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Anthropogenic influence on silicon behavior in an estuary member of the Biosphere Reserve in Southeastern Brazil

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Abstract

The Cananéia-Iguape estuarine-lagoon complex (CIELC), located in the State of São Paulo, Brazil, is considered an area of the Biosphere Reserve. However, an artificial channel built in the northern sector of the system (Iguape) has promoted an unnatural input of fresh water into the system, leading to enhanced drainage of terrestrial material into the estuary and influencing silicon biogeochemistry within the complex. This study used the distribution of different fractions of silicon along the system as a proxy for the freshwater input. The samples were collected during August, 2012 (winter) and February 2013 (summer) and analyzed for dissolved silicate, biogenic silica, and lithogenic silica. Dissolved silicate reached values above 200 µmol L^{-1} in the two seasonal periods, indicating the constant supply of terrestrial material in the northern sector of the system associated with fresh water. Southward, where the system is more preserved (Cananéia-Ararapira), the concentration decreased dramatically. Lithogenic silica (LSi) reached extremely high values of ~700 µmol L^{-1}. Biogenic silica (BSi) showed concentrations up to 120 µmol L^{-1} with distribution more dependent on assimilation processes and the nature of the biological communities than on the source of fresh water. The availability of different forms of Si revealed remineralization, deposition, adsorption, and uptake mechanisms with different dynamics in the northern and southern sectors of the system, evidencing the environmental impact by the Valo Grande Channel.

Keywords: Silicon Biogeochemistry, Silicate, Lithogenic Silica, Biogeonic Silica, Estuaries, Valo Grande

INTRODUCTION

The biogeochemical cycle of silicon (Si) in coastal waters is of great significance due to its association with the global carbon cycle and its potential as an indicator of anthropogenic activities. Silicon, along with nitrogen and phosphorus, is considered an essential nutrient supporting primary production in coastal and marine ecosystems. It plays a crucial role in the constitution of rigid structural parts for certain terrestrial and aquatic organisms, particularly in the basal levels of the marine food chain. Understanding the biogeochemical cycle of silicon and its connection to the carbon cycle is essential for comprehending marine organic matter dynamics and assessing the impacts of human activities.

The input of silicon to coastal regions is largely dependent on the contribution of watersheds and the dynamics of rivers and estuarine systems. Approximately 80% of silicon supplied to the oceans comes from rivers in the form of dissolved silicon (DSi), particulate lithogenic silica (LSi), and biogenic silica (BSi) (Tréguer et al., 1995). Natural processes such as rock weathering contribute to DSi in water systems, while human-induced

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factors like land use changes and hydrological modifications can alter the leaching processes and affect silicon inputs. For instance, the construction of dams can lead to higher silica sedimentation in reservoirs, reducing silicon supply to the oceans (Lauerwald et al., 2013), while soil erosion and climate change may increase the input of particulate silicon (LSi) to coastal environments.

The behavior of DSi varies across estuaries, ranging from conservative transport to almost complete retention (DeMaster, 1981). Estuaries play a crucial role in the consumption of DSi, with an estimated global average of 15% of DSi being consumed within these systems (Tréguer et al., 1995). Changes in the proportion of nutrients transported to coastal seas can have significant effects on the composition of phytoplankton communities, potentially reducing the dominance of diatoms and altering the structure and functioning of aquatic ecosystems (Ragueneau et al., 2005; Ittekkot et al., 2006).

Silicifiers, such as diatoms, are important organisms that utilize biogenic silica (BSi, SiO_2) as a structural component (Maldonado et al., 2019; Moriceau et al., 2019). Diatoms consume substantial amounts of silicon, nitrogen, phosphorus, and inorganic carbon, linking the biogeochemistry of these elements and contributing to the sequestration of atmospheric CO_2 in the ocean (Tréguer and Padovan, 2000). Seasonal variations in nutrient availability, including dissolved silicon, play a crucial role in primary production within coastal systems. Apart from river inputs, sediment-water flux also influences nutrient dynamics, as demonstrated by previous studies (Lerat et al., 1990). Additionally, microzooplankton and estuarine phytoplankton communities contribute to the regeneration and utilization of silicon (Birrien et al., 1991). Silicoflagellates and diatoms (silicifers organisms) use this essential nutrient to construct the rigid structures (BSi) and constitute important groups in the estuarine phytoplankton community.

The transport of silicon into estuaries is primarily carried out through the deposition of silicon-rich particles, with an average of 16% biogenic silica (BSi) content. These particles mainly consist of frustules from diatoms and phytoliths, the latter being BSi structures produced by higher plants (Roubeix et al., 2008). A significant portion of BSi originating from rivers can dissolve in estuaries, ultimately influencing the amount of dissolved silicon entering the ocean (Roubeix et al., 2008).

During the spring and summer seasons, diatom blooms may occur in rivers and estuaries, leading to substantial reductions in dissolved silicate levels and increased concentrations of BSi. In fact, biogenic silica can account for up to 70% of the total silicon load in rivers. Its transport can occur in suspended form, sinking and accumulating in sediment (resulting in silica retention within the ecosystem), or undergoing dissolution, which depends on factors such as salinity and bacterial activity (Roubeix et al., 2008; Loucaide et al., 2008; Carbonnel et al., 2013).

It is essential to acknowledge the presence of different forms of silicon within the hydrological system, as they indicate its relationship with the surrounding environment, including biota, sediments, and soil. However, studies focusing on the biogeochemical cycle of silicon often overlook these various forms and their environmental significance in relation to anthropogenic influences and associated evidence (Roubeix et al., 2008; Loucaide et al., 2008; Carbonnel et al., 2013).

Estuaries are areas where seawater mixes with fresh water and represent an interface among terrestrial and marine systems. As a result, they are very complex environments, where signals carried by the rivers are subjected to a variety of physical, chemical, and biological processes (Chester, 2003). Estuaries are highly dynamic environments, often with high biological productivity and, hence, high absorption of dissolved silicon by diatoms (Hughes et al., 2010). The most typical feature of estuaries is the salinity gradient generated by the mixing of freshwater and seawater. This gradient impacts the flow of Si to the coastal region as it influences the uptake of silicon by phytoplankton and modifies the interaction between DSi and suspended particulate matter (Roubeix et al., 2008).

The Cananéia-Iguape Estuarine-Lagoon Complex (CIELC) is a large coastal region characterized by distinct differences between its northern and southern parts. In the northern region, the estuarine-lagoon system experiences freshwater input from the Ribeira de Iguape River through the man-made Valo Grande Channel, resulting in a pronounced salinity gradient and significant terrestrial material intrusion from the Ribeira River watershed. In contrast, the southern portion of the system exhibits more pristine characteristics, making it an ideal area for studying the presence and distribution of different forms of silicon and their association with anthropogenic and natural activities. It is worth noting that this region is part of the UNESCO Biosphere program and is listed as an environmentally relevant wetland area under the RAMSAR Convention (https://rsis.ramsar.org/ris/2310).

Quantification of biogenic and lithogenic silica in aquatic environments has been scarce, especially in Brazilian waters where such studies are almost non-existent. This study aims to explore the potential use of silicon forms in relation to environmental parameters to elucidate the influences of both anthropogenic and natural factors on the hydrological system. To achieve this objective, various parameters were measured, including temperature, salinity, turbidity, pH, dissolved silica (DSi), biogenic silica (BSi), lithogenic silica (LSi), suspended particulate matter, and chlorophyll-*a* concentration. The findings of this study will contribute to a better understanding of the relationships among these parameters and the estimation of silicon biogeochemical processes occurring within the estuary. The different forms of silicon will serve as proxies to differentiate natural freshwater inputs from the contributions of anthropogenic influences.

METHODS

Study area

The Cananéia-Iguape estuarine-lagoon complex (CIELC) (Figure 1) is located on the southern coast of the State of São Paulo, Brazil. It is considered a protected environmental area and declared a Biosphere Reserve (UNESCO, 2005). The complex is separated from the ocean by the Comprida Island, a barrier island 70 km long (Tessler and Furtado, 1983). The channels that form the complex have a surface area of approximately 115 km^2 and are connected to the ocean by the inlets of Ararapira, Cananéia, and Icapara (Miyao et al., 1986).

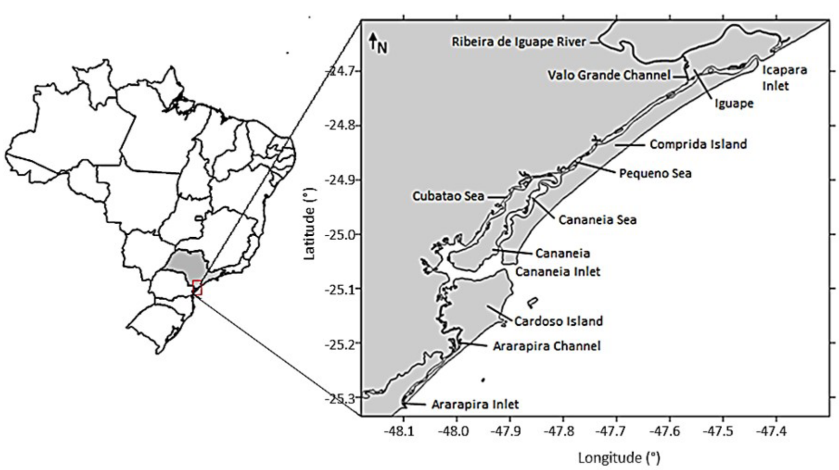

Figure 1. Map of the Cananéia-Iguape estuarine-lagoon complex (CIELC), indicating the sites where the fish were collected in the northern and southern areas.

In 1841, an artificial channel called Valo Grande, which connects the Ribeira de Iguape River to the Pequeno Sea (channel that separates Comprida Island from the mainland), was built to facilitate the transport of rice to the port of Iguape (Figure 1). Currently, the Valo Grande Channel is responsible for the largest fresh water inflow to the complex, what is responsible for the hydrochemical properties in the system resulting in gradient of salinity influencing the biogeochemical cycles of elements. The basin of the Ribeira de Iguape River has a drainage area of 23,350 km^2.

The artificial channel was closed in 1978 and remained closed for a few years until the dam was breached during the floods that occurred in 1983. Although it was later rebuilt, the Valo Grande Channel was reopened in February 1995, when heavy rains again caused the breaking of the dam (Filho and Miranda, 1997). At the time of its construction, the channel was 4 m wide, today it is over 250 m, due to erosion. It drains 70% of the matter and freshwater load from the Ribeira de Iguape River into the complex (Eschrique et al., 2014).

The circulation in the complex is driven by the tidal wave entering the inlets of Icapara and Cananéia, as well as, by the contribution of freshwater from rivers (Miyao et al., 1986). The tide is classified as mixed with semidiurnal dominance and the estuary as partially mixed. The Cananéia region has an average annual air temperature of 21.4 °C. The rainy season extends from December to April, with a monthly average of 200 mm; and the dry period from May to November, with monthly mean values of 80 mm. The annual precipitation can reach 2,000 mm.

Considering this complex system, that maintain important preserved areas, including a part of the Atlantic Forest, mangroves and a diversity of aquatic species, this area is relevant being included in the RAMSAR preservation sites. This study intends to evaluate the effect of the anthropogenic intervention via Valo Grande Channel in it system by the input of fresh water on silicon forms along the system.

Sampling and analyses

The samples were collected during August 2012 (winter) and February 2013 (summer) in the Cananéia-Iguape estuarine-lagoon complex, in the context of the Projects: FEBIOGEOQUIM CNPq 478890/2011-7 and INCT- TMCOcean CNPq 573.601/2008-9. The sampling was performed on board of the R/V Albacora, a vessel of the Oceanographic Institute of the University of São Paulo (IO-USP). The locations of the sampling points are shown in Figure 2. The samples outside the system (external stations MY_1-MY_3 and MC_1-MC_4) were only collected during summer. The samples were collected at surface, medium and bottom waters, normally at 0, 3, 5, 8 and 10 m depending on the total depth.

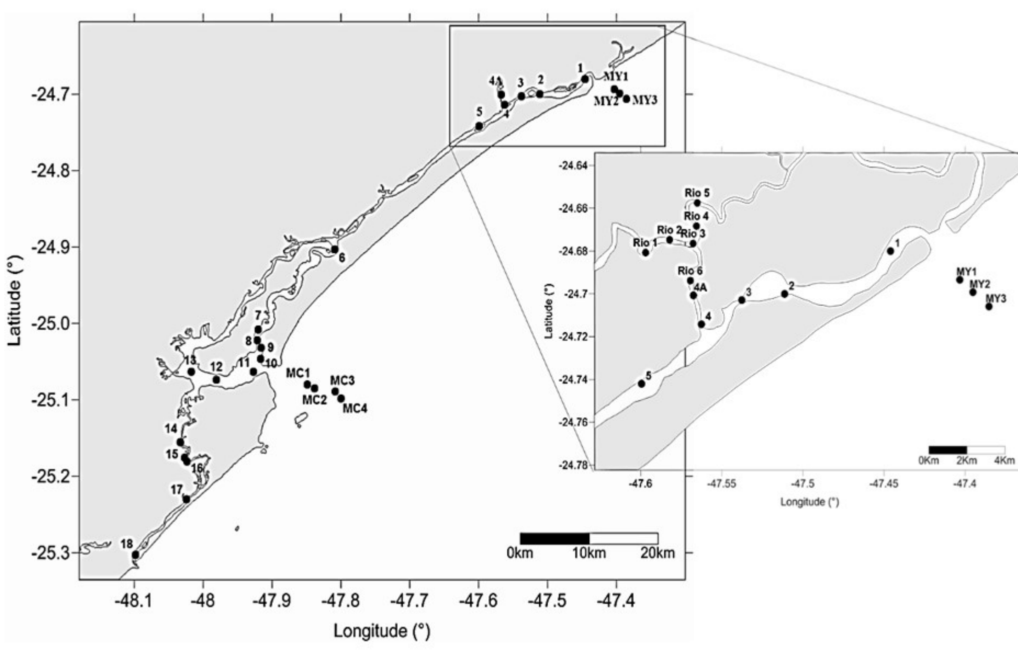

Figure 2. Location of the sampling stations in Cananéia-Iguape Estuarine-Lagoon Complex, São Paulo, Brazil.

Water temperature was measured in situ with protected reversal thermometers, Kahl Scientific Instrument Corporation®, accuracy of 0.02 °C. Salinity was determined using an inductive salinometer Beckman RS10, calibrated with Standard Seawater Ocean Scientific International Ltda., precision of ± 0.005. Water pH was measured with an Orion® 290A pHmeter, accuracy of ± 0.001, following the recommendations of Aminot & Chaussepied (1983). Turbidity was analyzed with 2100P Turbidimeter, Hach®.

Samples for the analyses of dissolved silicate, suspended particulate matter (SPM), and chlorophyll-*a* were filtered with Whatman® GF/F filters, porosity of 0.45 µm. Filtered water samples were preserved in polyethylene bottles at -20 °C. Silicate was analyzed following the colorimetric method of Grasshoff et al. (1983), precision of ± 0.01 µmol L^{-1}. The filters were used to determine the SPM content, via the gravimetric method (precision of ± 0.01 mg L^{-1}); and chlorophyll-*a*, through the colorimetric method (precision of ± 0.01 mg m^{-3}), both described in Strickland & Parsons (1968).

Biogenic silica was obtained by the digestion method presented by Ragueneau & Tréguer (1994). The material retained on a polycarbonate filter (porosity of 0.45 µm - Millipore®) was dried for 12 hours at 60 °C and treated with 4.0 mL of NaOH 0.2 µmol L^{-1} at 100 °C for 40 min in a plastic tube. After cooling, 1.0 mL of HCl1 µmol L^{-1} was added. The sample was then centrifuged for 10 min at 1,500 rpm, then 1.0 mL of supernatant was removed and diluted to 50 mL with distilled water. The dissolved silicate was analyzed according to Grasshoff et al. (1983) and yielded the apparent biogenic silica (BSi_a). To eliminate the interference of lithogenic silica, the following correction was made: $BSi = BSi_a - k.LSi_a$, where k is a constant depending on the mineralogy of the area. In this study, a mean of 0.15 was used as a linear coefficient of relationship between the mineral silicate and hydrolizated silicate in the study area (0.14-0.16 was obtained by Ragueneau and Tréguer, (1994) for Bay of Brest and for the western English Channel). LSi_a corresponds to the apparent lithogenic silica, whose determination is described below. The accuracy of the method is ± 0.05 µmol L^{-1}.

After BSi digestion, the supernatant was removed and discarded, then 12 mL of distilled water was added. The tubes were shaken and centrifuged for 10 min at 1,500 rpm and then 12 mL supernatant extracted and discarded. If the concentration of BSi was greater than 5.0 µmol L^{-1}, the procedure was repeated. The tube containing the filter was then covered with a sheet of aluminum foil and dried at 80 °C for 12 h. Next, the sample was then treated with 0.2 mL of HF 2.9 µmol L^{-1} for 48 h. Then, 10 mL of distilled water was added, the tubes were stirred, and the remaining solution was diluted until the HF concentration was less than 0.002 µmol L^{-1}. The analysis of dissolved silicate as described in Grasshoff et al. (1983) was made, yielding the apparent silicon lithogenic (LSi_a). The LSi concentration was calculated by the expression: LSi = TSi - BSi, where TSi is the total concentration of silicon present in the filter (BSi_a + LSi_a). The accuracy of the method is ± 0.1 µmol L^{-1}. Pearson's correlation coefficient was applied to measure the statistical relationship between two continuous variables and graphic treatment using Surfer® software.

RESULTS

Winter (August, 2012)

During the sampling period, in the winter of 2012, water temperature ranged from 20.25 to 24.00 °C (Table 1), with the highest values observed in the surface water, except at stations 10 and 12. Water temperature decreased from Iguape (stations 1 and 2) toward the Ararapira Inlet (station 18). Stations located in the Ribeira de Iguape River showed more homogeneous temperature around 21 °C. There was a small thermal stratification in the Cananéia sector, while the Ararapira Channel (stations 14–18) showed more thermic stability.

The waters of the Ribeira de Iguape River (stations Rio 1 to Rio 6 and 4A) showed salinity values between 0.03 and 0.04, characteristic of freshwater. Along the estuarine-lagoon complex, the values ranged from 0.49 to 32.75 (Table 1). The northern sector of the system is strongly influenced by freshwater inflow, characterized by salinity lower than 5 (stations 2–5), due to the contribution from the Ribeira de Iguape River, through the Valo Grande Channel. The salinity at station 1 was 6.73, showing the entry of more saline waters through Icapara Inlet.

The salinity increased toward Cananéia, following the largest marine influence held in the southern sector. The maximum of 31.20 was reached at station 10, located near the Cananéia Inlet. The influence of more saline water (> 30) was also observed from stations 15 to 18 in the Ararapira Channel.

Water pH (Table 1) was lowest at the river stations, 4A and 4; the minimum was 6.23 (station 4), increasing toward the southern area. The highest values were found at stations where marine influence is greater (stations 10, 11, 12, 17, and 18), reaching a maximum of 8.63 (stations 17 and 18).

The levels of SPM varied between 4.20 and 82.75 mg L^{-1} (Table 1), and its distribution was the reverse of turbidity in the northern sector. While in the southern sector, the distribution pattern of these parameters was similar. This must be due to the higher river inflow into the northern sector of the system, characterized by the entry of finer fractions of sediment (silt and clay), leading to lower SPM values and increased turbidity. In the southern sector, slightly coarser sediment resuspension (silt and fine sand) probably contributed to the SPM, increasing SPM and reducing turbidity. The Chlorophyll-*a* had a maximum of 12.89 mg m^{-3} at station 2 and a minimum of 0.04 mg m^{-3} obtained in Ararapira Channel (Table 1).

Table 1. Descriptive statistics (maximum, minimum, mean, median and standard deviation - SD) of the parameters: temperature (°C), salinity, pH, turbidity (NTU), silicate (µmol L^{-1}), BSi (µmol L^{-1}), LSi (µmol L^{-1}), SPM (mg L^{-1}) and chlorophyll-*a* (mg m^{-3}) and analyzed the estuarine-lagoon complex of Cananéia-Iguape (SP), during winter (August 2012), n = 42.

		T	*S*	*pH*	*Turb.*	*Silicate*	*BSi*	*LSi*	*SPM*	*Chl-a*
		(°C)			*(NTU)*	*(µmol L⁻¹)*	*(µmol L⁻¹)*	*(µmol L⁻¹)*	*(mg L⁻¹)*	*(mg m⁻³)*
Iguape (River stations, 4A and 1-5), n=16	Maximum	24.00	6.73	7.86	60.60	260.91	25.92	343.97	39.00	12.89
	Minimum	21.10	0.03	6.83	12.90	115.45	2.60	25.80	4.83	2.24
	Mean	21.84	0.88	7.07	37.37	216.06	10.91	111.19	16.63	4.70
	Median	21.30	0.09	6.99	41.25	224.09	10.35	65.61	9.44	3.37
	SD	±1.10	±1.92	±0.31	±13.99	±37.32	±7.16	±103.45	±12.75	±3.44
Cananéia (stations 6- 13), n= 17	Maximum	22.60	31.20	8.58	12.80	55.27	77.88	275.06	82.75	5.64
	Minimum	20.45	13.21	7.65	1.30	8.50	3.12	4.98	25.90	1.80
	Mean	21.45	25.83	8.31	5.12	20.08	21.43	61.81	45.52	3.78
	Median	21.46	28.78	8.37	4.44	16.64	15.42	29.43	43.20	3.86
	SD	±0.52	±6.03	±0.27	±2.92	±13.81	±19.65	±78.76	±14.50	±1.13
Ararapira (stations 14- 18), n=9	Maximum	21.10	32.75	8.63	23.40	23.36	41.50	254.33	68.44	4.01
	Minimum	20.25	28.87	8.10	0.85	7.95	3.12	5.28	24.90	0.04
	Mean	20.60	31.03	8.32	6.85	14.63	13.82	49.87	37.81	2.09
	Median	20.63	30.56	8.28	1.46	15.30	5.39	7.42	30.63	1.52
	SD	±0.25	±1.41	±0.19	±8.04	±5.20	±14.32	±80.04	±16.76	±1.74

Summer (February, 2013)

In February 2013, the water temperature ranged from 24.47 to 30.25 °C (Table 2) and was practically vertically homogeneous inside the estuary. The thermal stratification throughout the water column in the external stations (stations MY and MC) became more pronounced as the distance from the coast increased.

Salinity ranged from 0.02 in the river to 35.17 at external stations (seaside) (Table 2). Iguape values remained close to zero due to the entry of water from the Ribeira de Iguape River via the Valo Grande Channel, except at station 1 that, being located near the Icapara Inlet, was influenced by more saline waters, resulting in a salinity of 20.59. The salinity increased toward Cananéia, reaching a maximum value in station 10 (31.52 at the bottom). At stations 11, 12, and 13, also located in Cananéia, the salinity was slightly lower, around 25, because these stations were sampled during the lowest tide, when the influence of the river water was greater. In the Ararapira Channel, at stations 14, 15, and 16, the salinity was low (~ 15), due to heavy rains that occurred the night before sampling (rainfall of 130 mm). At stations 17 and 18, salinity increased again due to the entry of more saline waters through the Ararapira Inlet.

The distribution of pH was similar to the behavior of salinity, with lower values in Iguape (except station 1), with a minimum of 6.61 (Table 2) at station Rio 6, increasing toward the south, where marine influence is greater. The maximum pH of 8.42 was observed at station 9.

Turbidity showed wide variation, from 0.48 NTU to 164.00 NTU (Table 2). The highest values were in Iguape, decreasing toward Cananéia, the Ararapira Channel, and at the external stations.

The concentration of dissolved silicate ranged from 3.99 µmol L^{-1} to 250.96 µmol L^{-1} (Table 2). The distribution was the reverse of that of salinity and pH, i.e., the greater the marine influence, the lower the dissolved silicate, indicating continental input of this nutrient. Station MY1 displayed the maximum value of silicate (> 100 µmol L^{-1}), demonstrating an input from the system to the ocean.

Table 2. Descriptive statistics (maximum, minimum, mean, median and standard deviation - SD) of the parameters: temperature (°C), salinity, pH, turbidity (NTU), silicate (µmol L^{-1}), BSi (µmol L^{-1}), LSi (µmol L^{-1}), SPM (mg L^{-1}) and chlorophyll-*a* (mg m^{-3}) and analyzed the estuarine-lagoon complex of Cananéia-Iguape (SP), during summer (February 2013).

		T	*S*	*pH*	*Turb.*	*Silicate*	*BSi*	*LSi*	*SPM*	*Chl-a*
		(°C)			*(NTU)*	*(µmol L^{-1})*	*(µmol L^{-1})*	*(µmol L^{-1})*	*(mg L^{-1})*	*(mg m^{-3})*
Iguape (River stations, 4A and 1-5), n=18	Maximum	29.50	20.59	8.05	164.00	250.96	98.00	731.40	187.27	14.75
	Minimum	27.10	0.02	6.61	73.50	94.20	3.47	68.23	64.25	1.34
	Mean	27.66	1.30	6.87	113.26	204.10	59.05	271.30	116.19	5.46
	Median	27.35	0.03	6.76	133.00	210.71	57.00	261.05	113.39	5.30
	SD	±0.71	±4.83	±0.32	±38.87	±35.24	±23.61	±143.92	±32.31	±3.13
Cananéia (stations 6-13), n= 19	Maximum	29.11	31.52	8.42	87.60	47.84	119.13	284.63	189.67	25.71
	Minimum	27.50	3.94	7.03	4.20	10.96	2.58	12.65	34.00	5.62
	Mean	28.23	23.24	7.98	14.97	28.05	33.84	67.83	65.57	12.09
	Median	28.35	24.89	8.07	8.35	31.08	25.54	40.25	56.10	11.81
	SD	±0.45	±8.30	±0.42	±19.90	±12.24	±28.33	±78.07	±34.72	±4.49
Ararapira (stations 14-18), n=10	Maximum	28.07	31.51	8.32	11.10	40.00	28.35	149.79	68.29	20.15
	Minimum	27.20	13.91	7.36	4.11	5.80	2.58	18.69	34.00	6.45
	Mean	27.68	20.53	7.82	7.03	25.82	12.48	66.99	48.48	11.59
	Median	27.75	16.09	7.67	5.91	36.52	11.78	43.99	45.17	11.40
	SD	±0.28	±6.93	±0.37	±2.28	±14.91	±6.99	±49.88	±11.31	±4.44
External Stations (MY1-MY3 and MC1-MC5), n=19	Maximum	30.25	35.17	8.26	4.02	101.44	12.24	56.24	75.45	9.99
	Minimum	24.47	21.46	8.01	0.48	3.99	0.00	0.86	29.06	0.54
	Mean	27.18	32.18	8.13	1.96	16.42	3.70	11.20	47.72	3.59
	Median	27.04	33.79	8.14	1.90	9.30	2.34	8.78	48.10	2.65
	SD	±1.63	±3.34	±0.07	±1.01	±21.95	±3.33	±12.95	±9.89	±2.70

BSi values peaked at 119.13 µmol L^{-1}, while the minimum was lower than the limit of detection (0.05 µmol L^{-1}) (Table 2). LSi concentrations varied widely from 0.86 µmol L^{-1} to 731.40 µmol L^{-1}. (Table 2) The highest values of both BSi and LSi were in Iguape. Station 5 had a minimum BSi at the bottom along with the maximum value of LSi and turbidity, indicating the effects of erosion or sediment remobilization.

The SPM content, which ranged between 29.06 mg L^{-1} and 68.48 mg L^{-1}, (Table 2) was higher at stations with greater influence of fluvial input and where resuspension of sediment is possible (stations 5 and 11). The turbidity and LSi also displayed this behavior.

The concentration of chlorophyll-*a* was higher in the Cananéia sector and in the Ararapira Channel, with a maximum of 25.71 mg m^{-3} (Table 2) at station 1, where a maximum BSi was also observed. The values declined toward Iguape and at the external stations, with a minimum of 0.54 mg m^{-3} in MC5, located at the farthest point from the coast.

Seasonal highlights

To better understand the relationship between the parameters, a Pearson correlation analysis was applied. The results are provided in Tables 3 (winter) and 4 (summer). The statistically significant results ($p < 0.05$) are marked in red. Furthermore, the parameters values were interpolated between stations 1 to 18 (Figures 3 to 8).

Table 3. Linear correlation r between the analyzed parameters in Cananéia-Iguape estuarine-lagoon complex, during winter (August, 2012), n = 25. The significant correlations, $p < 0.05$, are marked in red.

	Temp.	*Sal.*	*pH*	*Turb.*	*Silicate*	*BSi*	*LSi*	*SPM*	*Chl-a*
Temp									
Sal	-0.34								
pH	-0.11	0.95							
Turb.	0.20	-0.73	-0.67						
Silicate	0.16	-0.95	-0.94	0.75					
BSi	-0.03	0.35	0.42	-0.05	-0.33				
LSi	0.24	-0.12	-0.01	0.48	0.11	0.65			
SPM	-0.01	0.72	0.80	-0.44	-0.76	0.77	0.41		
Chl-*a*	0.51	-0.19	0.20	0.34	0.14	0.14	0.18	0.08	

Table 4. Linear correlation r between the analyzed parameters in Cananéia-Iguape estuarine-lagoon complex, during summer (February, 2013), n = 47. The significant correlations, $p < 0.05$, are marked in red.

	Temp.	*Sal.*	*pH*	*Turb.*	*Silicate*	*BSi*	*LSi*	*SPM*	*Chl-a*
Temp									
Sal	-0.09								
pH	0.06	0.96							
Turb.	-0.04	-0.76	-0.78						
Silicate	0.04	-0.89	-0.89	0.87					
BSi	0.20	-0.61	-0.57	0.59	0.63				
LSi	0.02	-0.68	-0.68	0.83	0.74	0.64			
SPM	0.04	-0.58	-0.59	0.73	0.71	0.74	0.87		
Chl-*a*	0.27	0.01	0.11	-0.09	-0.20	0.26	-0.02	0.08	

Temperature was significantly correlated ($p < 0.05$) only with chlorophyll-*a* in winter. The temperature distribution throughout the system (stations 1 to 18) in winter (a) and summer (b) are in Figure 3. During summer, the values were higher throughout the system, reaching temperatures above 30 °C at a few points, such as those near the inlets (1, 10, 11, and 17). During summer, the salinity was generally lower than in winter and there was a formation of a slight haline stratification due to higher rainfall in this period. A significant increase in salinity southward was observed in both seasonal periods (Figure 3 c, d).

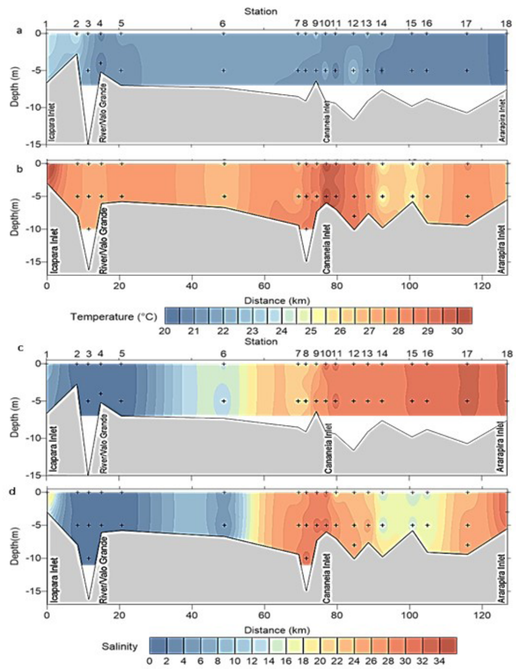

Figure 3. Temperature (a, b) and salinity (c, d) distribution through Cananéia-Iguape estuarine lagoon complex, during winter (August 2009) (a, c) and summer (February 2013) (b, d).

The pH values showed a strong positive correlation with salinity in both periods, with r = 0.95 in winter and r = 0.96 in summer (Tables 3 and 4). On average, the pH was lower in summer (7.72) than in winter (7.83) due to increased freshwater inflow from increased rainfall. Figure 4 (a, b) charts the pH distribution throughout the system. In both periods, the pH values were lower in the northern sector of the system. During the summer, in station 6, the values were slightly lower due to higher river inflow.

Turbidity had significant negative correlations with salinity and pH in both periods (Tables 3 and 4). The zone of maximum turbidity was located at stations 2 and 3 in winter and between stations 1 and 5 in summer (Figure 4 c, d).

Dissolved silicate showed a significant negative correlation with salinity and pH in the two seasons (Tables 3 and 4), indicating that their primary source for the estuary is the Ribeira de Iguape River through the Valo Grande Channel. The same correlation was observed for BSi and LSi, but only in the summer period. During the winter, rainfall is lower, decreasing the carrying capacity of the Ribeira de Iguape River and hence the SPM, BSi, and LSi loads arriving in the estuary via fluvial transport. This leads to the particulate fractions of silicon not having a statistically significant correlation with salinity.

Figure 5 shows the theoretical dilution of silicate with salinity based on conservative and non-conservative behaviors (Liss, 1976) during winter (a) and summer (b). This parameter indicated a removal behavior (points that are below the theoretical dilution line).

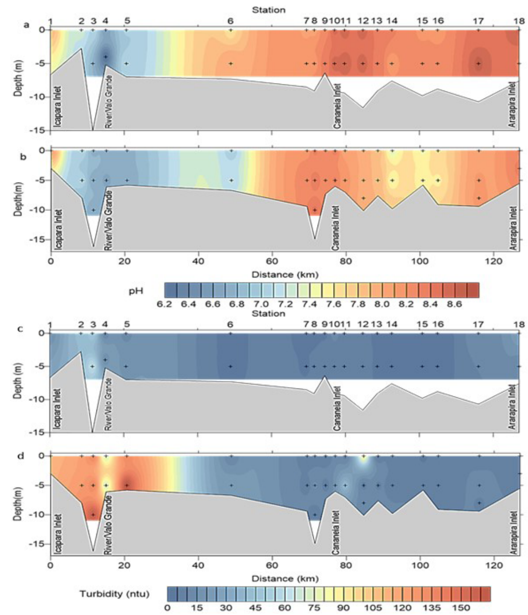

Figure 4. pH (a, b) and turbidity (NTU) (c, d) distribution through Cananéia--Iguape estuarine-lagoon complex, during winter (August 2009) (a, c) and summer (February 2013) (b, d).

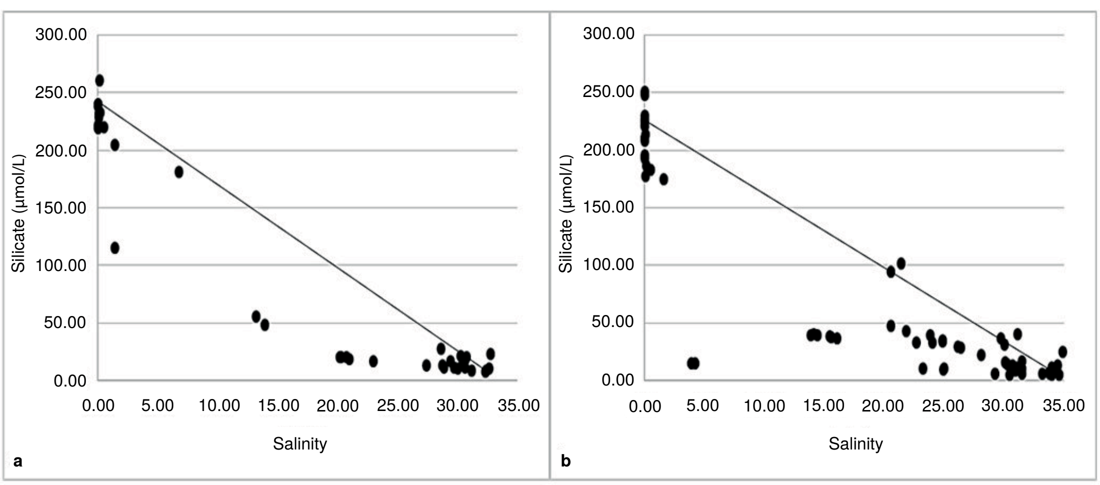

Figure 5. Scatterplot of the silicate by salinity with the theoretical dilution line during winter (a) and summer (b).

During winter, at stations 1, 2, and 3, the turbidity was high, and salinity was less than 8, increasing rapidly toward station 1. Normally, this condition favors the dissolved silicate passage to particulate forms. Following from Iguape to Cananéia, there was a decrease in the concentrations of dissolved silicate, BSi, and LSi, during both seasons (Figure 6), reaching local minimums at station 6.

Cananéia and Ararapira Channel stations (7–18), both in winter and in summer, displayed relatively low concentrations of silicate and higher values of BSi and LSi, especially in the stations near the Cananéia Inlet and at the bottom. Higher values of LSi at station 18 near the Ararapira Inlet were also observed. This distribution indicates a possible sediment remobilization (corroborated by greater values of SPM), wherein the dissolved silicate may have been removed by abiotic processes to form LSi or biotic processes to form BSi.

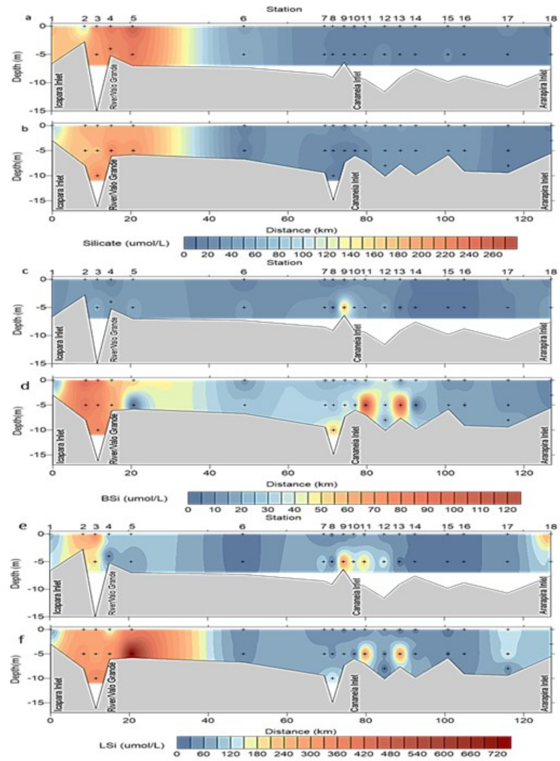

Figure 6. Dissolved silicate (a, b), biogenic silica (BSi) (c, d) and lithogenic silica (LSi) (e, f) distribution through Cananéia-Iguape estuarine-lagoon complex, during winter (August 2009) (a, c, e) and summer (February 2013) (b, d, f).

The distribution of SPM was quite different in the sampled periods. During the winter (Figure 7a), the highest concentrations occurred in the southern sector (Cananéia and Ararapira Channel), and the lowest in the northern sector and, unlike the expected values observed for turbidity. This occurred because in this period the rainfall was lower, reducing the carrying capacity of suspended material in the river, leading to the input of finer fractions of sediment (silt and clay) in the north of the system, resulting in lower values of SPM and higher turbidity. In the southern sector, the input of SPM was mainly due to resuspension of sediments a bit thicker (fine sand and silt), causing higher values of SPM and lower turbidity.

In summer, the distribution of SPM was reversed (Figure 7b), i.e., higher in the northern sector and lower in the southern sector. In this period, the rainfall was higher, increasing the transport capacity of the river and the input of coarser fractions of sediment to the system. The SPM showed significant positive correlations with silicate, BSi, and LSi, indicating that during this period these parameters had common sources (fluvial and sediment resuspension).

Chlorophyll-*a* exhibited no significant correlation with BSi during both seasonal periods (Tables 3 and 4). In the winter, the chlorophyll-*a* concentrations (Figure 7c) were relatively higher in the northern sector, while BSi was highest in the Cananéia region. This may be due to the production by non-siliceous organisms in the northern sector (leading to higher concentrations of chlorophyll-*a* and lower BSi). In Cananéia, the resuspension of detrital BSi may have caused high BSi and relatively low chlorophyll-*a*.

During the summer (Figure 7d), the concentrations of chlorophyll-*a* and BSi were higher in the southern sector indicating higher phytoplankton production, mainly by the presence of diatoms as being reported by Teixeira (1969), Kutner (1972), Braga (1995) in the Cananéia region, and showing in the recent research in process. Matta and Flynn (2015) also indicated the dominance of diatoms in this region until medium salinity (19), that correspond the end of the Cananéia Island.

The same process was observed by Shen et al. (2008) in areas of low salinity and maximum turbidity in the Changjiang Estuary. During summer (Figure 7b, d, and f), the distribution of the particulate and dissolved fractions of silicon is the inverse of salinity and pH in these stations.

In the northern sector, BSi had higher values accompanies by lower levels of chlorophyll-*a*, suggesting a contribution of phytoliyhs and/or detrital BSi introduced by Valo Grande Channel. Barrera-Alba et al. (2008) showed a contribution in chlorophyll-*a* in this region due to the diatoms presence that corroborate the BSi presence, but also noticed the euphotic layer at this region is limiting for an intense development.

However, the intense rice cultivation in the region occurred in the XIX century (Braga, 1999) allowed the inclusion of the presence of phytoliths and microphytoliths contribution from the leaching soil through the Valo Grande Channel to BSi reservoir. Phytoliths are vegetal structures formed by silicon and present in some vegetal, including the rice plants. Rice plants produce three distinctive phytoliths: bilobate phytoliths from rice leaves and stems, double-peaked phytoliths from the rice husk, and bulliform phytoliths from the rice leaves. Anjum and Nagabovanalli (2021) observe that the rice cultivation as an important Silicon (Si) accumulator and also produce a C occluded phytolitic (PhytOC) that represent an important agent in the Biogeochemical cycles of C and Si, acting in the C sequestration.

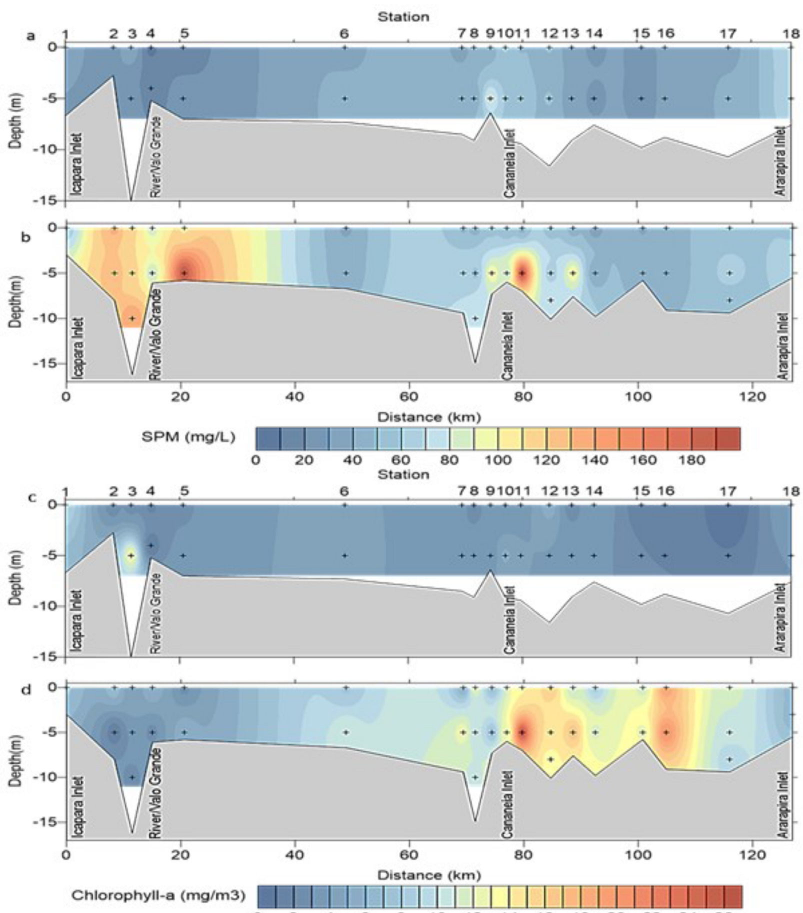

Figure 7. Chlorophyll-*a* (mg m^{-3}) distribution through Cananéia-Iguape estuarine-lagoon complex, during winter (August 2009) (a) and summer (February 2013) (b).

DISCUSSION

Silicon plays a crucial role in aquatic environments, affecting water buffer capacity, sedimentation, benthic flux, and serving as a structural component for siliceous organisms. This multifunctional element, which is mainly sourced from the terrestrial system, is influenced by climate change and anthropogenic activities. The biogeochemical cycle of Si involves different species, including dissolved and particulate forms such as silicate, biogenic silica (BSi), and lithogenic silica. Environmental parameters such as temperature, salinity, and pH influence the cycling of these forms. Therefore, the behavior of Si can serve as a proxy for detecting environmental changes.

In this study, temperature exhibited a seasonal pattern, with higher values in summer and lower values in winter, consistent with observations by other authors (Aguiar et al., 2013; Sutti et al., 2023). Homogeneous thermal conditions were observed in most of the water samples collected at various stations. Salinity values were higher in winter compared to summer, primarily due to increased river flow during the rainy season. Salinity values also increased from north to south within the Cananéia-Iguape Estuarine-Lagoon complex. The historical opening of the Valo Grande Channel significantly influenced regional salinity and chemical parameters in the system. Previous reports by DAEE (1989) indicated salinity values between 16 and 34 when the Valo Grande Channel was closed and between 0 and 32 when it was open. Seasonally, Souza et al. (2012) observed lower salinity values in the Cananéia sector during summer compared to winter, possibly due to high rainfall and increased freshwater influence in the southern sector. pH values were generally around 8, except in areas influenced by river waters, where pH decreased below 8, primarily in the northern part of the system. Some low pH values were recorded in the southern sector during the summer period, but overall, pH values were directly correlated with salinity values observed in other estuarine waters (Sutti et al., 2023). Turbidity, influenced by terrestrial input, exhibited higher values in summer, consistent with the findings of Marquez et al. (2007) in the Cananéia region, where turbidity was lower than 50 NTU in June 2002 and greater than 150 NTU in January 2004.

Dissolved silicate concentrations in the estuary were slightly higher in winter compared to summer, while particulate silicon showed higher values in summer, considering both biogenic (BSi) and lithogenic (LSi) forms. BSi concentrations were similar to those reported in the Scheldt estuary (between 7 µmol L^{-1} and 10 µmol L^{-1}) by Carbonnel et al. (2013), as well as at the mouth of the Danube River (~50 µmol L^{-1}) by Ragueneau et al. (2002). Lower BSi concentrations ranging from 2.0 µmol L^{-1} to 56.0 µmol L^{-1} were reported by Vieillard et al. (2011) in the Plum Island Estuary in the USA. The variation in dissolved silicate associated with seasonal periods, influenced by river discharge and spatial distribution, has been observed by Zhang et al. (2020) in other estuaries.

Silicate, BSi, and LSi concentrations showed different behaviors depending on the environmental conditions and locations within the estuarine system. The dilution tendency, characteristic of environmental components exhibiting conservative behavior with minor biological assimilation, was observed for silicate, indicating its stability and limited biological removal. This behavior differed from observations by Braga et al. (2009), who noticed conservative behavior of silicate in the study area but with lower maximum concentrations. This suggests an increasing input of silicate to the system, potentially due to erosion processes. The opening of the Valo Grande Channel facilitated the transport of silicate from the northern area, leading to increased sedimentation and silicate concentrations in the sediments (Cornaggia et al., 2018).

Turbidity, particularly in areas of low salinity, was associated with the abiotic removal of dissolved silicate to the particulate form (abiotic uptake). This behavior was observed at some stations, especially near the river influence (Station 2), and was linked to decreased dissolved silicate concentrations, low BSi, and high LSi levels. Similar observations were made by Shen et al. (2008) and Ran et al. (2018) in the turbid and low salinity areas of the Changjiang Estuary.

Lower concentrations of silicate, BSi, and LSi were observed in Station 6, which can be attributed to sedimentation processes in this middle area of the CIELC, characterized by low hydrodynamics. Similar observations were reported by Ragueneau et al. (2002) in the mixing zone between the Danube River and the Black Sea, where low salinity and pH hindered the solubilization of particulate silicon. Silicon removed through primary production or adsorbed to suspended particulate matter had limited return to the dissolved form, resulting in decreased dissolved silicate concentrations. This behavior was attributed to the biological assimilation of Si, which can occur independently of photosynthesis, utilizing energy from respiration processes. Heterotrophic organisms, such as rhizarians, choanoflagellates, and sponges, produce BSi regardless of the photoautotrophic processing of carbon and nitrogen (Maldonado et al., 2012, 2019; Monferrer et al., 2020).

In a eutrophic bay, Zhang et al. (2020) observed higher dissolved silicate values during the wet season and lower values in autumn and winter. Tropical watersheds, including the study area, play a significant role in the transfer of terrestrial dissolved silicate to the ocean, with approximately 74% of riverine Si input originating from these regions (Tréguer et al., 1995). Understanding the Si cycle is crucial for comprehending marine food webs, biogeochemical cycles, and the biological carbon pump (Tréguer et al., 2021).

The contribution of Si forms from coastal regions to adjacent oceans is essential for maintaining the input/output balance and stability of Si. Changes in regional and global biogeochemical cycling of Si, influenced by climate change and anthropogenic modifications, can impact the burial rates of Si (Tréguer et al., 2021). For instance, Braga et al. (2004) reported a benthic dissolved silicate anomaly (~4,000 m depth) in the Congo margin, indicating the transfer of Si from land to the ocean through the Congo River Canyon. Although studies in coastal tropical areas are scarce, Bastos and Braga (2018) observed dissolved silicate concentrations of up to 14.40 µmol L^{-1}, maximum LSi of 25.76 µmol L^{-1}, and BSi concentrations of 7.39 µmol L^{-1} in the coastal area of Recife, influenced by fluvial inputs from the Capibaribe and Beberibe rivers.

In the estuarine system under study, dissolved silicate reached values above 200 µmol L^{-1} during both seasonal periods, while LSi exhibited extremely high values, reaching ~700 µmol L^{-1}. BSi concentrations reached up to 120 µmol L^{-1} and were more dependent on assimilation processes and the nature of biological communities than on the source of fresh water.

Chlorophyll-*a* concentrations showed significant negative correlations with temperature and salinity, while positive correlations were observed with dissolved silicate and BSi in a study by Bastos and Braga (2018), confirming the link with siliceous organisms. Suspended particulate matter (SPM) exhibited significant correlations with silicate, BSi, and LSi, indicating their association. However, these correlations were not observed in the present study. The presence of microphytoliths resulting from the old agricultural practice of intensive rice crops (Holanda, 1947) may contribute to BSi levels independent of chlorophyll-*a* data.

The internal cycling of Si within the estuarine system involves terrestrial input, sedimentation, the contribution of siliceous organisms (such as diatoms, rhizarians, silicoflagellates, and various choanoflagellate species), macroorganisms (siliceous sponges), erosion, dams, agricultural Si signals (e.g., microphytoliths), and output to the coastal area. These processes have implications for future coastal and marine primary production and are influenced by anthropogenic activities.

CONCLUSION

The difference in rainfall between winter and summer resulted in increased material inflow from the Valo Grande Channel, particularly during the summer season. This is reflected in the concentrations of silicate, BSi, and LSi, which are notably high during this period, primarily in the northern sector of the estuary. Fluvial input, along with sediment remobilization processes, serves as the main source of BSi and LSi in the estuary.

Dissolved silicate, BSi, and LSi undergo removal processes along the salinity gradient that forms within the system. These removal processes are likely associated with interactions with suspended particulate matter (SPM) and sedimentation, leading to their retention within the estuary and limiting their export to the adjacent coastal area during the study period.

Despite being designated as a protected nature reserve, the Cananéia-Iguape estuarine-lagoon complex exhibits signs of anthropogenic impact, particularly in its northern sector (Iguape area), resulting from the opening of the Valo Grande Channel. This channel facilitates erosion processes and introduces material into the estuary. By enabling a significant inflow of water from the Ribeira de Iguape River into the northern sector, the Valo Grande Channel reduces salinity to freshwater values and increases the input of silicon into the system.

Maintaining a balance among different forms of silicon in the system is essential for monitoring anthropogenic activities at the continent-ocean interface. The studied estuarine-lagoon area demonstrates the potential of silicon to identify erosion, resuspension, primary production processes, sedimentation, dilution processes, and input/output balance in the coastal area.

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AUTHOR CONTRIBUTIONS

A.T.C.C.B.: Investigation; Methodology; Formal analysis; Writing – review & editing.

E.S.B.: Funding acquisition; Supervision; Resources; Project administration; Writing – review & editing.

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