

# Benthic aerobic respiration and nutrient fluxes in Cananéia-Iguape Estuarine-Lagoon complex along a salinity gradient

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## ABSTRACT

Estuaries are important features for global biogeochemical understanding, due to their highly coupled interaction between sediment and water. In those places, the land-sea transect sometimes has a gradient of physical and chemical characteristics, influencing the availability of nutrients and consequently primary production. This study aimed to observe the benthic aerobic respiration and sediment-water nutrient fluxes in a freshwater to marine transect in the Cananéia-Iguape Estuarine-Lagoon Complex (CIELC) on the southeastern Brazilian Coast. This area contains the most pristine mangrove at the limit between tropical and subtropical zones, providing an ideal observatory for ecological research programs. Intact sediment cores were incubated in laboratory to determine fluxes of  $O_2$ ,  $TCO_2$ , and dissolved nutrients. Three different sites with different salinities were sampled during the four seasons of the year. Sediment characteristics of the sites were compared, showing higher organic matter in the lowest saline (LS) site and higher phytopigments in the highest saline (HS) site, as expected. Benthic aerobic respiration,  $O_2$  and  $CO_2$  fluxes, ranged from  $-0.4$  to  $-3.2$   $mmol\ m^{-2}\ h^{-1}$  and  $0.1$  to  $1.5$   $mmol\ m^{-2}\ h^{-1}$ , respectively, and exhibited statistically significant variations between seasons and in a salinity gradient. Dissolved inorganic nitrogen and silicate, ranging from  $-228.7$  to  $544.8$   $\mu mol\ m^{-2}\ h^{-1}$  and  $-205.8$  to  $4,173.5$   $\mu mol\ m^{-2}\ h^{-1}$ , respectively, were generally released from the sediment, whereas phosphate ranged from  $-25.2$  to  $29.6$   $\mu mol\ m^{-2}\ h^{-1}$  with more variation in time and space. The LS site was characterized as a nitrogen sink and a silicate and phosphate releaser, and the HS site was characterized as a nitrogen producer and a phosphorus consumer. However, seasonal and spatial variations were observed, and the interaction between space and time factors was always highly significant, indicating that the metabolic behavior of the benthic compartment depends on both trophic and physicochemical conditions.

**Keywords:** Benthic-pelagic coupling, Benthic metabolism, Estuary, Subtropical climate

## INTRODUCTION

Coastal and estuarine waters are characterized by exceptionally high rates of primary production

(Boynton et al., 1982; Cloern et al., 2014). In these shallow systems, nutrient fluxes across the sediment-water interface and benthic respiration are important links between benthic and pelagic environments (Cowan and Boynton, 1996). The sediment may support 15–32% of the N and 17–100% of the P required by phytoplankton (Bonaglia et al., 2014; Carstensen et al., 2014; Boynton et al., 2018). Nevertheless, estuarine sediments can play

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a dual role, in which benthic nutrient inputs can prevent an estuarine ecosystem from seasonal nutrient limitation and estuarine sediments can act as a nutrient trap (Hellemann et al., 2017) by reducing the excess carbon and nutrients load that could otherwise imbalance the delicate estuarine ecosystem (Zhang et al., 2010; Evans and Scavia, 2013). The supply of organic matter (OM) to the benthic compartment, the macromolecular quality of this OM, the availability of oxygen, the salinity, and the water temperature are considered primary environmental and biological factors that control the direction and magnitude of solute fluxes (Banta et al., 1995; Hopkinson et al., 2001; Smith et al., 2012). These factors can operate on a variety of temporal and spatial scales (Twilley et al., 1999) and can exhibit a seasonal pattern of sediment fluxes of nutrients, normally high values in summer and low values in winter (Kemp and Boynton, 1984; Cowan et al., 1996). Estimating nutrient fluxes across the sediment-water interface is significant to understand the ecosystem functioning and assess the biogeochemical cycling of nutrients, sedimentary environment, trophic state, and quality of an ecosystem (Zhang et al., 2019). The estuarine biogeochemistry and ecosystem functioning can be largely controlled by benthic-pelagic coupling by which estuaries remain pristine, productive, and efficient ecosystem service providers (Barbier et al., 2011; Thrush et al., 2013).

Despite the abundant literature describing benthic nutrient fluxes, most studies have been conducted in temperate estuaries. Boynton et al. (2018) specifically mentioned that studies such as this one on benthic biogeochemistry of tropical and subtropical estuaries are rare. Tropical and subtropical estuaries characteristically differ from the temperate ones, owing to their contrasting hydrology, solar radiation, temperature, terrestrial input, turbidity, and type of fringing vegetation (Eyre and Balls, 1999). Higher temperature makes the microbe-driven respiration processes faster (Helder and De Vries, 1983; Eyre and Balls, 1999). The type of vegetation (mangrove versus coniferous vegetation) changes the quality and quantity of organic carbon, and the flux rates and mineralization of tropical and subtropical estuaries significantly vary from those

in temperate estuaries (Hopkinson et al., 1999; Humborg et al., 2003). For example, the high amount of OM from terrestrial sources (Pradhan et al., 2014; Sarma et al., 2014) and the organic-rich sediments below a thin top oxic layer can be strongly reducing (Pratihary et al., 2009; Gomez-Ramirez et al., 2019). On the other hand, due to high temperature and consequent high microbial and faunal activity, OM mineralization tends to be faster than temperate estuarine sediments (Helder and De Vries, 1983). Additionally, information is limited about benthic fluxes in varying salinity environments that have strong gradients of environmental parameters (Boynton et al., 2018).

Estuaries drain continental river basins into coastal waters, and tidal seawater is diluted by riverine freshwater inputs flowing seaward, creating an environmental gradient along the main channel (Barletta and Dantas, 2016). These coastal systems often display strong gradients of salinity, nitrate concentrations, and sedimentary organic carbon sources and characteristics, far from river mouths, and the consequent strong availability of terminal electron acceptors. The quality of organic matter (OM) reaching the sediment is also likely to vary along the salinity gradient. Structurally complex terrestrial detritus with high C:N dominates at the freshwater end, and phytoplankton detritus with low C:N dominates at the marine end (Hopkinson et al., 1998; Fellman et al., 2011). The lack of extensive biogeochemical process studies in tropical and subtropical estuaries (Cloern et al., 2014; Boynton et al., 2018) and in a salinity gradient leaves a gap in our understanding of global carbon and nutrient cycling. Better understanding of benthic biogeochemical processes in those estuaries is necessary for appropriate ecosystem management.

Many estuaries in the tropical zone are found in Brazil, which is the country with the second largest mangrove area in the world (Basha, 2018; Nabeelah et al., 2019). However, despite the importance of these systems for understanding the global patterns of biogeochemical changes, the study of the biogeochemical cycles in these environments is still lacking (Boynton et al., 2018). Some studies were found about the benthic metabolism and sediment-water nutrient fluxes

in an estuarine system in the Amazon region (Matos et al., 2022) and in coastal lagoons in the states of Rio de Janeiro (Machado and Knoppers, 1988; Knoppers et al., 1996, 2004) and Paraná (Niencheski and Jahnke, 2002; Knoppers et al., 2004), but no previous study, to our knowledge, has been carried out at the Cananéia-Iguape Estuarine Complex (CIELC).

The CIELC was included in the Ramsar's List of Wetlands of International Importance in 2017 (<https://rsis Ramsar.org/ris/2310>) and in the UNESCO Biosphere Reserve. The CIELC contains the most pristine mangrove at the limit between tropical and subtropical zones in the southwestern Atlantic, where sensitivity to climate change is higher. Thus, it is an ideal observatory for ecological research programs. The Cananéia region has great ecological importance since it contains highly diversified environments, fauna and flora biodiversity, and a significant preservation of the biota (Diegues, 1987). On the other hand, the artificial channel, Valo Grande, constructed in the 19<sup>th</sup> century has been responsible for an important introduction of fresh water into the system, and a salinity gradient decreasing from Cananéia to Iguape region can now be observed (Mahiques et al., 2009). The CIELC is in a transitional area between the tropical and subtropical climates and is characterized as a wet subtropical climate, with a very humid spring/summer and a drier autumn/winter, leading to variable seasonal inflow of freshwater from continental drainage of rivers (Mahiques et al., 2009).

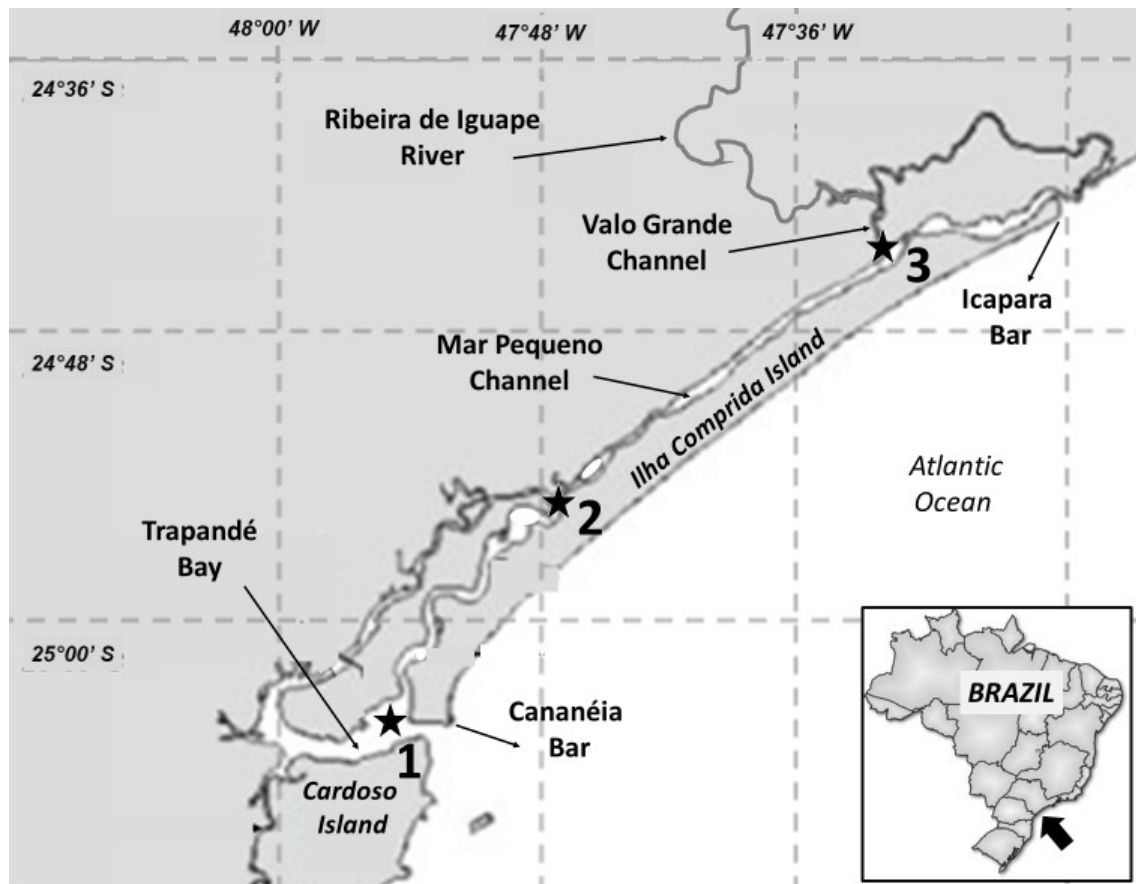
Due to the great ecological importance of the region and the lack of studies in tropical and subtropical areas, this study aimed to analyze the benthic oxygen consumption and the nutrients flow through the sediment-water interface in a salinity gradient in the CIELC region. For that, intact sediment cores were incubated *ex situ* at three different salinities, in four different periods from August 2021 to June 2022.

## METHODS

### STUDY AREA

The study was carried out at the Cananéia-Iguape Estuarine-Lagoon Complex (CIELC) in

the state of São Paulo on the southeast coast of Brazil (Figure 1). The system is composed of an extended coastal plain, with an intricate set of channels and interconnected coastal lagoons, in the municipalities of Iguape (northern sector), Ilha Comprida, and Cananéia (southern sector), as well as Cardoso Island. The islands are isolated from the continent by interconnected channels, the Pequeno, Cubatão, and Cananéia Seas and the Trapandé Bay, and are connected to the Atlantic Ocean through channels at the northern (Barra de Icapara) and southern (Barra de Cananéia) end of Comprida Island (Tessler and Souza, 1998). In the northeastern portion of the system, the Pequeno Sea channel is strongly influenced by freshwater from the artificial channel of Valo Grande (located in the municipality of Iguape), which connects it to the Ribeira de Iguape River (Italiani and Mahiques, 2014). Tidal cycles associated with freshwater inflows and atmospheric precipitation cause wide variations of salinity along the CIELC. The Ribeira de Iguape River is the main freshwater source in the complex, and its flow rate responds synchronously to rainfall variations (lowest in June with an average of  $218 \text{ m}^{-3} \text{ s}^{-1}$ , which triples during the rainy season to an average of  $634 \text{ m}^{-3} \text{ s}^{-1}$ ) significantly influencing the salinity of the lagoon waters (Departamento de Águas e Energia Elétrica do Estado de São Paulo, 2019). The southern region has eutrophic conditions to support a primary production and the richness of a preserved area influenced by the marine hydrodynamic and micro-tide regimes (Azevedo and Braga, 2011; Pecoraro et al., 2019). The general pattern of water circulation depends on tides, which are semidiurnal with a mean of 0.8 m and maximum amplitude of 1.25 m (Bernardes and Miranda, 2001). The nutrient dynamics of the lagoon region are influenced by inorganic nutrient runoff from the Tropical Atlantic Forest, dissolved and particulate organic matter input, phytoplankton biomass, and decomposition in tidal creeks of the upper estuary (Schaeffer-Novelli et al., 1990). The estuarine channels are surrounded by exuberant mangrove vegetation, and mangrove litter significantly contributes to OM production, where the highest values of chlorophyll and organic carbon are observed (Garcia et al., 2018).



**Figure 1.** Location of the Cananéia-Iguape Estuarine-Lagoon Complex (CIELC) showing High Salinity (1), Intermediate Salinity (2) and Low Salinity (3) sampling site (star).

### SAMPLING AND EXPERIMENTAL SETUP

Water and sediment were collected four times from August 2021 to June 2022 in three stations along a salinity gradient in the CIELC: high salinity station (Trapandé, S25°03.988 W47°92.241), intermediate salinity station (Pedrinhas, S25°88.594 W47°79.351), and low salinity station (Valo Grande, S24°16.050, W47°56.273) (Figure 1). At each station, sediments were sampled with minimum disturbance by scuba divers using transparent plexiglass liners (internal diameter = 7 cm, length = 35 cm), to have approximately equal heights (15–17 cm) of sediment and water column. Eight intact sediment cores were taken at each station, and the bottom water was characterized for temperature and salinity. Also, ~100 L of water were collected from each site for maintenance, preincubation, and incubation of the cores. Additionally, two cores were sliced in five sediment layers (0–2, 2–4, 4–6,

6–8, and 8–10 cm depth), homogenized, placed in dark vials, and frozen (–18 °C) for sediment characterization (density, porosity, organic matter content, and phytopigments).

The cores were stored vertically in the dark and immediately transferred to the laboratory. Different tanks were used for the different stations. During overnight preincubation, the cores were maintained submersed with the top open and under stirring, and the water in the tank was maintained at *in situ* temperature and at 100% oxygen saturation. The day after sampling, dark incubations began by sealing each core with gas-tight lids. A Teflon-coated magnetic bar driven by an external motor at 40 rpm was put on each core, which were suspended 10 cm above the sediment-water interface. Solute concentrations were measured at the beginning and at the end of the incubation, assuming that their uptake or release rate during

the incubation was linear. The incubations were set for 4–5 hours for flux measurements of dissolved gases (total oxygen and carbonic gas) and inorganic nutrients (ammonium, nitrite, nitrate, phosphate, and silicate). Water samples were collected at the beginning and at the end of the incubations using plastic syringes from each core water phase. The dissolved gas in the water samples was analyzed immediately, and samples for nutrients were filtered through Whatman GF/F glass fiber filters into 20 mL plastic vials and frozen (–20 °C) until analysis.

## ANALYTICAL PROCEDURES

Sediment density and porosity was determined by the weight of a 3 mL sediment aliquot before and after being maintained at 60 °C for 48 hours. Density was calculated by weight of dry sediment per milliliter of sediment (g/mL), and porosity was calculated by water content and density. The OM was measured by combustion in a muffle furnace at 400 °C for 4 hours and expressed in percentage. The concentrations of chlorophyll-a and phaeopigments were determined by the spectrophotometric method by extraction with 90% acetone and measured using a Thermo® Evolution 200 spectrophotometer, following Plante-Cuny (1978) recommendations and Lorenzen (1967) equations. The pigment content was calculated in micrograms per gram of dry sediment (mg g<sup>-1</sup>).

Dissolved O<sub>2</sub> was measured using the Winkler method. The TCO<sub>2</sub> was calculated by measuring total alkalinity with HCl (0.1 N) titration of the samples by using a Metrohm® Titrand, following the recommendations of Dickson et al. (2007). These analyses were performed between 8 and 12 hours after collection. Dissolved inorganic nutrient concentrations were measured using colorimetric methods. Nitrite and nitrate were measured using a continuous flow analyzer Seal® AutoAnalyzer II, as described by Tréguer and Le Corre (1975) with a 0.02 mmol L<sup>-1</sup> precision. The N-ammonium concentration was also determined following the method of Tréguer and Le Corre (1975), using a Thermo® Evolution 200 spectrophotometer with a ± 0.02 µmol L<sup>-1</sup> detection limit and a ± 0.01 µmol L<sup>-1</sup> precision. Dissolved phosphate and silicate concentrations

were determined by using the recommendation of Grasshoff et al. (1983) based on the molybdenum blue complex with a detection limit of 0.01 for phosphate and 0.02 µmol L<sup>-1</sup> for silicate and a precision of ±0.01 and ±0.1 µmol L<sup>-1</sup>, respectively. Fluxes of dissolved gases and nutrients were calculated from the change in concentrations in the cores with time and expressed based on area (µmol m<sup>-2</sup> h<sup>-1</sup> or mmol m<sup>-2</sup> h<sup>-1</sup>) according to equation of Dalsgaard et al. (2000):

$$F = \frac{(C_f - C_i) \cdot V}{A \cdot T}$$

where F is the flux of measured solutes (mmol/µmol m<sup>-2</sup> h<sup>-1</sup>), C<sub>i</sub> is the concentration at time zero (mmol/µmol L<sup>-1</sup>), C<sub>f</sub> is concentration at the end of incubation (mmol/µmol L<sup>-1</sup>), V is the volume of water in the core (l), A is area of sediment surface in the core (m<sup>2</sup>), and T is the incubation time (h). Fluxes directed from the sediment to the water column were considered as positive.

## STATISTICAL ANALYSIS

Differences between fluxes of dissolved gas and nutrients were analyzed by two-way analysis of variance (ANOVA), with time (T, n = 4; winter, spring, summer, and autumn) and salinity (S, n = 3; high salinity – HS; intermediated salinity – IS; and low salinity – LS) as factors. The normality and homogeneity of variance were checked using the Shapiro-Wilk test and the Levene median test, respectively. In the case of heteroscedasticity, the data were 1/x, ln(x), log(x<sup>2</sup>), or log(x) transformed. Pearson product-moment correlation matrix was performed to determine relationships between variables (significance level p < 0.05). Principal component analysis (PCA) was performed separately for environmental variables and fluxes. Statistics and graphics were done in Sigma Plot 11.0 and Past 4.03.

## RESULTS

### GENERAL FEATURES AND SEDIMENT CHARACTERIZATION

The water and sediment samples were collected on the same day for all the stations, keeping the location and time the same throughout the

seasons. (Trapandé around 8:00 AM, Pedrinhas around 10:00 AM., and Valo Grande around 12:00). With this, we tried to observe how the change in tidal dynamics and climatic conditions, such as rainfall and temperature, are influencing the benthic population at this specific place. Water temperature

over the survey period followed a typical seasonal pattern, ranging from 26 °C in summer/spring to 20 °C in winter/autumn (Table 1). The salinity gradient (from 0 to 30) was typical and reflected the pattern observed in the CIELC, with lower values in the rainy seasons (summer/spring, Table 1).

**Table 1.** Physic-chemical information of stations at the sampling times.

Season	Station	Salinity	Depth (m)	Temperature (°C)
Winter (August 2021)	Trapandé	30	2.5	20
	Pedrinhas	12	3.2	21
	Valo Grande	0	2.5	21
Spring (November 2021)	Trapandé	20	2.3	26
	Pedrinhas	3	3	26
	Valo Grande	0	3	25
Summer (March 2022)	Trapandé	25	1.5	26
	Pedrinhas	2	1.5	26
	Valo Grande	0	2	27
Autumn (June 2022)	Trapandé	26	2.5	20
	Pedrinhas	5	3	20
	Valo Grande	1	2.5	21

Sediments demonstrated higher porosity and total organic matter (TOM) content and lower density in stations with LS, whereas lower porosity and lower density was observed in IS station at all sampled times (Table 2). Chlorophyll-a and phaeopigments were more variable between sites

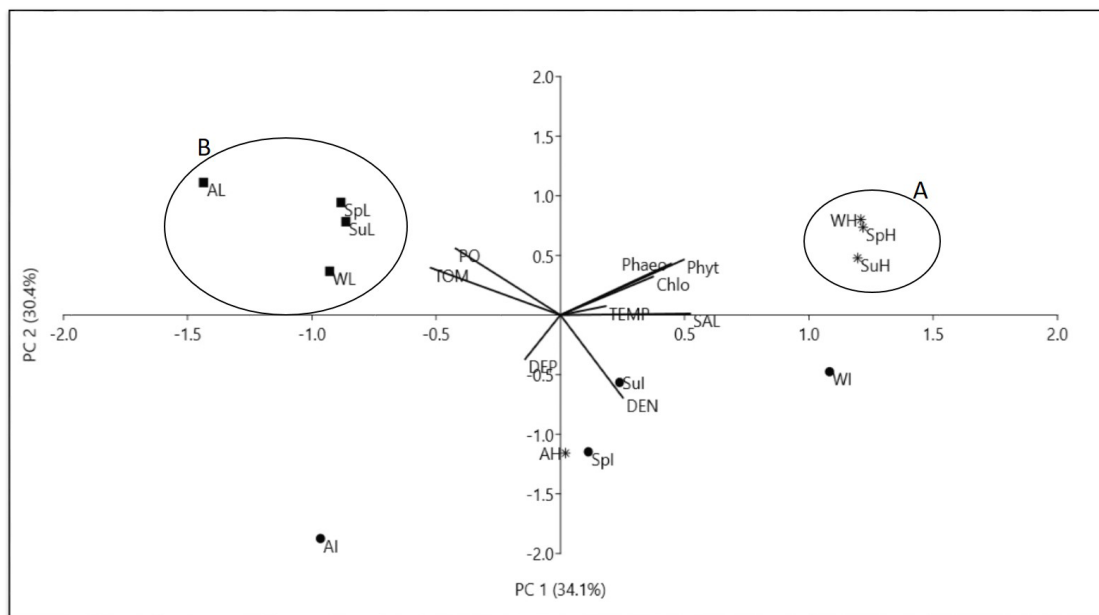
and showed a temporal variation, with the highest value at the IS station in winter and the lowest at the same station in autumn (Table 2). The HS station showed higher values of phaeopigments at almost all times, except in autumn, when the LS station showed the highest values (Table 2).

**Table 2.** Sedimentary features (average and standard error) measured in the upper 10 cm layer of stations in the sampling seasons. HS: high salinity site; IS: intermediate salinity site; LS: low salinity site.

	Winter			Spring			Summer			Autumn		
	HS	IS	LS	HS	IS	LS	HS	IS	LS	HS	IS	LS
Porosity	0.41 0.06	0.28 0.01	0.51 0.02	0.37 0.05	0.29 0.02	0.60 0.01	0.37 0.01	0.33 0.01	0.63 0.01	0.36 0.02	0.32 0.04	0.55 0.14
Density (g cm <sup>-3</sup> )	1.46 0.04	1.74 0.01	1.38 0.03	1.28 0.12	1.73 0.00	1.28 0.02	1.60 0.02	1.68 0.04	1.34 0.08	1.72 0.05	1.79 0.00	1.24 0.00
Chlorophyll-a (µg g <sup>-1</sup> )	14.45 0.92	33.90 7.84	12.06 1.09	29.24 4.53	19.65 8.71	17.52 5.72	29.18 9.95	17.06 1.36	16.80 0.88	11.75 4.47	2.65 1.37	23.89 6.52
phaeopigments (µg g <sup>-1</sup> )	65.88 8.29	35.81 9.40	27.92 2.66	42.57 0.18	14.81 4.45	21.05 6.82	30.12 7.07	26.84 2.95	29.50 2.53	10.43 0.29	2.88 0.02	15.85 6.33
Phytopigments (µg g <sup>-1</sup> )	80.3 7.3	69.7 10.2	39.9 3.7	71.8 4.3	34.4 13.1	39.5 1.7	59.3 17	43.9 4.3	46.3 3.4	22.1 4.1	5.5 1.3	18.1 6.8
MOT (%)	7.61 0.28	2.84 0.31	15.36 2.07	3.26 0.61	3.16 1.78	17.45 0.35	4.97 1.78	4.81 0.29	18.54 3.09	6.69 0.95	8.87 0.92	36.34 3.78

Pearson correlation analysis showed a positive correlation between TOM and porosity ( $r = 0.780$ ,  $p = 0.002$ ) and a negative correlation with sediment density ( $r = -0.731$ ,  $p = 0.006$ ). Negative correlations were observed between sediment density and porosity ( $r = -0.889$ ,  $p = 0.000$ ). Principal Component analysis (PCA) was used to observe the general distribution of

the values due to the environmental parameters. The PCA explained 64.5% of the total sample variance in the two first axes and clearly separated it into two distinct groups (Figure 2). The first group (A) comprised all samples at the HS site and the second group (B) included all the LS site. The IS site showed more variable parameters (Figure 2).



**Figure 2.** Principal Component Analysis (PCA) was performed with the environmental parameters in the stations and seasons. The two first axes (PC1 and PC2) explained 64.5% of the variation. Two groups A (high salinity stations) and B (low salinity stations) were observed. W: winter; Sp: spring; Su: Summer; A: autumn; H: high salinity; I: intermediate salinity; L: low salinity; DEP: Station depth; DEN: Sediment density; TOM: Total organic matter; CHLO: Chlorophyll-a; Phaeo: phaeopigments; Phyt: Phytopygments (chlorophyll-a + phaeopigments); TEMP: temperature; SAL: Salinity.

## BENTHIC AEROBIC RESPIRATION AND NUTRIENT FLUXES

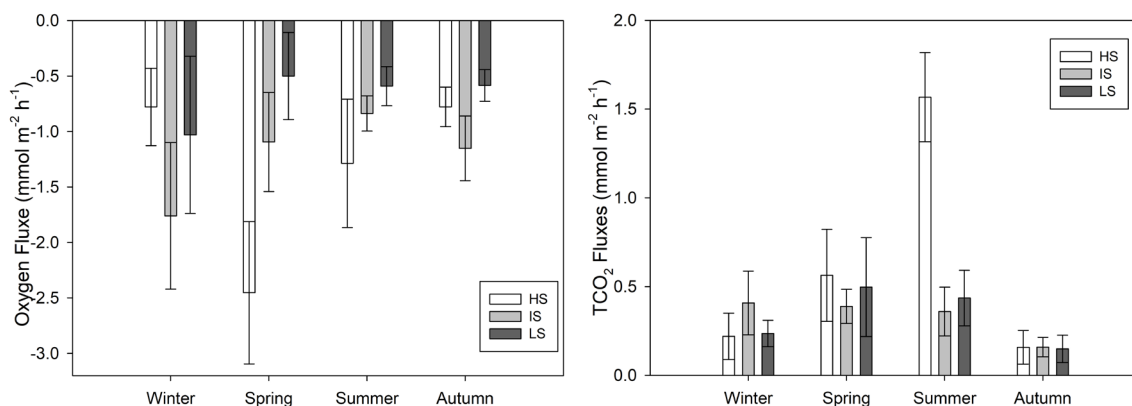
Benthic aerobic respiration (oxygen consumption and  $\text{CO}_2$  efflux) displayed significant variations between seasons and in the salinity gradient (Table 3, Figure 3). Oxygen consumption ranged from 0.4 to 3.2  $\text{mmol m}^{-2} \text{h}^{-1}$  and showed a significant interaction between the factors of salinity and seasonality (Figure 2, Table 3). The IS showed significantly higher values in winter and autumn, whereas oxygen consumption in summer and spring was significantly higher in HS station. (Figure 3, Table 3). Generally, oxygen consumption was significantly higher in spring ( $1.6 \pm 0.1 \text{ mmol m}^{-2} \text{h}^{-1}$ ) and lower in autumn

( $0.90 \pm 0.08 \text{ mmol m}^{-2} \text{h}^{-1}$ ); the HS site had the highest value ( $1.30 \pm 0.08 \text{ mmol m}^{-2} \text{h}^{-1}$ ) and LS site the lowest ( $0.80 \pm 0.08 \text{ mmol m}^{-2} \text{h}^{-1}$ ) (Table 3). The  $\text{TCO}_2$  liberation ranged from 0.1 to 1.5  $\text{mmol m}^{-2} \text{h}^{-1}$ , showing a similar pattern to the oxygen consumption, and a significant interaction between time and spatial factors was observed (Figure 3, Table 3). The marine site showed the greatest seasonal variation with significant higher  $\text{CO}_2$  efflux in summer and lower liberation in autumn (Figure 3, Table 3). Average  $\text{TCO}_2$  efflux was significantly higher in the HS site ( $0.60 \pm 0.08 \text{ mmol m}^{-2} \text{h}^{-1}$ ) and in summer ( $0.70 \pm 0.06 \text{ mmol m}^{-2} \text{h}^{-1}$ ) than the other seasons and stations (Figure 3, Table 3).

**Table 3.** Results of the two-way ANOVA on the effects of the factors sampling season, sampling stations and of their interaction on benthic fluxes. Significant differences in the two-way ANOVA and Tukey HSD tests were set at  $P < 0.05$ . Dashed border means similar concentrations. Dissolved Inorganic Nitrogen (DIN)=( $\text{NO}_2^- + \text{NO}_3^- + \text{NH}_4^+$ ), H: high salinity site; I: intermediate salinity site; L: low salinity site; Su: Summer; A: Autumn; Sp: spring; W: winter.

Dependent variable	Independent variable	F	P	Tukey HSD test			
O <sub>2</sub> flux	Station	8.710	<0.001	H	I	L	
	Season	10.785	<0.001	Sp	W	Su	A
	Interaction	6.797	<0.001				
CO <sub>2</sub> flux	Station	2.515	0.087				
	Season	44.73	<0.001	Su	Sp	W	A
	Interaction	6.574	<0.001				
NO <sub>2</sub> <sup>-</sup> flux	Station	17.639	<0.001	I	L	H	
	Season	7.486	<0.001	Su	W	A	Sp
	Interaction	3.806	0.002				
NO <sub>3</sub> <sup>-</sup> flux	Station	7.442	0.001	I	L	H	
	Season	40.621	<0.001	Su	A	W	Sp
	Interaction	21.149	<0.001				
NH <sub>4</sub> <sup>+</sup> flux	Station	46.214	<0.001	H	L	I	
	Season	20.075	<0.001	A	W	Sp	Su
	Interaction	47.013	<0.001				
DIN flux	Station	22.49	<0.001	I	L	H	
	Season	43.073	<0.001	Su	A	W	Sp
	Interaction	29.806	<0.001				
Si(OH) <sub>4</sub> flux	Station	24.14	<0.001	L	I	H	
	Season	36.57	<0.001	Su	W	Sp	A
	Interaction	8.296	<0.001				
PO <sub>4</sub> <sup>-3</sup> flux	Station	53.073	<0.001	L	I	H	
	Season	29.348	<0.001	Su	Sp	A	W
	Interaction	54.814	<0.001				





**Figure 3.** Dark O<sub>2</sub> and TCO<sub>2</sub> fluxes (mmol m<sup>-2</sup> h<sup>-2</sup>) in the sampling seasons at three salinity stations. Average (n=8) and standard deviation are reported. HS. High salinity, IS. Intermediate salinity, LS. Low salinity

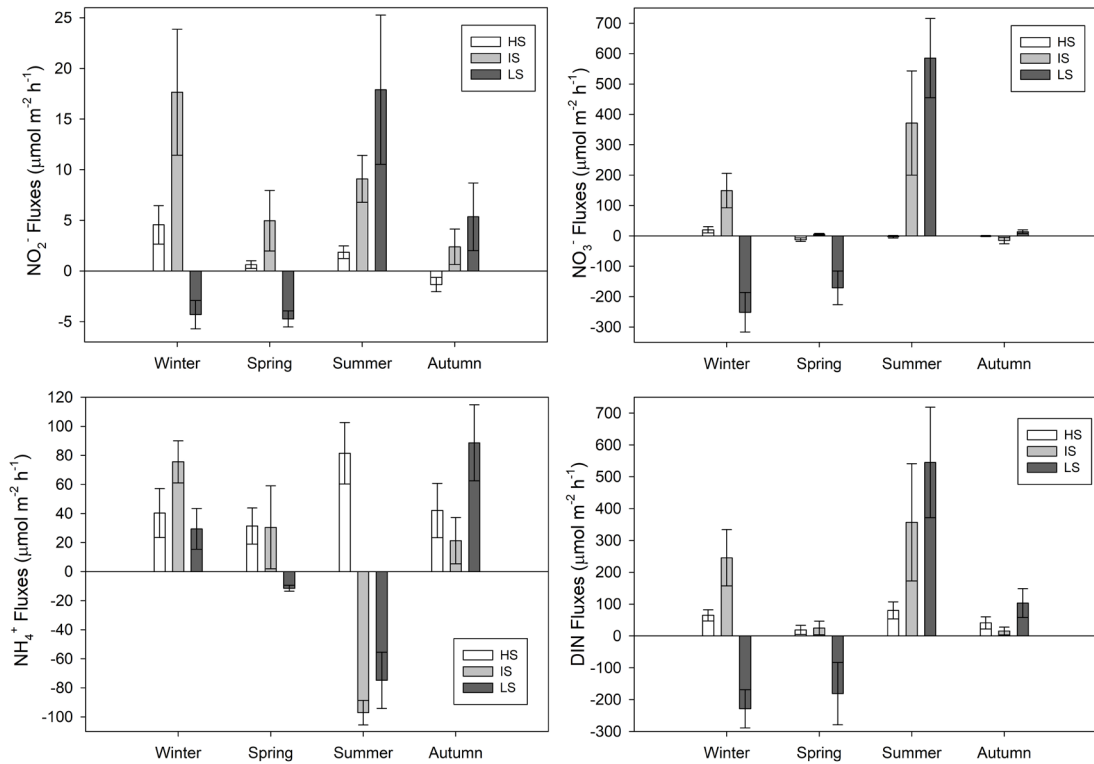
Dissolved N fluxes were high and had a very variated pattern (Figure 4). Nitrite (NO<sub>2</sub><sup>-</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) ranged from -4.7 to 17.8 and -251.3 to 585.3 mmol N m<sup>-2</sup> h<sup>-1</sup>, respectively, and showed similar uptake or efflux patterns, with significant variation in space, time, and in the interaction between time and space (Figure 4, Table 3). Both displayed sediment release to the water column in the temporal balance at all salinity values, with significantly higher average efflux at the IS site (8.5 ± 0.8 and 127.5 ± 24 mmol N m<sup>-2</sup> h<sup>-1</sup> for NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>, respectively) and lower efflux at the HS (1.4 ± 0.8 and 1.1 ± 22 mmol N m<sup>-2</sup> h<sup>-1</sup> for NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>, respectively) (Table 3). Significant consumption of both N forms was observed at the LS site in winter and spring (Figure 4, Table 3). On the other hand, at the IS site, NO<sub>2</sub><sup>-</sup> was always released from the sediment and exhibited significant liberation of both forms in winter and summer (Figure 4, Table 3). The HS site showed very low fluxes, which characterized a balance between efflux and influx of both N forms (Figure 4). Ammonium (NH<sub>4</sub><sup>+</sup>) fluxes ranged from -97.1 to 81.3 mmol N m<sup>-2</sup> h<sup>-1</sup> and displayed significant differences between sites, seasons, and in the interaction of factors (Table 3). In general, NH<sub>4</sub><sup>+</sup> flux was directed from the sediment to the water column (Figure 3), with statistically higher annual average efflux at the HS and lower at the IS sites (48.7 ± 4 and 7.5 ± 4 mmol N m<sup>-2</sup> h<sup>-1</sup>, respectively) (Figure 3, Table 3). Higher NH<sub>4</sub><sup>+</sup> consumption by the sediment was significant in summer (average -25.9 ± 5 mmol N m<sup>-2</sup> h<sup>-1</sup>) at the IS and LS sites

(Figure 4, Table 3). The HS site showed the lowest variation between seasons, with NH<sub>4</sub><sup>+</sup> fluxes oriented towards the water column (Figure 4). Total dissolved inorganic nitrogen (DIN = NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup> + NH<sub>4</sub><sup>+</sup>), which ranged from -228.7 to 544.8 mmol N m<sup>-2</sup> h<sup>-1</sup>, was essentially driven by high NO<sub>3</sub><sup>-</sup> flux (Figure 4). Significant variation in time, space, and interaction of factors was observed (Table 3). In general, N was released from the sediment to the water column, with higher efflux in summer and at the IS site (327.4 ± 26 and 160.7 ± 22 mmol N m<sup>-2</sup> h<sup>-1</sup>, respectively) (Figure 4, Table 3). The HS site had the lowest flux variation in time, whereas the LS site showed the highest variation, with influx of N in winter and spring, and efflux in summer and autumn (Figure 4).

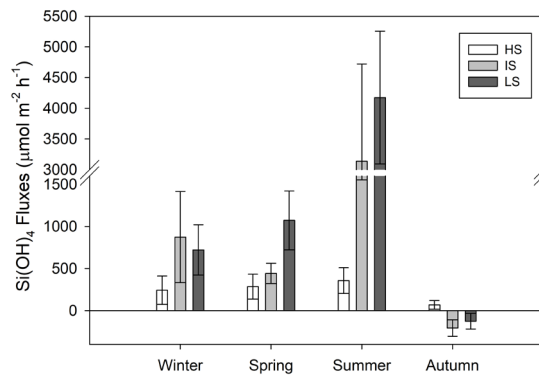
Silicate fluxes (Si(OH)<sub>4</sub>) ranged from -205.8 to 4,173.5 mmol m<sup>-2</sup> h<sup>-1</sup> with a generally large release from the sediment to the water column, showing a significative variation in time and space (Figure 5, Table 3). Significantly higher average efflux was observed at the LS site and in summer (1,460 ± 140 and 2,556 ± 0166 mmol m<sup>-2</sup> h<sup>-1</sup>, respectively) (Figure 5, Table 3). The HS site showed less variation in time, with a small efflux of Si to the water. However, the IS and LS sites had a significant seasonal variation with higher efflux in summer and a sediment Si consumption in autumn (Figure 5, Table 3). Phosphate fluxes were very variable, ranging from -25.2 to 29.6 mmol m<sup>-2</sup> h<sup>-1</sup>. A significant difference was observed in time and space, with significant interaction between factors (Figure 6, Table 3). The mean total flux showed an

efflux of P from the sediment to the water column with statistically higher values at the LS site and in summer ( $11.1 \pm 1.5$  and  $15.8 \pm 2$   $\text{mmol m}^{-2} \text{h}^{-1}$ , respectively) (Figure 6, Table 3). Phosphate uptake by the sediment was observed at station HS during most of the samplings (Figure 6). Likewise, in winter

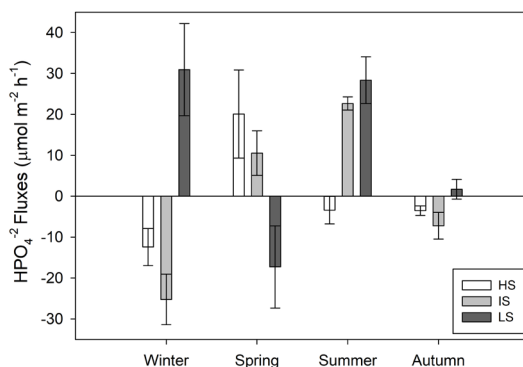
and autumn, both the HS and IS stations had a significant uptake of P by the sediment (Figure 6, Table 3), which showed an inversion in spring, when the HS and IS stations showed a release of P whereas the LS showed uptake of P from the water column (Figure 6, Table 3).



**Figure 4.** Dark fluxes of N ( $\text{mmol m}^{-2} \text{h}^{-2}$ ) derivate nutrients ( $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and DIN-sum of N fluxes) in the sampling seasons at three salinity stations. Average ( $n=8$ ) and standard deviation are reported. HS: High salinity; IS: Intermediate salinity; LS: Low salinity.



**Figure 5.** Dark  $\text{Si(OH)}_4$  flux ( $\mu\text{mol m}^{-2} \text{h}^{-1}$ ) in the sampling seasons at three salinity stations. Average ( $n=8$ ) and standard deviation are reported. HS: High salinity; IS: Intermediate salinity; LS: Low salinity.



**Figure 6.** Dark  $\text{PO}_4^{3-}$  flux ( $\mu\text{mol m}^{-2} \text{h}^{-1}$ ) in the sampling seasons at three salinity stations. Average ( $n=8$ ) and standard deviation are reported. HS: High salinity; IS: Intermediate salinity; LS: Low salinity.

Pearson correlation test showed a positive correlation between  $\text{NO}_2^-$  flux and depth, and a negative correlation between depth and  $\text{CO}_2$  liberation (Table 4). Fluxes of  $\text{Si}(\text{OH})_4$  were significantly

correlated with almost all other nutrient fluxes. Positive correlations were observed between Si,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and DIN (Table 4), whereas the pairs Si and P and  $\text{NO}_3^-$  and P were negatively correlated (Table 4).

**Table 4.** Pearson product-moment correlation coefficients showing the significant correlated fluxes. Significant correlation is observed when  $p < 0.05$ . Dissolved Inorganic Nitrogen (DIN) =  $(\text{NO}_2^- + \text{NO}_3^- + \text{NH}_4^+)$ .

		$\text{CO}_2$	$\text{NO}_2^-$	$\text{NO}_3^-$	DIN	$\text{PO}_4^{3-}$
$\text{Si}(\text{OH})_4$	r	-	0.588	0.838	0.728	-0.853
	p	-	0.004	0.001	0.007	0.000
$\text{NO}_2^-$	r	-	-	0.838	0.887	-
	p	-	-	0.000	0.000	-
$\text{NO}_3^-$	r	-	-	-	0.982	-0.615
	p	-	-	-	0.000	0.033

## DISCUSSION

### GENERAL ENVIRONMENTAL CHARACTERIZATION

This work aimed to verify if there were any significant differences among processes measured along the salinity gradient inside the CIELC. Normally, the salinity of an estuary exhibits a decreasing trend from closer to an ocean to up a river channel; thus, the system can be classified according to the salinity variations. Polyhaline are regions where salinity varies from 30 to 35; mesohaline shows salinity variations around 15; and the oligohaline systems ranges from 0 to 5 (Day et al., 1989). At CIELC, tidal cycles associated with

freshwater inflows and atmospheric precipitation cause wide amplitudes of salinity variation throughout the estuarine system. The Ribeira de Iguape River is the main freshwater source that reaches the complex and has the most significant influence on the salinity of the estuarine-lagoon waters. The Valo Grande station is in the Ribeira Iguape River and exhibited salinity values from 0 to 1, characterizing a predominantly freshwater system; thus, it was chosen as the oligohaline site in this study. Trapandé Bay, in the southern part of the CIELC, was chosen as the saline site, ranging from 20 to 30 of salinity, in spring and winter, respectively. Despite evidence indicating the relative seasonal persistence of saltwater within the southern estuary and Trapandé Bay (Miyao

et al., 1986), short-term episodes of intense continental runoff may move the saltwater wedge toward the southern area (Conti et al., 2012) mainly in wet seasons, and the average salinity in the region is 22.5, classifying it as a polyhaline water body (Perina and Abessa, 2020). The salinity in Pedrinhas station ranged from 2 to 12, in summer and winter, respectively, and is characterized as a mesohaline site. The flow rate of the Ribeira de Iguape River responds synchronously to variations in rainfall, which are lowest in June, when it averages  $218 \text{ m}^{-3} \text{ s}^{-1}$ , and triplicate during the rainy season, when it averages  $634 \text{ m}^{-3} \text{ s}^{-1}$  (DAAE, 2019). This characteristic has important implications for the distribution and deposition of fine sediments, organic matter, and contaminants in the CIELC and clearly separates the south (greater marine influence) from the north (greater river influence), as we observed (see Figure 2).

Normally, lithogenic sediments (continental origin) are carried to the ocean through a fluvial flux, and areas closer to the continental water flux are mainly composed of coarser sediments and retain less OM. During this study we observed that the density, porosity, and TOM distribution were significantly correlated, with lower sedimentary density associated with a higher degree of porosity and greater OM accumulation. However, the freshwater station showed the highest porosity and TOM concentration. This was also observed in previous studies in the region, which showed higher OM concentrations closer to the Ribeira de Iguape River (Barcellos et al., 2009). This can be in part explained by the strong tidal wave propagation observed in the high and intermediate salinity sites, which leads to the higher hydrodynamic circulation and greater variation in granulometric and organic matter values within the system (Barcellos et al., 2009). On the other hand, the low salinity site is submitted to a higher sedimentation deposition ( $1.46 \text{ cm year}^{-1}$ ) (Saito et al., 2001) and has more homogenous OM content (Barcellos et al., 2009). This OM is associated with terrestrial input from the Ribeira de Iguape River and presents higher C:N and C:P values (Barcellos et al., 2009). Except in autumn, this site showed the lowest chlorophyll-a values, and the high salinity station always showed higher

phytopigments (chlorophyll-a + phaeopigments) (Table 3). Phytopigment concentrations normally have an inverse relationship to the salinity (Aquino et al., 2012), mainly in sediment where a lower concentration of suspended particulate matter in water allows greater light intrusion, increasing the production of microphytobenthos.

## BENTHIC RESPIRATION AND SEDIMENT-WATER FLUXES

The combination of dissolved oxygen and  $\text{CO}_2$  fluxes in the dark is the best proxy for heterotrophic respiration, including diffusive (microbial) and total (microbial + macrofaunal) uptake. In sediment overlaid by oxygen saturated waters, benthic respiration includes both the oxygen consumption by aerobic organisms and microbial mediated oxidation of reduced compounds (Mackin and Swider, 1989), and it closely reflects the rates of oxic and anoxic decomposition in the sediment. The oxygen sedimentary consumption values in this study are within the range observed in similar subtropical estuarine systems (Chau, 2002; Grenz et al., 2003, 2010; Liu et al., 2009; Alongi et al., 2011; Buzzelli et al., 2013; Ferguson and Eyre, 2013). To our knowledge, no published data regarding nutrient or sediment oxygen flux measurements at the sediment-water interface in CIELC are available, and tracing a pattern of benthic respiration is difficult with a single study. This is due to the large number of variables that control benthic oxygen consumption. Benthic respiration rates depend on factors such as dissolved oxygen content of the overlying water, organic load, benthic biomass, temperature, sediment type, and redox conditions. Normally, temperature combined with OM concentration controls the benthic mineralization, but physical and biological factors mediated by disturbances, including the impact of macro- and meiofauna, also affect the exchange rates between sediment and water column (Kristensen et al., 1992). Additionally, the OM quality and quantity in sediment control benthic respiration rates (Jahnke et al., 2005; Burdige, 2006; Alongi et al., 2011; Pastor et al., 2011).

The main results that emerge from this CIELC data are the large spatial and temporal

heterogeneity of sediment-water fluxes, which reflect, in part, the high diversity of habitats, like all large estuarine ecosystems. In general, higher oxygen consumption was observed in spring at the HS site, which coincides with high chlorophyll-a content in the sediment. Normally an increase in primary production and chlorophyll content are followed by an increase in benthic metabolism. The stations with intermediate and low salinity showed similar seasonal variations, with higher values in autumn/winter and lower in spring/summer. Our observations showed highest OM content in these moments, which can explain the higher values of oxygen consumption. The IS cores in winter stood out due to the large presence of tubes on its surface (Figure 7), which after analysis were found to be of *Tanaisidacea*. The bioturbation by macrofauna affects oxygen consumption not only due to respiration but also by increasing the solute exchange by sediment reworking, by building holes and tubes, and by bioirrigation, feeding, and excretion (Kristensen et al., 2012). Furthermore, other estuaries also showed higher oxygen consumption by the sediment at sites characterized by intermediate salinity values (Boynton and Kemp, 1985; Buzzelli et al., 2013). The greater variety of habitats and consequently the greater variety of metabolisms can lead to greater metabolic activity of the sediment in this area.

The general pattern of  $\text{TCO}_2$  efflux was somewhat similar to the  $\text{O}_2$  consumption, although no correlation between these two parameters was found (Figure 4, Table 4). The relationships between dark  $\text{O}_2$  uptakes and  $\text{TCO}_2$  effluxes in benthic systems result from a complex 3D mosaic of biogenic and chemical reactions, and  $\text{TCO}_2$  is produced by both metabolism and calcium carbonate dissolution/precipitation (Ferguson et al., 2003). Therefore,  $\text{O}_2$  and  $\text{CO}_2$  are not likely to be well correlated in a dynamic system. The  $\text{TCO}_2:\text{O}_2$  rate (Table 5) was calculated to observe how much of the  $\text{CO}_2$  liberation was due to heterotrophic respiration ( $\text{TCO}_2:\text{O}_2 = 1:1$ ). The ratio 1:1 was observed only on one occasion, and in general the  $\text{TCO}_2:\text{O}_2$  flux ratio was less than 1 throughout the study region, indicating that either sulfide-oxidation or nitrification

may significantly influence the benthic fluxes. Furthermore, both sulfide-oxidizing and nitrifying bacteria are predominantly chemoautotrophic and may therefore lower the  $\text{TCO}_2:\text{O}_2$  flux ratio via carbon fixation, especially in coastal areas where a large OM quantity limits the oxygen to the first centimeters of the sediment column.



**Figure 7.** Sediment core of the intermediate salinity station in winter (August 2021) with a high number of *Tanaisidacea* tubes.

**Table 5.** Average ratios of  $O_2:TCO_2$  fluxes at stations and in seasons.

	High	Intermediate	Low
Winter	-0.300	-0.375	-0.269
Spring	-0.239	-0.347	-0.417
Summer	-1.395	-0.460	-0.802
Autumn	-0.225	-0.142	-0.253

Sediments play a major role in controlling the cycling and availability of nitrogen in estuaries (Giblin et al., 1997; Hopkinson et al., 1999). Although sediments are generally considered a significant internal source of nutrients in shallow coastal ecosystems, several studies have shown that they may be a net sink of dissolved nitrogen at least during certain times of the year (Sundbäck et al., 2000; Tyler et al., 2003). Coastal ecosystems have been characterized as nitrate sinks, resulting in gaseous ( $N_2$ ) losses from high rates of denitrification (Galloway et al., 2008). This study observed that, in general, N was liberated from the sediment to the water column. The efflux of  $NO_x$  ( $NO_2^-$  and  $NO_3^-$ ) during most of the sediment incubation period indicated that nitrification was an important process within the CIELC estuarine sediments. Nitrification, which is the oxidation of ammonium to nitrate, is an important process in the water column and in sediments of many estuaries around the world (Wilde and Bie, 2000; Dai et al., 2008; Damashek et al., 2016). The higher  $NO_x$  efflux was observed in summer at the IS and LS sites. Despite the absence of significant correlations between  $NO_x$  and  $NH_4^+$  fluxes, at this time, the liberation was coupled with a large consumption of  $NH_4^+$ , indicating large nitrification rates.

At the HS site, the most dominant compound in the DIN flux was attributed to  $NH_4^+$ , and the  $NO_x$  flux was very low at all flux measurements (Figure 3). At this site,  $NH_4^+$  was always released from the sediment, mainly in spring and summer, when higher oxygen consumption was observed, and when the primary production in the water column was maximum (Barrera-Alba et al., 2008). The dominant  $NH_4^+$  efflux observed during the study can indicate higher benthic faunal respiration, excretion, and a degradation

of sedimentary organic N (Belias et al., 2007). Ammonification is an important process adding ammonium in estuarine systems, and it is very active in sediments with abundant OM like estuarine sediments (Li et al., 2015). In addition, the dissimilatory nitrate reduction to ammonium (DNRA) could contribute to the accumulation of ammonium in anaerobic sediments (An and Gardner, 2002; Gardner et al., 2006). The DNRA is indicated to replace denitrification in marine sediments due to an inhibition in the activity of denitrifying organisms (Wang et al., 2018). On the other hand, the salinity gradient can also directly affect DIN fluxes at the sediment-water interface (Zhou et al., 2017). Under freshwater or low saline conditions, a greater portion of the pore-water  $NH_4^+$  pool remained adsorbed in sediment clay minerals and was possibly nitrified, resulting in very low benthic  $NH_4^+$  release. However, with increasing salinity,  $NH_4^+$  could be paired with seawater anions, and the adsorption sites could be blocked by seawater cations. Consequently, the pore-water  $NH_4^+$  largely escapes nitrification, which leads to higher upward diffusion of  $NH_4^+$  across sediment-water interface (Gardner et al., 1991; Seitzinger et al., 1991). Other estuarine systems also showed the decrease in benthic  $NH_4^+$  efflux with decreasing salinity (Rysgaard et al., 1999; Weston et al., 2010).

Nevertheless, some other factors, such as temperature, sediment organic content, and macroinvertebrate assemblages, also affect sediment DIN flux. For example, the large DIN release observed in the IS station in winter could be due to the high density of Tanaidacea found in the sediment (Figure 7). As previously stated, oxygen consumption and the release of  $NO_x$  and  $NH_4^+$  largely increased at this time. Bioturbation affects the transport of nutrients and often increases oxygen penetration into the sediment, which enhances mineralization processes and stimulates the nitrification and denitrification rates (Kristensen et al., 2012; Moraes et al., 2018; Bartoli et al., 2020).

Silicate is commonly released from the sediments as a diffusion flux controlled by its concentration gradient at the sediment-water interface (Willey, 1978). This study found, on two

occasions, an influx of silicate to the sediment (in IS and LS, in autumn). The concentration of the water column silicate in the area were not analyzed but we sampled water from the sites for the experiment. These values were our time zero concentration. We observed that in the moments in which silicates showed an influx to the sediment silicates were in high concentration on the water. These unusual  $\text{Si(OH)}_4$  influxes related to high water column silicate were also recorded by Niencheski and Jahnke (2002) in the Patos lagoon (Brazil) and by Grenz et al. (2019) in Laguna de Términos (Mexico). For all other observations,  $\text{Si(OH)}_4$  fluxes were directed toward the water column and correlated with the DIN,  $\text{NO}_x$ , and  $\text{PO}_4^{3-}$  fluxes. Other factors that possibly influence the benthic silicate release are the abundance, distribution, and dissolution rate of biogenic silica (diatom frustules) in the estuarine sediments. High diatom abundance in the estuary during high productivity seasons is common (Barrera-Alba and Moser, 2016) and results in higher availability of diatom frustules in the sediments and their consequent dissolution. Dissolution of biogenic silica in sediments and benthic  $\text{Si(OH)}_4$  efflux is stimulated by temperature and salinity (chemical composition) of the overlying water (Pratihary et al., 2021).

Sediment-water  $\text{HPO}_4^{2-}$  fluxes were directed both into and out of sediments, with values in the range of estuarine systems (Boynton et al., 2018). The  $\text{HPO}_4^{2-}$  flux varied greatly between the sediment and the water column, always with the inverse pattern between the HS and LS stations. Whereas the first presented phosphorus consumption by the sediment in winter and autumn and release in summer and spring, the second had an inverse pattern, with liberation from the sediment in winter and autumn and consumption in spring and summer. Often, when  $\text{HPO}_4^{2-}$  efflux is observed in estuarine systems, it is accompanied by reduced dissolved oxygen in the water column (Cowan et al., 1996; Didonato et al., 2006). No low oxygen concentration were observed in the CIELC in this study or in the consulted literature. Normally, an estuary with high saline sediments retains very little regenerated P (10%), whereas

freshwater sediments can retain 80 to 90% (Roden and Edmonds, 1997; Gächter and Müller, 2003), and increasing salinity can mobilize the sedimentary  $\text{HPO}_4^{2-}$  facilitating its release to the overlying water (Caraco et al., 1990; Gunnars and Blomqvist, 1997; Jordan et al., 2008). Still,  $\text{SO}_4^{2-}$  reduction in anoxic sediments can increase alkalinity and pH, which can inhibit  $\text{HPO}_4^{2-}$  adsorption onto Fe-oxide minerals (Caraco et al., 1989), and Fe-oxide minerals are known to adsorb/co-precipitate  $\text{PO}_4^{3-}$  (Krom and Berner, 1980; Boström et al., 1988; Gunnars and Blomqvist, 1997). As in the water column, in this system, the sediment remains well oxidized throughout the year, surface sediments are not likely to ever become anoxic, and the benthic flux of  $\text{HPO}_4^{2-}$  could be limited and coupled strongly with Fe-oxyhydroxide.

## CONCLUSION

Benthic respiration and nutrient exchange rates varied considerably along the salinity gradient and seasonally at Cananéia-Iguape Estuarine-Lagoon Complex (CIELC), São Paulo, Brazil. Benthic respiration was low but comparable with those found in estuarine sites at the same latitude, although few studies showed similar conditions of system preservation. The CIELC is a pristine environment with very low human impact, and it is part of a large preservation area. Normally, studies found in the literature refer to estuaries with high human impact, different from the condition of the studied area. We observed a dominance of nitrate efflux that suggest a big importance of benthic nitrification in the region. In general, the sediment was a net DIN source to the water column, releasing large quantities of nitrate ( $\text{NO}_3^-$ ) and ammonium ( $\text{NH}_4^+$ ). While the estuarine sediments behaved as both  $\text{HPO}_4^{2-}$  sink and  $\text{HPO}_4^{2-}$  source to the water column, showing that this nutrient must not be limited to the primary production, benthic silicate was always liberated in large quantities to the estuary water, showing that the sediment is a  $\text{Si(OH)}_4$  source for the water column. Benthic faunal activity possibly enhanced the benthic exchange, causing the IS in winter to show a very particular behavior. Overall, this study showed that benthic exchange played an important role in the

biogeochemistry and ecology of the CIELC, as well as seasonal and spatial variations. The interaction between space and time factors was always highly significant, showing that the metabolic behavior of the benthic compartment depends on both trophic and physicochemical conditions. In general, the freshwater site was characterized as a nitrogen sink and a silicate and phosphate release, despite some seasonal variations. The sediment of the marine site was characterized, in general, as a nitrogen producer and a phosphorus consumer. However, further studies on compound-specific isotopic composition, water column, and sediment analysis are necessary to provide a more precise understanding of benthic metabolism and N cycling, its control of benthic nutrient release, and its impact on the pelagic biogeochemistry of the estuary.

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## AUTHOR CONTRIBUTIONS

P.C.M.: Conceptualization; Investigation; Methodology; Writing – original draft; Writing – review & editing;  
 B.O.S.: Sampling; Formal analysis; Writing – review & editing;  
 V.G.C.: Methodology; Formal Analysis; Writing – review & editing;  
 E.S.B.: Supervision; Project Administration; Writing - review & editing.

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