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Metal concentration in ghost shrimp and contamination levels of sandy beaches contrasted with anthropogenic impacts in Southeast Brazil

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Abstract This study evaluates the contrast in the concentration of seven potentially toxic elements (As, Cd, Cr, Cu, Hg, Mn, and Pb) in tissues (G, gonads; H, hepatopancreas; and M, muscle) of the ghost shrimp Callichirus corruptus, as a response to sediment contamination in two sandy beaches in Southern Brazil with different anthropogenic status (JUR, Juréia; and STS, Santos). The biotic and abiotic samples were collected with a suction pump and subjected to metal quantification by atomic absorption spectrophotometry technique. In JUR, the sediment had Cr, Cu, and Mn concentrations two times lower when compared to STS ($t \le 7.80$; $p \le 0.01$), while STS had Hg concentrations between the Interim Sediment Quality Guideline (ISQG) and probable effect level (PEL) parameters. Three metals (Cd, Cr, and Cu) presented concentrations above the maximum tolerated

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J. José-Silva · M. A. A. Pinheiro Postgraduate Program in Coastal Environment Biodiversity, UNESP IB/CLP, São Vicente, Brazil e-mail: marcelo.pinheiro@unesp.br limit indicated by the Brazilian Health Regulatory Agency (Anvisa), with prawn bioaccumulation up to eight times greater in STS than JUR ($t \ge 4.42$; p \leq 0.03). Therefore, this study confirms higher metal concentrations ($\mu g/g$) in the biotic (Cd = 7.86 Cr = 11.95 and Mn = 19.38) and abiotic (Cd = 0.45, Cr = 3.13, Cu = 0.59, Hg = 0.49 and Mn = 45.61) compartments of Santos, which has a high human population density and a significant industrial and port complex, in contrast to Juréia, which is located in a highly conservation ecological station. Furthermore, the research presents novel information on trace elements in the sandy sediments of the studied sites. Additionally, it provides unprecedented evidence on metal concentration for C. corruptus, which can be used in monitoring programs for sandy beaches due to its metal bioaccumulation potential.

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Toxicity	

Abbreviations

As	Arsenic
ANOVA	Analysis of variance
ANVISA	Brazilian Health Regulatory Agency
Cc	Callichirus corruptus
Cd	Cadmium
CETESB	Environmental Company of the State of
	São Paulo
CIATox	Toxicological Information and Assis-
	tance Center
CL	Carapace length
Cr	Chromium
CLP	São Paulo Coastal Campus
CRUSTA	Crustacean Biology Research Group
Cu	Cupper
ESECJI	Juréia-Itatins Ecological Station
G	Gonads
GR	Gravel
Н	Hepatopancreas
HC1	Hydrochloric acid
HF	Sulfuric acid
Hg	Mercury
HNO ₃	Nitric acid
IB	Institute of Biosciences
IBGE	Brazilian Institute of Geography and
	Statistics
ISOG	Interim Sediment Quality Guideline
JUR	Juréia
LBC	Laboratory of Conservation Biology of
	Crustaceans and Coastal Environments
LD	Limits of detection
LO	Limits of quantification
M	Muscle
MTL	Maximum tolerable limits
Mn	Manganese
MGS	Median grain size
NIST	National Institute of Standards and
	Technology
ОМ	Organic matter
Pb	Lead
PEL	Probably effect level
RDSB	Sustainable Development Reserve of
	Barra do Una
RJ	Rio de Janeiro state
S	South

SA	Sand
SE-A	Upper stratum
SE-B	Lower stratum
SESSV	Santos-São Vicente Estuarine System
SI	Silt
SP	São Paulo state
SRM	Standard reference material
STS	Santos
UNESP	São Paulo State University
W	West
WW	Wet weight

Introduction

Sandy beach environments are subject to intense anthropogenic activity due to high population density in coastal regions, significant coastal development, and consequent pollution (Defeo et al., 2009; McLachlan and Defeo, 2018; Buzzi et al., 2022). Coastal ecosystems have undergone significant physicochemical changes, affecting the distribution of several invertebrate species (Belan, 2004; Wu et al., 2014; Cardoso et al., 2016; Cabrini et al., 2017; Wu et al., 2023), in terms of abundance (Osuala et al., 2018; Koziol et al., 2022) and diversity (Nwabueze et al., 2020; Wu et al., 2023). The unique characteristics of marine and estuarine beaches serve as important natural barriers to pollutants (Karlonienė et al., 2021; Hyndes et al., 2022; Corte et al., 2023) and provide other relevant ecosystem services such as organic and nutrient cycling and water purification (Defeo et al., 2009, 2021; Buzzi et al., 2022; Liang et al., 2024).

Despite the importance of marine coastal ecosystems, studies on pollutants in sandy beaches are scarce (Jonathan et al., 2011; Santhiya et al., 2011; Nagarajan et al., 2013; Corte et al., 2023). Metals stand out among such pollutants due to their wide distribution and association with industrial development (Cajaraville et al., 2000; Costa et al., 2021; Buzzi et al., 2022), which leads to persistence in the environment and toxicity to sediments and biota (Ahearn et al., 2004; Rainbow, 2007; Luoma and Rainbow, 2008; Cesar et al., 2012; Duarte et al., 2017; Pinheiro et al., 2017). Some metals are considered essential (e.g., Cu, Cr, and Mn) as they participate in biological processes, but they become toxic at high concentrations (Duarte et al., 2016). Other elements are non-essential (e.g., As, Cd, Pb, and Hg) and contaminate the environment and biota even at low concentrations (Eisler, 2009; Duarte et al., 2017).

Water acts as a transport matrix for potentially toxic elements, which can dissolve in water and undergo chemical changes, varying widely over time and distance from pollution sources (Harris and Santos, 2000; Raknuzzaman et al., 2016; Lin et al., 2021). These elements are also attracted to sediments, which become persistent and increase toxicity levels (Ahearn et al., 2004; Rainbow, 2007; Vilhena et al., 2013; Banci et al., 2017; Perina et al. 2018). Similarly, these contaminants accumulate in organisms and biomagnify throughout the food chain, causing irreversible damage to local biota (Luoma and Rainbow, 2008; Duarte et al., 2017; Trevizani et al., 2023). Thus, only 1% of pollution is associated with water, while the remaining 99% persists in beach sediments (Gaur et al., 2005; Bartoli et al., 2012; Vetrimurugan et al., 2016).

The main route of contamination for benthic invertebrates is through gills, direct skin contact, or ingestion of contaminated sediment and food (Rainbow, 2007; Duarte et al., 2016, 2017, 2020), resulting in low environmental preservation status and deleterious effects on the biota (García-Alonso et al., 2011; Castiglioni et al., 2018). Various invertebrate species have been shown to respond physiologically and genetically to different levels of metallic contaminants, reflecting the environmental contamination status of the studied location (Ryu et al., 2011; Rumisha et al., 2012; Cabrini et al., 2017). Therefore, several studies recommend using invertebrates to assess and monitor anthropogenic impacts and have confirmed physiological and genetic alterations (e.g., Goulart and Callisto, 2003; Pinheiro et al., 2012; Duarte et al., 2016, 2017; Pinheiro et al., 2017; Costa et al., 2021). Among the benthic invertebrates of sandy beaches, ghost shrimp deserve special attention as they are considered a "key species" for studying scenarios that promote changes in physicochemical parameters and the local community (Birkeland, 1989; Jones et al., 1994; Valls et al., 2015).

Callichirus corruptus (Hernáez et al., 2022) is a ghost shrimp (Callianassidae) endemic to Brazil, which promotes bioturbation of sandy beach sediments, causing significant changes to their textural and chemical composition (Klerks et al., 2007; Costa et al., 2022). Distributed along the entire 594

Brazilian coast (Hernáez et al., 2022), it excavates burrows and alters the structure of local communities by changing the biogeochemical cycles of the sediment (Posey, 1986; Ziebis et al., 1996; Rodrigues and Shimizu, 1997; Rosa et al., 2018; Constantino et al., 2024). Additionally, its burrows allow a high flow of water and incorporation of organic matter and associated pollutants (Abu-Hilal et al., 1988; Klerks et al., 2007), which interfere with various functional processes of marine sandy beaches (Rodrigues and Shimizu, 1997). This shrimp is also recognized as an important fishery resource due to its widespread use as bait in various coastal areas (Borzone and Souza, 1996). Its popularity can be attributed to its high attractiveness to fish and the ease with which it can be collected on sandy beaches (Peiró and Mantelatto, 2016).

Studies related to metal contamination have already been conducted on mangrove sediments (Pinheiro et al., 2012, 2017; Duarte et al., 2016) and dredging materials (Torres et al., 2009; Buruaem et al., 2013; Kim et al., 2016) from the Santos-São Vicente Estuarine System (SESSV). However, no research has yet assessed the concentration of these elements in the sandy matrix of local beaches. Similarly, there is a gap in studies quantifying metals in crustacean species living in beaches, with intensified studies developed in mangrove areas, especially with "uçá" crab species (Ucides cordatus), which is applied as sentinel species of this environmental quality. Therefore, the present study provides novel data on the metal concentration in a shrimp species (Callichirus corruptus) from the local beach environment, as well as in the sandy sediment of Santos' beaches (SP), in addition to aligning with Goal 14: Life Below Water, of the UN Sustainable Development Goals (United Nations, 2015).

Considering the significant contrast with human population density and anthropogenic activities along the Brazilian coast, comparing preserved and contaminated areas allows for assessing the effects of different concentrations of potentially toxic elements that cause irreversible damage to the local biota (Duarte et al., 2016, 2017). We hypothesize that the concentration of potentially toxic elements in the sediment and tissues of C. corruptus is higher on beaches with greater anthropogenic impact (Santos, SP) compared to an ecological station (Peruíbe, SP), with the following hierarchy of contamination in tissues: hepatopancreas > gonads > muscle.



The objective of this study is to quantify the concentrations of seven potentially toxic elements (As, Cd, Cr, Cu, Hg, Mn, and Pb) in the sediment and in three tissues (gonads, hepatopancreas, and muscle) of the ghost shrimp (*C. corruptus*) and to compare data obtained from two sandy beaches in southeastern

Fig. 1 Location map of two beaches in São Paulo state coast (Brazil), known as Juréia (JUR) and Santos (STS), sampled on April 7 and May 10, 2017. Description: The image consists of four maps. The two smaller maps provide location context: the map on the left illustrates the country and state where the research was conducted, while the map on the right pinpoints the two sampling areas within São Paulo state. Additionally, the image includes two larger maps: the upper map focuses on Santos Beach (STS), highlighting key enterprises and structures in the region, such as the Port of Santos (pink), the Subaquatic Dredged Material Disposal Area (yellow), VLI (lilac), Cosipa (purple), and the Cubatão Industrial Complex (orange). Conversely, the lower map depicts Juréia Beach (JUR), featuring the Juréia-Itatins Ecological Station (ESECJI) (dark yellow line) and the Barra do Una Sustainable Development Reserve (RDSB) (red line)

Brazil with different levels of anthropization: Juréia-Itatins Ecological Station Beach (less impacted environment) vs. Santos Beach (contaminated environment).

Material and methods

Studied areas

Samples were collected from two sandy beaches in southeastern Brazil, both located in the State of São Paulo: (1) Santos Beach (STS) sampled in April 2017 and (2) Juréia Beach (JUR) sampled in May 2017 (Figure 1). Santos Beach is in the municipality of Santos, on the central coast of São Paulo State, which has a high population density (418,000 inhabitants-IBGE, 2022). It hosts one of Brazil's most significant industrial hubs, such as the petrochemical industries (e.g., the Cubatão Industrial Complex), steel industries (e.g., Cosipa), and port transport and logistics (VLI) (Galvão-Filho, 1987; CETESB, 2021), as well as the Port of Santos, the largest in South America (Angeli et al., 2021). Consequently, it experiences various anthropogenic impacts and presents pollution sources, which significantly contaminate ecosystems and their organisms (Oliveira et al., 2008; Torres et al., 2009; Kim et al., 2016; Perina et al., 2018). Juréia Beach, on the other hand, is located in the municipality of Peruíbe, on the southern coast of the same state, located within the Juréia-Itatins Ecological Station (ESECJI) (Law no. 5.649/1987 - São Paulo, 1987; Sanches, 2004) and the Barra do Una Sustainable Development Reserve (RDSB) (Law no. 14.982/2013 - São Paulo, 2013), a Mosaic of Conservation Units (Law No. 12.406/2006 - São Paulo, 2006) governed by state legislation. The human population comprises 162 inhabitants, according to Duarte et al. (2016).

Sediment and crustacean sampling

A sampling area was established at the midpoint of each beach, where sediment and crustacean samples were collected (Figure 2). Twelve shrimps were captured using a simple suction pump positioned over the opening of each burrow, with 5 continuous suctions per burrow (see Rodrigues and Shimizu, 1997). The material (sediment/water) was deposited on a sieve (diameter: 60 cm; mesh: 12 mm). Intact specimens were placed in individual plastic bags, kept in thermal boxes with ice, and transported to the Laboratory of Conservation Biology of Crustaceans and Coastal Environments (LBC), part of the Crustacean Biology Research Group (CRUSTA) at UNESP IB/CLP, São Vicente.

Sediment for analysis was obtained from composite samples using the same suction pump positioned between the openings of three burrows to avoid bioturbation by the shrimp (JUR = $24^{\circ}26.23'$ S/04°73.55'W; STS = $23^{\circ}58.25'$ S/46°19.36'W). For each sample (*n* = 6/beach), five sediment columns (45 cm) were suctioned from each beach, with a minimum distance of 5 m between them. They were carefully placed on a plastic sheet, reserving the upper (SE-A: 0 to 15 cm) and lower stratum (SE-B: 30 to 45 cm). Each composite sediment sample (SE-A: n = 3; and SE-B: n= 3; for beach) comprised a mixture of five portions of upper and lower stratum, respectively, which were homogenized and reduced to 1 kg each (see Batley and Simpson, 2016). In the laboratory, each sediment sample was frozen until lyophilization. Three subsamples (15 g per stratum/beach) were kept, placed in labeled Falcon tubes (15 mL), and stored for metal quantification.

For each sediment sample, three replicates (100 g each) were reserved for granulometric analysis by beach following the methods indicated by Negreiros-Fransozo et al. (1991). These replicates were dried in a forced-air oven (60 °C for 72 h) until the dry weight was stabilized, followed by differential sieving into seven granulometric fractions (GR, gravel: ≥ 2 mm; sand (SA): very coarse sand, 2–1 mm; coarse sand, 1–0.5 mm; medium sand, 0.5–0.25 mm;



Fig. 2 Sampling design of the study developed in each beach studied in São Paulo state (Brazil), concerning to tissues from *Callichirus corruptus* (Cc) and of sediment stratum (SE-A: upper stratum; and SE-B: lower stratum). Description: the image is a schematic representation of the sampling design. On the left, there are nine test tubes representing three animals, vertically labeled as Cc I, Cc II, and Cc III. The test tubes are color-coded for different tissues: green for muscle, followed

by pink for gonads, and yellow for the hepatopancreas. In the center, there is a circle with a sand-like texture containing three smaller circles, each representing one of the animals. On the right, there is a rectangular section of sand, with a 45-cm ruler on its left and a suction pump on its right. Above and below the rectangle are test tubes, symbolizing the sediment replicates from the upper and lower strata, respectively

fine sand, 0.25–0.15 mm; very fine sand, 0.15–0.05 mm; and SI + CL, silt and clay: < 0.05 mm). Each beach's average weight (in grams) was calculated for each granulometric fraction, and the total weight for all fractions was summed to 1000 g. These data were processed using the *Sysgran* program (see Camargo, 2006) for verbal categorization of sediment composition and for the calculation of mean grain size (MGS), expressed by the equation MGS = $(\varphi 84 - \varphi 16)/4 + (\varphi 95 - \varphi 5)/6.6$ (see Folk & Ward, 1957). In this study, φ values were converted to millimeters using the equation MGS (mm) = $1/2\varphi$.

For each sample, five replicates (10 g each) of stabilized dry sediment were subjected to a muffle furnace (500 °C for 3 h) to quantify the organic matter (OM) content of the sediment (%) using the ash-free dry weight method. Processing of crustacean tissue samples

In the laboratory, each shrimp's carapace length (CL), from the postero-orbital margin to the posterior margin of the cephalothorax, was measured with a precision analogic caliper (0.05 mm). After blotting with absorbent paper, the total wet weight was recorded using a precision digital balance (0.01 g).

For metal analysis, three females per beach were separated due to their large size compared to males of this genus (Hernáez et al., 2019). They were dissected with scissors and tweezers to remove the three tissues under study (muscle, hepatopancreas, and gonads). Due to the small size of the first chelipeds in ghost shrimps, the muscle was removed from the abdomen. At the same time, gonads and hepatopancreas were extracted after a median-dorsal longitudinal incision of each specimen. Each tissue was placed in labeled Falcon tubes (15 mL) and frozen until analysis.

Quantitative analysis of metals

Tissue samples (muscular, gonadal, and hepatopancreatic) were immediately frozen after removal. All sediment samples (n = 6/beach) and each shrimp tissue sample (n = 3/tissue/beach) were lyophilized using a VirTis BenchTop Pro[®]-Scientific Products[®] equipment. Subsequently, samples underwent specific digestion and metal quantification procedures. For the analysis of the seven metals (As, Cd, Cr, Cu, Hg, Mn, and Pb), minimum masses were used for raw dried macerated sediment samples (1 g), dried macerated gonads, hepatopancreas (0.5 g each), and dried macerated muscle (2 g). Samples were mineralized after homogenization and weighed, followed by the addition of 6 mL of 65% HNO3 PA (Merck®) in a PTFE® reaction vessel, performing microwave digestion in a PROVECTO® DGT 100 plus, with a previously validated heating program specific to each matrix type. Calibration curves were obtained using certified primary standards (Fluka®, Merck®, and Sigma/Aldrich®) for each chemical element. Certified reference materials were used following NIST standards: SRM 1646a for sediment samples and SRM 1566b for tissue samples. Specific standard curves were defined according to detection and quantification limits using a hydride generator for Hg determination (Table 1). Qualitative/ quantitative metal readings in samples were conducted

Table 1 Limits of detection (LDs) and limits of quantification by atomic absorption technique (LQs) for seven potentially toxic elements (As, arsenic; Cd, cadmium; Cr, chromium; Cu, copper; Hg, mercury; Mn, manganese; Pb, lead) studied, as well the percentual (%) of recovery in tissues and sediments samples, according the methodology for quantifying metallic concentration ($\mu g/g$)

Metals	LD	LQ	% recovery of tissues	% recovery of sedi- ments
As	0.400	4.00	95	97
Cd	0.010	0.20	102	101
Cr	0.050	2.00	96	98
Си	0.020	1.00	98	99
Hg	0.005	0.05	105	101
Mn	0.020	1.00	99	101
Pb	0.050	0.50	98	101

with a GBC-AA 932 atomic absorption spectrophotometer, optimized according to the manufacturer's recommendations for each chemical element. All processes were conducted at the Toxicological Information and Assistance Center (CIATox) laboratory, IB/UNESP Botucatu.

Statistical analysis

Results were organized in spreadsheets and submitted to *R Studio* 2023.12.1 + 402 in the R environment (R Core Team, 2023) for graph construction and statistical analysis. Metal concentrations (μ g/g) recorded in dried sediment and dried shrimp tissues were subjected to homogeneity of variances (Levene's test) and normality (Shapiro-Wilk test). After confirming data as homoscedastic and normal (p > 0.05), variables were subjected to a parametric test (*t* test) comparing means of the same variable between the two beaches (STS vs. JUR).

Sediment contamination assessment for each beach per metallic element and its concentration in dried shrimp tissues were determined by comparing each metal concentration with regulatory threshold levels. For sediment, metal concentrations were compared to ISQG (Interim Sediment Quality Guidelines) and PEL (Probable Effect Levels) values provided by the Canadian Environmental Quality Guidelines (CCME, 2002). For shrimp, given that the entire animal is consumed, the sum of metal concentrations in the three analyzed dried tissues was compared to the maximum tolerable limit (MTL) for crustaceans provided by the Brazilian Health Regulatory Agency (ANVISA) (Brazil, 2022).

The hierarchy of metal concentration in dried shrimp tissues was established for each beach by comparing the mean values recorded for gonads, hepatopancreas, and muscle of the species based on ANOVA results and confirmed by Tukey's post hoc test. All statistical analyses were conducted with a minimum significance level of 5%.

Results

Shrimp biometrics

The females of *C. corruptus* at Juréia Beach (JUR) had a carapace length (CL) of 12.0 ± 1.5 mm (mean

 \pm standard deviation), which did not statistically differ from those at Santos Beach (STS), which measured 13.6 \pm 1.1 mm (t = 2.37; p = 0.08). This was also observed with the wet weight (WW) of these specimens, which did not differ between beaches: JUR: 4.7 \pm 2.6 g; STS: 14.1 \pm 4.9 g (t = 2.91; p = 0.06).

Mean grain size (MGS) and organic matter (OM) in sediment samples

The sediment from Santos Beach (STS) was classified as very fine sand (MGS: 0.078 ± 0.001 mm) with an organic matter content of $0.137 \pm 0.049\%$. In contrast, sediment from Juréia (JUR) was classified as fine sand (MGS = 0.129 ± 0.002 mm) and had an organic matter content of $0.032 \pm 0.006\%$. Statistical analysis revealed that the sediment from STS is significantly finer (t = 53.32; $p \le 0.01$) and contains a higher organic matter content (t = 6.62; $p \le 0.01$).

Metal concentration in sediment

All potentially toxic elements showed a normal distribution ($W \ge 0.89$; $p \ge 0.33$) and homosce-dastic variance ($L \ge 0.13$; $p \ge 0.12$), allowing their

Table 2 Concentrations (mean \pm standard deviation, in µg/g) of each metallic element (Cd, cadmium; Cr, chromium; Cu, copper; Hg, mercury; Mn, manganese) registered in the beach sediment samples (n = 6/beach) of Juréia (JUR) and Santos (STS), in São Paulo state coast (Brazil), obtained in May and April 2017, respectively. Quality parameters of the sediment

concentrations to be evaluated by parametric tests. The concentration of potentially toxic elements did not differ significantly between sediment strata (SE-A = SE-B) both for JUR (Cr, Cu, and Mn: $t \le 2.51$; $p \ge 0.13$) and STS (Cd, Cr, Cu, Hg, and Mn: $t \le 1.59$; $p \ge 0.09$). Therefore, these samples could be evaluated without differentiating strata (n = 6/ beach).

In STS, 71.4% of the studied potentially toxic elements was recorded (n = 5: Cd, Cr, Cu, Hg, and Mn), while only 42.9% occurred in JUR (n = 3: Cr, Cu, and Mn) (Table 2). The metallic element richness was 1.7 times higher in STS. The concentrations of Cu, Cr, and Mn were also significantly higher in STS than in JUR ($t \le 7.80$; $p \le 0.01$), varying from 1.5 to 3.8 times. In JUR, the hierarchical order of metallic element concentration in sediment was Mn > Cr > Cu, similar to that observed for STS, where two other non-essential potentially toxic elements were added: Mn > Cr > Cu > Cd > Hg.

Except for the Hg concentration in STS sediment (0.15 μ g/g), categorized as contaminated, the other potentially toxic elements presented concentrations below ISQG and PEL and were considered safe for both beaches.

are represented by ISQG (Interim Sediment Quality Guidelines) and PEL (probable effect levels), according to CCME (Canadian Environmental Quality Guidelines), where Min, minimum; Max, maximum; x, mean; s, standard deviation; t, t test

Metal	Beach	Concentrat	ion of metals (µg	/g)	t	CCME (2002)	
		Min	Max	$x \pm s$		ISQG	PEL
Cd	JUR	-	-	< LDM	_	0.70	4.20
	STS	0.25	0.61	0.45 ± 0.16			
Cr	JUR	1.21	2.74	$1.79 \pm 0.58a^{a}$	3.90	52	160
	STS	2.48	4.22	$3.13 \pm 0.61b$			
Си	JUR	0.26	0.56	$0.39 \pm 0.11a$	3.84	19	108
	STS	0.49	0.67	$0.59 \pm 0.07 b$			
Hg	JUR	-	-	< LDM	-	0.1	0.7
	STS	0	0.49	0.15 ± 0.23			
Mn	JUR	9.49	17.31	$12.03 \pm 3.03a$	7.80	-	-
	STS	34.66	61.12	$45.61 \pm 10.10b$			

^aMean concentration in the same metal, followed by distinct lowercase letters, differed significantly between the beaches studied ($p \le 0.05$)

Table 3 Concentrations (mean \pm standard deviation, in µg/g) of each metallic element (Cd, cadmium; Cr, chromium; Cu, copper; Mn, manganese) by *C. corruptus* tissues (*n* = 9/tissue: G, gonads; H, hepatopancreas; and M, muscle) obtained in two

studied sandy beaches (JUR, Juréia and STS, Santos), in São Paulo state coast (Brazil), obtained in May and April 2017, respectively

Metal	Local	Concentration of metals (µg/g)							
		G	Н	М	Total				
Cd	JUR	$0.25 \pm 0.08 \text{ A(a)}^{a}$	0.73 ± 0.16 B(a)	< LDM	$0.98 \pm 0.11a$	0.5			
	STS	$4.93 \pm 0.77 \mathrm{B(b)}$	$1.66 \pm 0.33 \text{ A(b)}$	$1.27 \pm 0.77 \; \text{A}$	7.86 ± 1.42b				
Cr	JUR	1.62 ± 0.93 A(a)	1.04 ± 0.41 A(a)	1.47 ± 0.35 A(a)	4.12 ± 1.04a	0.5			
	STS	$7.80 \pm 1.87B(b)$	2.43 ± 2.21 A(a)	1.72 ± 0.54 A(a)	$11.95 \pm 2.88b$				
Си	JUR	25.44 ± 9.60 A(a)	108.74 ± 120.20 A(a)	23.13 ± 5.94 A(a)	157.31 ± 130.00a	30.0			
	STS	109.66 ± 51.69 A(a)	145.33 ± 233.15 A(a)	$32.45 \pm 10.08 \text{ A(a)}$	339.69 ± 203.42a				
Mn	JUR	$1.07 \pm 0.07 \text{ A}(a)$	1.01 ± 0.44 A(a)	$3.37 \pm 0.74 B(a)$	$5.45 \pm 0.65a$	_			
	STS	$11.94 \pm 2.99B(b)$	2.72 ± 0.73 A(b)	4.73 ± 2.36 A(a)	$19.38 \pm 4.89 \mathrm{b}$				

^aMean concentrations of the same metal, followed by distinct lowercase letters, differed significantly between studied beaches ($p \le 0.05$) and those of a same metal and beach, followed by distinct uppercase letters, contrasting significatively among the tissues studied ($p \le 0.02$). Brazil (2013) presents the maximum allowable contamination limit for metals in crustaceans established by the "Agência Nacional de Vigilância Sanitária" (Anvisa)

Concentration of metals in dried shrimp tissues

Four potentially toxic elements (Cd, Cr, Cu, and Mn) were recorded in shrimp tissues (Table 3). Copper was the metal with the highest concentration in all evaluated tissues, ranging from 13.61 to 321.7 µg/g, although its total average concentration in the three tissues did not differ significantly between STS (339.6 ± 203.4 µg/g) and JUR (157.3 ± 130.0 µg/g) (t = 1.30; p = 0.21). This was also the case for each tissue when analyzed separately ($t \le 2.77$; $p \ge 0.10$). For the other potentially toxic elements (Cd, Cr, and Mn), the total average concentrations in shrimp from STS were three to eight times higher than in JUR ($t \ge 4.42$; $p \le 0.03$).

There was a differential accumulation of Cd, Cu, Cr, and Mn in the tissues of *C. corruptus* at the studied beaches. In gonads, Cd, Cr, and Mn accumulation differed significantly ($t \ge 5.12$; $p \le 0.01$). It was up to 10 times higher in shrimp from STS than from JUR. This was also observed in the hepatopancreas, with a significant contrast in the accumulation of Cd and Mn. The means in STS were higher than in JUR ($t \ge 3.45$; $p \le 0.03$), although there was no significant difference between the means of Cu and Cr between both beaches ($t \le 1.07$; $p \ge 0.40$). For muscle, there was no significant difference between the beaches for Cr, Cu, and Mn ($t \le 1.30$; $p \ge 0.25$). Regarding the maximum tolerable limits (MTL) of metals as established by ANVISA (Brazil, 2022), all shrimp tissue samples (n = 18) showed Cr contamination regardless of the beach, while for Cd, it was 61.1% (JUR: 55.6% > STS: 33.3%) and for Cu, it was 50% (STS: 88.9% > JUR: 44.4%). ANVISA does not present an MTL for Mn in crustaceans, making it impossible to evaluate the contamination percentage of this metal or compare the beaches.

Comparing the tissues of C. corruptus, the highest accumulation of Cd, Cr, and Mn occurred in the gonads of shrimp from Santos ($F \ge 3.86$; $p \le 0.02$), with concentrations 2.5 to 4.6 times higher than those of the other studied tissues. In Juréia, the highest Cd accumulation occurred in the hepatopancreas ($F \ge 4.59$; p = 0.02), surpassing the concentration recorded in the gonads by 3.5 times. There was also significant Mn accumulation in the muscle ($F \ge 5.61$; $p \le 0.02$), about 3.1 times higher than the concentrations in the other analyzed tissues. Thus, in STS, the hierarchy of Cd, Cr, and Cu accumulation in the tissues was G > H > M, contrasting with JUR, which was the inverse (H > M> G). However, the total average concentration of each metal in tissues showed a similar accumulation hierarchy for shrimp from Juréia (Cu > Mn = Cr > Cd) compared to those from Santos (Cu > Mn> Cr > Cd).

Discussion

The sediments from the studied beaches exhibited a distinct contrast in the concentrations of Cr, Cu, and Mn, which were consistently higher at Santos Beach (STS) than Juréia Beach (JUR). Cadmium (Cd) and mercury (Hg) were detected exclusively at Santos Beach. Notably, mercury levels at Santos Beach fell between the Interim Sediment Quality Guidelines (ISQG) and probable effect levels (PEL), indicating a threshold for the absence of adverse effects on associated biota. This observation underscores Santos as an area with higher environmental impact due to its greater human population density and the historical influence of anthropogenic activities, such as industrial (Cosipa, Cubatão Industrial Complex, VLI see Figure 1) and port complexes, relative to Juréia, which is situated within a less impacted area. The study also confirms the metal accumulation capacity of the ghost shrimp (C. corruptus), with variations observed among the analyzed dried tissues, particularly in the hepatopancreas, but also in the gonads and muscles. Human consumption of this crustacean from Santos Beach is not recommended due to elevated concentrations of Cd, Cr, and Cu, which exceed the levels set by the Brazilian Health Regulatory Agency (ANVISA). Cadmium is of significant concern.

Abiotic variables: metal concentration in sediment

The concentrations of the five potentially toxic elements (Cd, Cr, Cu, Hg, and Mn) were higher in sediments from Santos Beach than in those from Juréia Beach. This finding aligns with our hypothesis and is consistent with previous studies conducted in adjacent coastal environments. Notably, Banci et al. (2017) reported that sediment metal concentrations in mangrove areas were up to 2.4 times higher in Cubatão (Santos-São Vicente Estuarine System) compared to Juréia (Ecological Station), particularly for chromium $(6.1 \text{ vs. } 3.0 \text{ } \mu\text{g/g})$ and copper $(3.3 \text{ vs. } 1.4 \text{ } \mu\text{g/g})$. In the present study, average concentrations were lower for these two metals, likely due to differences in particle size between the sediments of these beaches. However, chromium concentrations (3.1 vs. 1.8 μ g/g) and copper (0.6 vs. 0.4 μ g/g) remained higher at Santos Beach compared to Juréia Beach. The elements Cr and Cu were found in higher concentrations in Santos, which may be related to the presence of the Port of Santos and untreated industrial effluents (Gonçalves et al., 2013; Angeli et al., 2021).

Surface estuarine sediments, especially from port channels, can exhibit even higher metal concentrations. For instance, Bordon et al. (2011) reported metal levels in the Santos Port Channel as follows: Cr (20.0 μ g/g), Hg (0.3 μ g/g), and Mn (272.5 μ g/g), which are up to 33 times higher than those found in the sandy sediments of Santos Beach (3.13, 0.15, and 45.61 μ g/g, respectively). The concentrations in dredging sediments from the Santos Port Channel are comparable to those in the region's mangroves (Buruaem et al., 2013; Cesar et al., 2014; Kim et al., 2016; Perina et al., 2018), regarding Mn (348.50 µg/g), Cd $(0.1 \text{ to } 3.1 \text{ } \mu\text{g/g})$, Cr (18.0 to 32.20 $\mu\text{g/g})$, Hg (0.3 to 0.5 μ g/g), and Cu (12.6 to 15.7 μ g/g). These values reflect similar magnitudes to those observed in the sandy sediments of the studied beaches. The highest concentrations of metals in surface estuarine sediments can be attributed to the average grain size and organic matter content (Perina et al., 2018), as sediments with smaller average grain sizes (MGS) and higher percentages of organic matter (OM) tend to exhibit higher metal concentrations (Uchimiya et al., 2010), as explained in detail in the paragraph below.

In these studies, metal concentrations in sediments are associated with particle size and organic matter content, with higher concentrations in finer and more organic sediments (Martinčić, et al., 1990). Martinčić, et al. (1990) and Uchimiya et al. (2010) confirmed that Cd, Cu, Pb, and Zn concentrations in dredging sediments showed a significant negative association with mean grain size (MGS) and organic matter content (OM) (n = 19; $r \ge -0.90$; p > 0.01). This is attributed to the high mobility, deposition, and complexation of metals in mangrove sediments, which are three to four times more organic than continental sediments (Jennerjahn and Ittekkot, 1997). Thus, OM and MGS are key factors influencing metal redistribution in sediments (Rahman et al., 2024).

The variation in metal concentrations across studies is linked to sediment particle size and organic matter content. Mangrove sediments, with higher organic matter content (6–15%) and smaller mean grain size (MGS < 0.063 mm), contain a significant percentage of finer-grained sediment (silt and clay, 38–51%), according to review of articles (Jennerjahn and Ittekkot, 1997; Sanders et al., 2012; Gomes et al., 2013; Tue et al., 2018; Allais et al., 2024). In dredging sediment studies, metals are associated with finer sediment fractions, particularly silt and clay (MGS < 0.063 mm), with percentages ranging from 80 to 95% and OM% between 8 and 19%, according to review articles (Kronvang and Cristiansen, 1986; Oyarzún et al., 1987; Holland and Elmore, 2008; Torres et al., 2009; Buruaem et al., 2013; Hamouche and Zentar, 2020). For the sediments analyzed in the study, sand was the predominant granulometric fraction at both beaches, differing in classification as very fine sand (MGS: 0.078 \pm 0.001 mm) in Santos and fine sand (MGS: 0.128 \pm 0.002 mm) in Juréia.

The organic matter (OM) content in the sediments of STS ($0.137 \pm 0.049 \%$) and JUR ($0.032 \pm 0.006 \%$) beaches also influences the concentration of potentially toxic elements (Sauve et al., 1998). Santos Beach is categorized as a low-energy dissipative beach due to its embayment and lower hydrodynamic activity, which allows for more significant organic matter deposition (Hernáez et al., 2019), which promotes metal complexation. In contrast, Juréia Beach has high-energy dissipative morphodynamics (Souza, 2012), where stronger longshore drift currents reduce sedimentation and organic matter incorporation, leading to lower metal retention.

At Juréia sediment beach, the hierarchy of average concentration for essential potentially toxic elements was Mn > Cr > Cu, whereas Santos Beach exhibited Mn > Cr > Cu > Hg > Cd. This hierarchy is consistent with previous studies in the same region (e.g., Bordon et al., 2011: Mn > Cu > Cr > Hg > Cd; Cesar et al., 2014: Mn > Cr > Cu; Perina et al., 2018: Cr >

Cu > Hg > Cd), although there were some inversions, especially for Hg and Cd at lower concentrations.

Contamination of coastal environments by potentially toxic elements is related to historical occupation and human population density, particularly in port regions and industrial complexes, such as in the municipality of Santos (Torres et al., 2009; Pinheiro et al., 2017). The Port of Santos (Figure 1), with industries like (VLI), plays a significant role in generating concentrations of Cu and Cr, which are highly adsorbed by sediments due to fuels (Costa, 2004; Angeli et al., 2021). Kim et al. (2016) noted that these metals (Cu, Cr, and Pb) frequently occur at high concentrations in untreated or poorly treated industrial effluents, likely due to the high number of petrochemical industries (Cubatão Industrial Complex) and steel industry (Cosipa) (see Figure 1) in the Santos-São Vicente Estuarine System (CETESB, 2021).

Mercury in Santos Beach sediment is particularly concerning due to its high frequency in the analyzed samples (66%) and concentrations between ISQG and PEL values (0.1 and 0.7 μ g/g, respectively), reflecting its high toxicity. Mercury contamination in Santos is associated with port activities (Hortellani et al., 2008) and industrial sources, such as petrochemicals, fertilizers, and landfills (Perina et al., 2018).

A global comparison of metallic element concentrations in sandy beaches reveals that the sediments in the present study showed lower values for Cr and Cu compared to other locations (Table 4). However, the average Cd concentration in Santos Beach $(0.45 \ \mu g/g)$ is comparable to that of other urban beaches, ranging

Table 4	Concentration	(mean, in $\mu g/g$)	of metals (Cd,	cadmium; Cr	, chromium; (Cu, copper;	Hg, mercury; M	(n, manganese)	in sandy
beach se	diments around	the world. High	ner concentratio	on values of ea	ich metal are	represented	in bold face		

Beach	Country	Concentration of metals (µg/g)					Type of metal digestion	Authors (year)	
		Cd	Cr	Cu	Hg	Mn			
Acapulco	Mexico	-	17.9	42.8	-	26.6	HCl	Jonathan et al. (2011)	
Aqba	Jordan	7.8	92.1	14.0	-	321.5	HNO ₃ , HC1O ₄ and HF	Abu-Hilal et al. (1988)	
Chennai	India	0.3	14.1	4.0	-	46.8	HCl and HNO ₃	Santhiya et al. (2011)	
Durnford	South Africa	0.4	11.4	5.0	-	107.1	HNO ₃ and HCl	Vetrimurugan et al. (2016)	
Espinho	Portugal	-	44.0	371.4	-	476.1	HCl, HNO3 and HF	Vidinha et al. (2006)	
Kerela	India	3.6	80.9	76.7	-	-	HNO ₃	Suresh et al. (2015)	
Miri City	Malaysia	-	126.2	42.9	-	26.6	HNO ₃ and HCl	Nagarajan et al. (2013)	
Rio del Plata	Uruguay	0.3	15.1	-	-	-	HCl	Castiglioni et al. (2018)	
Juréia	Brazil	-	1.8	0.4	-	12.0	HNO ₃	Present study	
Santos	Brazil	0.5	3.1	0.6	0.2	45.6	HNO ₃	Present study	

from 0.30 μ g/g (Chennai, India—Santhiya et al., 2011; Montevideo Bay—Castiglioni et al., 2018) to 0.40 μ g/g (Richards Bay, South Africa—Vetrimurugan et al., 2016). Conversely, Kerala Beach in India (Suresh et al., 2015) exhibited a Cd concentration of 3.60 μ g/g, approximately seven times higher than that at Santos Beach. The average Mn concentration at Santos Beach (45.61 μ g/g) was like that of Chennai Beach, India (46.80 μ g/g—Santhiya et al., 2011). However, concentrations at beaches under intense port influence and with high levels of untreated domestic and industrial waste can be seven to 10 times higher (Abu-Hilal et al., 1988; Vidinha et al., 2006).

Biotic variables: concentration of potentially toxic elements in *C. corruptus*

At Santos Beach, the highest concentrations of four potentially toxic elements (Cd, Cr, Cu, and Mn) were recorded in the tissues of the shrimp C. corruptus. These concentrations were up to eight times higher than those at Juréia Beach, particularly for Cd, Cr, and Cu, which exceeded the maximum tolerable limit (MTL) established by ANVISA (Brazil, 2022) at both beaches. Copper is an essential metal for decapod crustaceans, primarily associated with hemocyanin, a hemolymph protein responsible for oxygen transport (Rainbow, 2002; Terwilliger, 2015). In addition to its role in respiration, hemocyanin helps maintain relatively stable copper concentrations in crustaceans, facilitating the transport and accumulation of this metal in other tissues (Rtal and Truchot, 1996). The higher Cu concentrations in shrimps from Santos Beach (339.69 µg/g) compared to Juréia (157.31 µg/g) clearly illustrate this phenomenon. Excess copper was immobilized in the hepatopancreas of C. cor*ruptus*, regardless of the beach (JUR: $108.74 \mu g/g$; STS: 145.33 μ g/g). Such high copper concentrations in the hepatopancreas have been previously reported for other decapod crustaceans, including the lobster Homarus gammarus (Clark, 2001).

For the non-essential metals that exceeded the MTL (Cd and Cr), *C. corruptus* specimens from Santos exhibited concentrations up to eight times higher than those from Juréia (Cd: 7.86 vs. 0.98 μ g/g; Cr: 11.95 vs. 4.12 μ g/g). Cadmium concentrations were highest in the gonads of shrimps from Santos (4.93 μ g/g), followed by the hepatopancreas and muscle

(1.27 µg/g), while in Juréia, cadmium levels were much lower and not detectable in the muscle, accumulating only in the hepatopancreas (0.73 µg/g) and gonads (0.25 µg/g). According to Vig (2003) and Cabrini et al. (2018), Cd is highly toxic to biota and ranks third in hierarchical toxicity among eight metals (Luoma and Rainbow, 2008). This metal is generally found at higher concentrations in the base of the food chain, in producers and primary consumers (Bargagli, 1998; Sun et al., 2020) and is depurated in brachyuran crustaceans during molting (Reichmuth et al., 2010).

Chromium was found at high concentrations at both beaches (JUR: 4.12 μ g/g; STS: 11.95 μ g/g). In Santos, the highest concentration was observed in the gonads, whereas in Juréia, it bioaccumulated more in the hepatopancreas of shrimps. Chromium has no biological function and has been reported to reduce survival and fecundity and even inhibit growth (Ochiai, 1995; Cabrini et al., 2018; Honig et al., 1980).

When comparing the same tissues in shrimps from the two studied beaches, the concentrations of Cr, Cu, and Mn in the hepatopancreas and muscle did not exhibit significant differences between individuals from JUR and STS. This finding suggests that the hepatopancreas effectively fulfils its biological detoxification role in C. corruptus, as supported by studies such as Ahearn et al. (2004), Zhu et al. (2018), and Rodrigues et al. (2022). The absence of significant differences in metal concentrations in the muscle between individuals from Santos and Juréia can be attributed to the biological functions of these elements, particularly manganese. Mn is an essential metal that participates in key metabolic pathways such as glycolysis and the Krebs cycle (Napierska and Skorkowski, 2001), which explains the higher concentrations observed in muscle tissues with high energy demands (Thibodeaux et al., 2009). Copper, on the other hand, is a critical component of hemocyanin, the oxygen-transport pigment in the hemolymph, which plays a vital role in supporting the metabolism of these animals (Terwilliger, 2015).

The hierarchy of metal accumulation in *C. corrup*tus tissues followed H > M > G for the four elements (Cd, Cr, Cu, and Mn) at Juréia Beach. At Santos Beach, the hierarchy was G > H > M for three metals (Cd, Cr, and Mn). Pinheiro et al. (2012) reported a similar sequence (H > M) for tissues of the crab *Ucides cordatus*, endemic to mangroves, though they did not analyze metal concentrations in gonads. The highest concentration of potentially toxic elements in crustaceans typically occurs in the hepatopancreas (Ahearn et al., 2004), which serves as the primary detoxification organ (Metian et al., 2010; Zhu et al., 2018; Rodrigues et al., 2022). This observation was confirmed in the present study based on the proportions and hierarchy of contamination among the tissues of *C. corruptus*, especially in Juréia. At Santos, metal contamination surpassed the detoxification capacity of the hepatopancreas, leading to greater bioconcentration in the gonads and even in the muscle of the shrimps.

Luoma and Rainbow (2008) and Liao et al. (2022) attribute this phenomenon to the biochemical composition of the hepatopancreas, which includes (1) lipids, particularly during the fattening phase of decapod crustaceans when the hepatopancreas enlarges (Wu et al., 2008; Lobato et al., 2013); (2) metallothioneins, sulfur-rich proteins responsible for sequestering potentially toxic elements, regulating metal homeostasis, and redistributing these elements to other tissues (Pourang et al., 2004; Liao et al., 2022; Baudrimont et al., 2003); and (3) glutathione-S-transferase, isoenzymes with detoxifying capacity that convert xenobiotic compounds into less toxic forms (Habig and Jakoby, 1981; Lobato et al., 2013). The higher metal accumulation in the ovaries of female C. corruptus from Santos can be attributed to increased lipid content due to vitellogenesis, which characterizes the ovaries of decapod crustaceans (Jeckel et al., 1996). The hepatopancreas's detoxification capacity, with redistribution to other tissues, has been documented for other decapod crustacean species (Metian et al., 2010; Zhu et al., 2018; Rodrigues et al., 2022) and may potentially cause reproductive damage (as suggested for Ucides cordatus by Duarte et al., 2016, 2017).

The high metallic concentrations found in ghost shrimps are likely due to their contact with external and interstitial water in their burrows, branchial respiration, and feeding (Morrison et al., 2011). This was particularly evident for *C. corruptus* at Santos Beach, where Cd and Cr concentrations (7.9 and 11.9 μ g/g, respectively) were up to five times higher than those recorded for *Callichirus laurae* (1.7 and 3.2 μ g/g, respectively) in Aqaba, Jordan (Abu-Hilal et al., 1988), due to the port activity in that location. Conversely, bioconcentrations of Cu and Mn were similar between these species, as they are essential metals for crustacean metabolism (Baden and Eriksson, 2006),

especially in antioxidant defense (Frías-Espericueta et al., 2022).

The maintenance of the bioconcentration hierarchy of potentially toxic elements by C. corruptus (Cu >Mn > Cr > Cd) at both beaches shows some similarity with results obtained by Cabrini et al. (2018) for two species of mole crabs (Hippidae) on the beaches of the State of Rio de Janeiro (RJ) (see Figure 1). Like ghost shrimps, Hippidae are filter-feeding decapod crustaceans associated with similar abiotic matrices (water and sediment). The metal hierarchies in their tissues are Cu > Cr > Cd and Cu > Cd > Cr, respectively. The high bioconcentration of copper (an essential metal) and low concentrations of cadmium and chromium (non-essential metals) observed in this study are consistent with findings from these studies. Similarly, the bioconcentration hierarchy for Callichirus laurae studied by Abu-Hilal et al. (1988) on Aqaba Beach (Jordan) was Cu > Mn > Cr > Cd.

Conclusion

The concentration of potentially toxic elements in the sediment of Santos Beach is notably higher compared to Juréia Beach. This is particularly concerning due to mercury levels falling between the ISQG and TEL parameters, suggesting potential risks. The elevated levels of pollutants in Santos Beach are likely associated with the high population density in the region, which contributes to pollution from various sources, including industrial effluents from the industrial complex and polycyclic aromatic hydrocarbons from ships at the Port of Santos, impacting the Santos-São Vicente Estuarine System.

The bioconcentration of potentially toxic elements in specimens of *C. corruptus* from Santos is also significantly higher than in those from Juréia. Notably, the concentrations of three metals (Cd, Cr, and Mn) exceed the maximum tolerable limits established by the Brazilian Health Regulatory Agency (Brazil, 2022). The absence of contrast in the concentrations of Cr, Cu, and Mn in the muscle tissue between individuals from both beaches suggests that these elements are essential for the physiology of these shrimps. The similar concentrations observed in individuals from both less-impacted and more-impacted environments likely reflect the indispensable metabolic roles of these elements. In Juréia, the metal concentration in ghost shrimps follows a hierarchy (H > M > G) like that reported for other decapod crustaceans. The hepatopancreas, known for its role in metal detoxification, appears to be operating beyond its capacity in Santos. Consequently, metals are being transported to other tissues, with significant accumulation observed in the gonads (ovaries) of females due to their high lipid content. This pattern is comparable to what occurs in the hepatopancreas and may have detrimental effects on the species in the study area.

These findings provide new insights into the concentration of potentially toxic elements in *C. corruptus* and highlight the importance of sandy beach conservation, as exemplified by the Juréia-Itatins Ecological Station.

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Data Availability No datasets were generated or analysed during the current study.

Declarations

Competing interests The authors declare no competing interests.

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