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CONCENTRATIONS OF PB, CD AND ZN IN SEDIMENTS OF AN ESTUARINE COMPLEX AFFECTED BY ANCIENT MINING ACTIVITIES IN SOUTHEAST BRAZIL

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ABSTRACT: An artificial canal, built in 1852, diverted 60% of the flow of the Ribeira de Iguape River (RIR) into the northern region of the Estuarine-Lagoon Complex of Iguape-Cananéia (ELCIC), Southeast Brazil. Since then the river has become the main contributor of fresh water and suspended matter into the system. Additionally, the RIR was contaminated by mining activities, especially of Pb, which disposed their wastes directly into this river from their beginning until its cease in 1996. Thus, unknown quantities of metals began to be continuously introduced into the ELCIC. This study evaluated lead, cadmium and zinc concentrations in the surficial sediment at 10 points sampled along the ELCIC, 15 years after the closure of the mining. Zinc concentrations were in accordance with legislation and similar across the ELCIC regions, ranging from 10.4 to 22.8 $\mu g.g^{-1}$. Lead concentrations ranged from 19.3 to 67.9 $\mu g.g^{-1}$, with higher concentrations in the northern ELCIC region, especially in areas near to the canal and the mouth of the RIR. These values were above the Level I limits established by the Brazilian Environmental Agency, suggesting the possibility of a sediment toxicity. Cadmium was only detected (up to 3.6 $\mu g.g^{-1}$) in the northern region, exceeding Level I limits too. However, Pb and Cd values were not above the Level II limits. Results revealed areas of moderate lead and cadmium contamination in the northern ELCIC region, still indicating a strong contribution from the ancient mining activities and from other current anthropogenic activities such as agriculture or an incorrect disposal of sewage and residues. Therefore, a continuous assessment of metal concentrations in the sedimentary record is important to monitor the ELCIC environmental quality.

Keywords: contamination, estuary, metals, surficial sediments, Ribeira de Iguape River, Brazil.

RESUMO: Um canal artificial, construído em 1852, desviou 60% do fluxo do rio Ribeira de Iguape (RIR) para a região norte do Complexo Estuarino-Lagunar de Iguape-Cananéia (CELIC), sudeste do Brasil. Desde então, o rio tornou-se o principal contribuinte de água doce e material em suspensão no sistema. Adicionalmente, o RIR foi contaminado por minerações, especialmente de Pb, que descartavam os resíduos diretamente no rio desde o início das atividades até 1996. Assim, quantidades desconhecidas de metais começaram a ser continuamente introduzidas no CELIC. Este estudo avaliou as concentrações de chumbo, cádmio e zinco no sedimento superficial em 10 pontos amostrais ao longo do CELIC, 15 anos após o encerramento das minerações. As concentrações de zinco estavam de acordo com a legislação e foram similares em todo o CELIC, variando de 10,4 a 22,8 $\mu g.g^{-1}$. As concentrações de chumbo variaram de 19,3 a 67,9 $\mu g.g^{-1}$, com maiores concentrações no norte do CELIC, especialmente nas áreas próximas ao canal e a foz do RIR. Esses valores estiveram acima dos limites do Nível I estabelecidos pela Agência Ambiental Brasileira, sugerindo a possibilidade de toxicidade dos sedimentos. O cádmio (até 3,6 $\mu g.g^{-1}$) foi detectado apenas na região norte, excedendo também os limites do nível I. No entanto, os valores de Pb e Cd não estavam acima dos limites do nível II. Os resultados revelaram áreas de contaminação moderada por chumbo e cádmio no norte do CELIC, indicando ainda uma forte contribuição das antigas minerações e de outras atividades antrópicas atuais, como agricultura e disposição incorreta de esgoto e resíduos. Assim, a avaliação contínua das concentrações de metais é importante para se monitorar a qualidade ambiental do CELIC.

Palavras-chave: contaminação, estuário, metais, sedimento superficial, Rio Ribeira de Iguape, Brasil.

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1. INTRODUCTION

Metals are naturally occurring elements in the environment and many are essential for metabolism and life, but when in excess, they can become toxic (De Groot 2018). The presence of metals in water, soil or sediment is often associated with a geographical location (Fadigas *et al.*, 2006). Nevertheless, anthropic activities alter the distribution of these elements in the planet, with the industrial development being one of the main factors responsible for environmental contamination by metals (Duruibe *et al.*, 2007, Alvarez-Iglesias and Rubio 2012, Machado *et al.*, 2016, Lü *et al.*, 2018, Vardhan *et al.*, 2019).

The introduction of materials, including metals, into an aquatic system constitutes a disturbance that can start a complicated series of chemical and biological reactions (Hadzi *et al.*, 2018). Aquatic systems are very sensitive to pollutants as they have longer trophic chains that favor the distribution and accumulation of metals and other contaminants into the biota (Fernandez *et al.*, 2014, Yilmar *et al.*, 2017). Certain organisms accumulate metals, and bioaccumulation and/or biomagnification processes are observed. Therefore, metal contamination can be considered a direct threat due to habitat destruction, such as in the case of particle inputs from mining activities, and indirect due to the transfer of contaminants through the food chain (Machado *et al.*, 2016, Yilmar *et al.*, 2017, Cabrini *et al.*, 2018).

Contamination by metals in aquatic systems can be detected from the analysis of water, sediments and/or organisms (Ferreira *et al.*, 2010, Yilmar *et al.*, 2017, Cabrini *et al.*, 2018, Hadzi *et al.*, 2018). Generally, dissolved metals are first absorbed by organic or inorganic particles, and then incorporated into the sediment by particle settling (La Colla *et al.*, 2015, Machado *et al.*, 2016). Bays and estuaries act as geochemical barriers, intensifying the fixation and accumulation of metals (by processes such as flocculation) into sediments. It especially occurs when these regions are associated with mangrove areas. Such areas present sediments with abundance of organic matter and fine-grained particles, such as clay and silt (Semensatto-Jr *et al.*, 2007, Amorim *et al.*, 2008, Álvarez-Iglesias and Rubio 2012, Cruz *et al.*, 2019). However, several biotic processes (*e.g.* human interference – dredging; decomposition; some metabolic reactions) and abiotic processes (*e.g.* changes in environmental conditions – pH, temperature, salinity, redox potential, organic and inorganic complexing agents) can remobilize metals from sediments (La Colla *et al.*, 2015, De Groot 2018, Vardhan *et al.*, 2019).

Sediment analysis becomes an indispensable tool for assessing environmental quality of aquatic environments (De Groot 2018). Current values can be assessed by analyzing surface sediments, which are in direct contact with the water column (Semensatto-Jr *et al.*, 2007, Salgado *et al.*, 2018a, Azevedo and Salgado 2019). Ancient concentrations can be determined from deeper layers of the sedimentary record (Mahiques *et al.*, 2009, Cruz *et al.*, 2019). These assessments may also allow the identification of the main sources of pollution within a given aquatic system (Mahiques *et al.*, 2009, Salgado *et al.*, 2018a).

Metal pollutants cause great concern as coastal environments receive large amounts of discharges from human activities that contain these contaminants (Rubio *et al.*, 2010, La Colla *et al.*, 2015, Machado *et al.*, 2016, Yilmar *et al.*, 2017). Diverse Brazilian estuarine regions have registered metal contamination problems (*e.g.* Choueri *et al.*, 2009, Ferreira *et al.*, 2010, Garcia *et al.*, 2018, Cruz *et al.*, 2019, Vezzone *et al.*, 2019). Thus, the study of metal concentrations and their monitoring in coastal waters is necessary to provide tools for decision-makers so that they can promote protective actions and a sustainable use of marine resources, as well as the protection of the human health.

Many authors have studied contamination by metals in surface sediments from sheltered environments, such as basins, lagoons and estuaries (*e.g.* Semensatto-Jr *et al.*, 2007, Amorim *et al.*, 2008, Salgado *et al.*, 2018a, Cruz *et al.*, 2019). The Estuarine-Lagoon Complex of Iguape-Cananéia (ELCIC), Southeastern Brazil, is among the most environmentally relevant areas in the South Atlantic and is recognized by UNESCO as part of the Biosphere Reserve of the Atlantic Rainforest (Morais and Abessa 2014, Salgado *et al.*, 2018a). However, over the years, this region went through several changes that have affected its environmental quality. The most important was the opening of an artificial canal which increased the fresh water input, allowing the Ribeira de Iguape River (RIR) to enter the estuarine complex. Metal mining and refining affected this river for decades. These activities ceased in 1996. Among the consequences, the sediments of the RIR and of some points of the ELCIC contain significant levels of metals, such as Zn, Cr, Pb and Cu, which may be of concern (Vukan *et al.*, 2012, Abessa *et al.*, 2012, Mahiques *et al.*, 2009, 2013, Morais and Abessa 2014, Tramonte *et al.*, 2016, 2018, Salgado *et al.*, 2018a, Cruz *et al.*, 2019, Azevedo and Salgado 2019).

Therefore, the objective of this study was to investigate the concentrations and distribution of Pb, Cd and Zn in surficial sediments from the Estuarine-Lagoon Complex of Iguape-

Cananéia, 15 years after the closure of the mining activities in the region, as well as to compare them with the present Brazilian legislation, generating new data on the local environmental health. This research addresses not only metal inputs from the local watershed due to natural processes, but also possible inputs from different anthropogenic activities.

2. MATERIALS AND METHODS

2.1 Study Area

The Estuarine-Lagoon Complex of Iguape-Cananéia (Figure 1) has a total area of 2,500 km^2 and is located in the São Paulo State, Southeastern Brazil, between latitudes 24º 50' to 25º 10'S and longitudes 47º 25' to 48º 00'W. It's a complex system, between four large islands (Cardoso, Cananéia, Comprida and Iguape), with long narrow channels that extend approximately parallel to the coast. These are called Mar de (sea of) Cubatão, Mar de Cananéia and Mar Pequeno with average depths of 6, 10 and 6 m, respectively. The Comprida Island separates the estuarine system from the Atlantic Ocean, with the southern and northern limits of the Cananéia and Icapara mouths, respectively (Tessler and Souza 1998, Tramonte *et al.*, 2016, 2018).

The region is influenced by the Brazil Current, which carries Tropical Water, South Atlantic Central Water, Antarctic Intermediate Water and Upper Circumpolar Deep Water thought the southeastern coast of Brazil (Bilo *et al.*, 2014). The hydrodynamic pattern inside the estuarine complex is influenced by tidal currents and freshwater inputs wich causes periodic changes. These tidal currents determine the variation in salinity, oxygen content and other water conditions in the region, also influencing the plankton distribution.

In the south, the tidal stream splits into two branches after passing through the Cananéia mouth, one though the Pequeno channel and the other though the Cubatão channel. In the north, the tidal stream penetrates the mouth of the Icapara and flows through the Pequeno channel until the tidal currents

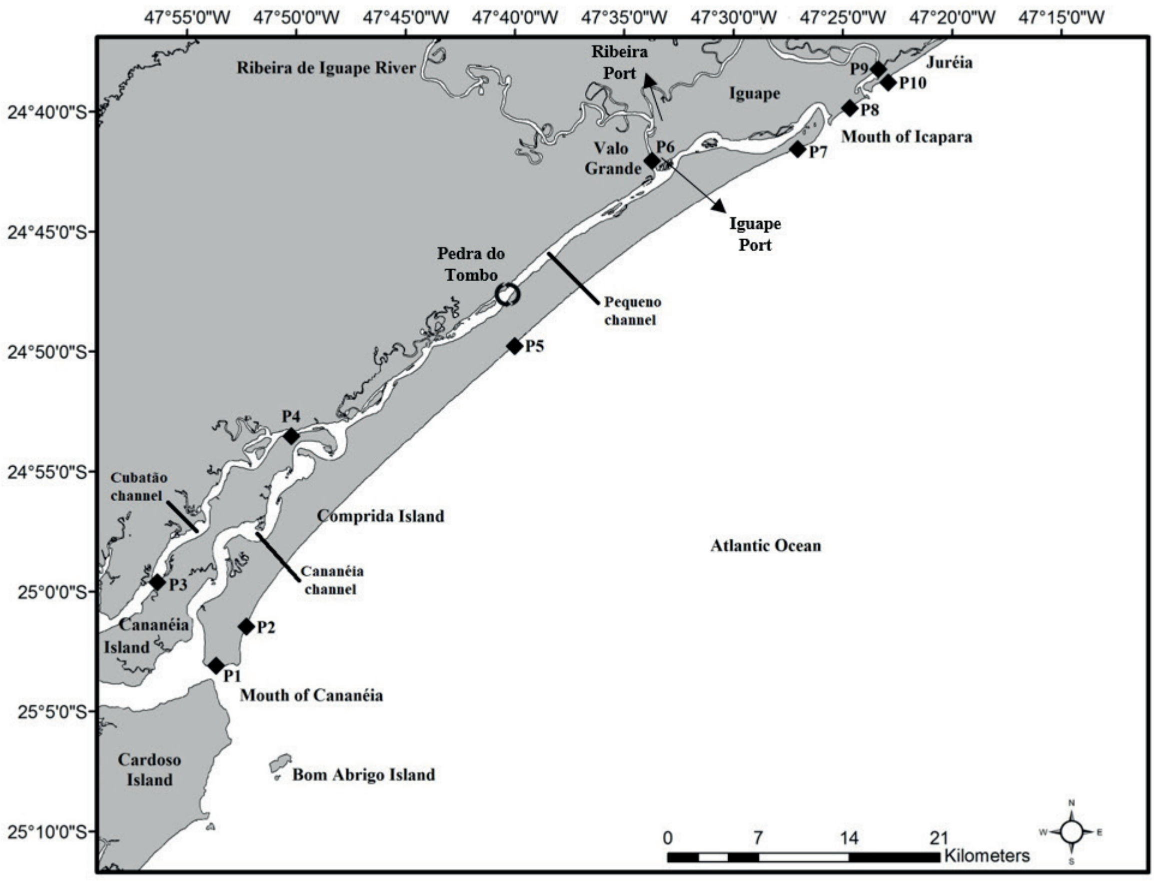

Figure 1. Map of the Estuarine-Lagoon Complex of Iguape-Cananéia, with emphasis on the sampling points of surficial sediments.

meet in the Pedra do tombo region (Figure 1), where the estuary waters are reversed. During ebb tide, the waters flow in the opposite direction (Tessler and Souza 1998, Salgado *et al.*, 2018a). An intense erosion occurs on the concave margins and sediment depositions takes place on the convex margins of the channels (Tessler and Mahiques 1998, Tramonte *et al.*, 2016). Sedimentation rates differ among locations and range from 5 to 10 mm yr^{-1} (Saito *et al.*, 2001a, 2001b, Mahiques *et al.*, 2013).

The climate of the region is divided in two well-defined seasons with dry winters and rainy summers (Cunha-Lignon *et al.*, 2009). The area is characterized by a low population density, a lack of large-scale economic activities and the presence of several terrestrial and aquatic protected areas, due to the large Atlantic Forest Reserve and extensive mangrove areas (Cunha-Lignon *et al.*, 2009, Morais and Abessa 2014, Tramonte *et al.*, 2016, 2018). However, the ELCIC suffered a major anthropogenic interference from mining activities and the opening of an artificial channel which caused many environmental changes in the region-, before the creation of environmental protection areas (Mahiques *et al.*, 2013, Morais and Abessa 2014, Cruz *et al.*, 2018).

The mouth of the Ribeira de Iguape River (RIR) is located near the city of Juréia (Atlantic Ocean). However, to shorten the path between the two old ports of the region (Iguape Port - located in the estuary and the Ribeira Port - located in the river) and maximize the transport and export of local agricultural products, an artificial canal called Valo Grande was built in 1852 (Figure 1). This construction caused, among many problems, the detour of the 60% of the RIR waters into the estuarine complex altering the salinity pattern (that decreased drastically), and the modification of the sedimentation patterns (generating new erosion and deposition areas), and the input of contaminants in the ELCIC (Saito *et al.*, 2001a, 2001b, Mahiques *et al.*, 2009, 2013; Tramonte *et al.*, 2018, Salgado *et al.*, 2018a).

Thus, nowadays the ELCIC presents quite distinct environmental characteristics between its southern and northern regions (Mishima *et al.*, 1985, Bonetti-Filho and Miranda 1997). Near the Cananéia Island (South) there is a strong marine influence. In this place the fluvial discharge (on average 50 $m^3.s^{-1}$) comes from the rivers Taquari, Mandira, das Minas, Itapitangui and several streams that drain an area of about 1,339 km^2 (Mishima *et al.*, 1985, Bonetti-Filho and Miranda 1997, Mahiques *et al.*, 2009). Near Iguape city (North) the characteristics are typically fluvial due to the freshwater inputs (on average 443 $m^3.s^{-1}$ - measured at Iguape) made by the RIR and its tributaries, which drain a basin of 23 350 km^2.

Nonetheless, the RIR basin has several metal deposits, which were exploited since the 17^{th} century, most intensively between 1945 and 1995 (Moraes *et al.*, 2004, Mahiques *et al.*, 2009, 2013; Tramonte *et al.*, 2018). Lead, Zn, Au, Ag, As and Cu were extracted, and mines were operated for years discarding the refuses and slags from the smelting furnace indiscriminately into the river (Guimarães and Sígolo 2008, Mahiques *et al.*, 2013). It was estimated that during the mining period the river received about 5.5 tons per year of metal-rich wastes (Guimarães and Sígolo 2008).

This occasioned the contamination of the water and the sediments along the course of the RIR, especially by Pb (Moraes *et al.*, 2004, Cunha *et al.*, 2005, Guimarães and Sígolo 2008, Abessa *et al.*, 2012, Mahiques *et al.*, 2013). Lead contamination in the RIR and its effluents has been reported since the 70`s (Morgental *et al.*, 1975, Tessler *et al.*, 1987, Eysink *et al.*, 1988, Corsi and Landrim 2003, Moraes *et al.*, 2004, Cunha *et al.*, 2005, Cotta *et al.*, 2006, Alba *et al.*, 2008, Abessa *et al.*, 2012), including points were Pb concentrations exceeded up to 100 times the limit established by Prates and Anderson (1977) for non-contaminated sediments of 40 $\mu g.g^{-1}$ (Eysink *et al.*, 1988).

Mining activities ceased in 1996 due to a decrease in profitability and environmental problems (Tramonte *et al.*, 2016, 2018). After the closure of the mines, residues were deposited on the banks of the river in the form of piles of wastes that were exposed to the weather and consequently leached. Some of these piles remain in the area nowadays (Cruz *et al.*, 2019). Even after the 2000s, studies continue to show contamination points into the RIR area (Cotta *et al.*, 2006, Alba *et al.*, 2008, Abessa *et al.*, 2012, 2014).

Released metals can absorb to suspended matter and underwent mobility through the RIR and, as consequence, reach the ELCIC (Mahiques *et al.*, 2009, 2013, Tramonte *et al.*, 2016, 2018, Cruz *et al.*, 2019). Previous publications indicated that Pb, Cu and Zn were the main elements of concern in the region (Mahiques *et al.*, 2009, 2013, Tramonte *et al.*, 2018, Cruz *et al.*, 2019, Azevedo and Salgado 2019).

Mahiques *et al.*, (2009) showed that this estuarine environment was significantly polluted by lead, and that even after mine closure pollution continued, indicating contributions from the tailings piles still existing in the upper RIR. In addition, they indicated that Pb values in those samples recovered from the upper layers of the sedimentary column affected bymining activities were twice as high as those found in the contaminated sediments of the Santos estuary, one of the most industrialized areas off the Brazilian coast.

The analysis of sediment cores from the estuarine complex by Mahiques *et al.*, (2013) revealed an increase in Pb inputs between the 1930s and the 1990s. These authors also traced the anthropogenic influence at locations within 20 km of the Valo Grande Canal, and indicated that the suspended load caused by the artificial canal may not be the only factor controlling the distribution of metals from anthropogenic sources.

Nowadays the area is still under an increasing anthropogenic pressure and faces numerous environmental management problems. In addition to natural inputs and mining, the disposal of garbage and domestic effluents, the existence of agricultural activities in the nearby areas and the presence of vessels are among another possible metal sources to this ecosystem (Alba *et al.*, 2008, Amorim *et al.*, 2008, Morais and Abessa 2014, Tramonte *et al.*, 2016, 2018, Salgado *et al.*, 2018a, Cruz *et al.*, 2019).

2.2 Sampling procedures

Samplings were carried out on April 2011, the 9th and the 11th. Surficial sediments were sampled in 10 points under different anthropogenic pressures along the ELCIC (Figs. 1 and 2). Four of them were located in Comprida Island facing the open sea (P1, P2, P5 and P7), two of them in Cananéia Island facing the Cubatão Sea (P3 and P4), one in the Valo Grande Canal in Iguape (P6), one in the Juréia beach facing the open sea (P10), another at the mouth of the Ribeira de Iguape River in Juréia (P9), and the last one near the mouth of Icapara (P8). All sampling points corresponds to areas of briny-salty waters (salinity in the range 0.5-30 ‰) in the ELCIC, except that located at the Valo Grande canal (P6) which corresponds to fresh waters (salinity <0.5‰) according to salinity values determined in the ELCIC in previous studies (Bonetti-Filho and Miranda 1997, Maluf 2009) and considering the waters classification established in the Resolution No. 357 of March 15, 2005, of the Brazilian National Environment Council (CONAMA, which is the consultative and deliberative Agency that disposes about the National Environmental Policy).

The surficial sediments were collected manually with a plastic corer (15 cm length), at a distance of approximately 2 meters from the coast. Due the different sedimentation rates in the ELCIC (Saito *et al.*, 2001a, 2001b, Mahiques *et al.*, 2013), only the first 2 cm of sediment samples were considered for metal analysis. Samples were stored in plastic bags with no fixing reagent and conditioned in thermal containers at 4˚C during transportation. Afterwards they were kept in a freezer at -20˚C until analysis according to the Guide of sampling and preservation of samples of the Environmental Company of the State of São Paulo (CETESB 2011).

2.3 Determination of metal contents

Each sediment sample was homogenized by the quartering method and dried in an oven at 60°C for 12 hours. Then 50 g of the sediments were sieved at 32 tyler/mesh to remove the coarser fractions such as shells, animals and roots. The sieved fraction of each sediment sample (lower than 32 μm) corresponded to 93% to 97% of the bulk sample. These sieved fractions were divided into triplicates of 2g and then used for metals' determination according to the 3050B method proposed by the U.S. Environmental Protection Agency (U.S. EPA 1996). The procedure implies an acid digestion with HNO3, H2O2 and HCl. This pseudo-total digestion allows obtaining the environmental available metal fraction. All the reagents used were of analytical grade and the materials used were previously decontaminated by washing with neutral detergent and bathing in a nitric acid solution (10%) for 24h. Lead, Cd and Zn contents were determined by Flame Atomic Absorption Spectrometry (FAAS) in a Shimadzu AA6800 equipment, respecting the limits of quantification for each of the metals (Table 1). Standard solutions were prepared by successive dilutions using stock solutions of each metal of analytical grade (1.000mg L^{-1}), using 13% v/v HNO3. Analytical blanks were used and determinations were performed in triplicate.

The exactitude of the method was verified with CRM used to check the consistence of the internal standards in the laboratory. The RTC-CRM031-040 (sewage sludge) from Sigma-Aldrich was used with an analytical result of: 217.39 $\mu g.g^{-1}$ for Cd; 882.22 $\mu g.g^{-1}$ for Zn; and 126.48 $\mu g.g^{-1}$ for Pb; which were in accordance with their certified values of: 212 $\mu g.g^{-1}$ for Cd; 908 $\mu g.g^{-1}$ for Zn; 121 $\mu g.g^{-1}$ for Pb. The coefficient of variation (CV) was: of 1.78% for Cd; 2.03% for Zn and 3.13% for Pb. Metal concentrations were expressed in $\mu g.g^{-1}$ dry weigh.

2.4 Data treatment

The mean concentrations found in the sediment at each sampling point were compared to the limits determined by the CONAMA Resolution No. 454 of November 1, 2012, which establishes general guidelines and minimum procedures for assessing the material to be dredged from the Brazilian jurisdiction waters, and also gives other steps, once there is no

Figure 2. Sampling points of surficial sediments. P1: River at Ponta da Trincheira beach, extreme south of Comprida Island. P2: River on Boqueirão Sul beach, Comprida Island. P3: Cananéia-Continent ferry, Cananéia Island. P4: Cananéia-Continent Bridge, Cananéia Island. P5: River on Vilarégio beach, Comprida Island. P6: Valo Grande Canal, Iguape. P7: Beach at the extreme north of Comprida Island. P8: Mouth of Icapara. P9: Mouth of the Ribeira de Iguape River, Juréia. P10: Juréia beach.

Table 1. Intervals of linearity (IL) of the calibration curve, method linearity (r^2) and limits of quantification (LQ) for the analysed metals.

Metal	IL ($mg.L^{-1}$)	r^2	LQ ($mg.kg^{-1}$) Sediment
Pb	0.25 – 1.25	0.9984	12.5
Cd	0.01 – 0.4	0.9998	0.5
Zn	0.2 – 1.2	1.0000	10.0

specific federal legislation that deals with the maximum limits allowed for the concentration of metals in estuarine sediments. This resolution establishes two quality criteria, where values below the quality criterion I (Level I) indicate a non-expected toxicity of the sediments to the aquatic life. Values above the quality criterion II (Level II) indicate a probable toxicity of the sediments. Intermediate values (between Levels I and II) indicate a possible sediment toxicity. These values established by the CONAMA national legislation are present in Table 2. Values < LQ were excluded from groups of samples to generate the averages of the different regions.

Table 2. Limits of lead, cadmium and zinc established by the Resolution No. 454 of the CONAMA for surficial sediment (in $\mu g.g^{-1}$).

CONAMA	Pb		Cd		Zn	
	Level I	Level II	Level I	Level II	Level I	Level II
Salt water sediments	46.7	218	1.2	7.2	150	410
Fresh water sediments	35	91	0.6	3.5	123	315

For statistical analyses, sampling points were grouped according to their proximity: Southern region (P1, P2 and P3), central region (P4, P5 and P6) and northern region (P7, P8, P9 and P10). The STATISTICA 7.0 program was used. A single-factor Analysis of Variance (ANOVA) statistical test was applied to compare results between regions, followed by a Least Square Difference (LSD) test, considering 0.05 as the level of significance. To compare dissimilarities between regions, an Agglomerative Hierarchical Cluster Analysis (AHCA) method was applied using the Bray Curtis distance proximity type with the Ward agglomeration method. The product of this analysis was a dendrogram by using the statistical program XLSTAT.

3. RESULTS

Average concentrations of Pb, Cd and Zn for the studied samples are presented in Table 3.

Table 3. Mean (n=3) and standard deviation of the concentrations of lead, cadmium and zinc in the surficial sediments of the Estuarine-Lagoon Complex of Iguape-Cananéia. Those samples exceeding the Level I limits established by the Resolution No. 454 of the CONAMA are marked by an asterisk (in µg.g-1).

Points	Pb	Cd	Zn
P1	44.9 ± 10.0	<LQ	<LQ
P2	33.7 ± 3.5	<LQ	<LQ
P3	19.3 ± 4.1	<LQ	14.4 ± 1.0
P4	40.8 ± 6.1	<LQ	22.8 ± 6.3
P5	64.3* ± 10.0	<LQ	<LQ
P6	36.5* ± 5.6	<LQ	12.5 ± 2.2
P7	52.4* ± 15.2	<LQ	<LQ
P8	67.9* ± 10.9	3.6* ± 0.4	10.4 ± 1.3
P9	48.1* ± 4.1	2.6* ± 0.3	20.3 ± 1.4
P10	46.9* ± 5.3	2.4* ± 0.9	<LQ

< LQ - Values detected below the limits of quantification.
* Values above present Brazilian legislation.

3.1 Lead

Lead contents varied from 19.3 to 67.9 $\mu g.g^{-1}$ in the sampled points. The points P5, P6, P7, P8, P9 and P10 had concentrations above the Level I limit determined by the Brazilian legislation for fresh and salt water sediments (Table 3). When comparing values of lead in the three considered groups, an increase in concentrations to the north was evidenced: $F(2, 27)=6.9290$, $p=0.00373$ (Figure 3). The southern region (Mean=32.65 $\mu g.g^{-1}$ ± 12.54 $\mu g.g^{-1}$) had lower concentrations than the other two regions ($p<0.05$). However in the central (47.20 ± 14.50 $\mu g.g^{-1}$) and northern regions (53.85 ± 12.19 $\mu g.g^{-1}$) Pb contents were similar ($p>0.05$).

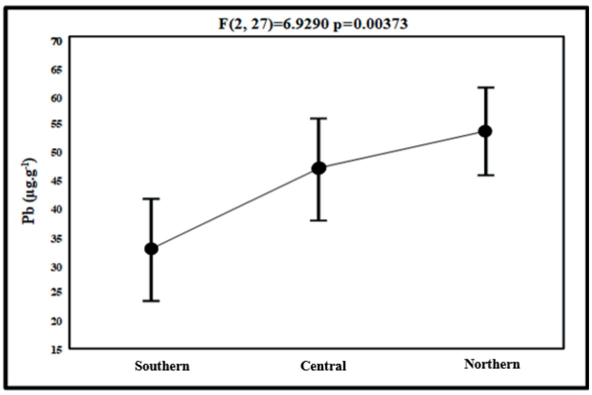

Figure 3. Mean + 0.95*. Reliability of intervals of lead concentrations in the southern, central and northern regions of the Estuarine-Lagoon Complex of Iguape-Cananéia.

3.2 Cadmium

Regarding the cadmium, concentrations were below its LQ in samples from the central and southern regions and in sample P7. However, values ranging from 2.4 to 3.6 μg.g^{-1} were observed at points P8, P9 and P10, located at the northern region. These values were higher than the Level I limit defined by the Brazilian legislation for salt water sediments (Table 3). Comparing the cadmium concentrations in the three regions, the northern region had higher cadmium concentrations than the other two regions of the estuarine system.

3.3 Zinc

Zinc concentrations of five of the analyzed points (P1, P2, P5, P7 and P10), all facing the open sea, did not exceed its LQ. However, Zn was detected in the other samples (P8 and those located in the inner part of the estuarine system-P3, P4, P6 and P9) ranging from 10.4 to 22.8 μg.g^{-1}. These concentrations were below the Level I limits for fresh and salt water established by the CONAMA legislation (Table 3). When comparing Zn contents in the three considered regions differences are not evidenced: F(2, 27)=2,8183, p=0.07734, p>0.05 (Figure 4). The central region (14.25 ± 11.98 μg.g^{-1}) had higher concentrations of Zn than the southern region (7.68 ± 5.18 μg.g^{-1}; p<0.05). However, it was similar to the northern region (11.98 ± 5.20 μg.g^{-1}; p>0.05). Nevertheless, the North and South regions did not differ in the concentrations of Zn in the surface sediments (p>0.05).

3.4 Comparison of the metal concentrations in the surficial sediments of the three regions

Summarizing, this study found lower concentrations of Pb, Cu and Zn in the surficial sediments from the southern region and higher concentrations in those from the northern region of the estuarine system, near the Iguape City. It was observed that Pb and Zn contents were more similar between the central and northern regions. According to the AHCA method, these two regions presented a dissimilarity of 0.089, while the southern region presented a dissimilarity of 0.285 from the other two regions (Figure 5).

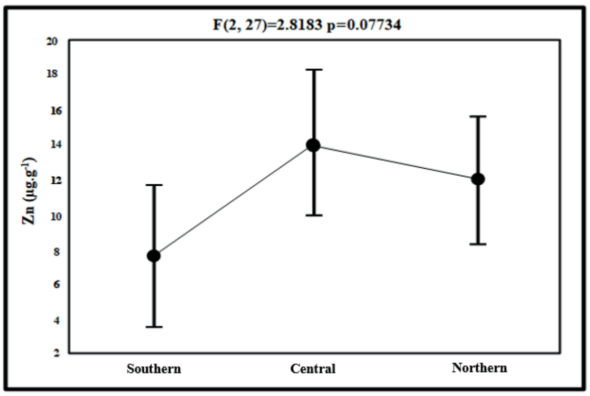

Figure 4. Mean + 0.95*. Reliability of intervals of zinc concentrations in the southern, central and northern regions of the Estuarine-Lagoon Complex of Iguape-Cananéia.

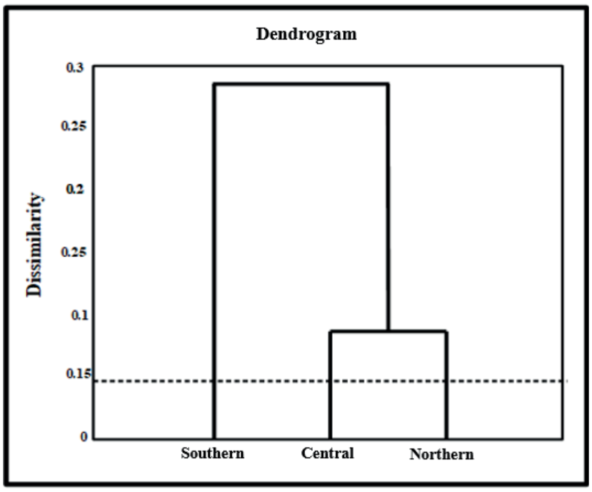

Figure 5. Dendrogram showing the dissimilarity in the Pb, Cd and Zn concentrations in surficial sediments from the three considered regions (southern, central and northern) of the Estuarine-Lagoon Complex of Iguape-Cananéia.

4. DISCUSSION

Lead concentrations in ELCIC surface sediments did not exceed the Level I limit established by the CONAMA legislation in four of ten analyzed points, in particular, in the southernmost points (P1, P2, P3 and P4). Then, sediments from the southern ELCIC region are not expected to cause toxicity. These results corroborated previous findings by Semensatto-Jr *et al.*, (2007), Mahiques *et al.*, (2009) and Salgado *et al.*, (2018 a, b) in the same region in sediments from near Cananéia Island.

However, Pb concentrations in the other six analyzed points exceeded the Level I limits of CONAMA legislation, indicating the possibility of a sediment toxicity to aquatic life (CONAMA, 2012). In particular, five of them (P5, P7, P8, P9, P10) presented values up to 45% higher than the limit value for briny-salty waters, while the sampling point located at the mouth of the Valo Grande Canal (P6), showed values exceeding in a 4% the fresh water sediment limit. All these points, excepting P5 are located in the northern region of the ELCIC, near the Valo Grande Canal (Iguape city) and the original Ribeira de Iguape River mouth (Juréia beach), thus indicating the contribution from this river to the Pb inputs in the area.

These results are in accordance with the previous literature of the area that indicates Pb contamination in the RIR basin happened since the 1970s (Morgental *et al.*, 1975, Tessler *et al.*, 1987, Eysink *et al.*, 1988, Corsi and Landrim 2003, Moraes *et al.*, 2004, Cunha *et al.*, 2005, Cotta *et al.*, 2006, Alba *et al.*, 2008, Abessa *et al.*, 2012, 2014). In addition to the natural contribution from the local river basin, all previous studies have highlighted metallic inputs to sediments caused by intensive mining activities, which thus constitute the main source of lead along the river area.

Although different authors have also observed a significant decrease in Pb concentrations in RIR waters and sediments following the mines closure in 1996, recent studies indicate that the local environment still remains affected by mineral waste inputs (Guimarães and Sígolo 2008, Rodrigues *et al.*, 2012, Abessa *et al.*, 2012, Tramonte *et al.*, 2018, Cruz *et al.*, 2019) including metal contributions from the tailings' piles still existing in the upper RIR (Mahiques *et al.*, 2009). These facts may explain the Pb contamination observed at those points near the mouth of the RIR (Iguape and Juréia city) in the present study 15 years after mines closure.

Nevertheless, a contribution of lead from another sources may also occur (Alvarez-Iglesias *et al.*, 2012). The RIR drains large areas of banana and tea cultivation along its course, and a contribution from the leaching of fertilized soils can be expected (Barcellos *et al.*, 2005). In addition, this river runs through the urban center of the city of Iguape and is influenced by various anthropogenic activities along its route, such as untreated effluents inputs.

Since the RIR waters reached the ELCIC through the Valo Grande Canal, the Pb contamination in the estuarine complex has also been evidenced in different studies over the years (Vukan *et al.*, 2012, Mahiques *et al.*, 2009, 2013, Morais and Abessa 2014, Tramonte *et al.*, 2016, 2018, Salgado *et al.*, 2018a, Cruz *et al.*, 2019, Azevedo and Salgado 2019). As observed in the RIR, the Pb values found in the present study in the northern ELCIC region (P5 to P10) were lower than those described years ago by other researches (Mahiques *et al.*, 2009, 2013, Tramonte *et al.*, 2016, 2018). This is probably because there is a natural tendency for these values to decrease over time after mining activities have ceased with the arrival of new and less contaminated sediments (Cunha *et al.*, 2005). However, the lead residence time in the soils is quite high, close to decades, or even higher than 100 years in the marine environment (Kabata-Pendias and Pendias 1985), explaining its persistence after over a decade.

Moreover, these high concentrations of lead in the estuarine area may still indicate the contribution of waste piles left on river banks that contaminate sediments entering the system through the Ribeira de Iguape River (Mahiques *et al.*, 2013) and the contribution of coastal cities and anthropogenic activities within the estuarine complex. These include the disposal of waste and effluents, agricultural and mariculture activities and the presence of boats. All ELCIC coastal cities have insufficient infrastructures for proper collection and treatment of their effluents and wastes, causing sewage to be discharged into streams and rivers without any prior treatment (Morais and Abessa 2014, Gusso-Choueri *et al.*, 2015, Salgado *et al.*, 2018a). Thus, the supply of Pb to the ELCIC may be influenced by these problems.

The anthropogenic influence on the concentrations of metals in the surficial sediments were observed by Mahiques *et al.*, (2013) at locations within 20 km of the Valo Grande Canal indicating that the suspended load made by the artificial canal was not be the only factor controlling the distribution of metals from anthropogenic sources in the ELCIC, corroborating the results found in the present research. Thereby, the high concentration of Pb observed at point P5, located in the central region of the system, can be explained by the anthropic presence in the area. This point is located at the beach of Vilarégio (Comprida Island), at the mouth of the river that crosses the neighborhood, and similarly to the other cities of the estuarine system, the villages of Comprida Island do not have sewage systems. Thus, this may be a possible source of lead contamination in this area.

As a consequence of the large quantities of Pb-enriched particles discharged to the RIR and the local atmosphere, which deposited afterwards on soils and sediments surfaces, Pb bioaccumulation was verified in RIR mollusks (Guimarães and Sígolo 2008, Rodrigues *et al.*, 2012), and in edible products (vegetables, eggs and milk) that grown in areas near the RIR (Cunha *et al.*, 2005, Lammoglia *et al.*, 2010). Furthermore, human lead contamination has been detected in some communities along the RIR, especially near the mining areas and near the ancient main refinery, although a non-alarming situation has been evidenced (Figueiredo *et al.*, 2004, Cunha *et al.*, 2005). However, the authors warn that these local populations live with environmental hindrances, are exposed to harmful substances and need to be assisted by local and state health and environmental authorities (Figueiredo *et al.*, 2004, Cunha *et al.*, 2005, Lammoglia *et al.*, 2010).

In the estuarine region, previous studies indicate the incorporation of Pb by aquatic animals, such as edible fishes (Duarte *et al.*, 2016, Gusso-Choueri *et al.*, 2015) and dolphins (Salgado *et al.*, 2018b). Lead values up to 14.64 $\mu g.g^{-1}$, were reported in muscle tissue from Cathorops spixii fish species from the ELCIC (Gusso-Choueri *et al.*, 2018) well above the 0.3 $\mu g.g^{-1}$ allowed by the Brazilian legislation (ANVISA, 1998). Then, an accentuated consumption of these fishes by the local population may pose risks to human health (Gusso-Choueri *et al.*, 2018). In Sotalia guianensis dolphins the lead mean concentration (3.17 $\mu g.g^{-1}$) were the highest described for this species, suggesting a trophic transfer, which may also affects the human population (Salgado *et al.*, 2018b). However, there are no studies involving metal contamination in inhabitants from the estuarine complex.

Regarding Pb toxicity in ELCIC, previous studies showed that this metal is among the major contaminants responsible for toxic effects on crustaceans (Duarte *et al.*, 2016), fishes (Gusso-Choueri *et al.*, 2015, 2018, Salgado *et al.*, 2018a) and possibly in aquatic mammals (Salgado *et al.*, 2018b). Such indications corroborate the findings of the present study, which indicate the possibility of sediment toxicity to aquatic life in the ELCIC (CONAMA, 2012).

Cadmium contamination may occur associated to lead mining (Cardoso and Chasin 2001). In the present study, most of the sampled points showed Cd contents below the LQ. Nevertheless, three points in the northern region (P8, P9 and P10), showed Cd values up to 3 times above the limits defined by the Brazilian legislation. These points were located at the original mouth of the Ribeira de Iguape river (Juréia), corroborating previous studies that found higher values of Cd in the northern region of the estuarine complex and values below the LQ in the southern ELCIC region (Maluf 2009, Salgado *et al.*, 2018a, 2019).In addition high concentrations of Cd in the waters of the estuarine complex were reported near the Iguape city (Maluf 2009) while low values of Cd were observed in the estuarine waters of the southern region (Souza *et al.*, 2012). Sediment analyses in one of the tributaries of the Ribeira de Iguape river held by Cotta *et al.*, (2006) found only one point with detectable Cd concentrations, and analyses on surficial sediments from the Comprida and Cananéia islands (Salgado *et al.*, 2018a, Azevedo and Salgado 2019) showed low Cd values too.

However, concentrations of Cd of 8,8 $\mu g.g^{-1}$ were found in the sediments from the Cardoso island by Semensatto-Jr *et al.*, (2007). These authors indicated that these concentrations were not related to an anthropic interference, since there is not known activity in the region that would release this metal. Thus, this high value was attributed to the predominance of mangroves in the area, which have a substantial quantity of clay, silt and organic matter that absorbs metals (Semensatto-Jr *et al.*, 2007). The Cd concentrations found by the present study were in the range of those presented in the bibliography, however the high concentrations found in the norther region can be attributed to anthropic interference (Semensatto-Jr *et al.*, 2007, Maluf 2009, Salgado *et al.*, 2018a, Azevedo and Salgado 2019).

Cadmium is a non-essential metal, highly toxic, considered dangerous to the health of organisms in general (Cardoso and Chasin 2001). However, studies on aquatic biota from Ribeira de Iguape River (Guimarães and Sígolo 2008) and the estuarine ELCIC region (Machado *et al.*, 2002) report that average Cd levels were below the limit value of 1.0 $\mu g.g^{-1}$ allowed for filter feeding organisms by the Brazilian National Health Surveillance Agency - ANVISA Ordinance 685/1998 and at low levels in the liver of the Guiana dolphins from the ELCIC (Salgado *et al.*, 2018b). In addition, Cd concentrations in blood samples from populations along the RIR did not arouse special concern (Figueiredo *et al.*, 2004).

Regarding Zinc, this metal is found associated to lead in the mineral deposits along the Ribeira de Iguape River basin and was also a target for mining activities (Cunha *et al.*, 2005, Cotta *et al.*, 2006). Thereby, high values of this metal have already been reported for sediments in the RIR basin (Corsi and Landrim 2003, Cunha *et al.*, 2005, Cotta *et al.*, 2006, Alba *et al.*, 2008). However, the present study found that Zn concentrations throughout the estuarine complex were up to 14 times lower than the limit set by CONAMA for briny salt water and 9 times lower than the limit set for freshwater. As previously described for Pb, there is a tendency for decreasing zinc concentrations in sediments from the ELCIC with time.

Previous studies have not revealed Zn contamination in the estuarine area (Semensatto-Jr *et al.*, 2007, Souza *et al.*, 2012, Salgado *et al* 2018, Azevedo and Salgado 2019). Semensatto-Jr *et al.*, (2007) indicated Zn concentrations ranging from 5 to 50.4 $\mu g.g^{-1}$ in sediments from the Cardoso Island, whereas Salgado (2009) obtained values averaging 11.01 $mg.kg^{-1}$ in sediment and 0.5 $mg.L^{-1}$ in surface water samples from the southern region of the estuarine complex; and Souza *et al.*, (2012) also found no high Zn (II) concentrations in the waters from the entire system.

However, zinc bioaccumulation has been reported in clams

(Corbicula fluminea) from the Ribeira de Iguape river (Guimarães and Sígolo 2008), in oysters (Crassostrea brasiliana) from the estuarine region of Cananéia Island (Machado *et al.*, 2002), and in the liver of estuarine fishes (Mugil curema) from the ELCIC (Fernandez *et al.*, 2014). In these three cases the Zn concentrations were above the 50.0 $\mu g.g^{-1}$ limit allowed in food by the National Health Surveillance Agency (ANVISA, 1998).

Regarding the possibility of metals causing adverse effects on local biota, Azevedo and Salgado (2019) analyzed the bioavailability of Fe, Zn, Mn, Co, Cu, Cr, Cd, Pb and Ni in the ELCIC sediments and observed that sediments presented toxicity at all points, being more toxic those from the northern region of the ELCIC due to the presence of the Valo Grande Canal. Thus, as observed in the present study, there is the potential of these sediments to cause adverse effects to aquatic biota. In addition, those authors highlight a possible metal contribution from other anthropogenic activities in ELCIC, such as urban and agricultural activities. As previously mentioned, incorporation of metals by the ELCIC aquatic biota occurs, including animals that are also intended for human consumption (Duarte *et al.*, 2016, Gusso-Choueri *et al.*, 2015).

In summary, in the present study zinc concentrations in the surficial sediments of the ELCIC were similar in the different system regions, while cadmium and lead concentrations showed a clear differentiation between the south (Cananéia Island) and north (Iguape) regions. In the southern region the concentrations of the three studied metals in the surficial sediment did not exceed the limits recommended by the Brazilian Environment Agency (CONAMA) for the preservation of aquatic life and for the sediment. Thus, the southern region can be characterized as slightly influenced by these metals. In the northern region, at those points mainly influenced by the Ribeira de Iguape River (Valo Grande Canal and the RIR mouth in Juréia), Pb and Cd concentrations exceeded the Level I limits established by the national legislation. This indicates a moderate contamination in the sediments of the area that have a potential toxicity to cause adverse effects to local biota.

In the aquatic environment, metals predominantly associate with suspended matter before depositing in the sediment where they are usually retained. However, under certain physicochemical conditions, such as the modification of pH, salinity, potential redox or low content of organic matter, solubilization of metals to the aqueous phase is possible (Álvarez-Iglesias and Rubio 2008, Souza *et al.*, 2012, La Colla *et al.*, 2015, De Groot 2018). Therefore, the residence time of metals in sediments depends on the changes of these variables in a given aquatic system and on the sediment composition (Cunha *et al.*, 2005).

According to previous studies, ELCIC sediments are predominantly sandy. Azevedo and Salgado (2019) observed 97% of sand, 2% of silt and 1% of clay in the grain size distribution of the analyzed points in the ELCIC. Tessler and Souza (1998) also observed a majority of sandy sediments (75% of the samples). This sediment distribution is influenced by local hydrodynamics: the ELCIC channels show low fine-grained particles contents due to the strong dynamics of the currents that occur near the bottom because of the proximity of the estuary mouths (Cananéia and Icapara), while those areas with lower hydrodynamics have higher silt and clay contents (Tessler and Souza 1998, Tessler and Mahiques 1998, Azevedo and Salgado, 2019). Due to the typical association of organic matter to these fine-grained particles (Fadigas *et al.*, 2006, Álvarez-Iglesias and Rubio 2008, Amorim *et al.*, 2008, De Groot 2018) higher levels of organic matter and nitrogen are detected in those low hydrodynamic areas of the ELCIC (Barcellos *et al.*, 2005, Azevedo and Salgado 2019).

For the studied region, many authors highlighted that climate, sedimentation processes and biogeochemical and hydrodynamic processes can cause differences in the concentrations of the elements at some points seasonally (Amorim *et al.*, 2008, Tramonte *et al.*, 2016, 2018, Azevedo and Salgado 2019, Cruz *et al.*, 2019). Thus, due to the set of variables that control this process, an extrapolation from the results obtained in the present study to another areas should be done with caution.

The obtained data corroborate that environmental conditions and anthropogenic impact levels are different between the southern (Cananéia) and northern (Iguape) regions of the Estuarine-Lagoon Complex of Iguape-Cananéia. These differences are related to typical estuarine characteristics in the Cananéia region and predominantly fluvial characteristics in the Iguape region, due to the impact of the Valo Grande Canal (Bonetti-Filho and Miranda 1997, Tramonte *et al.*, 2018). Moreover, in this last region, the anthropic presence is more evident and the waters register low salinity, high phosphate and silicate values (Maluf 2009), and as evidenced in this and previous studies, sediments are contaminated bylead and cadmium (Bonetti-Filho and Miranda 1997, Maluf 2009, Mahiques *et al.*, 2009, 2013, Morais and Abessa 2014, Tramonte *et al.*, 2016, 2018, Cruz *et al.*, 2019).

5. CONCLUSIONS

The present study evidenced that even fifteen years after the closure of the mining activities in the Ribeira de Iguape river, the lead (from 19.3 to 67.9 $\mu g.g^{-1}$) and cadmium (2.4 to 3.6 $\mu g.g^{-1}$) contents in those sediments from the Estuarine-Lagoon Complex of Iguape-Cananéia (ELCIC) sampled near the Iguape city and Juréia beach exceeded the limits of the Brazilian environmental legislation. This may be a matter of concern as sediment toxicity is expected. Although the measured values were lower than those found in previous studies, suggesting that restoration processes are underway, they still indicate the influence from the former mining activities and the environmental hindrances left behind, added to the persistent characteristics of metals in the environment. In addition, the contribution of another anthropogenic activities, such as agriculture and the contamination generated by sewage and wastes from local urban centers, may contribute to metal inputs into sediments. Thus, studies on metals' contents in the ELCIC continue to be of great importance. The authors encourage the continuous monitoring of the environment quality of the region and the evaluation of possible adverse effects in the local biota. This study generated new data on local environmental health, in order to contribute to the development of public policies for the preservation and/or improvement of the environmental, life and public health quality of the ELCIC region.

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