 $mgC.m^{-2}.d^{-1}$ (Fig. 8d, N=389), showing peaks during the winter of 2017 (900 $mgC.m^{-2}.d^{-1}$), early summer 2018 (700.0 $mgC.m^{-2}.d^{-1}$) and fall 2018 (942.0 $mgC.m^{-2}.d^{-1}$). GPP maximums were recorded in periods that presented rainfall accumulations above 100, 40 and 20 mm (highlighted by the numbers in figure 8d - 1, 2 and 3, respectively). The NEP ranged from -200 to 300 $mgC.m^{-2}.d^{-1}$, the lowest values occurred in spring 2017 (Fig. 8c). The RESP ranged from -8.38 to -889 $mgC.m^{-2}.d^{-1}$ (Fig. 8b), with negative values indicate oxygen withdrawal from water. During winter 2017 and summer and fall 2018, RESP exceeded -800 $mgC.m^{-2}.d^{-1}$.

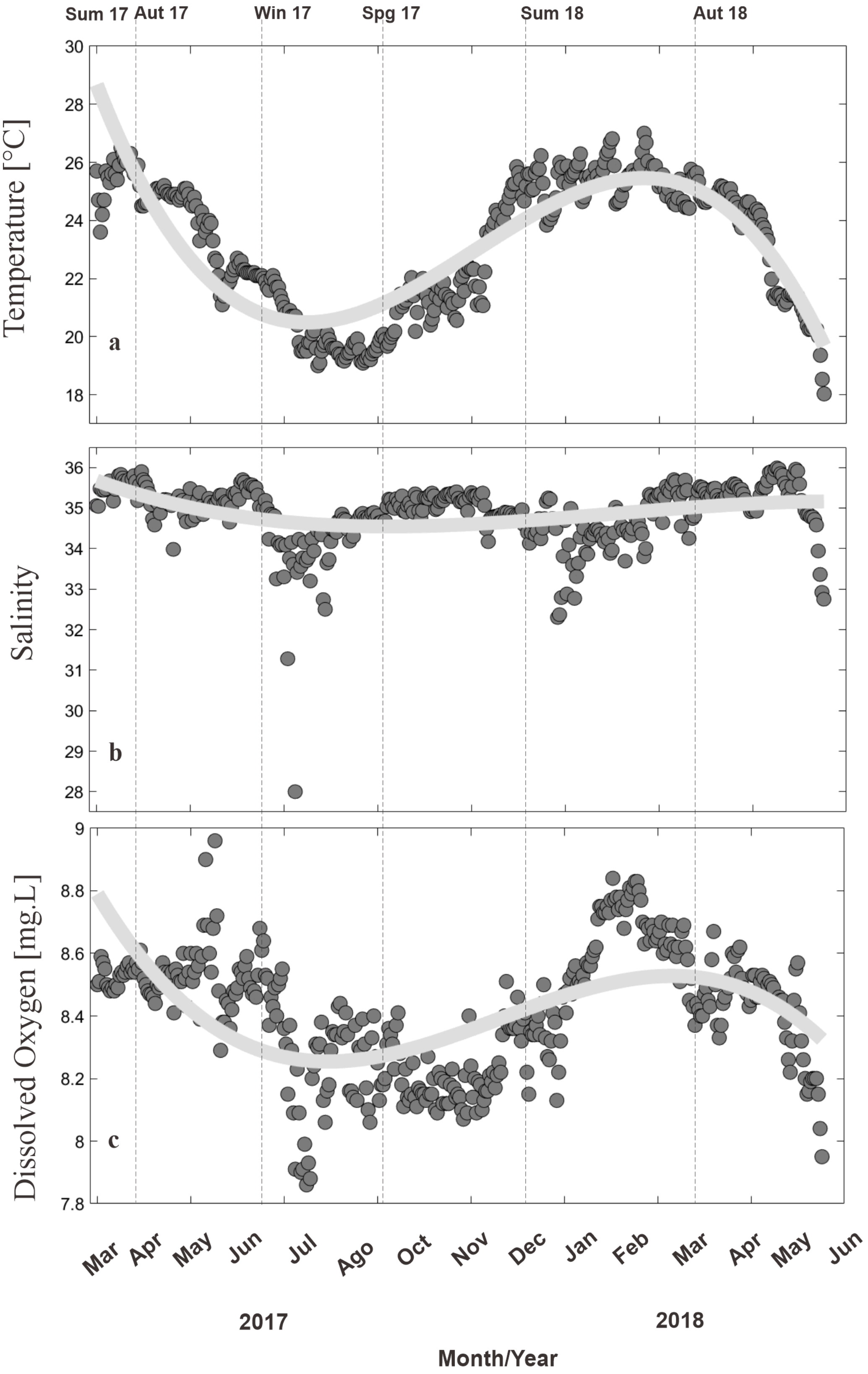


Figure 7. Time daily series of the physical (Temperature, a, Salinity, b) and chemical (Dissolved Oxygen, c).

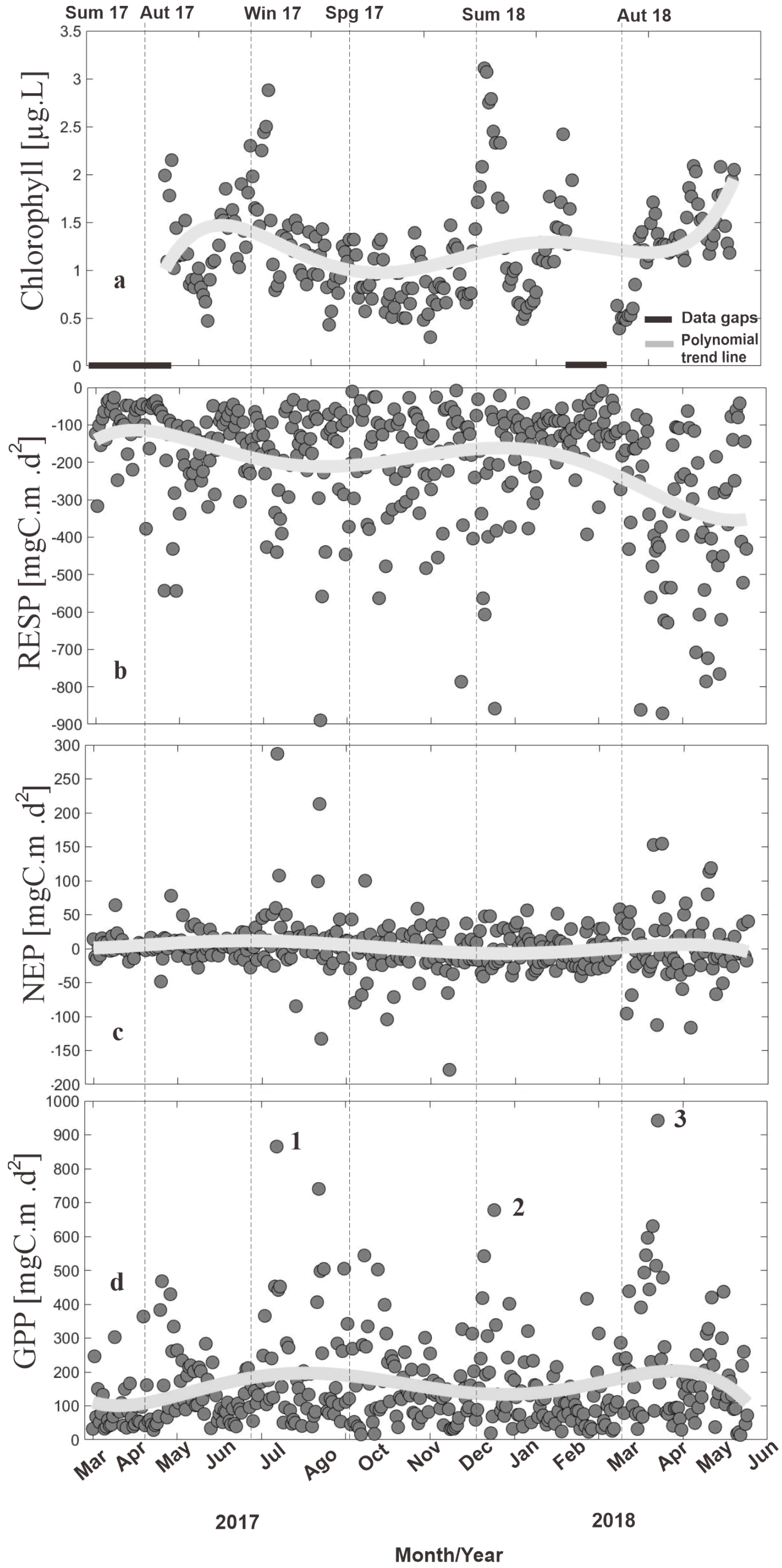


Figure 8. Time daily series of the biologic variables (Chlorophyll, a, Resp, b, NEP, c, and GPP, d).

### Multivariate association among meteo-oceanographic events, biogeochemistry and the ecosystem metabolism

GAM analysis showed that precipitation and atmospheric PAR best described the temporal variation of GPP, among all the variables used (Tab. 3).

Table 3 Results of the GAM test for the meteo-oceanographic variables in relation to the GPP, showing the variables that best correlated and were more significant.

| Explanatory variables | Coefficient | Std. Error |
|---|---|---|
| ***Intercept*** | *< 2e-16* *** | *12.89* |
| **Precipitation** | 0.0002 *** | 3.715 |
| **PAR** | 0.0245 * | -2.259 |

**R-sq.(adj)** = 0.04 **Deviance explained** = 4.9%
**GCV** = 16878 **Scale est**. = 16748 N = 389

**Signif. codes:** 0 ‘***’ 0.001 ‘**’ 0.01 ‘*’

The dbRDA indicated a separation between winter and summer (Fig. 9). Seasonal separation is clearer on the axis 1, where temperature (r = -0.61) and oxygen (r = -0.57) correlated best. The samples that presented the highest GPP rates, concomitant with the chlorophyll peak, especially in winter, are located in the positive part of axis 1. Spring showed similar pattern to winter, but in the autumn, there was no clustering (Fig. 9). PAR and salinity were inversely correlated (r = -0.26, $p<0.05$), indicating that freshwater flux might limited light penetration.

Multivariate analysis of discrete data also showed a separation between winter and summer (Fig. 10). $CO_2$ (r = -0.39) showed an inverse correlation ($p < 0.05$) with temperature. Nitrate was directly correlated ($p < 0.05$) with $CO_2$ (r = 0.75) and inversely (r = -0.50) with DO. DIP, on the other hand, showed an inverse correlation ($p<0.05$) with temperature (r = -0.37) and DO (r = -0.43) and a direct correlation with chlorophyll (r = 0.40).

GPP strongly correlated with discrete chlorophyll-a data (Fig. 11A), measured in the laboratory, and poorly with daily in situ data from the SIMcosta buoy (r = 0.23, p = 0.00, N = 389). This trend was also observed in the dbRDA, where the GPP and chlorophyll vectors converge to the positive side of axis 1 (Fig. 9).

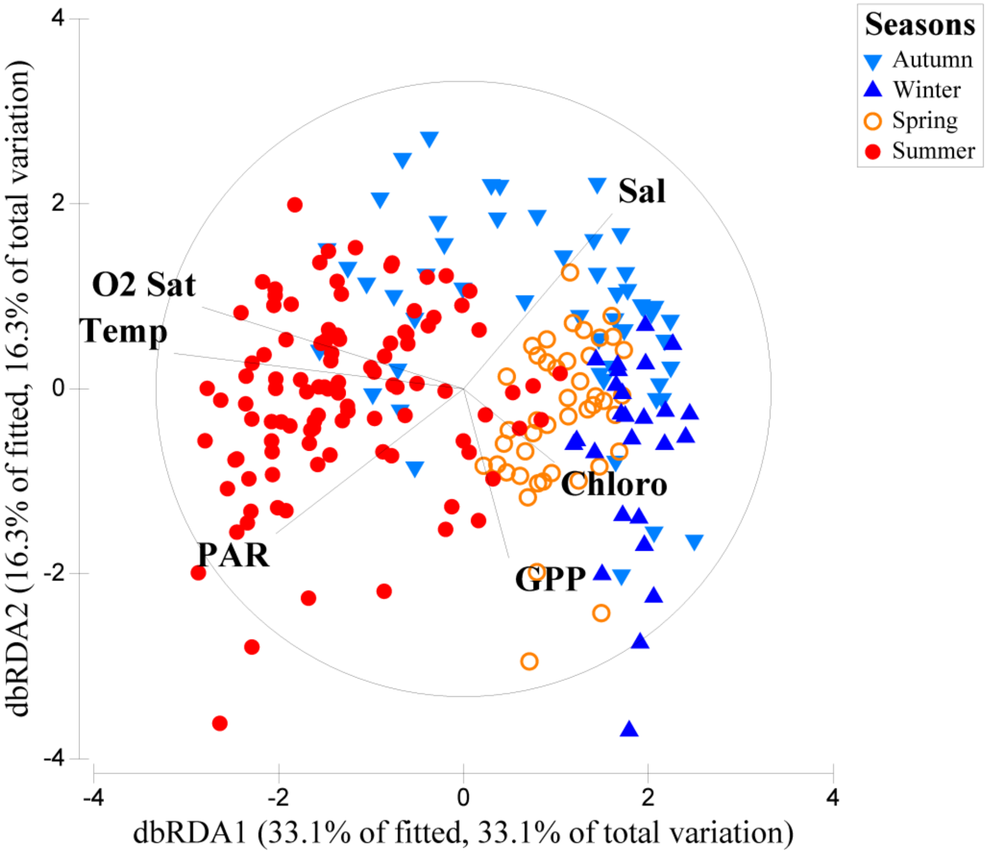


Figure 9. Distance-based Redundancy Analysis (dbRDA) of the continuous data, measure by sensors and estimated by ecosystem metabolism model. The similarity matrix (N = 225) was generated from samples that presented all data lines for Salinity (Sal), Temperature (Temp), Water Photosynthetically Active Radiation (PAR), Oxygen Saturation ($O_2$ Sat), Chlorophyll-a (Chloro) and Gross Primary Production (GPP).

The inverse correlation between water temperature and RESP reinforces the tendency for higher heterotrophic conditions in the winter (Fig. 11C). DIC showed an inverse trend with NEP (Fig. 11B) and directly with TRIX (Fig. 11D). It is, the highest DIC concentrations were found during periods of heterotrophy and high trophic state (Fig. 11). DIC was also correlated ($p < 0.05$) with ammonium ($r = 0.59$), and the highest ammonium concentrations were found in the periods of low salinity ($p < 0.05$, $r = -0.44$).

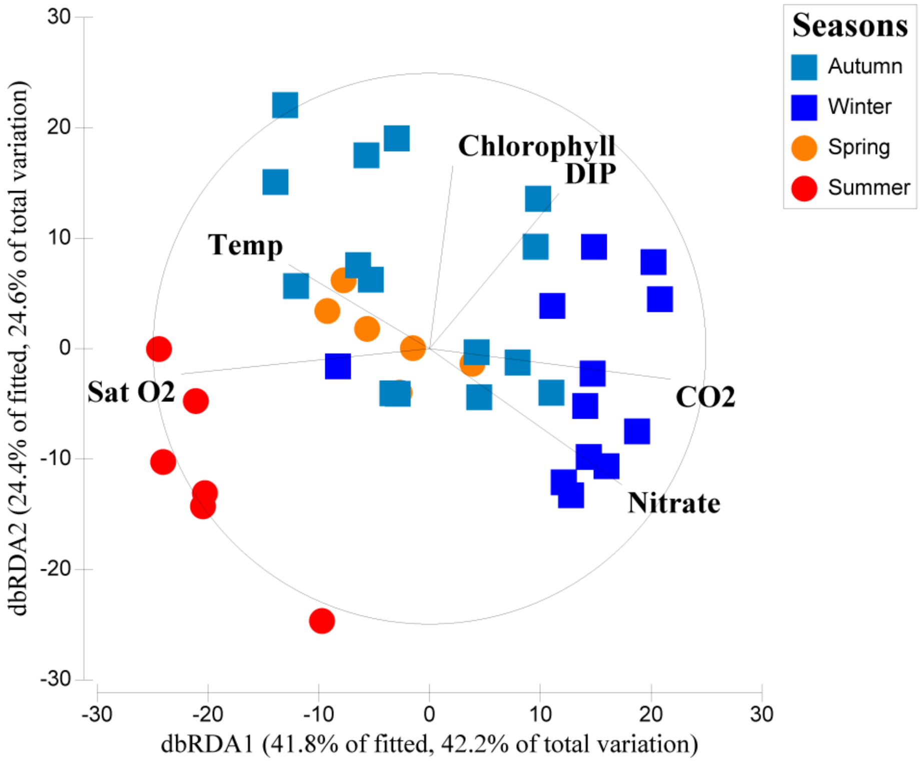


Figure 10. Graph generated from Distance-Based Redundancy Analysis (dbRDA) of discrete data collected in situ. The similarity matrix (N = 39) was generated from samples that presented all data lines of Temperature, Oxygen Saturation, Carbon Dioxide, Dissolved Inorganic Phosphorus, Nitrate and Chlorophyll.

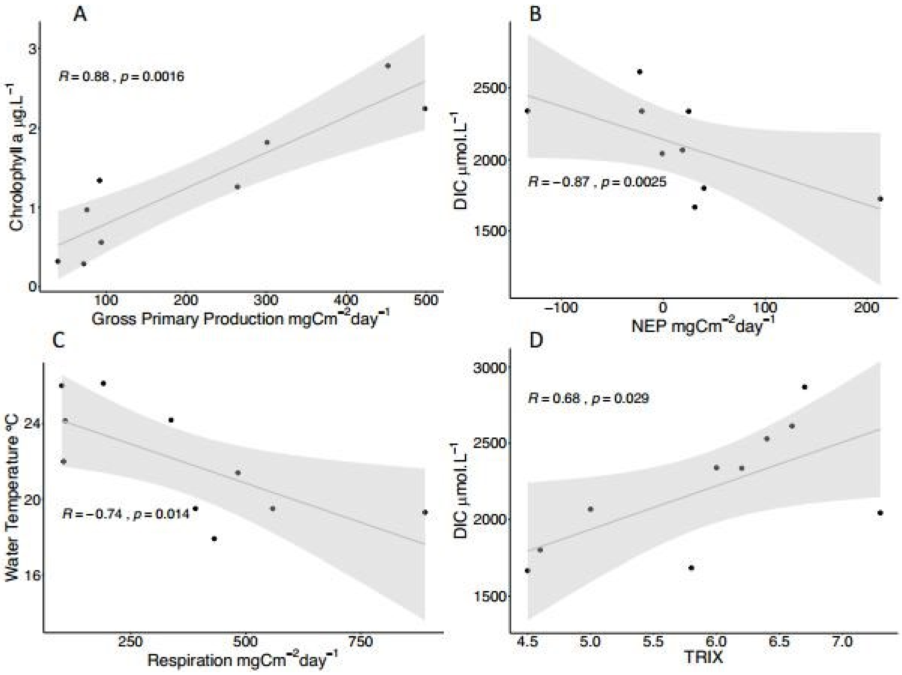


Figure 11. Spearman linear correlations of a) chlorophyll-a (discrete data *in situ*) and GPP, b) DIC and NEP, c) water temperature and respiration and d) DIC and TRIX. The gray bands indicate the 95% confidence interval.

## DISCUSSION

### Mesoscale dynamics

The Subtropical Shelf Water (STSW) dominates throughout the study, which influenced the metabolism and biogeochemical proprieties of water column. According to Moller et al. (2008), the STSW has temperature (T) higher than 14°C and salinity (S) between 33.5 and 35.3 in the winter (Figure 12). In the summer, STSW has T>18.5 °C and 35.3<S<36. STSW is influenced by different water masses, such as Tropical Water (TW) in summer and the PPW in winter (Moller et al., 2008).

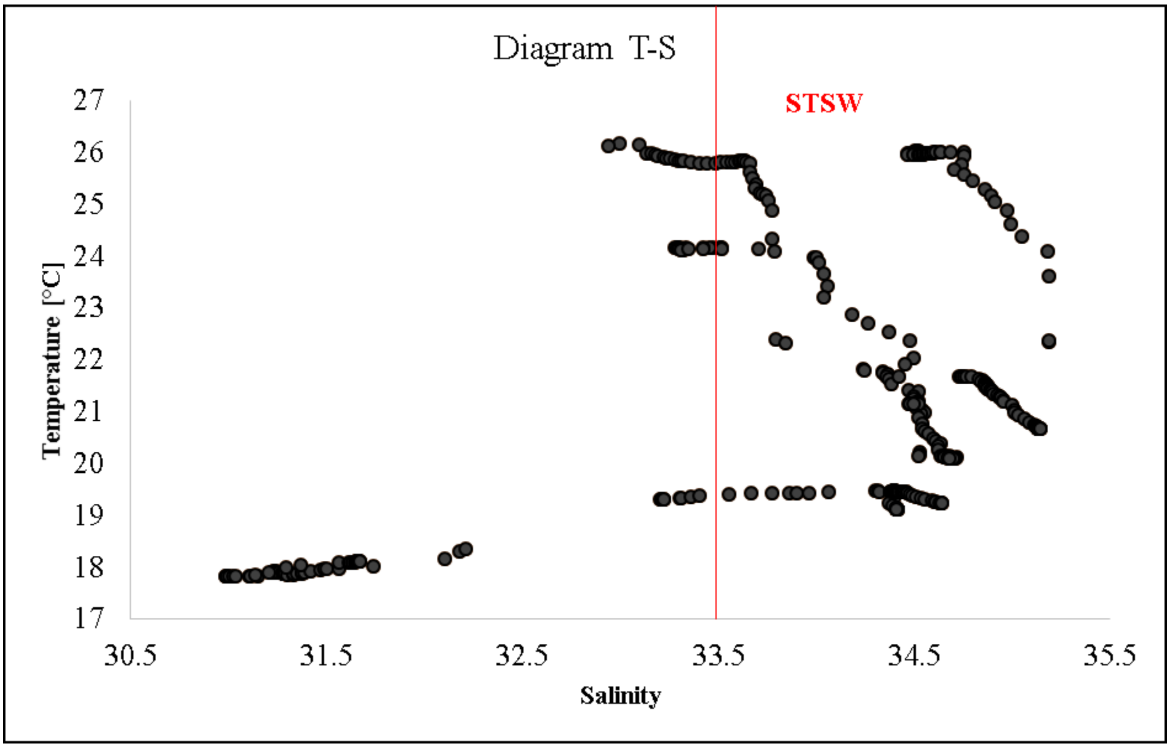


Figure 12: Diagram T-S made with the vertical profiles of CTD in the water column identifying the water mass STSW at the point where the float is. Profiles were made from July 2017 to June 2018.

The seasonal dynamics of surface waters in the SBB promotes eutrophic conditions in the winter and oligotrophic in the summer (Braga et al., 2008; Bordin et al., 2018). Also, the influence of PPW in the SBB during winter is usually associated with the highest concentrations of chlorophyll-*a* and DIP in the surface waters. In this study, the GPP presented a positive trend with phytoplankton biomass, associated with high DIP concentrations in autumn-winter, suggesting that the ecosystem metabolism is related to mesoscale events.

We found that low water temperatures in winter were correlated with high respiration and DIC, indicating regeneration processes. Nitrate was high in this period too, corroborating with regeneration processes. Also, the supersaturated oxygen conditions found in the surface water is probably fueling nitrification, it is, ammonium to nitrate (Lutz et al., 2018). Bordin et al. (2018) and Lutz et al. (2018) indicated the importance of regeneration processes for nutrient availability to primary producers in the SBB, mainly in the winter. The heterotrophic pattern was also evidenced in our study, not only in the winter season, but in the summer too. In the winter, OM mineralization exceeded autotrophic production, indicating that the metabolism is dependent of regenerative processes. Thus, the internal continental shelf water acts as a source of nutrients to the adjacent open ocean, as indicated in other regions (Ito et al., 2016; Chen et al., 2003).

SBB is influenced by continental runoff throughout the year, including the PPW (from Plata river basin of 3.1 x 106.km$^2$) and South Brazil Atlantic Watersheds (0.2 x 106.km$^2$), this runoff contributes with high amounts of allochthonous organic matter and nutrients to the continental shelf (Bordin et al., 2018). The heterotrophic pattern along the coast has been described in systems that receive riverine inputs, such as the Louisiana Continental Shelf (LCS/USA), from the Mississippi river (2.9 x 106 km$^2$), and the East China Sea, from the Changjiang river (1.8 x 106 km$^2$) (Chen et al., 2006; Murrel et al., 2013). The organic carbon inputs from riverine sources is what makes up the heterotrophy of nearshore regions (Duarte et al., 2013), While the open ocean regions is usually autotrophic (Williams et al., 2013).

Although the seasonal pattern of the ecosystem metabolism is more elucidate in temperate regions (Blight et al., 1995; Serret et al., 1999), its importance in subtropical regions is unclear (Williams et al., 2013). In our study, respiration dominated the NEP in 99% of the samples, suggesting that the region is source of $CO_2$ to the atmosphere (Ito et al., 2005; Padin et al., 2010). This condition was already reported in other regions of SBB, using in situ measurements of $CO_2$ fluxes (Ito et al., 2016). Other studies have found similar results of $CO_2$ fluxes in atmosphere-ocean interface of Atlantic continental shelves (0-30°S), which are typically source of $CO_2$ to the atmosphere (Chen and Borges, 2009; Laruelle et al., 2010;

Laruelle et al., 2014; Ito et al., 2016). Ito et al. (2016) indicates that the SBB is source of $CO_2$ to the atmosphere, i.e. respiration > production, while oceanic waters (> 1000 m) acts as a $CO_2$ sinks, associated to the autotrophic behavior (R < P). Lutz et al. (2018) corroborates Ito et al. (2016), showing high PP values and autotrophic NEP in shelf break of Atlantic continental, where new primary production dominates.

The trophic state of the internal SC shelf, according to TRIX, varied from mesotrophic (4.5) to eutrophic (7.4). Bordin et al. (2018) found mean TRIX values of 5.6±1.3, characterizing the system as mesotrophic, under the influence of the STSW. According to Cloern et al. (2014), GPP between 0.27–0.81 $gC.m^{-2}.d^{-1}$ classifies the system as mesotrophic and between 0.81–1.36 $gC.m^{-2}.d^{-1}$ as eutrophic. The daily GPP found in this study ranged from 0.01 $gC.m^{-2}.d^{-1}$ (oligotrophic) to 0.94 $gC.m^{-2}.d^{-1}$ (eutrophic). However, average values indicate an oligotrophic system (0.16 $gC.m^{-2}.d^{-1}$). The waters of the internal shelf of SC have been described as heterotrophic, it is, nutrient regeneration is more important than the assimilation by primary producers (Metzler et al., 1997). In this context, it would be expected that the high nutrient availability and the elevate trophic state boost productivity rates, however GPP values suggest that the system is oligotrophic, as addressed by Lutz et al (2018) over the waters of the Southeast and South of Brazil, between São Tomé cape and Chuí. That is, there is a potential for primary production that does not match the measured values. Although the potential for primary production is high, other mechanisms might be limiting the ecosystem to achieve its fully productivity capacity.

In an overview on the primary production (PP) rates of the Southwestern Atlantic (Lutz et al., 2018), which includes the SBB, a total of 211 measurements of PP between 1982–2009 were made were gathered and separated by seasons (Number of measurements (N in Summer, N=70; Autumn, N=32; Winter, N=42; and Spring, N=67). The higher GPP rates were registered during in autumn-winter, as a result of high nutrient input, mostly from anthropogenic and Eolic sources. According to these authors, it is possible to recognize some areas of higher GPP, associated to the shelf-break of southwestern Atlantic (>0.55 $gC.m^{-2}.d^{-1}$, mesotrophic), Grande Bay in the Argentine shelf (>0.30 $gC.m^{-2}.d^{-1}$, mesotrophic) and the southeast of the Brazilian shelf (>0.19 $gC.m^{-2}.d^{-1}$, oligotrophic) (Lutz et al., 2018). The ecosystem metabolism rates found here are in accordance with those measured by and Brandini (1990); Saldanha-Correa and Gianesella (2008); Ciotti et al.

(1992) and Gonzalez-Rodrigues et al. (1992), highlighting the few records in the internal and median SBB (Tab. 4).

Table 4. Gross Primary Production rates in the Brazilian continental shelf, LSC (Louisiana Continental Shelf) and East China.

| Region | Sector | mgC.m$^{-3}$.d$^{-1}$ | N date | Reference |
|---|---|---|---|---|
| SBB | Brazilian Internal Continental shelf | 1-104 | 389 | This study |
| Southeast Brazil | Coast | 0.1-97 | 0 | Brandini (1990) |
| Cabo Frio | Brazilian Continental shelf | 24-168 | 2 | Gonzalez Rodrigues et al.(1992) - Unpublished data |
| Chuí and Santa Marta Cape | Brazilian Internal Continental shelf | 235 | 24 | Ciotti et al 1992 |
| São Sebastião | Brazilian Internal Continental shelf | 30.4-108 (in seasons) | 11 | (Saldanha-Correa and Gianesella, 2008) |
| East China Sea | Continental shelf | 2.6 – 9.4 | 56 | Chen et al 2006 |
| Louisiana | Continental Shelf | 3.6 | 341 | Murrel et al 2013 |

The NP ratios measured in our study and by Freire et al. (2017) indicate that primary production is mostly limited by DIN, that could be an important feature to control the GPP, as observed in other continental shelves, such as the Northern Gulf of Mexico and the North Atlantic Ocean (Fennel, 2010). Deviations in the NP ratio are triggered by the different biogeochemical processes, considering that for phytoplankton productivity these ratios need to be constant, following the Redfield ratio of 16N:1P or preferably between 10 and 20 (Duce et al., 2008). High phytoplankton productivity and biomass were measured in SBB during NP ratios in accordance to Redfield (Gaeta and Brandini, 2006). In our study, the NP ratio was 6.6±5.1, close to the values found in other studies in the region (Simonassi et al., 2010; Freire et al., 2017; Bordin et al., 2018). The predominance of values below 10 in the waters the continental shelf are due to nitrogen losses, as denitrification (Gaeta and Brandini 2006, Bordin et al., 2018).

Effects of meteorological events in the ecosystem metabolism

High precipitation (100 mm in 12 days), associated with light availability, promoted max GPP in the Autumn of 2017, 0.86 $gC.m^{-2}.d^{-1}$, and NEP of 0.28 $gC.m^{-2}.d^{-1}$. Concomitantly, decrease in DO was observed, indicating mineralization of allochthones organic matter. Freire et al. (2017) indicated the influence of eutrophic waters from the Tijucas River and North Bay Channel under precipitation events, fertilizing the continental shelf with organic matter and nutrients. The increase of anthropogenic influence on coastal areas affect the structure of the aquatic communities (Fennel, 2010) and its metabolic processes (Doney et al., 2012). In another rainy event, 39 mm in 11 days, autotrophic metabolism was associated to the NEP reaching high values, up to 0.21 $gC.m^{-2}.d^{-1}$, indicating nutrient assimilation by primary producers, while the GPP was 0.74 $gC.m^{-2}.d^{-1}$. Overall, rainfall events can increase organic matter runoff into coastal regions (Fontes et al., 2015).

Metabolism and the free-water diel DO method (FWM)

The estimation of ecosystem metabolism by the free water technique, through the variation of DO, is not usually applied in the continental shelves, when compared to incubations with $^{14}C$ (Cloern et al., 2014; Lutz et al., 2018). Bottle incubations effects could be a source of uncertainty to measure the gross primary production (GPP) and net primary production (NEP), due to the insertion of errors from sampling, manipulation and containment inherent of incubation methods (Quay et al., 2010). In the other side, the inaccuracy of our methodology could be associated with under- or overestimation of air-sea gas exchange by diffusion and turbulence (Emerson et al., 2008; Williams et al., 2013). Water masses fluxes between two consecutive DO measurements might also cause error in FWM. Those fluxes could be promoted by the tidal influence, for example, or wind patterns. Our study site is located in a microtidal zone and it is expected that the hourly oxygen budget, the basis of FWM calculations, represented the same water mass during a given day. Beside the differences between methods, our study showed pertinent results when compared with other studies in the SBB (Table 4).

The estimates must be further validated and adjusted with field experiment, such as $^{14}C$ or $^{13}C$ methods, in order to better understand the uncertainties of the methodology applied in this study. Recent studies used in vitro DO incubation to measure the metabolism in the study site and they also showed a heterotrophic metabolism in the winter (Cabral, person. comm. It corroborates with our results, presenting a better reliability. Moreover, a few other studies have also used high-frequency DO measurements to estimate the GPP, e.g. Moore et al. (2011) in the South Atlantic, Stanley (2010) in the equatorial western Pacific and Emerson (2008) in Hawaiian coast.

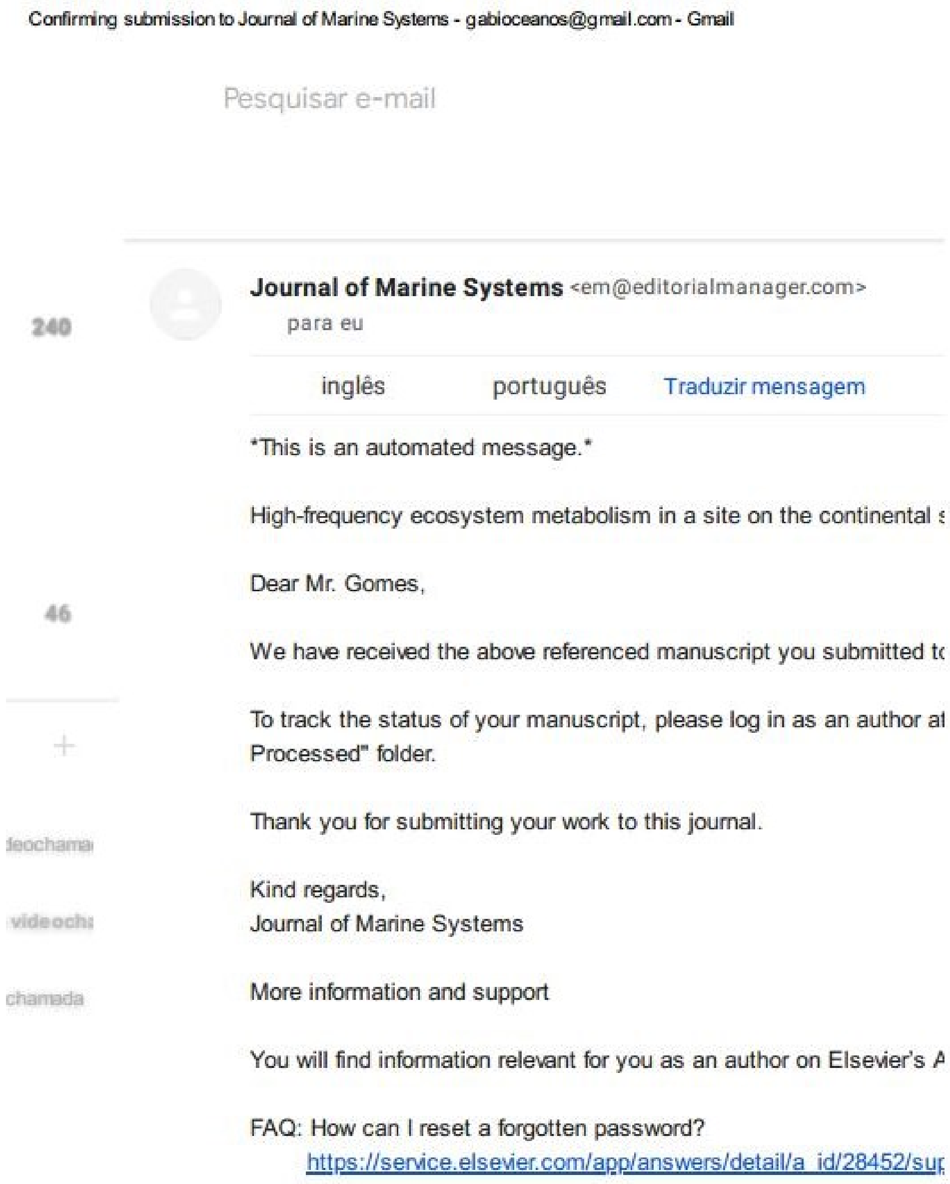
### Implications of the ecosystem metabolism to the Arvoredo Marine Reserve (AMR) management and conservation

In the Brazilian coast, continuous monitoring of the high-frequency meteorological and oceanographic properties are scarce and punctual. Also, the buoy that we used to collect the data is the first installed in a marine protected area, the AMR (SIMCosta, 2019). The Arvoredo Marine Reserve is an Integral Protection Conservation Unit (UCPI), restricted natural area intended for the conservation of local fauna and flora. The great productivity and richness of AMR is attributed to the seasonal oceanographic dynamic, as observed in our study, and its position in the subtropical area of Brazil, the transition zone between tropical and temperate climates (Freire et al., 2017). It is noteworthy mentioned that the continent next to the AMR has the highest urbanization density in the state of Santa Catarina, approximately 1.5 million people live in the region, where sewage collection and treatment are inefficient or non-existent (Garbossa et al., 2017). This condition could be an important drive to increase the trophic potential from oligotrophic to meso or eutrophic, mainly during high precipitation events, damaging the local biodiversity by causing environmental problems, such algal blooms, usually reported in the Bay of SC (Proença, et al., 2017).

A review by Hoellein et al. (2013) showed that the results obtained on aquatic metabolism can be valuable for the management and restoration of environments and their surroundings. Red tides are periodic events that occurred mainly during the end of autumn and beginning of winter in the Santa Catarina (SC) coast (Proença et al., 2017). The enclosed systems of SC internal shelf have optimal conditions for algal bloom, including toxic species, damaging the local economy, where aquaculture play an important role, up to 90% of the Brazilian oysters is produced in the SC state (Proença et al., 2017). Algal toxic bloom are reported due to the increases of nutrients (Smayda, 2008; Hattenrath-Lehmann et al., 2015), changes in wind direction and velocity, that affect water column stability (Whyte et al., 2014b) and synergistic interactions of the ecosystem metabolism and meteorological patterns (Ajani et al., 2016; Martínez et al., 2017). Therefore, it is necessary to monitor AMR and the surrounding region to understand the oceanographic processes in association with pressures from anthropogenic activities and climate change.

# APPENDIX

Figura 1 A1: Confirmação de submissão do artigo apresentado nos resultados da dissertação na revista Jornal of Marine Systems.



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High-frequency ecosystem metabolism in a site on the continental

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Table 1 A1: DO (mg.L$^{-1}$) and chlorophyll-a (µg.L$^{-1}$) data registered by the sensors were adjusted/corrected using data from the analytical procedures obtained by discrete sampling. The mean DO (N = 8) and chlorophyll-a (N = 10) values recorded by the buoy at the three times nearest to the field collection were used in the linear regression, with the purpose of establishing the trend between the data series. The equation of the line served to adjust the recorded buoy data as a function of the analytical data, being for OD and chlorophyll: where y is the discrete analytical data and x is the float measured data, with the respective r squares of each correlation equation. Corrected values were used in GPP, R and NEP calculations and statistical analyzes.

| FIT EQUATIONS | |
|---|---|
| DO | $y = -0.5298x + 8.334$; $R^2 = 0.6$ |
| CLO | $y = 1.0928x + 0.0503$, $R^2 = 0.58$ |

```
%% GABRIELA GOMES - SCRIPT FOR CALCULATING VARIABLES USED IN ESTIMATING ECOSYSTEM METABOLISM IN MATLAB

%%%%%%%%%%%%%%%%%%%%%%


%First step>>open the working file and specify each variable that will be used;
%The data used were taken from SIMCOSTA buoy and the precipitation data, speed
%and wind direction from revisions obtained from Era-Interim (ECMWF).
%%
clc; clear all; close all  %clear command window, to workspace and close all windows;
%%
var = load ('calculo_completo.txt');  %opening the file and creating a data array VAR;

date = var(:,1:3); %date, all rows from column 1 to 3;
hour = var(:,4); %hour (time data);
wind_era = var(:,6); %Wind speed (m.s-1);
press = var(:,8); %Atmospheric pressure;
sal = var(:,9); %Salinity;
```

```
temp = var(:,10); % Temperature (°C);
DO = var(:,12); %Dissolved oxygen (mg.L);
tempk = temp + 273.15 %temperature conversion to kelvin;
zmix_md = var(:,13); %medium mixing zone(9 m);
%zmix_max = var(:,14); % maximum mixing zone (16 m);
%zmix_min = var(:,15); % minimum mixing zone (2 m);
PAR = var(:,16);  %LIGHT (ATM 100%) umol photon.m-2.s-1;

%%
%% 1.Calculated variables for ocean-atm interface flow calculation

Sc = 1920.4+(-135.6.*temp)+(5.2122.*temp.^2)+(-
0.10939.*temp.^3)+(0.00093777.*temp.^4); %schimodt number (constants taken from
whanninkof, 2014)
%%
Sc_660 = (660./Sc).^0.5; %calculation needed to find the k660;
  U10 = UZ x alfa        %Calculation of wind speed adjustment for a height of 10
                                                          m from the ocean surface;
alfa  = 1 .4125 z–0.1 5                    %z is sensor depth;

k0 = 2.718281.^(-
58.3877+85.8079.*(100./(tempk))+23.8439.*(log(tempk./100))+(sal.*(-
0.034892+0.015568.*((tempk)./100)-0.0019387.*((tempk)./100).^2)));

%O2 Solubility Constant
k660_Ecmwf = 0.251.*wind_era.*Sc_660; %Wind speed function at 10 m (m.h–1)
DO_sat = exp(-173.4292+249.6339.*100./tempk+143.3483.*(log(tempk./100))-
21.8492.*tempk./100+sal.*(-0.033096+0.014259.*tempk./100-
0.0017.*(tempk./100).^2)).*1.423;
%%calculated to transform DO into saturated oxygen (mg.L)
DOsat_corr = DO_sat.*(press.*0.0987-0.0112)/100 %corrected atm pressure;(Staehr,
2010)
 %%
% 2.Ocean-atm interface flow calculation (g O2 m–2 h–1)

F_Era = k0.*k660_Ecmwf.*( DOsat_corr-DO);

%% Criando matriz de variação da concentração de od (mg.L)
   for i = 2:8108  %from line 2 to the last line;
      var_DO2 (i,1)= DO_lab(i)- DO_lab(i-1); %creating matrix var_od equals end
position minus initial od;
```

```
   end
%%
%% 3.Calculation of NEP hourly
NEPhr_b1 = (var_DO-F_Era)./zmix_md;
NEPhr_b2 = (var_DO-F_Era)./zmix_max;
NEPhr_b3 = (var_DO-F_Era)./zmix_min;

%%
%% 4.Next step was done in R script, which will generate the files of:
%mdRESP,maxRESP,minRESP(median of R (night) with 3 different mixing zones (average, maximum and minimum);
%mdNEP,maxNEP,minNEP(median of NEP (day) with 3 different mixing zones (average, maximum and minimum);

%% 5.Final calculation to estimate metabolism per day;

S = load ('md_era.txt'); %open the file of each result generated in R;
night_fration = S (:,4); %night time;
dayfration = S(:,5); %day time;
mdPAR = S(:,6); %average radiation each day;
SumPAR = S (:,7); %radiation sum each day;
mdRESP = S(:,8);
maxRESP = S(:,9);
minRESP = S(:,10);
mdNEP = S(:,11);
maxNEP = S(:,12);
minNEP = S(:,13);

%% 5.1 RESPdaytime[gO2 m–3 daylight period–1] (Respiration between  sunrise and over day length)

rdaytime_md = night_fration.*mdRESP;
rdaytime_max = night_fration.*maxRESP;
rdaytime_min = night_fration.*minRESP;
%% 5.2 NEPdaytime[gO2 m–3 daylight period–1] (Net integrated daylight hours)

ndaytime_md = dayfration.*mdNEP;
ndaytime_max = dayfration.*maxNEP;
ndaytime_min = dayfration.*minNEP;
%% 5.3 Rday[gO2 m–3 d–1] (Extrapolated respiratory rates to 24h)
 rday_md = mdRESP.*24;
```

```
rday_max = maxRESP.*24;
rday_min = minRESP.*24;

%% 5.4 GPP[gO2 m–3 d–1] (Calculation of Gross Primary Production)

GPP1_md = ndaytime_md - rdaytime_md;
GPP2_mx= ndaytime_max - rdaytime_max;
GPP3_min = ndaytime_min - rdaytime_min;
```

XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXxX

R script: Calculation needed for step 4. in matlab

```
#script to generate data from RESP hr[g O2 m-3 hr-1], NEPdaytimeg[O2 m-3
daylight period-1], dayfration e nightfration.

rm(list=ls()) #clean and restart
setwd("C:/Users/GABRIELA/Desktop/R") #workbook location

library(readxl)
library(dplyr)

filenames <- list.files(pattern='xlsx', full.names=F)
tabela<-data.frame(matrix(ncol = 12, nrow = 0))
names(tabela)<-
c("Arquivo","Data","n.Noite","n.Dia","mdPAR","sumPAR","mdRESP","maxRESP","minRE
S","mdNEP","maxNEP","minNEP")

for (i in 1:length(filenames)) {
 mydata <- read_xlsx(filenames[i], col_types = c("date","date","numeric",
"numeric","numeric","numeric"))
 arq<-data.frame(mydata)
 arq$d<-as.Date(arq$d)

 dias <-unique(as.Date(arq$d)) #multiple data from the same day

 for (j in 1:length(dias)) {
  id<-subset(arq, arq$d == dias[j])
  tab.vec<-rep(NA,12)
  tab.vec[1]<-filenames[i]             # source file
  tab.vec[2]<-as.Date(dias[j])                                   #  date
```

```
          tab.vec[3]<- nrow(id[which(id$PAR == 0),]) # n. of readings where the PAR = 0
          tab.vec[4]<- nrow(id[which(id$PAR != 0),]) # n. of readings where the PAR diff 0
          tab.vec[5]<- mean(id[which(id$PAR != 0),3],na.rm = T) # median of PAR diff 0
          tab.vec[6]<- sum(id$PAR,na.rm = T)                 # sum of PAR
          tab.vec[7]<- mean(id[which(id$PAR == 0),4],na.rm = T) # median of NEPMED
when PAR = 0
          tab.vec[8]<- mean(id[which(id$PAR == 0),5],na.rm = T) # median of NEPMAX
when PAR = 0
          tab.vec[9]<- mean(id[which(id$PAR == 0),6],na.rm = T) # median of NEPMIN
when PAR = 0
          tab.vec[10]<- mean(id[which(id$PAR != 0),4],na.rm = T) # median of NEPMED
when PAR diff 0
          tab.vec[11]<- mean(id[which(id$PAR != 0),5],na.rm = T) # median of NEPMAX
when PAR diff 0
          tab.vec[12]<- mean(id[which(id$PAR != 0),6],na.rm = T) # median of NEPMIN
when PAR diff 0
          tabt<-t(tab.vec) #transpose the vector for it to become a line
          tabela<-rbind(tabela,tabt)
         }
        }
        names(tabela)<-
c("Arquivo","Data","n.Noite","n.Dia","mdPAR","sumPAR","mdRESP","maxRESP","minRE
S","mdNEP","maxNEP","minNEP")
        tabela
        head(tabela)
        tail(tabela)
        write.csv(tabela, "MEDIAS_NEP.csv", row.names=F)#saving the averages in table
        write.csv(dias, "date.csv", row.names=F)#saving the dates in table
```

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# 5. CONCLUSÕES E CONSIDERAÇÕES FUTURAS

- As propriedades meteo-oceanográficas e o metabolismo ecossistêmico foram influenciadas por processos de mesoescala como a influência da ASTP durante todo o período de estudo e processos pontuais como eventos de chuva.

- O sistema foi heterotrófico em 99% das medidas, sugerindo que a região é uma fonte de $CO_2$ para a atmosfera.

- Durante eventos de chuva, as entradas de água costeira (ricas em matéria orgânica e nutrientes) influenciaram nos máximos de produção primária bruta (PPB) e clorofila, principalmente durante baixas temperaturas no inverno.

- De acordo com o índice trófico (TRIX), o sistema foi caracterizado como mesotrófico, e pela medida de PPB o sistema foi oligotrófico. Apesar das diferenças entre os diferentes métodos utilizados para estimar o metabolismo ecossistêmico.

- A limitação da produção primária fitoplanctônica pelo N, observada pode estar relacionada com processos de denitrificação.

- Os resultados aqui encontrados corroboram as poucas estimativas de produção primária e de metabolismos feitos na Plataforma Subtropical Brasileira, podendo servir de referência para a compreensão da dinâmica desse processo em maior detalhamento temporal (N=389).

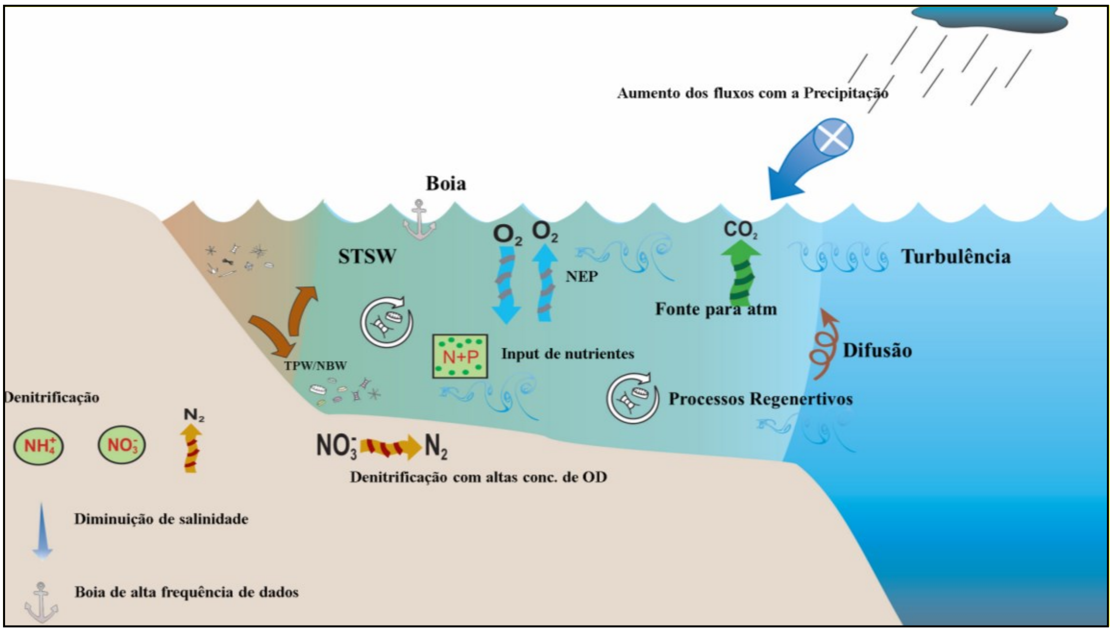

Figura 13 Modelo conceitual dos resultados dos processos encontrados neste trabalho citados nos tópicos da conclusão.

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