

Contamination and toxicity in a subtropical Estuarine Protected Area influenced by former mining activities

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ABSTRACT

The present paper reviews information about sources, fate, concentrations and toxicity of the metals found in the Cananéia-Iguape Estuarine Complex (CIEC), which is within a Ramsar site, the Cananéia-Iguape-Peruíbe Environmental Protected Area (CIP-PA). The main sources of metals to CIEC are the former mining sites located upstream, on the Ribeira de Iguape River basin. Pb is reported as the element of primary concern, but Cu, Zn, Cr and As have been detected in sediments and biota. In general, higher levels of metals are associated with muddy sediments, in depositional portions of the estuary. Metals appear to be bioavailable, as sediment toxicity has been reported, together with bioaccumulation and sub-chronic effects in fish and invertebrates. Areas with higher concentrations of metals and more severe sediment toxicity are not necessarily the closest to the sources. The worse conditions occur in depositional sites, which depend on rainfall in catchment basin and hydrological processes in the estuary. In fact, during the flooding season the deposition of particles seems to move southward, carrying metals to the southern portion of the CIEC. The results suggest that the protection objectives are not being fully achieved, demanding actions to ensure control of both internal and external sources of contaminants for the CIEC. Additionally, new enforcements and actions are required to control the contamination sources of mining residues located upstream. The current review highlights that estuarine and marine protected areas may be impacted by contaminants released from distant sources, and this situation should be properly addressed in management plans.

Descriptors: Sediment, Metals, Pollution Sources, Bioaccumulation, Ecotoxicology.

INTRODUCTION

Estuaries are coastal transition zones between fresh-water and seawater that present substantial gradients of abiotic parameters and which are most highly affected by freshwater inflows and tidal regimes. Therefore, large variations in salinity, pH, temperature and geochemical conditions may occur in

these transitional environments, even in relatively short spatial and temporal scales (Elliott and McLusky, 2002). The hydrodynamics of estuaries favor the retention of nutrients and consequently the primary production, thus placing these environments among the most biologically productive coastal ecosystems on the planet (Miranda et al., 2002; McLusky and Elliott, 2004).

Estuaries also exhibit geomorphological and physical-chemical characteristics that favor material deposition such as organic material and man-made contaminants (Du Laing et al., 2009). Estuarine areas normally present low energy from waves and

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currents making it difficult for the chemicals to disperse, frequently resulting in accumulation of organic and inorganic substances in the sediments. Once in the sediment, contaminants may directly affect the benthic biota, but they may also return to the water column through various physical, chemical and biological processes, thus resulting in even greater ecological effects (Chapman and Wang, 2001). These characteristics make estuaries very sensitive; and one of the most significantly affected ecosystems by human activity (Lewis et al., 2011).

Changes in salinity, temperature, pH and oxidation/reduction potential regulate the retention, and release of metals associated with the finest sediment fraction, organic material, iron oxides and sulfides (Caporale and Violante, 2016). The resuspension of contaminated sediments can occur naturally, as is observed in the turbidity maximum zone (TMZ). These zones mainly occur in estuaries in which salinity is partially stratified. The turbulent movement induced by currents close to the bottom causes sediment resuspension and increases the levels of suspended sediments; up to 100 times higher than those found upstream and downstream (Postma, 1967). Besides, the TMZ is displaced following the tidal cycles and the rainfall precipitation regime, being subject to daily and seasonal variations.

Metals in estuaries may come from natural sources involving both local geological composition and the leaching of soils and rocks present in the drainage basin. However, for the most of the toxic metals, the greatest contribution comes from human sources, such as domestic and industrial effluents, agricultural pesticides (Ebrahimpour and Mushrifah, 2008), atmospheric deposition (Pereira et al., 2006) and mining activities. It is important to note that, even when pollution sources are located at substantial distance away from estuaries, the contaminants may reach the estuarine ecosystems. Studies reported that mining activities located hundreds of kilometers upstream were responsible for the contamination of estuarine zones worldwide, largely due to the transport of residues and sediments containing absorbed metals (Johnson et al., 2005; Price et al., 2005; Masson et al., 2006; Osher et al., 2006).

Sediments are important indicators of environmental quality and can be considered one of the most complex matrices to exist in aquatic ecosystems

(Power and Chapman, 1992). Chemical analyses may provide information on specific levels of contaminants, which, if bioavailable, may lead to toxicity and bioaccumulation (USEPA, 2004). Nevertheless, different types of associations between sediments and contaminants may reduce their bioavailability (Simpson et al., 2016). Thus, chemical analyses indicate the nature of the contaminants present in the environment and quantify their concentrations; but they do not provide information on the possible effects on aquatic organisms. Therefore, a sediment quality assessment performed exclusively through chemical analyses is insufficient for estimating damages to biota. Hence, an ecotoxicological approach is required for evaluating sediment quality, since it provides information on the biological effects caused by contaminants (Chapman, 2016).

In order to evaluate the presence of metals in an important subtropical estuarine protected area, this paper reviews a series of studies on the contamination and toxicity of the sediments in Cananéia-Iguape Estuarine Complex (CIEC). The CIEC is located on the southern coast of Sao Paulo State, Brazil, and it is influenced by former mining activities along the Ribeira de Iguape River catchment basin. Thus, the current information on the extent of metal contamination in the Ribeira de Iguape River was also analyzed, since it is the most important freshwater and fine sediment contributor to the CIEC (Barcellos et al., 2009).

METHODS

This literature review considered studies on contamination carried out in the CIEC and in the Ribeira de Iguape River catchment basin (also known as the Ribeira Valley), which has a history of contamination by metals (Eysink et al., 1988; Guimarães and Sígolo, 2008a; Abessa et al., 2014). The criterion for inclusion of a paper into this review was that the study had to have analyzed field-collected samples to measure metal in sediments or biological effects of contaminants. To obtain articles that fit these criterion, we conducted sequential searches in the relevant databases (Scopus, Web of Knowledge and SciELO) by crossing the terms *contamin-*, or *pollut-*, or *toxic-*, or *bioacum-*, or biomarker against the terms "Cananeia Iguape Peruibe protected area", or "Cananeia", or "Ribeira de Iguape". We searched for additional studies by examining monitoring reports

available on databases of environmental agencies as well as academic thesis and dissertations that are available on digital libraries. We recognize that some of the information about metal contamination in the CIEC is unpublished (academic documents not available on the web) or part of monitoring reports.

This review selected only papers that have adopted analytical procedures widely accepted around the world and quality control procedures (quality assurance/quality control - QA/QC). Besides, this review did not aim to discuss differences among analytical methods employed in each of the selected papers, focusing on spatial and temporal variations of contamination. We also did not aim to discuss the experimental design adopted in each of the selected papers, such as field sampling techniques and the use of replicates; instead, we focused on the reported results, including contamination and biological data (bioaccumulation, toxicity, genotoxicity, cytotoxicity, or biochemical biomarker) indicating potential adverse effects on aquatic biota.

The information obtained from the literature was used to respond to a series of questions: Is the CIEC contaminated by metals? If so, which elements are the main contaminants? How are contaminants distributed along the estuary? Which are the primary contamination sources? Are concentrations high enough to cause adverse effects on the biota? If so, which types of effects and at which concentrations? How large is bioaccumulation of the different metals? Are there any implications to the public health? Based on the literature found, we produced a diagnostic for the studied area, including physical, geographical and socio-environmental aspects, the presence of sources of metals and other contaminants, and other information relevant to the comprehension of the pollution status of the study area. The compiled information was also used to produce recommendations to managers, stakeholders and authorities.

STUDY AREA

A protected area (PA) is defined by the International Union for Conservation of Nature as “A clearly defined geographical space, recognized, dedicated and managed, through legal or other effective means, to achieve the long-term conservation of nature with associated ecosystem services and cultural values” (Day et al., 2012). The coastal zone of Brazil

presents an extensive network of PAs, which forms a large ecological corridor, encompassing terrestrial, marine and estuarine areas. The Cananéia-Iguape-Peruíbe Protected Area (CIP-PA) is inserted in this network; this PA was created in 1984 through Brazilian Law No. 90.347; it covers the cities of Cananéia, Iguape, Peruíbe, Itariri, Pedro de Toledo, and Miracatu (IBAMA/SMA-SP, 1996). This protected area is part of the “Atlantic Forest Biosphere Reserve”, recognized as such by UNESCO as 1991 (Lino et al., 2011); in addition, the CIP-PA was recently included in the Ramsar’s List of Wetlands of International Importance (RSIS, 2017). The Ramsar Convention is the intergovernmental treaty that provides the framework for the conservation and wise use of wetlands and their resources (Ramsar Convention Secretariat, 2016). The CIP-PA Ramsar site includes the Cananéia-Iguape Estuarine Complex (Figure 1), which is part of a region known as Lagamar. Since 2000, the region has been part of the global list of UNESCO’s World Heritage Sites (Abdulla et al., 2013), as it is part of the “Atlantic Forest South-East Reserves” World Heritage site.

The Cananéia-Iguape Estuarine Complex (CIEC) is located on the southern coast of Sao Paulo State. It is comprised of the cities of Iguape, Ilha Comprida, and Cananéia, and it also includes Cardoso Island. CIEC has about 100km length and an approximate area of 200km²; this complex is located on a sandy coastal plain and has an intricate set of estuarine and lagoon channels (Figure 1). It was formed through five phases of transgression and regression of the ocean over the last 120,000 years (Suguio and Martin, 1978). The current configuration was obtained close to 5,100 years ago, when the average sea level was 4 meters above current levels and began to regress, thus forming the current system of channels and barrier islands (Suguio et al., 1988).

CLIMATE

The climate in the Lagamar region is classified as a humid subtropical climate (Cfa). Its average annual temperature is 21.2 °C, and the relative humidity in the air averages approximately 88%. Between spring and summer, tropical air masses prevail, while in the winter there is a predominance of polar air masses (Schaeffer-Novelli et al., 1990). Average annual precipitation exceeds 2200mm, with the highest amounts occurring from January to March (average

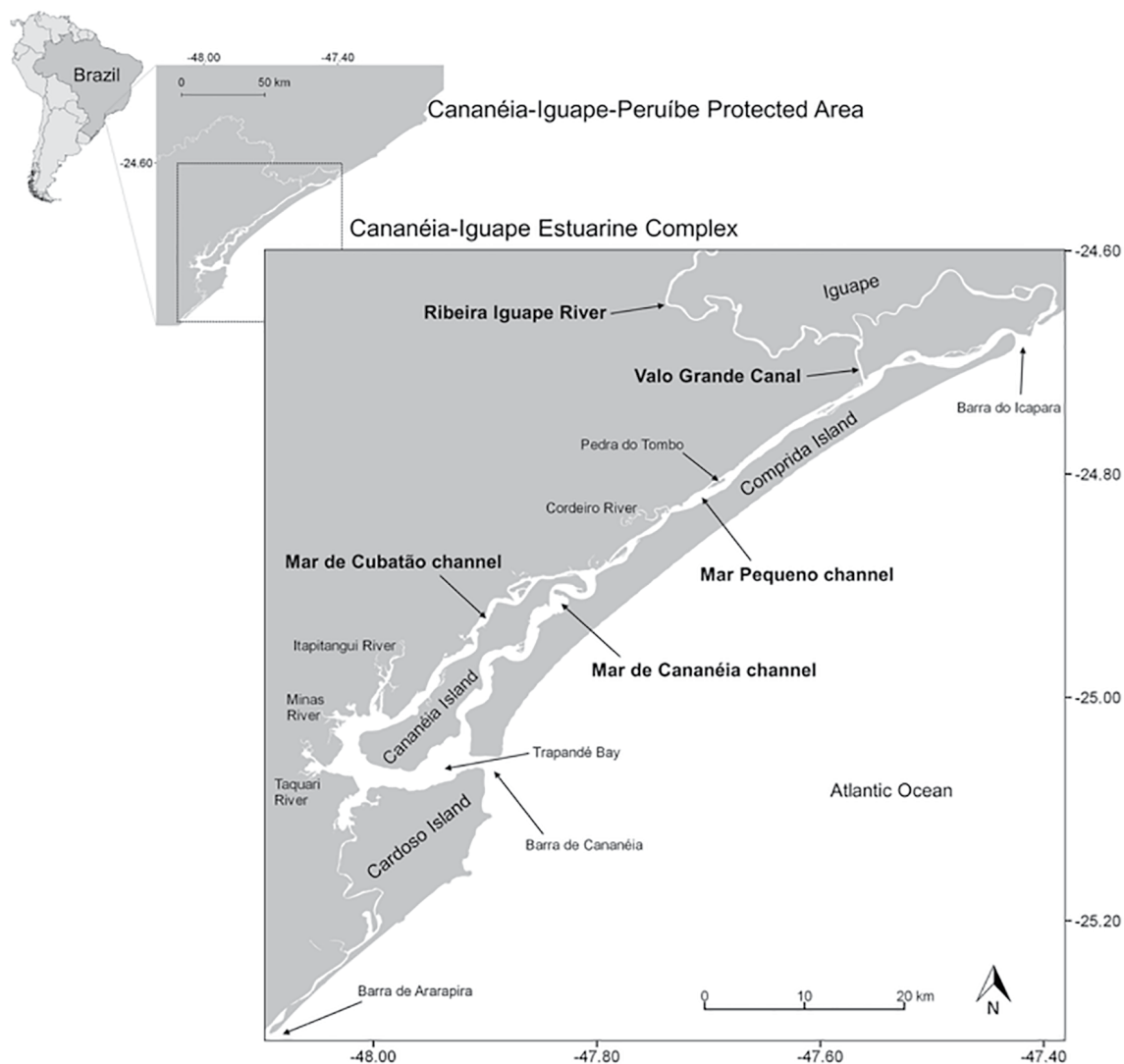


Figure 1. Cananéia-Iguape-Peruíbe Protected Area (CIP-PA) and overview of the Cananéia-Iguape Estuarine Complex (CIEC).

monthly rainfall of 266.9mm) and the lowest amount recorded in July and August, when the average is 95.3mm (Mishima et al., 1986; Silva, 1989).

HYDROGRAPHY AND HYDROLOGICAL DYNAMICS

Tidal cycles associated with freshwater inflows and atmospheric precipitation cause wide amplitudes of salinity fluctuation throughout the CIEC. The Ribeira de Iguape River (RIR) is the main freshwater course in the complex and has the most significant influence on the salinity of the lagoon waters. CIEC also receives contributions from a vast network of

smaller rivers, such as the Cordeiro River in the northern portion, the Taquari River, the Minas River, and the Itapitangui River in the southern portion (Figure 1). The flow rate of the RIR responds synchronously to variations in rainfall; it is lowest in June, when it averages $218\text{m}^3\text{s}^{-1}$, and it triples during the rainy season, when it averages $634\text{m}^3\text{s}^{-1}$ (DAEE, 2019). After the opening of an artificial canal known as the Valo Grande Canal (detailed below), the RIR inflow came to be almost completely directed to the CIEC through this canal.

The estuary connects to the ocean through three natural mouths known as Barra do Icapara, Barra

de Cananéia and Barra do Arapira (Figure 1). The longitudinal density gradient of the water and this freshwater inflow are the driving forces behind the stationary circulation in the CIEC; they are predominantly determined by tides (Miyao and Harari, 1989) and, to a lesser extent, by winds (Miranda et al., 1995). The tides in the estuary are semi-diurnal, with diurnal variations and maximum amplitudes of 1.25m (Bernardes and Miranda, 2001).

The average annual salinity gradient along the CIEC has a spatial structure on its shallow and the deeper portions (> 2m). This gradient begins at the mouth of the Valo Grande Canal and continues toward the Barra do Icapara and Barra de Cananéia, branching southward into two channels, separated by the Cananéia Island; these branches are known as the Mar de Cubatão and the Mar de Cananéia. In the southern portion of the CIEC, Trapandé Bay connects the Mar de Cananéia channel to the Atlantic Ocean between Comprida Island and Cardoso Island (Figure 1). The average flood tide and ebb tide current speeds reach 2 m s^{-1} and 1 m s^{-1} , respectively. Despite evidence indicating the relative seasonal persistence of saltwater within the estuary and in Trapandé Bay (Miyao et al., 1986) short-term episodes of intense continental runoff may move the saltwater wedge towards south (Mahiques et al., 2009; Conti et al., 2012).

The CIEC channels are known as the Mar Pequeno, the Mar de Cubatão and the Mar de Cananéia. The Mar Pequeno channel is bordered by the Barra do Icapara (northern estuary mouth) and by the confluence of the three channels in the middle of the estuary. The opening of the Valo Grande Canal is found within this channel. The tidal waves generally meet in the region known as Pedra do Tombo, which represents the central region of this water body (Miyao and Harari, 1989). The water column between the confluence of the three channels and the Valo Grande Canal is more homogenous than the southern portion (Fontes et al., 2019). Between the Valo Grande Canal and the Barra do Icapara, an abrupt increase in the saline gradient and current speeds are often observed due to the area's proximity to the ocean (Barrera-Alba et al., 2007).

The Mar de Cubatão channel extends from the northern area of Trapandé Bay to the confluence of the three channels in the middle section of the estuary. The average depth is 5 m, with a maximum depth

of 10m at the connection with Trapandé Bay (Tessler and Furtado, 1983; Tessler and Souza, 1998). It is characterized as a polyhaline channel with an average salinity of approximately 21.3. The freshwater inflows from the Taquari, Madrina, Minas and Itapitanguí Rivers create clear water column stratification, in which salinities gradually increase in the direction of the Mar Pequeno channel. Tidal current speeds vary from 0.7 to $1.0\text{ m}^2\text{ s}^{-1}$ (Miyao and Harari, 1989).

The Mar de Cananéia channel is bordered by the Mar Pequeno channel and by the southern portion of Trapandé Bay; its depth averages 6m. In this body of water, a gradual increase in depth has been identified from the Mar Pequeno channel to Trapandé Bay; it reaches 15m at some points (Tessler and Souza, 1998; Bernardes and Miranda, 2001). According to Miyao et al. (1986) the vertical salinity structure of the Mar de Cananéia channel underwent changes after the opening of the Valo Grande Canal. It came to be classified as partially mixed and weakly stratified estuary. Average salinity is approximately 22.5, which classifies this channel as a polyhaline water body. Imbalanced tidal wave behavior provokes induction currents in opposite directions between the Mar de Cananéia and the Mar de Cubatão channels (Miyao et al., 1986). This characteristic has important implications for the distribution and deposition of fine sediments, organic matter and contaminants since the MTZ shifts with the tidal excursion.

BIOLOGICAL PRODUCTIVITY

The arrangement of the bays and the mouths of the rivers within the CIEC allows the retention of large amounts of nutrients, which enables high primary productivity (Tundisi and Matsumura-Tundisi, 2001), with implications on the estuarine and marine food chains. The input of nutrients (dissolved and particulate organic material, as well as inorganic compounds) largely comes from mangrove swamps (Schaeffer-Novelli et al., 1990). Phytoplankton production is an important source of particulate carbon, especially during peaks in primary production during the rainy summer season (Tundisi and Matsumura-Tundisi, 2001). Furthermore, rates of secondary production of zooplankton exhibit clear seasonal variations that are largely influenced by the interaction between coastal waters and the elevated concentration of nutrients and organic material in estuarine

waters (Ara, 2004). For this reason, the CIEC is home to extensive biological diversity and is an important estuary in terms of its primary productivity and its role as a nursery for South Atlantic fish species (Kelleher et al., 1995; Costa Neto et al., 1997). The estuarine channels are surrounded by abundant mangrove vegetation and serve as a nursery for economically important marine species (Mendonça and Katsuragawa, 2001; Mendonça and Miranda, 2008).

SOCIO-ENVIRONMENTAL CONSIDERATIONS

Apart from the ecological relevance, one of the objectives of the CIP-PA is to protect cultural and historical value for traditional people. The traditional people living in the region include Brazilian indigenous, Maroons (known as Quilombolas), and fisher-farmers (known as Caiçaras). The culture of the Caiçaras is influenced by the miscegenation of Amerindians, European colonists, and African Brazilians, and their production system is based mainly on local indigenous knowledge (Hanazaki et al., 2007). The main economic activities among traditional people are subsistence agriculture, artisanal fishing, tourism-related activities and extraction of non-timber forest resources directed to commerce (Peroni et al., 2008). According to Hanazaki et al. (2007), the level of importance of each of those activities varies across communities in the same region.

One of the most important fishery resources on the estuary of Cananéia is the mangrove oyster (*Crassostrea* spp.). The principal technique of oyster exploitation is the “oyster fattening”, which is an intermediary method among extractivism and full culture (Henriques et al., 2010). This technique consists of setting adult oysters in the intertidal zone until they reach the appropriate size for commercialization (Pereira et al., 2001). This management method is environmentally essential since the animals spawn in the fattening farms, allowing the natural replenishment of stocks (Galvão et al., 2000; Pereira et al., 2001). The fattening culture at CIEC is economically viable compared to full culture, as it aggregates market value to the oysters (Henriques et al., 2010). According to Barbieri et al. (2014), oyster fattening culture in the CIEC displays low potential environmental impact and considerably more positive than negative impacts on the social-economic of Cananéia.

In general, the economy of the region is based mainly on fishing, tourism and oysters cultivation (Mendonça and Katsuragawa, 2001; Barbieri et al., 2014; Machado et al., 2015); thus the local economy relies on the ecological services and goods, strongly depending on the ecological conservation. Therefore, in addition to its unquestionable ecological function, the CIEC has socioeconomic importance (Machado et al., 2010; Barcellini et al., 2013). Household incomes and education levels are both relatively low in the region, as are the municipal GDPs of the three cities located within the CIEC (Cananéia, Iguape, and Ilha Comprida).

The demographic density of the cities located within the CIEC is low relative to the rest of the Sao Paulo coast (Morais and Abessa, 2014). However, due to its tourist attractions, the cities within the CIEC experience seasonal variation in their populations for two- to three-month periods during the year, though there is no official data on this fluctuation for the whole CIEC. Becegato and Suguio (2007) reported the number of tourists reached 150,000 people only in the city of Ilha Comprida, against 10,000 of inhabitants. Thus, in this region there is a considerable increase in population size and, therefore, there is also an increase in waste production and the input of urban effluents into the surrounding bodies of water. It is important to note that, in 2009, solid waste from the cities still lacked an adequate destination (CETESB, 2010a). Local sanitation and public health systems are also inadequate, and a substantial number of households are not included in the regional sewer system (Morais and Abessa, 2014). In addition, this region is currently the furthest away from the implementation of a Coastal Management Plan in the state of Sao Paulo, and more studies are needed on this topic (Morais and Abessa, 2014).

CHARACTERIZATION OF STRESSORS

THE OPENING OF THE VALO GRANDE CANAL

The natural mouth of the Ribeira de Iguape River (RIR) is located within the CIP-PA, north of CIEC. The river is 470km in length from its headwaters in the state of Paraná (within the Paranapiacaba Mountain Range) to the mouth in the Atlantic Ocean in the state of Sao Paulo (in the city of Iguape). With an area

of approximately 25,000km², the drainage basin of the RIR is almost completely distributed between the Atlantic Plateau and the coastal province. This region is characterized by slopes and embedded wetlands and also includes coastal plains, as well as marine and fluvial terraces (SIG-RB, 2012).

The RIR is the main contributor of suspended sediments, nutrients and contaminants into the CIEC (Barcellos et al., 2009). According to Mahiques et al. (2013), the CIEC has undergone significant environmental changes over the last 150 years due to the construction of a 4km artificial canal connecting the Ribeira de Iguape River to the inner portion of the estuary. The project, which was concluded in 1852, sought to diminish the costs of agricultural production and transportation to the main economic port located in the city of Iguape. Originally, the canal was 4.4m in width and 2m in depth, but after more than 150 years the width reached approximately 300m, and in some locations, depth can reach 7m.

The Valo Grande Canal was closed in 1978 in order to minimize financial losses to agriculture in areas located upstream. However, during the El Niño oscillation of 1983, the rock and sand barrier was destroyed by significant floods. The coastal plain where the canal was dug underwent erosion, leading to the silting of the port areas of Iguape and the deposition of sediments in adjacent lagoon areas. In addition, approximately 70% of the main flow of the RIR was transferred to the CIEC, a process that decreased the system's salinity (Mahiques et al., 2013). In the city of Cananéia, for example, which is located 60km to the south of the mouth of the canal, salinity can be found to be zero during the summer (Mahiques et al., 2009).

There is evidence that changes in salinity have affected the local biota since the opening of the Valo Grande Canal, with reports on the effects on ichthyofauna (Barcellini et al., 2013), phytoplankton (Kutner and Aidar-Aragao, 1986), foraminifera (Mahiques et al., 2009), and halophytes (Schaeffer-Novelli et al., 1990; Cunha-Lignon et al., 2011). According to Martinez et al. (2013), an abrupt change in the overall composition of molluscan fauna in the CIEC occurred after this canal was opened, as a consequence of the input of fresh water and contaminants.

The impact of the input of fresh water from the RIR is greater in the Mar Pequeno channel, which exhibits greater persistence under atypical conditions

of low salinity and more physical habitat destruction; mangrove swamps have been replaced by freshwater macrophytes, and there has been an overall reduction in depth due to intense silting (Cunha-Lignon et al., 2009; Cunha-Lignon et al., 2011; Mahiques et al., 2013). According to Saito et al. (2001a), the rate of sediment deposition in this area is approximately 0.5cm year⁻¹. Therefore, the Valo Grande Canal has clearly affected sedimentation patterns and the physical-chemical characteristics of the estuary, with increased transportation of silt and clay from the RIR into the southern portion of the CIEC (Barcellos et al., 2009). More drastically, the canal began to direct metals from mining areas of the Ribeira de Iguape River Valley to the inner portion of the CIEC (Mahiques et al., 2013), as described below.

THE RIBEIRA DE IGUAPE RIVER VALLEY AND ITS HISTORY OF METAL CONTAMINATION

Approximately 39% of the Ribeira de Iguape River catchment basin is located in the northeastern region of Paraná State while 61% of which is located in southeastern Sao Paulo state, where it occupies approximately 17,000km² (Theodorovicz and Theodorovicz, 2007). The Ribeira Valley is home to most of the remaining continuous Atlantic Forest in the country — out of the 7% of this biome that remains in Brazil, 21% is located in this valley. For this reason, UNESCO declared the region to be a National Heritage Site in 1999, and approximately 50% of the Ribeira Valley became an Environmental Protection Area (Santos and Tatto, 2008).

The Ribeira Valley region is currently slightly developed from a socioeconomic point of view; it has the lowest human development index in the state of Sao Paulo. However, due to its peculiar geology, the Ribeira River Valley has been one of Brazil's most important regions for mineral resources (Morgental et al., 1975). Mining along the upper course of the river (known as the Upper Ribeira Valley) began in the eighteenth century with manual gold and silver mining. In 1945, lead mining began on an industrial scale, followed by zinc mining (Lopes Junior, 2007).

Mining activities are recognized for their high impact on the environment, which results from the generation of toxic waste and acid or alkaline drainage that all come from the extraction and beneficiation of metals (Benedicto et al., 2008; Besser et al., 2009; Li et

al., 2014). In addition, the inadequate disposal of this waste into the environment may have contaminated soils, groundwater, atmosphere, and surface waters (Corsi and Landim, 2003; Riba et al., 2005; Melo et al., 2012). According to Guimarães and Sígolo (2008a), mining residues are the main source of contamination in the RIR. They are present in the form of waste from the mining process (ore) and also as metallurgical waste (slag).

Lead mining in the Ribeira Valley was halted in 1995 as a result of an exhaustion of reserves, technical difficulties, and economic and environmental factors. However, wastes from the two main mines operating in the region, which were known as Rocha and Panelas, still remain along the banks of the Ribeira River and its tributaries (Figure 2). Waste from the Rocha mine was deposited close to the Rocha River and with a volume of approximately 3,000m³. The volume of waste from the Panelas mine (Plumbum Mining Company) is approximately 89,000m³ (Franchi, 2004), and the waste may still

be found close to the bank of the RIR. It may be lixiviated or even eroded and transferred into the river (Abessa et al., 2014).

It is important to highlight that the concentrated waste from metallurgical activities performed by the Plumbum Mining Company was dumped into the RIR for more than forty years. Toxic waste dumping directly into the river was interrupted in 1991, and the material began to be deposited with mining waste on the banks of the RIR, with a total of at least 200,000m³ of waste (Franchi, 2004) containing aluminum (Al), arsenic (As), barium (Ba), calcium (Ca), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), potassium (K), nickel (Ni), manganese (Mn), magnesium (Mg), sodium (Na), lead (Pb), silicon (Si) and zinc (Zn) (Guimarães and Sígolo, 2008a). These materials were deposited into the soil without any prior treatment and apparently without any concerns over contamination, since significant concentrations of metals were found in the RIR after 1995.

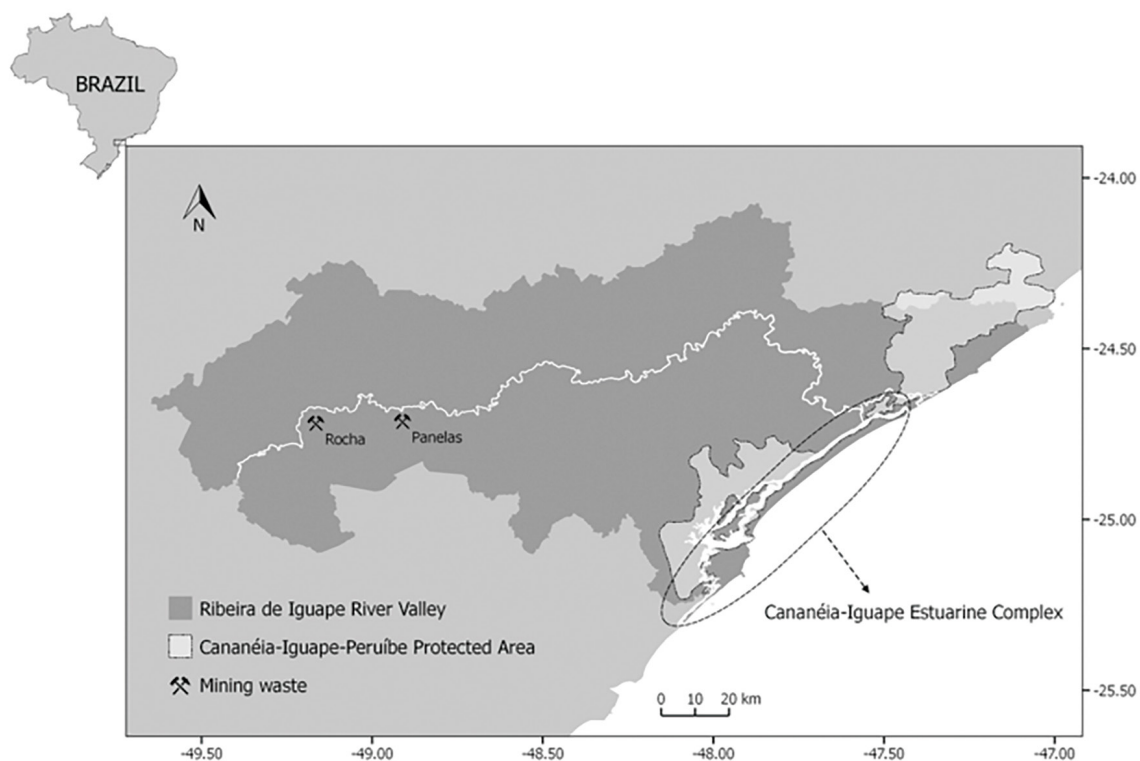


Figure 2. The Ribeira de Iguape River Valley showing the location in which mining wastes were deposited.

Studies conducted during the period in which beneficiation and mining activities were performed reported high levels of Pb in the sediments of the RIR and its tributaries. Eysink et al. (1988) reported that the Rocha River reached Pb levels of $2,750\mu\text{g L}^{-1}$ in the water and $1,440\text{mg kg}^{-1}$ in the sediment. In the RIR, the authors found high levels of Pb in the sediment — $4,000\text{mg kg}^{-1}$. Lead levels above 500mg kg^{-1} were also found at seven of the twelve sampling stations evaluated along the river in this study. The same authors reported high levels of Pb, Zn and Cu in the sediments along the Ribeira de Iguape riverbed, with a predominance close to the mining areas. At that time, the sediments that were collected close to the mines presented metal values at concentrations of 10^2 - 10^3mg kg^{-1} , while this concentration varied from 10mg kg^{-1} to 10^2mg kg^{-1} close to the estuary (Eysink et al., 1987; Eysink et al., 1988). In a further study, Eysink et al. (1991) reported Pb concentrations in sediments from the RIR between 105mg kg^{-1} and 358mg kg^{-1} .

The Environmental Company of Sao Paulo State (CETESB) published an assessment of the quality of the Ribeira de Iguape River and its tributaries based on data obtained in 1998. The document reported Pb concentrations between 41.7mg kg^{-1} and 389mg kg^{-1} in the sediments (CETESB, 2000). In 2002, the CETESB began to include sediment quality assessments in its “Sao Paulo State Surface Water Monitoring Program”. Because Brazil lacks standards for concentrations of contaminants in sediments, the CETESB uses quality criteria established by the Canadian Council of Ministers of the Environment, or the (CCME, 2002). This guide establishes two types of guideline values for toxic substance limits: one for threshold effect (Interim Sediment Quality Guidelines, or ISQG; also known as the threshold effect level or TEL), and the other for the probable effects level (PEL). According to the reports published by the CETESB, metal levels have been above ISQG/TEL every year, with the exception of 2002 and 2009 (CETESB, 2003; 2010b). In 2004 and 2006, values above the PEL were reported for Pb and As, respectively. Due to the origin of the sediment matrix of the river basin, Al, Fe and Mn have always been present in high concentrations in RIR sediment (CETESB, 2005; 2007). Only one site is monitored for ecotoxicity, and acute toxicity has thus far not been observed in the amphipod crustacean *Hyalella azteca*.

More recent studies have shown that the effects of lead metallurgy and mining are still present in the RIR and its tributaries (Corsi and Landim, 2002; Moraes et al., 2004; Cunha et al., 2005; Guimarães and Sígolo, 2008a). These studies have reported concentrations of metals in the sediments, particularly in the case of Pb, which was found above regional background levels proposed by Morgental et al. (1978). According to these authors, the range of Pb levels before the effects of human activity was 12 to 16mg kg^{-1} .

Cunha et al. (2005) found Pb concentrations as high as 175.5mg kg^{-1} in the RIR sediments and 527.2mg kg^{-1} in one of its tributaries (the Betarí River, close to the city of Iporanga, Sao Paulo state). However, the authors observed a decrease in Pb concentrations in sediments from the RIR and its tributaries relative to the results of previous studies (Eysink et al., 1988; Eysink et al., 1991; CETESB, 2000). Lopes Junior et al. (2007) have also suggested a decrease in Pb concentrations over time in both the waters and the sediments of the RIR. In addition, the CETESB (2007) reported that the RIR is going through a natural recovery process induced by the control measures imposed by environmental agencies. Indeed, Abessa et al. (2012) reported an absence of acute toxicity to the cladoceran *Daphnia similis*, for both water and sediment samples collected from six sampling stations in the upper course of the RIR. Morais et al. (2013) evaluated the presence of Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in sediment samples and reported concentrations below the ISQG.

Though the literature indicates the occurrence of an environmental recovery process along time in the RIR, recent studies have reported the persistence of metals in abiotic compartments (Guimarães and Sígolo, 2008a; Melo et al., 2012) and in the biota (Guimarães and Sígolo, 2008b; Rodrigues et al., 2012). Therefore, we can conclude that the contamination has not yet been completely removed. This finding has been corroborated by studies on the release of metals by soils in the region (Buschle et al., 2010; Kummer et al., 2011).

The recovery process aids in returning the ecosystem to a state similar to that which was observed before the contamination occurred (Bradshaw, 1997; Garten and Ashwood, 2004). In the case of the RIR, this process includes the natural removal of contaminated waste and its dilution through the physical

and chemical processes within the drainage basin. The waters of the RIR are slightly alkaline and present high levels of dissolved oxygen, resulting in a markedly oxidizing environment (Eh between +320mV and +440mV), which favors the incorporation of metals into the suspended particles. Metals are thus easily remobilized for the water column and transported downstream (Corsi and Landim, 2002; Melo et al., 2012). Guimarães and Sígolo (2008b) highlighted that metals are migrating along the course of the RIR; they are incorporated into suspended material and made bioavailable for filter feeder mollusks, as was observed in the freshwater clam *Corbicula fluminea*.

Moraes et al. (2004) used Pb isotope tracers to identify sources of metals in the sediments of the lower course of the RIR and in the CIEC. The authors concluded that the found contamination came from the Upper Ribeira Valley mines. According to the study, the sediments carried along the river may include a mixture of various types and eroded soils in the Ribeira Valley, but the isotopic signatures of these materials coincide with those of ore and mining wastes discarded along the banks of the RIR. The study also suggests that the transportation of Pb and other associated metals has occurred through solid particles from ore, as well as through particles absorbed by minerals in the fine-grained sediment fraction.

CLIMATE INFLUENCE ON SEDIMENTS AND CONTAMINANTS TRANSPORT TO THE CIEC

As some authors have demonstrated, the metals released in the Upper Ribeira Valley are transported downstream (Corsi and Landim, 2002; Melo et al., 2012; Guimarães and Sígolo, 2008b) and reach the CIEC (Moraes et al., 2004). Thus, during extreme weather events, this transport can be intensified, since larger amounts of sediments are remobilized along the drainage basin and redistributed, mainly in the estuarine region (Jonasson and Nyberg, 1999; Coppus and Imeson, 2002). According to Costa et al. (2009) the rainstorms have major role in removing contaminated sediments along the RIR basin.

In addition to transporting contaminants, episodes of strong rainstorms may also cause significant changes to the landscape and geomorphology of the CIEC. The geomorphological impacts of extreme weather events are closely related to factors such as

the erodibility of the material of origin, topography, vegetation and how the land is used (Bull et al., 2000; Belmonte and Beltrán, 2001). Then, the increase in flow and water volume along the drainage basins is a secondary factor that may increase sediment transport through the basin, since bottom particles can be resuspended as a physical consequence of the increase in energy (Morgan et al., 1998).

The flow rate of the RIR in its lower course varies from 300 to about 1,200m³ s⁻¹. The variation in flow is strongly influenced by rainfall, since the precipitation volumes are the main factor in regulating the hydrological balance of drainage basins, controlling the quantity of water that flows into the rivers through both surface runoff and underground drainage (Morgan et al., 1998; Zhang et al., 2004). The Ribeira Valley region experiences a relatively high rainfall in the summer, though it does not experience a defined dry season. Annual rainfall in the region vary from approximately 1,200 to 2,700mm (SSE/SP, 2010). However, the flow rate of the RIR frequently exceeds 2,500m³ s⁻¹; an extreme rate of 4,250m³ s⁻¹ was recorded in its lower course in 1999 (SIG-RB, 2012).

Episodes of flooding in the RIR basin are not uncommon, since the climatic conditions in the region are highly conducive to the occurrence of highly intense and long-lasting frontal precipitation. Additionally, the morphological characteristics of the basin are also conducive to the occurrence of major floods. In its middle course and upper course, the RIR and its tributaries flow through enclosed valleys at an elevated slope. In the lower course, in addition to receiving contributions from other rivers, the RIR acts as a typical lowland river, cutting through low wetlands on a very limited slope. The overlap of these two factors constitutes the basic cause of large-scale flooding, both in terms of peak flow rate and volume (DAEE, 1998).

Some studies showed that runoff might carry a series of contaminants that are deposited in the soil or associated with sediment particles (Bay et al., 1996; Allert et al., 2009). These contaminants tend to be deposited in areas of low energy, such as floodplains and estuaries (Du Laing et al., 2009). In these locations, the physical and chemical characteristics may alter the dynamic of the metals and, as a result, their bioavailability (Carr et al., 2000). Increased rainfall precipitation rates may contribute to seasonal variation

of metal concentrations in the biota. Lacerda et al. (1985) reported that higher concentrations of metals in macroalgae from the coast of Rio de Janeiro were associated to an increase of levels in seawater, which, in their turn, were associated to the terrestrial runoff that was augmented due to the increased rainfall volumes.

Extreme weather events are of special concern in regions where inadequate disposal of mining residues is made. A monitoring study of three decades of metal contamination in Sepetiba Bay (Brazil) indicated that during heavy rains, runoff waters enriched in Zn and Cd reached the bay after a massive spill of tailings material, causing a sudden increase on the concentrations of Cd and Zn in seaweeds and oysters (Lacerda and Molisani, 2006). We observed that the flooding in the RIR has the potential to make an even greater impact: the areas in which mining waste is located may be eroded, and contaminants may be transported in large quantities into the CIEC.

In a study conducted in the RIR, Abessa et al. (2014) compared metal concentrations in sediments collected along the RIR under different weather conditions. The collections were performed during a period of low indices of precipitation (less than 35mm over 20 days), after an extreme weather event in which precipitation above 220 mm in 24 hours was recorded, and after moderate rainfall (approximately 65mm in 7 days). Metal concentrations were highest in the fine sediments collected after the episode of intense rainfall and at a distance of approximately 150km from the areas where the mining activity waste had been deposited. The results revealed much lower metal concentrations in the sediments collected during the dry period, as the concentrations were below the ISQG and the background values for the Ribeira Valley region (Morgental et al., 1978). After the period of moderate rains, Pb and Cr concentrations were found to be above the ISQG. Meanwhile, in the samples collected after the 2011 floods, Cr concentrations also exceeded the ISQG and Pb concentrations were above the PEL. It is worth nothing that, in the extreme rainfall event, the river rose 14 meters in 24 hours and the flood was the second largest in the region's history (SIG-RB, 2012).

These data suggest that high rainfall precipitations may contribute to an enrichment of metals in the CIEC. Then, we can infer that this enrichment

occurs largely through the transportation and deposition of fine-grained sediments, which potentially carry higher quantities of metals.

EXPOSURE CHARACTERIZATION TO THE STRESSORS

METALS IN THE CIEC SEDIMENTS

The evidence obtained in this analysis revealed that the northern and southern portions of the estuary complex are subject to different consequences of human activity, as well as to other types of pressures. In the northern region, the effects are predominantly caused by former mining activities in the Upper Ribeira Valley. Some others have suggested that the presence of an abandoned gold mine close to the northern portion of the estuary and a fertilizer factory located in the city of Iguape are also important sources of metals in this region (Azevedo et al., 2012a). The southern portion is highly influenced by the urban area of Cananéia City (Cruz et al., 2014; 2019; Gusso-Choueri et al., 2016). The sources of metal vary; they include marine sources (particularly anti-fouling paints), gas stations, domestic sewage and urban drainage. The input of contaminants may have a seasonal influence, since the region experiences high levels of tourism and the population size undergoes changes during the year (Morais and Abessa, 2014). However, the southern portion may also be subject to the influence of mining activities, a possibility that will be discussed below.

In recent decades, many studies have reported the presence of metals in sediments from the CIEC (Table 1). The first metal concentration assessments using sediments from the CIEC was performed in the 1980s, when the Ribeira Valley mining activities were being performed. In the mid-1980s, Pb concentrations as high as 160mg kg⁻¹ were found in sediments from areas within the estuary (Piva-Bertoletti and Padua, 1986). Eysink et al. (1988) reported the presence of Pb at 82mg kg⁻¹ in sediment samples from the estuary close to the natural mouth of the RIR. In the southern portion, Tessler et al. (1987) found Pb concentrations varying from 0.30 to 247mg kg⁻¹, as well as Zn at 1.4 to 105mg kg⁻¹ and Cu at 0.05 to 292mg kg⁻¹. According to these authors, elevated metal concentrations may have caused by the transport of fine sediments through the RIR and into the estuary.

Table 1. Maximum concentrations (in mg kg⁻¹) of metals and arsenic reported in sediments in the Cananéia-Iguape Estuarine Complex and their respective ISQG and PEL values.

Location	As	Cd	Cr	Cu	Hg	Pb	Zn	Anal. proc.	Digestion method	Reference	
Close to the natural mouth of the RIR		<0.19		13.1	0.15	82.0	58.9	NR	APHA (1980)	Eysink et al. (1988)	
		0.13	7.8	9.83		29.04	31.16	ICPOES	EPA 821/R-91/100 (Allen et al., 1993)	Campos et al. (2016)	
						160.0		NR	NR	Piva-Bertoletti and Padua (1986)	
Mar Pequeno channel				292		247	105	NR	NR	Tessler et al. (1987)	
				46^b		197^b	135^b	ICPOES	Method 3050B (USEPA, 1996)	Mahiques et al. (2013)	
	3.49	<0.1	29.4	11.5		30.7	49.4	NR	Method 3051A (USEPA, 2007a)	CETESB (2014)	
		0.28	11.21	16.07		51.63	37.01	ICPOES	EPA 821/R-91/100 (Allen et al., 1993)	Cruz (2014)	
		0.07	20.38	5.47	0.06	13.08	23.32	ICPOES	EPA 821/R-91/100 (Allen et al., 1993)	Araújo (2014)	
		0.17	8.59	7.99		32.84	32.62	FAAS	EPA 821/R-91/100 (Allen et al., 1993)	Gusso-Choueri et al. (2015)	
	11	<0.6	70.1	16.73		72.7	176	NR	Method 3051A (USEPA, 2007a)	CETESB (2015)	
	0.16	9.13	10.95		33.41	33.57	ICPOES	EPA 821/R-91/100 (Allen et al., 1993)	Campos et al. (2016)		
			18.74		177.5	123.0	ICPOES	Pueyo et al. (2001)	Tramonte et al. (2018)		
Mar de Cananéia channel			52.2^b	32.1^b		68.2^b	92.1 ^a	ICPOES	Method 3050B (USEPA, 1996)	Mahiques et al. (2009)	
	12.1		76				96	INAA	-	Amorim et al. (2008)	
		5.3	280	35		56	74	GFAAS	Method 7010 (USEPA, 2007b)	Aguiar et al. (2008)	
					<0.10				ICPAES	Horvat (1996)	Azevedo et al. (2011)
	10	<0.1	38.8	12.9		25.7	57.2	NR	Method 3051A (USEPA, 2007a)	CETESB (2014)	
		0.76		61.7			71.6	FAAS	Method 3050B (USEPA, 1996)	Cruz et al. (2014)	
		0.14	31.97	16.27	0.12	40.24	45.18	ICPOES	EPA 821/R-91/100 (Allen et al., 1993)	Araújo (2014)	
6.23	<0.5	25	13		12.5	43	NR	Method 3051A (USEPA, 2007)	CETESB (2015)		
	0.04	3.84	1.97		8.68	3.84	FAAS	EPA 821/R-91/100 (Allen et al., 1993)	Gusso-Choueri et al. (2015)		
Mar de Cubatão channel		<0.20		3.16	<0.05	<3.95	11.3	NR	APHA (1980)	Eysink et al. (1988)	
	9.4		41				32	INAA	-	Amorim et al. (2008)	
		6.1	133	25		55	56	GFAAS	Method 7010 (USEPA, 2007)	Aguiar et al. (2008)	
					<0.10				ICPAES	Horvat (1996)	Azevedo et al. (2011)
	<0.14		<0.14		<0.14	<0.14		FAAS	Method 200.8 (USEPA, 1999)	Barros and Barbieri (2012)	

CONTINUATION TABLE 1.

Trapandé Bay	15.8		60		70	INAA	Method 3051A (USEPA, 2007)	Amorim et al. (2008)	
	5.2	94	16	24	56	GFAAS	Method 7010 (USEPA, 2007)	Aguiar et al. (2008)	
Close to Cardoso Island	<0.20		3.48	0.06	<3.87	19.4	NR	APHA (1980)	Eysink et al. (1988)
ISQG	7.24	0.7	52.3	18.7	0.13	30.2	124		CCME (2002)
PEL	41.6	4.2	160	108	0.7	120	271		

Values marked in bold are above the ISQG; italics indicate violation of PEL; Letters a and b: Concentrations obtained from cores dated at the time of depositions that occurred (a) after the opening of the Valo Grande Canal and (b) after the mechanization of the local mining activity; NR = Not reported; Analytical procedures: ICPAES = Inductively Coupled Plasma Optic Emission Spectroscopy; FAAS = Flame atomic absorption spectrophotometry; ICPAES = Inductively Coupled Plasma Atomic Emission Spectroscopy; INAA = Instrumental neutron activation analysis; GFAAS = Graphite furnace atomic absorption spectrophotometer.

In a more recent study, Moraes et al. (2004) used Pb isotopes and corroborated the geochemical studies performed previously, which contributed the high concentrations of metals in the Mar Pequeno channel sediments (north portion of CIEC) to the mining activities performed in the Upper Ribeira Valley. Saito et al. (2001b) evaluated the geochronology of the CIEC sedimentation using dating with ^{210}Pb and found that the RIR had a strong influence on sediment deposition. Other studies have reported that sedimentation rates are lower at north of Cananéia Island, since it does not receive direct freshwater inflows from the RIR. However, during the ebb tide, this location receives a high contribution of suspended sediments from the Mar Pequeno channel, which mainly come from the RIR by way of Valo Grande (Saito et al., 2001a). South of Cananéia Island, the sedimentation is more strongly influenced by tidal currents that may re-suspend fine sediments (Saito et al., 2001a).

Mahiques et al. (2013) analyzed the sediment profile in the north portion of the CIEC and found records of man-made metal input at a point located 20km from the mouth of the Valo Grande Canal (in the direction of Cananéia Island). The study identified 150 years of metal input into the estuary resulting from human activity. According to the authors, the highest contamination levels occurred between 1940 and 1990, coinciding with the decades in which industrial-scale mining was performed in the Upper Ribeira Valley, approximately 300km away from the Valo Grande Canal. Tramonte et al. (2018) performed the sequential chemical extraction of some metals on previously described sediment cores (Mahiques et al., 2013), and estimated the remobilization geochemical

behavior. Concerning Pb, the maximum available level (sum of all mobile fractions) was 177.55mg kg^{-1} . According to the study, Pb remains a concern in the system, since it presents strong association with Fe and Mn oxides, and can be remobilized in reducible conditions that dissolve those compounds. The authors highlighted the anthropic contribution of Pb, being the mining activity in the Ribeira Valley considered the only potential source of Pb in the region.

High levels of Pb are still being identified in surface sediments of the CIEC. Cruz et al. (2019) found values above 51mg kg^{-1} in the Mar Pequeno channel. This contamination is worrisome when it is compared to the guideline values proposed by the CCME (2002); ISQG is defined as 30.2mg kg^{-1} for coastal sediments. These levels are similar to those found in areas with a high degree of degradation, such as the Santos - São Vicente Estuarine System (Abessa et al., 2008) and Aratu Bay, in the state of Bahia, northeastern Brazil (Onofre et al., 2007).

In the southern portion of the CIEC, the main source of contaminants is attributed to the city of Cananéia (Cruz et al., 2014; Gusso-Chueri et al., 2015). However, the levels of metals reported in this area may have a contribution of the mining sites located upstream the Ribeira de Iguape River (Cruz et al., 2019), because the distribution of these contaminants in superficial sediments around the Cananéia Island presents a seasonal variation. Amorim et al. (2008) found levels of Cr, Hg, Zn, and As below the ISQG in sediments collected in the estuarine region. However, sediments from two stations (Mar de Cananéia channel and Trapandé Bay) presented high concentrations of As and Cr — amounts which exceeded ISQG values.

In another study performed around Cananéia Island, Aguiar et al. (2008) found high concentrations of Pb (19-56mg kg⁻¹), Cd (4-6.1mg kg⁻¹), and Cr (35-280mg kg⁻¹). The highest Pb levels corresponded to the sediments with the largest silt and clay fractions, which were collected north of Cananéia Island where the influence of continental drainage is more intense. The authors of the study found high levels of Cd, with a maximum value of 6.1mg kg⁻¹ found in the Mar Cubatão channel. In addition, the Cr levels obtained were elevated and reached 280mg kg⁻¹ in the northern portion of the Mar de Cananéia channel.

Though Aguiar et al. (2008) found extremely high Cd levels in the Mar de Cananéia channel, the same result was not found in the Mar de Cubatão channel in a study performed by Barros and Barbieri (2012). The authors reported an absence of this metal in surface sediments, and Pb, Cu and Zn concentrations were lower than those reported in the aforementioned studies (Table 1). These differences may be due to the analytical methodology used in each study, and particularly the effect of acid extraction used in the digestion of the sediment matrix. Nevertheless, the authors reported a predominance of Pb in 75% of the samples evaluated.

Fine sediment particles (e.g., clays and silts) and organic matter are known for having a higher electro-chemical affinity to metals, and thus for favoring the processes of sorption, complexation and co-precipitation between contaminants and the sediment (Moore et al., 1989). We analyzed the literature and concluded that both organic matter and muddy particles influence the spatial distribution of metals, especially in the southern portion of CIEC; published data show that the main zones of deposition (and consequently metals accumulation) are located in the Mar de Cananéia channel, following the seasonal shifts of the TMZ. This phenomenon may increase the sediment contamination southwards; in order that metals from the upper Ribeira de Iguape River basin reach the south portions of CIEC.

METALS IN THE CIEC BIOTA

Barros and Barbieri (2012) evaluated the concentrations of metals in oysters of the species *Crassostrea brasiliana*, which are collected and farmed for human consumption in the mangrove swamps in the CIEC. Lead concentrations in the soft tissues of the

animals varied from 0.230 to 0.236mg kg⁻¹ in the wet weight basis (ww) and were higher than those found in the sediments. Zinc concentrations were the highest among metals studied, with average levels varying from 20.1 and 24.1mg kg⁻¹ (ww). However, these values are below the maximum limits established for bivalve mollusks by Brazilian law and recommended by both the Brazilian Health Surveillance Agency (ANVISA) and European Commission (EC). The maximum tolerant limit value is established at 1.5mg kg⁻¹ (ww) in the case of Pb (EC, 2006; ANVISA, 2013) and 50.0mg kg⁻¹ (ww) in the case of Zn (Brazil, 1965). Though the concentrations are below those considered to be risk values, these animals interact extensively with the sediments and tend to accumulate metals in their tissues (Rebelo et al., 2003). Furthermore, the animals in the aforementioned study were collected from the Mar de Cubatão channel, where metal concentrations are lower than those reported in the Mar de Cananéia channel sediment (Table 1). According to the historical report, oysters were once found throughout the CIEC and are now limited to the southern portion (Mendonça and Machado, 2010). This impact was caused by changes to the physical and chemical properties of the waters in the northern portion, which were themselves caused by the opening of the Valo Grande Canal.

In another study, metal concentrations were measured in *C. brasiliana* tissues, in individuals collected from the Mar de Cubatão channel, and the concentrations found (ww) were 0.02mg kg⁻¹ of Hg, 0.08mg kg⁻¹ of Pb, 0.11mg kg⁻¹ of Cd, 2.6mg kg⁻¹ of Cu and 393mg kg⁻¹ of Zn (Machado et al., 2002). Only the Zn concentration was above the maximum limit of 50.0mg kg⁻¹ (ww) established by Brazilian law (Brazil, 1965). However, Zn is physiologically present at relatively high levels in the digestive glands and gills of bivalve mollusks (Viarengo et al., 1997).

Metal concentrations in oysters reported in other coastal areas of Brazil generally are presented in the dry weight basis of soft tissues. In order to perform a comprehensive comparison, we used a conversion factor of 6.8 for the dry weight to wet weight ratio for *Crassostrea* spp. (Wright et al., 1985). Thus, we observed that metal concentrations in oysters from CIEC are similar to those observed in animals from other estuaries under anthropogenic influence. Senez-Mello et al. (2020) found 0.11mg kg⁻¹ of Cd, 0.08mg

kg⁻¹ of Cr, 0.05mg kg⁻¹ of Pb and 294mg kg⁻¹ of Zn in the Potengi estuary (Northeast Brazil). However, concentration of Zn in oysters from CIEC was higher than in other coastal areas of the NE Brazil, such as 309mg kg⁻¹ in the Todos os Santos Bay (Amado-Filho et al., 2008) and 154mg kg⁻¹ in the estuary of Rio dos Cavalos, Rio Grande do Norte (Silva et al., 2003). On the other hand, Zn concentration reported in oysters from CIEC is about 30 times lower than that found in the Sepetiba Bay (SE Brazil), where the highest level reached 11,871mg kg⁻¹ wet weight (Rebello et al., 2003).

Some studies have been performed in recent years to determine the extent of metal contamination in the biota of the CIEC (Table 2). Most of these studies have used fish as bioaccumulation models. Fernandez et al. (2014) compared metal concentrations in tissues from the fish species *Mugil curema* collected in the CIEC and in another estuary in the southeastern region of Brazil (Santos, Sao Paulo). The presence of Pb was not evaluated in that study, but Cu and Zn levels in the animals collected around Cananéia Island were found to be extremely high; average (ww) values were 406mg kg⁻¹ and 116mg kg⁻¹, respectively. Unlike the concentrations that were found in oysters (Machado et al., 2002; Barros and Barbieri, 2012), these values were found to be above the maximum tolerance limits established for fishing products by Brazilian law (Brazil, 1965): they were 30.0mg kg⁻¹ in the case of Cu and 50.0mg kg⁻¹ in the case of Zn. It is worth mentioning that, although Cu is an essential metal, its concentration in these animals was 13 times above legal limits. In addition, Cu levels in the fish from the CIEC were higher than the amount found in fish from the Santos Estuary (282mg kg⁻¹), a location that is known to be heavily impacted by industrial and port-related activities. However, the concentrations that were above recommended limits were found in the fishes' liver tissue; normally, muscle is used for human consumption.

Fernandez et al. (2014) found elements' concentrations in fish tissues comparable to those from an impacted estuary (Santos - São Vicente Estuary). A similar observation was also made by Azevedo et al. (2012b). The authors evaluated the presence of metals in tissues from two species of catfish (*Cathorops spixii* and *Genidens genidens*) and did not find significant differences in Zn concentrations between the

animals collected from the two aforementioned estuaries. In another study, Azevedo et al. (2009a) identified the presence of Fe, Co, and Zn in tissues of *C. spixii* from the Mar de Cananéia channel. The animals collected in the CIEC had higher Fe levels than the animals collected in the Santos - São Vicente Estuary (4.84mg kg⁻¹ and 3.08mg kg⁻¹, respectively). The authors attributed this difference to the more efficient metabolism that may have been developed by the CIEC animals, given the role of Fe as a micronutrient in biological systems. Among the other elements analyzed by Azevedo et al. (2009a) in the animals from the CIEC, selenium was found at an average concentration of 12.73mg kg⁻¹ (ww) a value much higher than the limit of 0.03mg kg⁻¹ established for solid foods in the Brazilian legislation (Brazil, 1965).

Other studies compared the presence of metals in CIEC fish to those from the Santos - São Vicente Estuary; however, higher levels in the animals from the industrialized area were the most common finding. Mercury concentrations in muscles of *C. spixii* from the Santos Estuary were higher than those found in fish from CIEC (1.085mg kg⁻¹ (ww) against 0.231mg kg⁻¹ (ww), respectively) (Azevedo et al., 2009b). In a further publication, Azevedo et al. (2012c) reported maximum Hg values in muscle (0.19mg kg⁻¹) and in liver tissue (1.04mg kg⁻¹) from *C. spixii* specimens collected in the Mar de Cananéia channel. Though fish liver is not commonly consumed by humans, the amount of Hg in this organ was found to exceed the levels recommended by both Brazilian law (ANVISA, 2013) and international agencies (FAO/WHO, 2004; EC, 2006). Recommended values are consistent across the agencies; the limits of mercury that are safe for human consumption are 0.5mg kg⁻¹ in non-predatory fish and 1.0mg kg⁻¹ in piscivorous fish. Thus, elevated mercury concentrations may be transferred to other levels of the tropic chain within the CIEC.

According to Azevedo et al. (2012a), the presence of Hg in the CIEC could be partially explained by the presence of an abandoned gold mine and a fertilizer factory located close to the northern portion of the estuary. However, Hg could also come from different sources, such as atmospheric transport (Fitzgerald et al., 1998), dispersion through suspended sediments via continental drainage (Mol et al., 2001), or migratory aquatic species tissues (Wiener and Spry, 1996).

Table 2. Concentrations of metals and arsenic reported in biota of the Cananéia-Iguape Estuarine Complex. Data represent mean \pm SD to wet weight basis (ww) expressed in mg kg⁻¹. The extreme values (minimum and maximum) are also presented. Action levels for human consumption established by different health agencies are also given (the exceedances are presented in bold).

Species	n	As	Cd	Cr	Cu	Fe	Hg	Hg	Pb	Zn	Reference
<i>Crassostrea brasiliiana</i>	69		0.11 (0.02- 0.22)		2.8 (1.5- 7.7)		0.02 (<DL- 0.03)		0.8 (0.04- 0.17)	402 (145- 844)	Machado et al. (2002)
	NR		<DL		0.2 \pm 0.002			0.02 \pm 0.01	0.24 \pm 0.01	20.4 \pm 9.8	Barros and Barbieri (2012)
<i>Anomalocardia brasiliiana</i>	NR		1.01 (0.88- 1.46)								Cruz (2014)
<i>Genidens genidens</i> (muscle)	10		0.01 (0.003- 0.01)		0.04 (0.01- 0.07)		0.21 (0.01- 0.26)		0.06 (0.03- 0.07)	0.01 (0.01- 0.02)	Azevedo et al. (2012b)
<i>Cathorops spixii</i> (liver)	5					4,838 (3,419- 5,501)	0.25 (0.25- 0.26)			1.11 (0.95- 1.21)	Azevedo et al. (2009a)
	15		0.02- 1.24		1.08- 4.78				0.02- 0.58	100- 850	Azevedo et al. (2012a)
	20						1.04				Azevedo et al. (2012c)
	225	0.01	0.34 (0.11- 1.58)	10.21 (0.08- 39.28)	41.5 (0.1- 146.7)				<0.09	0.86 (0.11- 6.39)	243.82
<i>C. spixii</i> (muscle)	152						0.1 (<0.03- 0.35)				Azevedo et al. (2009b)
	60						0.08 (0.02- 0.35)				Azevedo et al. (2011)
	225	1.15 (0.0- 5.7)	4.54 (<0.11- 13.6)	0.08	0.1			119.53 (<0.1- 339.3)	14.64 (<0.1- 73.2)	23.07 (9.1- 65.57)	
<i>C. spixii</i> (gills)	15		0.001- 0.005		0.15- 0.83				0.04- 0.41	145- 926	Azevedo et al. (2012a)
<i>Micropogonias furnieri</i> (muscle)	11						0.24 (0.11- 0.44)				Curcho et al. (2009)
<i>Mugil curema</i> (liver)	156				406 \pm 182	791 \pm 260				116 \pm 17	Fernandez et al. (2014)
<i>M. curema</i> (kidney)	149				6.6 \pm 2.3	791 \pm 260				59 \pm 11	

CONTINUATION TABLE 2.

Action levels	n	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Zn	Reference
		1.0	1.0	0.1	30.0		0.5	5.0	2.0	50.0	Brazil (1965)
		1.0	0.05 to 0.3				0.5		0.3		ANVISA (2013)
Fish species		1.0	1.0				1.0		2.0		FAO/WHO (2004)
			0.1 to 1.0				0.5		0.2 to 2		EC (2006)
		1.0	0.05				0.5		0.3		MERCOSUL (2011)
Bivalve molluscs			1.0						1.5		EC (2006)
		1.0	2.0				0.5		1.5		MERCOSUL (2011)

*Bioaccumulation tests using animals from Trapandé Bay and exposed to CIEC sediments; NR = Not reported; DL = Detection limit.

In a recent paper, Gusso-Choueri et al. (2018) reported the presence of high levels of metals and As in muscle from *C. spixii* specimens collected in the Mar de Cananéia channel. These concentrations exceed the action levels for human consumption (Table 2). The maximum concentrations (wet weight basis) of metals in tissues from *C. spixii* specimens from the CIEC were reported by Gusso-Choueri et al. (2016). The levels found in the liver were 1.58mg kg⁻¹ of Cd, 39.28mg kg⁻¹ of Cr, 146.70mg kg⁻¹ of Cu, 6.39mg kg⁻¹ of Pb and 537.84mg kg⁻¹ of Zn. In muscle, the maximum concentrations (ww) found were 5.73mg kg⁻¹ of As, 13.64mg kg⁻¹ of Cd, 73.22mg kg⁻¹ of Pb and 65.57mg kg⁻¹ of Zn. Arsenic, cadmium and lead values were found to be above the limits recommended by both national and international regulatory agencies (Table 2), whose recommended limits are 1.0, 0.2, 0.05mg kg⁻¹, respectively (FAO/WHO, 2004; EC, 2006; ANVISA, 2013). The reported concentrations are alarming, particularly for having been found in the edible portions of a species commonly consumed in the region.

In addition to their presence in commercial species, metals were also found in *Sotalia guyanensis* cetaceans (Salgado, 2015) and *Chelonia mydas* turtles (Barbieri, 2009) from the CIEC. The main metals found in the liver of the *S. guyanensis* (ww) were Zn (37.7mg kg⁻¹), Pb (1.94mg kg⁻¹), Cu (14.18mg kg⁻¹), Cd (0.07mg kg⁻¹) and Cr (2.84mg kg⁻¹); the concentrations of Pb were higher than those found in livers of *Sotalia fluviatilis* off the coast of Ceará, northeast Brazil (Monteiro-Neto et al., 2003), while the concentrations of Cd were low and comparable in both studies. According to Salgado (2015), Pb showed the highest mean values

ever described for the species. Regarding *Chelonia mydas*, elevated levels of Cu and Ni were found in the liver, with average dry weight basis values of 39.9mg kg⁻¹ and 0.28mg kg⁻¹, respectively. The highest levels of Cd were found in the kidneys of these animals; the average concentration was 2.18mg kg⁻¹ (dry weight basis). Lead concentrations were relatively high in both the liver and the kidneys, with average values of 0.37 and 0.56 (dw), respectively (Barbieri, 2009). In general, concentrations were higher than those observed in sea green turtles (*C. mydas*) and hawksbill turtles (*Eretmochelys imbricata*) from northern coast of Bahia (Macêdo et al., 2015), but comparable or lower than those detected by Silva et al. (2014) in *C. mydas* from the S and SE coast of Brazil. In the case of APA-CIP, although these animals were found in the estuary, the sources of contamination may have been elsewhere, since turtles migrate long distances between feeding areas.

EFFECTS OF STRESSORS

SEDIMENT TOXICITY: ECOTOXICOLOGICAL STUDIES

Since 2010, the São Paulo State Environmental Agency (CETESB) has been monitoring the sediment quality of two water bodies in the CIEC (three stations in the Mar Pequeno channel and three in the Mar de Cananéia channel) through biannual samplings. This monitoring includes analyses based on specific indices for the microbiological, chemical and ecotoxicological quality of coastal sediments. The ecotoxicological assessment consists of chronic toxicity assays

with embryos of the sea urchin *Lytechinus variegatus* (sediment/water interface) and acute toxicity assays with the amphipod *Leptocheirus plumulosus* (whole sediment). According to the percent of affected organisms in the ecotoxicological assays, sediments were classified as presenting “very good,” “good,” “fair,” “poor,” or “very poor” quality. The 2015's CETESB's annual report of the quality of saltwater and brackish waters of the state of Sao Paulo (relative to data collected in 2014), sediments from the three sampling stations located in the Mar Pequeno channel presented acute toxicity and the sediment quality was considered “very poor” (mortality of *L. plumulosus* \geq 50%). Regarding Mar de Cananéia channel, acute toxicity was not observed. However, sediments from two stations showed chronic toxicity and the quality of the sediments was respectively classified as “fair” (51–70% of normal *L. variegatus* larvae) and “very poor” (normal larvae $<$ 25%) (CETESB, 2015).

Previous assessments performed by the CETESB showed that the quality of sediments from the Mar de Cananéia channel was occasionally classified as “poor” (for example, in 2010). In 2011, sediments did not exhibit evidence of toxicity, but in 2012 sediments from all the sampling stations of Mar de Cananéia channel were classified as “very poor”. There was evidence of *L. plumulosus* mortality above 50%, and less than 25% of *L. variegatus* larvae were normal (CETESB, 2012; 2013). In 2013, the quality of sediments from the Mar Pequeno channel was considered “good” (CETESB, 2014). In the second half of 2013, the concentration of Pb was 30.7mg kg⁻¹ in a sample located in the Mar Pequeno channel; this concentration is above ISQG for coastal sediments (CCME, 2002). As for the Mar de Cananéia channel, chronic toxicity was reported for one of the three tested sediments and the sediment quality was considered “poor”. Furthermore, the CETESB report (2014) notes the presence of metals with values below but close to ISQG.

In broader ecotoxicological studies, surface sediment toxicities in the Mar Pequeno and the Mar de Cananéia channel have also been conducted (Araújo, 2014; Cruz et al., 2019). In these studies, sediment samples collected close to the mouth of the Valo Grande Canal and from the central region of the Mar Pequeno channel (close to the Pedra do Tombo region) exhibited acute toxicity for *T. viscana* during the rainy seasons. Araújo (2014) points to the influence

of climatic factors on contaminated material transport. The author found higher toxicity levels in the sediments that were more strongly influenced by the Valo Grande Canal, areas which themselves respond synchronously to the increase in RIR flows during periods of high rainfall in the Ribeira Valley. Sediments from the Mar de Cananéia channel affected the embryo-larval development of *L. variegatus* during the rainy seasons (Cruz et al., 2019), results which also represent chronic toxicity. Besides, the samples collected during the dry season were more toxic in the Mar Pequeno channel, while those collected during the rainy season were more toxic in the Mar de Cananéia channel. This difference suggests that fine suspended particles from the RIR are transported into the southern portion of the CIEC; as previously discussed in the section “exposure characterization to the stressors” of this review.

In another ecotoxicological study at Mar de Cananéia channel, Cruz et al. (2014) found acute and chronic toxicity in surface sediments from areas surrounding the southern portions of Cananéia Island and Comprida Island. The acute toxicity was characterized by the lethal effects on the burrowing amphipod *Tiburonella viscana*, in stations located close to the urban center. Then, toxicity was attributed to sources located in the city of Cananéia. All of the sediment samples collected from a total of eight sampling sites exhibited chronic toxicity for the benthic copepod *Nitocra* sp. (effects on organism fecundity); the authors suggested that metals from the RIR were the cause of chronic toxicity.

As previously mentioned, some studies have associated changes in the hydrological regime of the RIR basin with seasonality (Corsi and Landim, 2003; Costa et al., 2009), with increased amounts of metals carried to CIEC during the rainy season (Cunha et al., 2007). Since the depositional areas along the CIEC may change throughout the year, the areas defined as having more extensive contaminated sediment deposition may change seasonally; and so do the areas of risk to the biota may change seasonally as well. The literature showed that toxicity is mainly associated with fine sediments, such as those collected at the Mar Pequeno and the Mar de Cananéia. Some authors suggested that metals can be transported southward (Tramonte et al., 2018; Cruz et al., 2019), and our analysis of the published information allow

us to conclude that depositional areas in CIEC change over time, being influenced by rainfall indices and the interaction between inputs of freshwater and currents waves. Therefore, greater freshwater inflow may influence the transport of sediments and contaminants, as the maximum depositional areas tend to migrate towards south during the rainy season.

In addition to the short-term and long-term lethal effects, the adverse effects of metals may cause damages at the molecular, biochemical, cellular, and physiological levels. Therefore, biological responses to environmental aggressions should not be identified only based on the structure of the ecosystem (such as biological populations and communities), but also at more basal levels of organization, such as intracellular biochemical reactions (Bayne et al., 1985). In this way, greater potential damages to biological organization can be anticipated.

In the CIEC, biochemical biomarkers were used by Azevedo et al. (2009b) on *C. spixii* collected in the Mar de Cubatão and Mar de Cananéia in order to assess exposure and the possible effects of metals. No changes to metallothionein content, lipid peroxidation (LPO), or δ -Aminolevulinic acid dehydratase enzyme (δ -ALAD) activity were observed. Given these results and the lack of significant Hg contamination in fish tissues ($0.09 \text{ mg kg}^{-1} \text{ ww}$), the authors did not consider the area to be impacted. Araújo (2014) analyzed biochemical biomarkers in the *Callinectes danae* crab collected in the CIEC, and the crustaceans exhibited changes in glutathione peroxidase (GPx) activity, glutathione S-transferase (GST) and LPO, as well as DNA damage (strand breaks). In an integrated multivariate approach to estuarine sediment contamination, the authors found that metal concentrations in these matrices are enough to produce negative effects on the native biota, especially due to the activation of depuration processes and the secondary production of reactive oxygen species. Metal contamination may have activated the antioxidant system, causing lipid peroxidation in the tissues of *C. danae*. They also affirmed that the animals collected during the winter exhibited more enzyme activity than those collected during the summer, thus providing evidence that seasonality has a strong influence on biomarker response in the animals studied. According to the study, the sediments collected in the central areas of the Mar Pequeno and the Mar de

Cananéia exhibited higher metal concentrations. The crabs collected in the Mar de Cananéia channel experienced a more substantial response to the biomarkers during the summer, as was observed through LPO and DNA damage. Meanwhile, organisms from the central area of the Mar Pequeno channel exhibited similar qualitative results in the winter, with an increase in GPx enzyme activity. The study also found acetylcholinesterase (AChE) inhibition during the summer. According to Devi and Fingerman (1995), AChE inhibition has great potential for serving as a biomarker for metal pollution. However, Araujo (2014) also stated this result could be caused by the use of pesticides along RIR basin.

In a more recent study assessing the environmental quality of the CIEC, a set of analyses was used in which biochemical biomarkers served as a tool in different organs from *C. spixii* (Gusso-Choueri et al., 2015). The authors analyzed GST, GPx and AChE activity and also quantified metallothioneins, GSH, LPO and DNA damage. They concluded that Pb may be highly relevant in the neurotoxicity experienced by *C. spixii*, as shown by the AChE activity in contaminated fish. In addition, they observed seasonal differences in the adverse effects on fish in the northern section of the CIEC relative to the southern section. During the dry season, metal concentrations in the organisms and their responses to biomarkers were greater in the southern section of the CIEC, a finding that reflects the influence of the city of Cananéia. However, during the rainy season, the most highly affected organisms were those collected close to the Valo Grande Canal, in the central area of the Mar Pequeno channel (the northern section), and from the Mar de Cananéia channel close to its meeting with the Mar Pequeno. These results reflect the influence of the Ribeira de Iguape River on toxicity.

The rainy period was also influential on the results of cytogenotoxicity studies on fish collected at the Mar de Cananéia channel. Kirschbaum et al. (2009) evaluated erythrocytes from *Centropomus parallelus* and found nuclear abnormalities (NAs) to be slightly higher in the summer (rainy season) than in the winter (dry season). However, these abnormalities were not high enough for the location to be considered impacted. Azevedo et al. (2012d) also identified higher NA frequencies (‰) in *C. spixii* during the summer. In light of the evidence outlined herein, it is possible

that metals are still being transported from the RIR to the southern portion of the CIEC, particularly during periods of high rainfall.

Although the entire region of the CIEC has often received a blanket description of an area of reference for environmental studies (Azevedo et al., 2009a; Azevedo et al., 2009b; Kirschbaum et al., 2009; Azevedo et al., 2011; Azevedo et al., 2012a; Azevedo et al., 2012c), the integration of data on metal sediment contamination and on the effects of this contamination on biological systems indicates that some portions of the estuary are clearly impacted. Furthermore, even if contaminants are at only moderate levels, they are still harmful to biota in many instances, such as cytogenotoxic and biochemical effects. In these cases, in addition to assessing the presence of stressors, such as metals the use of biomarkers provides useful information for protective management of CIEC.

Overall, the variations in toxicity relative to seasonality provide evidence of the influence of abiotic parameters on the bioavailability of contaminants in aquatic systems, since pH, salinity and temperature can all modify the bioavailability and/or the uptake of contaminants in these systems. The variations in toxicity also depend on spatial variation, which can occur as a function of the distribution and deposition of sediments. The samples with greater amounts of organic material and finer-grained sediment fractions (silt and clay) exhibited higher concentrations of most of the elements found in the CIEC sediments. Thus, any considerations regarding the environmental quality of the Cananéia-Iguape Estuarine Complex should consider the space-time variability of contamination.

CONCLUSIONS

As outlined in this review, studies on the CIEC suggest that contamination seems to be increasing in the region as a result of different sources. A set of contamination sources within the CIEC is close to the urban center of the city of Cananéia. On the other hand, metals associated with suspended fine particles are clearly introduced into the system through the Valo Grande Canal. This association indicates that the former mining sites are the primary sources of metals to the CIEC. Both particulate transport across the estuary and resuspension processes are

influenced by tidal movements and contribute to differences in surface sediment composition and toxicity, though they are not always established by local inputs. Therefore, areas with a higher presence of metals in the sediments are not always those, which are closest to the source.

The data available provides evidence of significant variation in metal concentrations between the northern and southern sections of the estuary. Concentrations of metals are clearly higher in the north portion of the estuarine complex. In the southern section, metals in sediments and biota of Mar de Cananéia are higher than Mar de Cubatão. This finding may be associated with the circulation of water within the estuary, which favors the sedimentation of particles and contaminants in the Mar de Cananéia channel, and its transport south during short-term episodes of extreme rainfalls.

An essential factor to highlight in this environmental protection area is that, though the CIEC is not highly polluted, some areas exhibit metal contaminations, which exceed sediment quality guidelines (CCME, 2002). Also, this finding was represented in the contamination found in species of fish that most commonly live on the bottom of the estuary channels but which may inhabit other strata, albeit on a small scale. The metal concentrations above the limits recommended for human consumption that were found in commonly consumed species are alarming and reflect the potential risk to the local human population. In some portions of the CIEC, the bioavailability of metals found in the sediments was reflected also through the ecotoxicological data. In these regions, metals are not only available to the point of causing negative effects on the biota, but can combine with other factors, such as ammonia, and produce toxicity. Moreover, toxicity tends to be associated with muddy sediments, indicating that depositional areas are of main concern within the estuarine system.

Marine protected areas (MPA) have been established as an important strategy to preserve ecosystems and to avoid negative impacts due to anthropic activities (Day et al., 2012). Brazilian legislation has also placed the CIP-PA in a protection category that should achieve a sustainable balance between the anthropic uses of the natural resources and the protection of the natural ecosystems (Moraes, 2004). However, occurrence of toxicity and metal

contamination in CEIC sediments represent threats to CIP-PA conservation objectives and indicate that the protection status is not being totally achieved. In fact, designating an area as protected, by itself, cannot ensure its protection; thus, pollution has been detected in MPAs (Terlizzi et al., 2004; Araujo et al., 2013; Rodrigues et al., 2013). This kind of situation has been discussed in recent years (Barber et al., 2004; Cicin-Sain and Belfiore, 2005; Lausche, 2011); and as Jameson et al. (2012) argue: “*an area is not magically or instantaneously ‘protected’ via an MPA designation process*”. Uncontrollable external pollutant sources are not situated in side MPA, and this disturb can affect the ecosystems situated within these areas (Kelleher, 1999). Such sources are frequently beyond the direct control of MPA managers and their impacts are not easily mitigated. Under such conditions, lack of effectiveness in MPAs may occur, and when the management of a protected area does not properly address the surrounding areas, protection may not be successful. According to Salm et al. (2000), one of the first steps taken is to design an appropriate management plan for controlling the sources and avoiding pollution should be developed. Such plan is required to guarantee the protection of CIP-PA, by the development of policies to control the contamination sources located upstream (especially former mining areas) and within the CIEC, such as those situated in the cities of Iguape, Cananéia and Ilha Comprida (sewage, urban drainage, marinas, among others).

The MPA plans must go beyond identifying sources of pollution and must search for information on potential pollutants, their concentrations, and their biological effects. The ecotoxicological data are limited to the point that ecological consequences of metals on biodiversity and productivity inside this area are still unknown, likewise of the majority of the MPAs around the world (Abessa et al., 2018). Furthermore, the current review highlights the importance of further research in this MPA, which include the use of biomarkers and others ecotoxicological tools, in order to associate the presence of contaminants with negative biological effects. Such tools provide information for making sound decisions regarding environmental health status and they support the development of management plan for the strategy of protection.

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AUTHOR CONTRIBUTIONS

F.C.P: Conceptualization; Data curation; Investigation; Writing – original draft; Writing – review & editing;
D.M.S.A.: Supervision; Funding acquisition; Methodology; Project administration; Writing – review & editing.

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