Accumulation of cadmium and lead in macroinvertebrates in relation to sediment concentration and the dynamics of environmental parameters in a tropical estuary of the Colombian Pacific

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Abstract

Estuaries provide a wide variety of ecosystem services; therefore, they are densely populated coastal regions with high activity and vulnerable to contaminants from natural and anthropogenic sources. The estuary of Buenaventura Bay is environmentally affected by liquid and solid wastes of anthropogenic origin, which arrive through the discharges of the main rivers of the region, as well as by gold mining and port activities, generating problems of environmental stress and contamination. For this reason, the main objective of the study was to determine how the environmental dynamics of the bay influences the processes of contamination and accumulation of heavy metals, cadmium (Cd) and lead (Pb), in sediments and in the muscle tissue of macroinvertebrates. For this purpose, macroinvertebrate samples were collected in two areas of Buenaventura Bay during three different climatic periods in 2018. In addition, sediment samples were collected for granulometric and organic matter data, and physicochemical water data were recorded. Cd and Pb concentrations in sediments and muscle tissue of four species were quantified. The concentrations of Cd and Pb in the sediments were undetectable and therefore did not exceed the maximum permissible values for marine sediment quality (Cd 0.6 mg/kg and Pb 35 mg/kg, TEL values, threshold effect level). The low levels of Cd and Pb in the sediments are due to their granulometric composition: high content of fine sand and low percentage of silt, clay and organic matter, conditions that do not favor the accumulation of metals in this matrix. The concentrations of Cd and Pb in the muscle of the organisms did not exceed the limit established for organisms for human consumption (crustaceans Cd 0.5 mg/kg and Pb 0.5 mg/kg; cephalopods Cd 1.0 mg/kg and Pb 0.3 mg/kg, fresh weight), indicating the absence of serious contamination by these two metals. It was found that the climatic seasons, as well as the peculiarities of each zone of the estuary and their interaction, influenced the dynamics of the physicochemical variables of the water and sediments of the bay. Climatic seasons also influenced the accumulation of Cd in the muscle of crustacean species, being higher under conditions of lower precipitation (dry and transitional seasons). Spatially, the outer zone of the bay showed a trend of higher Cd concentration in crustacean muscle. The environmental variables that best explained the Cd concentrations in the muscle of the four species were: temperature, salinity, and mean sand.

Introduction

Marine-coastal ecosystems, such as estuaries, are characterized by being complex and dynamic environments at the hydrological and oceanographic scales, with high biological richness (Day et al. 2013). They are of great global importance due to the wide range of ecosystem services they provide and are therefore highly populated coastal regions. As areas of high activity, they are sensitive and vulnerable ecosystems that act as filters and buffers of polluting substances and materials from the terrestrial system; either through natural phenomena or as a product of anthropogenic activities that take place there (Lu et al. 2018). Among the pollutants that can negatively affect these ecosystems are heavy metals, which have been the subject of research in recent decades (Cui et al. 2011; Thinh et al. 2018), especially those of a toxic nature that are not essential for any biological activity, functional or metabolic processes in organisms. These include arsenic (As), mercury (Hg), cadmium (Cd) and lead (Pb) (Bonsignore et al. 2018; Espina and Vanegas 2005; Páez-Osuna 2005; Ureña 2007). The last two, considered of high environmental priority at the international level, given the abundant natural contributions (geological weathering), as well as by the increase of those derived from various anthropic activities (Frías-Espericueta et al. 2010).

The main sources of anthropogenic contamination of Cd and Pb in river and marine systems are municipal, agricultural, and industrial wastes. For Cd, these are mainly those associated with the production of fertilizers (phosphates), lithium and nickel cadmium batteries, plastic stabilizers, pigments, alloys and galvanizing of metal objects (Frías-Espericueta et al. 2010; Páez-Osuna 2005). In the case of lead, waste from the production of batteries, especially for automotive use, paints, cables, plastics, metals, glass, ceramics, chemicals, and electronic equipment (Frías-Espericueta 2010; Sepúlveda 2018). When Cd and Pb enter the aquatic environment, like other heavy metals, they can form "insoluble precipitates as solutes bound to the surface of microparticles" (Barraza et al. 2018), or they can be soluble in water and react with organic matter, forming complexes and chelates that increase their solubility, availability, and dispersion (Barros-Barrios et al. 2016; Jorge-Panduro 2018). In this scenario, seafloor sediments play an important role as reservoirs of metals, thus their concentrations are higher than in water (Barraza 2018; Mero-Valarezo 2010; Rajeshkumar et al. 2018).

The process of heavy metal contamination in organisms, including Cd and Pb, begins in the tissues that facilitate their uptake. In invertebrates, the gills, digestive glands, and hepatopancreas are the organs where the greatest accumulation occurs (Kumar and Achyuthan 2007). Subsequently, metals are transported from the permeable surface to the different organs through the blood or hemolymph, binding non-specifically to the proteins present in this fluid (Ureña 2007). Normally, binding to these macromolecules can alter their conformation and biological activity, which is the main form of toxicity of metals (Ureña 2007). This is because metals have a high affinity to bind to the sulfhydryl (-SH), carboxyl (-COOH) and amino (-NH2) groups of proteins, inactivating enzymes (Amiard et al. 2006). Long-term exposure to high concentrations of metals causes changes in cell structure, physiological damage (alteration of osmotic pressure), genotoxic damage, changes in growth and reproduction of organisms, among others (Lu et al. 2018; Páez-Osuna 2005). For example, it has been observed in crustaceans and bivalves that Cd inhibits respiratory processes, decreases heart rate, deforms the shell, and that both Cd and Pb alter DNA repair mechanisms and can even affect the quantity and quality of sperm (Espina and Vanegas 2005).

It is important to mention that the availability, accumulation rate, and toxic effects of metals on organisms depend on various physicochemical and biological factors that vary both seasonally and geographically. First, the environmental variables alter the chemical speciation of metals in the environment, such as: temperature, pH, salinity, dissolved oxygen concentration, organic matter, adsorption, desorption and precipitation processes between water and sediment, etc. (Barraza et al. 2018; Bonsignore et al. 2018; Mero-Velarezo 2010; Shulkin et al. 2018). On the other hand, biological conditions also influence the rate of accumulation of heavy metals, such as, weight, size, sex, reproductive status, feeding habits, chemical affinities of the metals with the tissues of the species, absorption rate and capacity to purify toxic agents (Bonsignore et al. 2018; Páez 2005; Ureña 2007). All these biogeochemical processes that allow or not the bioaccumulation and biomagnification (via the food web) of metals occur during the environmental dynamics of estuarine circulation, in response to river runoff and seawater input, among other biogeochemical and hydrodynamic processes (Shulkin et al. 2018).

In the Southeast Pacific region, Colombia, Panama, Ecuador, Peru and Chile, environmental characterization studies were developed (between 1984 and 1986), focusing on physicochemical parameters of water quality (characterization of organic matter, suspended solids, nutrients, and microorganisms); gradually including the contribution of heavy metals and organochlorine pesticides in rivers, sediments, and typical organisms (Gutiérrez 1989). However, research on heavy metal contamination at the abiotic and biotic levels is still scarce. Specifically, for Colombia, these have been carried out in the bays of Tumaco and Buenaventura, focusing on mercury (Hg), a metal used in gold mining in the region (Espinosa 2010). Studies carried out in the 1980s on the Pacific coast of Colombia reported that in the tributaries of Tumaco Bay, Cd was not detected in most of the water samples; and in Buenaventura, this metal showed concentrations below the standard established for human consumption (0.01 μg/L). In the organisms studied, bivalve mollusks of the genus *Anadara*, Cd was found to exceed the limits established for human consumption (0.05 and/or 0.1 mg/kg), indicating serious contamination. Nevertheless, lead was not detected in the water, sediments, and organisms of Tumaco and Buenaventura bays (INDERENA 1987; Gutiérrez 1989). On the other hand, other studies in the Dagua River watershed and Buenaventura Bay have reported high levels of Cd, Pb, and Hg in water, sediments, marine macroinvertebrates (crustaceans and mollusks), and fish, exceeding the permissible limit for the time. The results indicated bioaccumulation in the organisms studied, suggesting a risk to consumers, although not to the ecosystem (Calero and Casanova 1997; Lucero-Rincón 2019; Velásquez and Cortés 1997).

Considering that the pollution problems of the Bay of Buenaventura are related to wastewater discharges from coastal populations, agricultural runoff, industrial waste, and waste from gold mining, which are transported to the estuary by the main rivers of the region, carrying various pollutants, including heavy metals (Casanova-Rosero et al. 2015; Díaz 2007; DIMAR-CCCP 2012; Invemar 2017; Tejada et al. 2003), that the sources of anthropogenic contamination of the heavy metals Cd and Pb are associated with the main pollution problems in the bay (Frías-Espericueta et al. 2010; Páez-Osuna 2005; Sepúlveda 2018); that the use of Cd and Pb in industrial derivatives of different anthropogenic activities is increasing, despite their toxic nature (Frías-Espericueta et al. 2010); and that Cd and Pb contamination has previously been reported in the Bay of Buenaventura, both in sediments and in organisms (Calero and Casanova 1997; Lucero-Rincón 2019; Peña-Salamanca et al. 2004; Velásquez and Cortés 1997), without regular monitoring in organisms. The objective of this research was to determine how the environmental dynamics of the bay influence the processes of contamination and accumulation of heavy metals, Cd and Pb, in sediments and in macroinvertebrate muscle tissue. Macroinvertebrates have been used as bio-indicator organisms to measure the environmental health of the ecosystem because they represent an integrated response to pollutant effects or environmental changes over time (Holt and Miller 2010; Marín-Guirao 2007), while physicochemical analyses of water and sediments only identify and quantify their environmental impact in isolation (Marín-Guirao 2007).

Materials and methods

Study area

This study was conducted in Buenaventura Bay (3°48'09.99" – 3°52'38.57" N; 77°06'30.75" – 77°09'25.96.96" W) (Fig. 1), one of the most important bays in the Colombian Pacific, classified as a complex tropical estuary due to its irregular geomorphology, variations in amplitude, depth and relief of the seafloor, bidirectional currents, fluvial and tidal currents, and alluvial beds (DIMAR-CCCP 2012). It has an approximate area of 70 km2 and an average depth of 10 m (Otero 2005; Peña-Salamanca 2008). It is located within the ITZ, which makes it a very rainy region (Cantera 2010; DIMAR-CCCP 2012), with a tidal regime between 3.7 and 5 m (Cantera and Blanco 2001), two annual rainfall periods, from April to June and September to November, with higher rainfall in the latter period of the year. Monthly precipitation of 300–850 mm (Cantera and Blanco 2001), together with the influence of the Dagua, Potedó and Anchicayá rivers (126 m3 /s and 112 m3 /s, respectively) (Díaz 2007; Gamboa-García et al. 2020), contribute to cloudy water conditions, low salinities (10–19 ups), sandy and muddy bottoms in the estuaries, given the contribution of sediment and organic matter, conditions that are accentuated during the rainy season in the vicinity of these tributaries (Cantera and Blanco 2001; Lemaitre and Alvarez-León 1992; Otero 2005).

Field phase

Macroinvertebrates and marine sediments were collected, and physicochemical parameters of the water were measured in two zones of Buenaventura Bay during three seasons throughout the year 2018, corresponding to different climatic seasons based on precipitation levels (Dry: March; Transition: July; Rainy: November). The two sampling zones were chosen based on the salinity gradient and the contribution of fluvial sediments: the Inner zone, characterized by a higher influence of fluvial discharges from the Dagua and Anchicayá rivers, and the Outer zone, by a greater influence of seawater (Fig. 1). To obtain the data, six replicates for each climatic period and sampling zone, for a total of 36 samples (6 replicates x 2 zones x 3 seasons = 36). Physicochemical water parameters were measured at a depth of one meter, while sediment and biological samples were collected at a depth not exceeding 6 meters, given the shallow conditions of the sampled zones.

Macroinvertebrates were sampled using the artisanal fishing method typical of the region, which is a trawl net with a working width of 8 m and a mesh size of 2.5 cm, in a moving boat for 10 minutes, at a speed between 3.1 and 4.0 km/h, with a trawling area of 900.7 m2. Before each trawl, the following parameters were recorded in the water: transparency, temperature, salinity, pH and dissolved oxygen using a Thermo Scientific portable multi-parameter probe and a Secchi disk for transparency. In addition, sediment samples were collected using a 4.5 cm diameter PVC tube. A time lag was allowed between replicates (10 min) to ensure that they were independent samples. Captured organisms and sediment samples were kept in cold storage at -20°C.

Laboratory phase

Captured macroinvertebrates were taxonomically identified to species level following the FAO Guide (Fischer et al. 1995) and the online database World Register of Marine Species (WoRMS 2022). The weight (g) and length (cm) of everyone were recorded. The length reported for crabs corresponded to the total length (TL) that encompasses the width of the carapace; for shrimp, the length from the rostral plate to the telson; and for cephalopods, the total mantle length.

Four of the most representative species of the bay, according to the Biological Value Index (BVI) calculated for this study, were sampled from the main muscle (approx. 2 g) for quantification of the heavy metals Cd and Pb, using sterile porcelain knives. For the swimming crab *Callinectes arcuatus*, the muscle sample was taken from the chelae; for the shrimp *Rimapenaeus byrdi* and *Squilla aculeata*, from the abdomen; and for the squid *Lolliguncula panamensis*, from the mantle. The quantification of these metals was carried out in muscle tissue, considering that the species studied are of fishery and food importance in the region, with muscle being the main consumption tissue. Therefore, the specifications of national and international standards that establish the maximum limits allowed in organism for human consumption were followed (European Commission 2021, EU Regulation 2021/1223; The Food and Agriculture Organization of the United Nations [FAO] and World Health Organization [WHO] 2019, CXS193-1995; Ministry of Health and Social Protection, Col 2012, Resolution 122).

At the same time, a subsample (approx. 2 g) of the first five centimeters of the sediment samples, previously homogenized with plastic spatulas, was extracted for the quantification of Cd and Pb. The first five centimeters of marine sediment were used, considering that a relationship has been demonstrated between the concentration of some metals and this portion of surface sediment; as well as an affection the benthic invertebrates and filter feeders in contact with these contaminated sediments (Hernández-Sánchez 2014). Both the muscle and sediment samples were arranged in Eppendorf tubes and submitted to the freeze-drying process at a temperature of -80°C, with a vacuum pressure of 0.120 millibars for 36 h.

The determination of the concentration of Cd and Total Pb (dry weight), in the muscle of macroinvertebrates and sediment, was carried out through the following steps: **Digestion process.** The sample was weighed and transferred to a beaker where 5 ml of nitric acid and 5 ml of perchloric acid were added to the muscle samples; and 7 ml of nitric acid and 7 ml of perchloric acid to the sediment samples. The samples were then heated at 200°C for three minutes for the muscle samples and for five minutes for the sediment samples. Once in solution, they were filtered through a 0.45 μm membrane and finally were calibrated to 50 ml with type 1 water. **Reading process.** The reading was performed in an atomic absorption spectrophotometer as recommended by Standard Methods for the Examination of Water and Wastewater 3111 B: Direct air-acetylene flame method. **Detection limits.** Sediment: L.D.Cd < 0.01151 mg/L and L.D. Pb < 0.12544 mg/L. Muscle tissue: L.D.Cd < 0.01267 mg/L and L-D. Pb < 0.07719 mg/L.

The remaining sediment samples were homogenized and separated into 2 fractions (approx. 50 g) and subsequently oven-dried in Petri dishes for 24 h at 110°C, until a constant weight was obtained. One of the fractions was used for the quantification of organic matter (OM) by the loss on ignition method, subjecting the dried sediment in a muffle at 450°C for 4h (Danovaro 2009; Luque 2003). The OM content of each sample was calculated following the equation proposed by Luque (2003). The other fraction was used for sediment granulometry by vibratory sieving for 7 min, with a set of sieves between 0.063 mm and 1.000 mm. The fraction retained on each sieve was weighed and classified according to the Udden-Wentworth scale (Wentworth 1922), as follows: coarse sand (> 0.500 mm), medium sand (between 0.500 and 0.250 mm), fine sand (between 0.250 mm and 0.063 mm), and silt-clay (< 0.063 mm). Finally, the grain-size profiles were plotted following the methodology proposed by Palacio-León et al. (2017).

Data analysis

Spatiotemporal variation of environmental parameters of water and sediments

Descriptive statistics were performed for all environmental variables of the water and sediments of the bay and normality (Shapiro Wilk) was assessed for the residuals of the models to be evaluated in the analysis of variance. The data that did not meet the assumptions of normality and heterogeneity of variance were transformed until the residuals of their models were normal. Next, an ANOVA was performed for each environmental variable, with climatic season, sampling zone and their interaction, as main factors; using a General Linear Model and the means of differences of squares, for which the type III error was analyzed. Subsequently, compliance with the alternate hypothesis was verified for each variable and factor separately; applying Tukey's test when the model was significant ($p < 0.05$). This, to identify between which climatic season or sampling zone, significant differences were found (Tukey, $p < 0.05$). The post-ANOVA results (Tukey, $p < 0.05$) were reported as letters, in the tables, together with the means and variances of each variable. All analyses were performed in RStudio.

Spatiotemporal variation of Cd and Pb content in muscle tissue of macroinvertebrates

The Biological Value Index (BVI) was calculated for all macroinvertebrate species, following the methodology proposed by Loya-Salinas and Escofet (1990), which indicates the most important species in the bay in terms of dominance, considering both relative abundance and frequency of occurrence of the species. Based on these results, four species were chosen for quantification of Cd and Pb in their muscle tissue (Fig. 2).

Figure 2 Invertebrate species used for Cd and Pb quantification in muscle. For each species, the results of the biological value index-BIVB are indicated. PUNT: Punctuation; RANK: ranking

Considering that the literature reports an effect of length (total length-LT) on the uptake and accumulation of Cd in macroinvertebrates (Páez-Osuna and Ruiz-Fernández 1995; Páez-Osuna 2011; Pourang et al. 2004), we proceeded to corroborate whether the length (LT) of the species of interest in this study, also presented such effect. For this purpose, the normality (Shapiro Wilk) of the residuals of the length (LT) variable was examined for each species. To the data sets that did not meet the assumptions of normality, the appropriate transformations were applied so that their distribution and homogeneity of variance were normal. Next, an ANOVA was performed for length, with the same criteria and specifications described in the previous section. Jointly, a

Pearson Correlation analysis (significant relationship, $r > 0.3$ and $p < 0.05$) and a Simple Linear Regression (significant model $p < 0.05$) were performed between the Cd content of the muscle of each species and the size of its individuals (LT). All analyses in RStudio.

Based on the results obtained in these analyses, the TL of each species was considered as a covariate in the analysis of variance-ANOVA for Cd content in muscle. But, before performing the ANOVA, the value of Cd concentration on LT of each individual was divided, thus reducing the effect of size, and being able to determine the specific effect of the climatic season and sampling zone on the Cd content in the muscle tissue of the four macroinvertebrate species. Next, the normality (Shapiro Wilk) of the residuals of the new variable (Cd/LT content) was examined and the analysis of variance (ANOVA) was performed. Both the normality test and the ANOVA were performed according to the specifications and criteria described above.

Influence of environmental parameters on Cd content in macroinvertebrate muscle tissue

To identify the influence of environmental parameters on the variation of total Cd concentration in the muscle of macroinvertebrates, a Stepwise Multiple Linear Regression was carried out for each species, including all environmental variables, except those collinear with each other. For each of the predictor variables, normality and heterogeneity of variance were previously verified, and when necessary, the appropriate transformations were performed. Collinearity was evaluated by examining the Variance Inflation Factor (VIF) for all predictor variables included in the model, eliminating those that did not meet the assumption of independence. Variables were considered independent if VIF values were close to 1 and collinear when the value was between 5 and 10. Additionally, Pearson's Correlation Coefficients, and Simple Linear Regression models, previously calculated, were taken into account to reduce problematic predictor variables, whose coefficient was high and significant between pairs of variables ($r > 0.8$; $p < 0.05$); and when in Simple Linear Regression the coefficient of determination was low (R^2) and the model for the variable was not significant ($p > 0.05$). All analyses were performed in RStudio.

The Stepwise Multiple Linear Regression Model was the model that best explained the variation of Cd content in muscle. This analysis starts without any predictor variable, then new variables are added, but, after each addition, variables that are not significant in the model are excluded. This addition and elimination are carried out considering the lowest AIC (Akaike information criterion) value in each step, allowing to establish in which order the variables are introduced. The results were presented considering the order in which the variables were introduced into the model and the value of Pr(>|t|), to identify the variable that contributed most to the value of R^2.

Results

Spatiotemporal variation of environmental parameters of water and sediment

Temporal variation in all water physicochemical parameters was significant, except for transparency (Temperature ANOVA Season, $F = 16.8911$, $p < 0.0001$; Salinity ANOVA Season, $F = 44.6541$, $p < 0.0001$; pH ANOVA Season, $F = 27.5262$, $p < 0.0001$; Dissolved oxygen ANOVA Season, $F = 21.5039$, $p < 0.0001$). Temperature, salinity, and pH values were significantly higher (Tukey, $p < 0.05$) during the dry season (Temperature 29.25 ± 0.55°C; Salinity 17.51 ± 2.07 ppt; pH 8.15 ± 0.24) and lower during higher rainfall seasons (Fig. 3). Dissolved oxygen presented an inverse pattern: higher mean values during the rainy season (7.49 ± 0.86 mg/L) and lower during the drier season (5.98 ± 0.3328.07 mg/L) (Fig. 3e). As for transparency, it followed a pattern opposite to salinity, with higher values when salinity is lower, and in the opposite direction (Fig. 3a).

The spatial variation for salinity and pH was significant (Salinity ANOVA zone, $F = 37.6358$, $p < 0.0001$; pH ANOVA zone, $F = 14.6658$, $p = 0.00061$). And despite not finding significant statistical differences for the other physicochemical parameters of the water, all presented the same trend, higher mean values in the outer zone of the bay (Transparency 82.72 ± 12.77 cm; Temperature 28.68 ± 0.78°C; Salinity 16.21 ± 2.59 ppt; pH 7.93 ± 0.36; Dissolved oxygen 6.79 ± 0.90 mg/L), contrasting with the inner estuarine zone (81.89 ± 19.36 cm; 28.59 ± 0.64°C; 13.75 ± 2.09 ppt; pH 7.68 ± 0.26; 6.53 ± 0.80 mg/L, respectively) (Fig. 3). On the other hand, it was found that the parameters temperature and salinity are directly related to pH levels, that is, pH increases when these variables also increase (Temperature-pH: $r = 0.52$, $p = 0.0012$; Salinity-pH: $r = 0.86$, $p < 0.0001$). For dissolved oxygen, a negative relationship was found with respect to salinity, i.e., it tends to decrease when salinity increases ($r = -0.33$, $p = 0.0464$).

The granulometric analysis indicated that the sediments of Buenaventura Bay are mainly composed of fine sand (0.250 mm-0.063 mm), since this type of particle predominated during the three climatic seasons, both in the inner and outer zones of the estuary, contributing between 37% and 68% of the sediment composition (Fig. 4). Followed by medium sand (0.500 mm – 250 mm) and silt-clay (< 0.063 mm) particles, which had a similar percentage contribution, but less than 30% (Fig. 4). Finally, coarse sand was the type of particle with the lowest percentage contribution, contributing values below 15%, both by climatic season and by sampling zone (Fig. 4).

The two types of particles with the highest percentage contribution to the sediment composition of the bay, fine sand, and fine sand, did not present significant statistical differences at the temporal or spatial level. But, in both cases, the particles obtained higher averages during the rainy season (fine sand = 56.41 ± 15.98%; medium sand = 23.66 ± 11.16%) (Table 1). With respect to the estuarine zone, medium sand obtained higher average in the inner zone (21.34 ± 10.38%), while fine sand obtained higher values in the outer zone (Table 1). For silts and clays, significant statistical differences were only detected at the temporal level (ANOVA season, $F = 7.5406$, $p = 0.002223$), finding that during the rainy season their contribution was much lower (Tukey, $p < 0.05$; 10.56 ± 10.28%), especially, if compared to the dry season, season during which higher values were obtained (24.21 ± 7.88%) (Table 1).

Regarding the analysis of organic matter (OM) content in the sediments, the values did not show statistically significant spatiotemporal differences either; even so, higher values were observed during the drier season (6.15 ± 1.97%) and in the inner zone of the bay (6.24 ± 3.61%) (Table 1). In addition, the percentage of OM was positively related to the silt-clay content, finding a higher percentage of OM when the silt-clay content was higher ($r = 0.83$, $p < 0.0001$); and a lower percentage, when the fine sand content increased ($r = -0.44$, $p = 0.0072$).

Table 1
Spatial-temporal variation (mean ± SD) of the environmental parameters of the sediments of Buenaventura Bay. Letters indicate significant differences (Tukey, $p < 0.05$)

	Coarse sand			**Medium sand**			**Fine sand**			**Silt-Clay**				**Organic material**		
	(%)			**(%)**			**(%)**			**(%)**				**(%)**		
Seasons																
Dry	9.93	±	7.11	18.98	±	16.64	46.88	±	17.03	24.21	±	7.88	**a**	6.15	±	1.97
Transition	11.40	±	8.60	18.51	±	5.99	50.44	±	14.82	19.66	±	9.15	**a**	4.89	±	2.17
Rainy	9.37	±	12.11	23.66	±	11.16	56.41	±	15.98	10.56	±	10.28	**b**	4.79	±	4.14
Zones																
Inner	7.39	±	6.74	21.34	±	10.38	50.26	±	12.76	21.01	±	10.84		6.24	±	3.61
Outer	13.08	±	10.70	19.42	±	13.60	52.23	±	19.05	15.27	±	9.80		4.32	±	1.58

Cd and Pb content in sediments and macroinvertebrate muscle tissue

All Cd concentration values and the most of Pb concentration values in the sediments were below the detection limit for the methodology used in this study (L.D. Cd < 0.01151 mg/L and L.D. Pb < 0.12544 mg/L). Regarding the quantification of Pb content in macroinvertebrate muscle tissue, it was found that most of the concentration values, for all four species, were below the detection limit (L-D. Pb < 0.07719 mg/L). On the contrary, in the quantification of Cd content in the muscle of the four species, the concentration values were above the detection limit (L.D. Cd 0.01267 mg/L). The species with the highest Cd concentration in its tissue was the mantis shrimp *Squilla aculeata aculeata* (0.85595 ± 0.61386 mg/kg, LT 10.2 ± 2.2 cm); and the species with the lowest average Cd was the carabali shrimp *Rimapenaeus byrdi* (0.22225 ± 0.10242 mg/kg, LT 9.7 ± 2.0 cm) (Table 2). No individual of the four species exceeded the equivalent in dry weight of the maximum concentration level (wet weight) established as a reference limit in organisms for human consumption, according to national and international standards (Table 2).

Table 2
Total Cadmium content in the muscle of four species of macroinvertebrates from Buenaventura Bay

Species	N	Biological Value Index	Total length			Cadmium in muscle		
		BVI	(cm)			[Cd] mg/kg - Dry weight		
Callinectes arcuatus(1)	66	Ranking 1	9.5	±	1.8	0.53353	±	0.52346
Swimming crab		Punctuation 57						
Rimapenaeus byrdi(1)	32	Ranking 2	9.6	±	2	0.22225	±	0.10242
Carabali shrimp		Punctuation 39						
Squila aculeata(1)	19	Ranking 4	10.2	±	2.1	0.85595	±	0.61386
Mantis shrimp		Punctuation 29						
Lolliguncula panamensis(2)	17	Ranking 5	4.1	±	1.2	0.44711	±	0.18688
Panamanian squid		Punctuation 26						

	Reference limits		Wet weight	Dry weight
	Maximum value in organisms for human consumption		[Cd] mg/kg	[Cd] mg/kg
(1) **Crustaceans**: Metal content flesh of the appendages and abdomen, excluding the cephalothorax.	**Colombia**	Minsalud-MSPS. Resolución 122/2012.	0.5	2.1*
	FAO – OMS	CXS 193–1995 2019.	0.5	2.1*
	CE	Reglamento (UE) 2021/1323.	0.5	2.1*
(2) **Cephalopods and Bivalves**: Metal content in the meat wihout, excluding viscera and shell.	**Colombia**	Minsalud-MSPS. Resolución 122/2012.	1.0	4.2*
	FAO – OMS	CXS 193–1995 2019.	2.0	8.3*
	CE	Reglamento (UE) 2021/1323.	1.0	4.2*
Moisture content in tissue of the species: average 76%.				
***** Equivalence in dry weight of the reference limit in wet weight, for organisms intended for human consumption. Conversion factor 0.24, calculated based on: Frías-Espericueta et al. 2010; Molina et al. 2012; Palomarez-García et al. 2009; Pourang et al. 2004.				

Influence of size on Cd content in macroinvertebrate muscle tissue.

Significant spatiotemporal differences were detected in the total length (TL) of three macroinvertebrate species, by climatic season and/or sampling zone (*C. arcuatus* ANOVA season $F = 4.007$, $p = 0.0233$, ANOVA zone $F = 23.92$, $p < 0.0001$; *R. byrdi* ANOVA season $F = 5.625$, $p = 0.00863$, ANOVA zone $F = 3.66$, $p = 0.0653$; *S. aculeata* ANOVA season $F = 4.074$, $p = 0.0371$, ANOVA zone $F = 2.362$, $p = 0.143$). For the same species, the existence of a significant, negative relationship between muscle tissue Cd concentration and size (LT) of individuals was detected, with high correlation and determination values, as well as significant models (*C. arcuatus* r= -0.47, $p < 0.0001$, $R^2 = 0.2182$, $p < 0.0001$; *R. byrdi* r= -0.45, $p = 0.010$, $R^2 = 0.2$, $p = 0.010$; *S. aculeata* r= -0.60, $p = 0.006$, $R^2 = 0.363$, $p = 0.006$). The only species that did not present significant spatiotemporal differences in length (LT), nor did it show a significant relationship between the concentration of Cd in its tissue and the size (LT) of its individuals, was the squid *L. panamensis* (ANOVA season $F = 0.837$, $p = 0.375$; r= -0.232, $p = 0.370$; $R^2 = 0.05$, $p = 0.3698$).

For the species *C. arcuatus*, *R. byrdi* and *S. aculeata*, it was confirmed that length (LT) has a significant effect on the variation of Cd levels, by climatic season and/or zone of capture, (*C. arcuatus* ANCOVA season $F = 6.05$, $p = 0.017$, ANCOVA zone $F = 0.68$, $p = 0.57$; *R. byrdi* ANCOVA season $F = 0.62$, $p = 0.439$, ANCOVA zone $F = 9.88$, $p = 0.004$; *S. aculeata* ANCOVA season $F = 7.23$, $p = 0.017$, ANCOVA zone $F = 15.3$, $p = 0.001$), contrary to what was observed for *L. panamensis* (ANCOVA season $F = 0.32$, $p = 0.581$, ANCOVA zone $F = 0.54$, $p = 0.473$).

Spatiotemporal variation of Cd content in macroinvertebrate muscle tissue

To determine the temporal and spatial differences in Cd content in the muscle tissue of the four species, first the concentration data for each species were standardized with respect to the size of their individuals, thus considering the variation because of length (LT). The Cd content in the muscle tissue of swimming crab *C. arcuatus* showed statistical differences by season (ANOVA $F = 4.452$, $p = 0.01574$) and by sampling zone (ANOVA $F = 8.66$, $p = 0.00462$), observing that the season of maximum precipitation (Rainy) presented a significantly lower mean value (Tukey, $p < 0.05$, 0.31726 ± 0.15907 mg/kg), compared to the other climatic seasons (Dry 0.52787 ± 0.37394 mg/kg; Transition 0.62064 ± 0.68988 mg/kg) (Table 3). At the spatial level, individuals captured over the inner zone of the estuary were characterized by having a lower average concentration of Cd in their tissue (Tukey, $p < 0.05$, 0.43322 ± 0.33165 mg/kg), contrasting with the outer zone of the bay, which boasted a significantly higher average concentration (Tukey, $p < 0.05$, 10.6 ± 1.8 mg/kg) (Table 3).

The carabali shrimp and mantis shrimp, only, presented temporal statistical differences (*R. byrdi* ANOVA season, $F = 15.69$, $p < 0.0001$, ANOVA zone $F = 0.054$, $p = 0.817$; *S. aculeata* ANOVA season $F = 4.45$, $p = 0.0291$, ANOVA zone $F = 0.001$, $p = 0.971$), even so, both temporally and spatially, the same pattern of results obtained for *C. arcuatus*: higher Cd averages in individuals captured during climatic seasons of lower precipitation (*R. byrdi* Dry Tukey, $p < 0.05$, 0.34193 ± 0.09583 mg/kg; *S. aculeata* Transition Tukey, $p < 0.05$, 1.41164 ± 0.74106 mg/kg) and significantly lower averages during the season of maximum rainfall (*R. byrdi* Rainy Tukey, $p < 0.05$, 0.17086 ± 0.05124 mg/kg; *S. aculeata* Rainy Tukey, $p < 0.05$, 0.60823 ± 0.40030 mg/kg) (Table 3). For individuals caught over the outer zone of the bay, higher Cd averages were observed (*R. byrdi* 0.22602 ± 0.09856 mg/kg; *S. aculeata* 0.92512 ± 0.51676 mg/kg), while for the inner estuarine zone individuals presented lower Cd concentrations within their tissue (*R. byrdi* 0.2109505, 0.22602 ± 0.09856 mg/kg; *S. aculeata* 0.80565 ± 0.69623 mg/kg) (Table 3). The Cd content in the Panamanian squid *L. panamensis* did not show statistically significant spatiotemporal differences. However, it was observed that the Cd concentration in its tissue followed a behavior contrary to that described for the other species, with higher mean Cd levels during the rainy season (0.58495 ± 0.19322 mg/kg), compared to the dry season (0.39368 ± 0.17031 mg/kg) (Table 3).

Table 3

Spatial-temporal variation and total Cadmium content in the muscle of four species of macroinvertebrates from Buenaventura Bay. For each species, the total length of the analyzed individuals is indicated (mean ± SD) together with the concentration of Cd in their tissue (mean ± SD). Letters indicate significant differences (Tukey, $p < 0.05$), considering the effect of the size (LT) of the individuals

	Callinectes arcuatus								*Rimapenaeus byrdi*							
	Total length				**Cadmium in muscle**				**Total length**				**Cadmium in muscle**			
	(cm)				**([Cd] mg/kg *)**				**(cm)**				**([Cd] mg/kg *)**			
Seasons																
Dry	9.2	±	1.7	**b**	0.52787	±	0.37394	**a**	7.9	±	1.3	**b**	0.34193	±	0.09583	**a**
Transition	9.5	±	2.1	**b**	0.62064	±	0.68988	**a**	10.3	±	2.0	**a**	0.19595	±	0.19322	**b**
Rainy	10.6	±	1.3	**a**	0.31726	±	0.15907	**b**	10.2	±	1.8	**a**	0.17086	±	0.05124	**b**
Zones																
Inner	10.6	±	1.8	**a**	0.43322	±	0.33165	**b**	8.5	±	1.3		0.21095	±	0.11976	
Outer	8.8	±	1.6	**b**	0.60744	±	0.62280	**a**	10.0	±	2.1		0.22602	±	0.09856	
	Squila aculeata								**Lolliguncula panamensis**							
	Total length				**Cadmium in muscle**				**Total length**				**Cadmium in muscle**			
	(cm)				**([Cd] mg/kg *)**				**(cm)**				**([Cd] mg/kg *)**			
Seasons																
Dry	9.8	±	2.1	**ab**	0.59401	±	0.31338	**b**	4.3	±	1.3		0.39368	±	0.17031	
Transition	9.1	±	1.3	**b**	1.41164	±	0.74106	**a**								
Rainy	12.2	±	2.0	**a**	0.60823	±	0.40030	**b**	3.7	±	1.6		0.58495	±	0.19322	
Zones																
Inner	9.6	±	2.1		0.80565	±	0.69623									
Outer	11.1	±	2.2		0.92512	±	0.51676						***Dry weight**			

Influence of environmental parameters on Cd content in macroinvertebrate muscle tissue

The results showed that 23% of the variation of Cd content in swimming crab *C. arcuatus* muscle was related to the environmental variables, temperature ($p \leq 0.05$) and mean sand ($p \leq 0.05$), with a significant model ($R^2 = 0.23$, $F = 6.08$, $p = 0.0011$) (Table 4). Cd concentrations in the tissue of this species tended to be higher when the temperature in the water was higher ($r = 0.34$, $p = 0.0052$) and when the percentage of mean sand in the sediments was lower ($r = -0.26$, $p = 0.0330$) (Table 4). The variation of Cd content in the muscle of the carabali shrimp *R. byrdi* was explained by 46% by the physicochemical variables of the water, salinity ($p \leq 0.05$) and dissolved oxygen ($p \leq 0.05$), also with a significant model ($R^2 = 0.46$, $F = 12.39$, $p = 0.0001$), where the higher the salinity and lower the dissolved oxygen in the water, the higher the concentration of Cd in tissue ($r = 0.62$, $p = 0.0002$; $r = 0.42$, $p = 0.0175$, respectively) (Table 4).

For the mantis shrimp *S. aculeata* it was found that 51% of the variation in Cd content was influenced, mainly ($p \leq 0.05$), by the environmental variables salinity and transparency ($R^2 = 0.51$, $F = 5.14$, $p = 0.01213$) (Table 4). Cd levels in muscle tissue of this species were higher when the water presented low salinity conditions ($r = -0.56$, $p = 0.0120$); but no significant correlation was detected with transparency ($r = -0.56$, $p = 0.0120$) (Table 4). Finally, for the squid *L. panamensis*, 77% of the variation of Cd content in muscle tissue was related to physicochemical variables of both water and sediment, all significant ($p \leq 0.05$): salinity, dissolved oxygen, organic matter, and mean sand. However, Pearson's Correlation Coefficients showed no significant relationship between tissue Cd content and the variables selected in the model (Salinity $r = -0{-}44$, $p = 0.0775$; Dissolved oxygen $r = 0.36$, $p = 1.1508$; Organic matter $r = 0.12$, $p = 0.6340$; Mean sand $r = -0.12$, $p = 0.6437$) (Table 4).

Table 4

Multiple Linear Regression Model (Stepwise) explaining the relationship of environmental variables with Cd content in the muscle tissue of four species of macroinvertebrates from Buenaventura Bay. The predictor variables are presented in the order in which they were included in the model, according to the lowest AIC value. Pearson Correlation Coefficients are indicated, with the sign of the relationship between Cd concentration and the variables included in the model.

	Callinectes arcuatus						
	Variable 1	**Variable 2**	**Variable 3**		**R^2**	**F Value**	**p Value**
	Temperature	Medium sand	Coarse sand		0.23	6.08	0.0011
p	**0.0057**	**0.0107**	0.1187				
Pearson's Coefficient							
r	0.34	-0.26	0.22				
p	0.0052	0.0330	0.0797				
	Rimapenaeus byrdi						
	Variable 1	**Variable 2**			**R^2**	**F Value**	**p Value**
	Salinity	Dissolved oxygen			0.46	12.39	0.0001
p	**0.0005**	**0.0495**					
Pearson's Coefficient							
r	0.62	-0.42					
p	0.0002	0.0175					
	Squila aculeata						
	Variable 1	**Variable 2**	**Variable 3**		**R^2**	**F Value**	**p Value**
	Salinity	Transparency	Silt-Clay		0.51	5.14	0.0121
p	**0.0128**	**0.0325**	0.1233				
Pearson's Coefficient							
r	-0.56	0.12	-0.17				
p	0.0120	0.6163	0.4930				
	Lolliguncula panamensis						
	Variable 1	**Variable 2**	**Variable 3**	**Variable 4**	**R^2**	**F Value**	**p Value**
	Salinity	Dissolved oxygen	Organic material	Medium sand	0.77	10.04	0.0008
p	**0.0005**	**0.0003**	**0.0003**	**0.0004**			
Pearson's Coefficient							
r	-0.44	0.36	0.12	-0.12			
p	0.0775	0.1508	0.6340	0.6437			

Discussion

Cd and Pb content in sediments

The concentrations of Cd and Pb in the sediments were below the detection limit, therefore, they did not exceed the maximum admissible in marine sediment quality, nor the reference values TEL (Threshold Effect Level) and ERL (Effect Range Low), which indicate the limit above which the concentrations of these metals can generate negative biological effects on organisms, according to the Sediment Quality Guidelines - SQGs proposed by NOAA of the United States and the Department of Environment of Canada, who establish as limits: 0.6 mg/kg for Cd and 35 mg/kg for Pb (TEL values); 1.2 mg/kg for Cd and 46.7 mg/kg for Pb (ERL values) (Buchman 2008; Burton 2002). The low concentrations of Cd and Pb in the bay could be explained by several reasons. One of these is that, generally, metals suspended in water are easily retained by the sediment when the sediment is mostly made up of a fraction smaller than 63 µm, i.e., the sediment is made up of a large percentage of clayey silt (Belabed et al. 2011; Mauro-Navarro 2014). This, due to a higher surface area/volume ratio and higher number of binding sites with clay silt sediments (Baggio, 2019; Mauro-Navarro 2014). This is not the case of the grain size composition obtained in this study, where the sediments of Buenaventura Bay were found to be mainly composed of fine sand (0.063 mm-0.250 mm), a sedimentary fraction that predominated during the three climatic seasons, both in the inner and outer zones of the estuary (37% and 68%), while clayey silt was less than 30%. Therefore, it could be said that the grain size composition of the sediment in the bay did not allow optimal conditions to easily retain these metals.

Another reason could be that biogeochemical and hydrological factors in the bay are generating a desorption process in the flux of Cd and Pb from benthic sediments to the estuarine solution (Shulkin et al. 2018), which may be subject to the low content of muddy sediments and organic matter (Mero-Valarezo 2010; Proaño-Alvarado 2016; Shulkin et al. 2018), as found in this study, where organic matter had a limited contribution between 4 and 6%, with a positive relationship with the presence of clayey silt material, which was also low (less than 30%). In addition to particle size and sedimentary organic matter, other factors that could affect the accumulation of these metals in the estuarine sediment are salinity, redox potential, or pH (oxide-reduction conditions), diffusion and adsorption processes, compaction, and bioturbation of sediments (Mauro-Navarro 2014; Mero-Valarezo 2010; Páez-Osuna 2005; Rajeshkumar et al. 2018). In the case of Cd, when it enters the marine environment, if the sediment pH is higher than 8.0, the metal will associate with the organic matter fractions, present in this matrix. When the pH is higher, Cd will form insoluble hydroxide compounds. On the contrary, when the pH is lower than 8.0 and under oxidizing conditions, Cd is to be found mainly in the form of exchangeable ions and carbonates, weakly bound to the sediments, therefore, small variations in environmental conditions may cause the re-suspension and dissolution of Cd into the water column (Vidal 2009).

Similar to the concentrations obtained in this study, other environmental monitoring conducted in Buenaventura Bay during the same year and nearby periods (2017), report concentrations below the quantification limits for Cd < 2.00 µg/g and Pb < 25.2 µg/g (Invemar 2019), values that also do not exceed the permissible environmental quality limits for marine sediments (TEL and ERL values). This indicates that contamination levels in the sediments of Buenaventura Bay remain low, even after environmental impacts such as dredging, whose control values for Cd and Pb content prior to its development were < 0.003 mg/kg Cd and < 0.01 mg/kg Pb (Autoridad Nacional de Licencias Ambientales [ANLA], 2013, Resolución 1071). If we compare this information with the results obtained in studies of heavy metal contamination in sediments in Buenaventura Bay during the 1990s, we observe a decrease in the content of these two metals over time, since the data reported for the time (Cd 2.1–5.1 ppm and Pb 5.2–52.3 ppm, Calero and Casanova 1997; Cd 2.0–3.6 mg/kg and Pb 20.6–38.6 mg/kg, Velásquez and Cortés 1997;) exceed current permissible limits (SQGs: Buchman, 2008; Burton, 2002). However, for that decade, it was considered that the concentration levels did not represent great stress for the ecosystem, determining lithogenic and anthropogenic causes as sources of contamination (Velásquez and Cortés 1997). In contrast to the contamination panorama of the Buenaventura Bay, Central Pacific, the sediments of the North Pacific, in Solano Bay and Nuquí, currently have extremely severe Pb enrichment, whose potential ecological risk index and geological indices indicated: a serious threat to aquatic biota, by exceeding the medium effect range (MRE) value; and that, the contamination problem is due to the periodic practices of extraction and recovery of precious metals such as gold, silver and platinum, activities characteristic of this region (Gutiérrez-Mosquera et al. 2018).

Cd and Pb content in muscle tissue of macroinvertebrates

The fact that Pb was not found in the muscle of macroinvertebrates could be due, in the first place, to the fact that it was not detectable in the sediments either, to assume that a transfer to the biota has occurred. But also, that the bioaccumulation of this metal, as has been found in invertebrates, is very variable between tissues, being another target tissue of greater accumulation: hepatopancreas > gills > muscle > shell, therefore, the accumulation of Pb in the muscle could only occur when an excess reaches them through the hemolymph of the gills and hepatopancreas (Munuera et al. 2021). Or, that the excess of this and other metals have been eliminated and/or stored through assimilation routines and detoxification mechanisms such as physiological regulation, intracellular capture of proteins such as metallothioneins, or phosphorus and/or sulfide granules (Jara-Marini et al. 2014; Sastre et al. 1999). Even, that Pb has been metabolized through calcium channels, therefore, as reported for this metal, it has accumulated in the carapace or exoskeleton, in the case of invertebrates (Barros et al. 2014), which, by molting during active growth, allows eliminating excess of the contaminant, influencing the distribution and accumulation of metals among soft tissues (Pourang et al. 2004).

As for Cd, this metal was present in the muscle tissue of the four macroinvertebrate species. The species with the highest mean Cd concentration was the mantis shrimp *S. aculeata*, and the species with the lowest concentration was the carabali shrimp *R. byrdi*. The fact that the mantis shrimp *S. aculeata*, presented higher Cd concentration in muscle tissue, can be explained because these crustaceans Stomatopods of the genus *Squilla*, tend to accumulate, preferably, Cd and Cu, among other metals (Bonsignore et al. 2018), finding high values of Cd in the soft tissue, and Pb in the cuticle (Blasco, et al. 2002). This last point would explain why Pb was not detected in the muscle of these organisms. Furthermore, it supports the argument that Pb is metabolized through calcium channels, accumulating in the exoskeleton in greater proportion than in the soft tissue (Barros et al., 2014; Pourang et al., 2004). The fact that the carabali shrimp *R. byrdi* had the lowest Cd content values among the other species, and that these values are below the maximum values established for consumer organisms, is indicative of the environmental health of the ecosystem, since the Peneid shrimp, a family to which the shrimp *R. byrdi belongs*, are used as environmental quality indexes, ideal for studies of toxicity and deterioration caused by heavy metals in coastal zones (Barros et al., 2014; Hossain and Khan, 2001; Páez-Osuna, 2011;).

On the other hand, no individual of the four macroinvertebrate species exceeded the equivalent in dry weight, of the maximum concentration level (wet weight) established as a reference limit in organisms for human consumption, according to national standards (Ministerio de Salud y Protección Social, Col, 2012, Resolución 122) and international (The Food and Agriculture Organization of the United Nations [FAO] and World Health Organization [WHO], 2019, CXS193-1995; Comisión Europea, 2021, UE Reglamento 2021/1223). These results contrast with data presented by Velázquez and Cortés (1997), in past decades, for Buenaventura Bay, who report Cd and/or Pb values in invertebrate tissue (*C. toxotes* Cd 1.5 μg/g. and Pb 1.6 μg/g) above the permissible limits for the time, even at present, considering that they represented danger for consumers in the region. On the contrary, a recent study in the lower basin of the Dagua River, in the Buenaventura Bay, revealed that, in filter-feeding invertebrates such as the piangua (*Anadara tuberculosa*), the bioconcentration of Pb is low (0.114 mg/kg) and infrequent (Lucero-Rincón 2019), with values lower than those reported by Velázquez and Cortés (1997). Unlike Pb, for which contamination indices have indicated moderate contamination in the bay, for mercury (Hg), indices have indicated severe contamination and a high potential for bioconcentration in filter-feeding organisms. This is evidence that over time both Cd and Pb have been decreasing their availability in the environment, especially lead, losing importance as a tensor within the bay (Lucero-Rincón 2019).

Although no detectable Cd was found in the sediments of the bay, for the reasons stated in the previous section, as to assume the transfer of this metal via sediment-biota, the Cd content present in the tissue of macroinvertebrates could have occurred by contact of this metal present in the water through the respiratory system or the body surface (Kang et al. 2012). Because "metal dissolved in water can cross permeable body surfaces and then, be incorporated into the fraction of metal content in the body, called accumulated, with the potential to have direct or indirect metabolic effects" (Paez-Osuna 2011). In addition, it should be considered, that metals enter the tissues of organisms not only through surfaces exposed to the environment (water and sediments), but also, through the transfer of the contaminant from their food sources, being susceptible to bioaccumulation and biomagnification through the trophic network (Barraza et al. 2018; Barros-Barrios et al. 2016; Bonsignore et al. 2018; Kumar and Achyuthan 2007; Mero-Valarezo 2010).

Influence of size on Cd content in macroinvertebrate muscle tissue

The effect of the size of individuals on the concentration of Cd in the muscle of the species is supported by the literature, where it has been determined that the relative accumulation rates of metals depend on the efficiency of osmoregulatory systems, variations in habitat change and diet of many species, which are correlated with age, size of the individual and biochemical variations associated with the reproductive stage (Páez-Osuna and Ruiz-Fernández 1995 ; Páez-Osuna 2011; Pourang et al. 2004). Regarding the negative relationship between the Cd concentration in the muscle tissue of crustaceans and the size of their individuals, this trend has already been described for invertebrates in general, observing that during rapid growth stages there is a decrease in metal concentrations in the tissues, and conversely, low growth results in higher concentrations (Pourang et al. 2004). For example, during the postlarval stage of Paneid shrimp, whose growth rate is more accelerated compared to adult stages, a decrease in body metal concentration is reported, due to the effect of growth dilution (Páez-Osuna 2011). Although, in this study, for the squid *L. panamensis* no such relationship was found, other studies in individuals of the same genus, have observed similar decreases (Lischka et al. 2018).

Spatiotemporal variation of Cd content in macroinvertebrate muscle tissue

The Cd content in the muscle of *C. arcuatus* crab exhibited spatiotemporal differences, where the seasons of lower rainfall, dry season, and transition season, presented significantly higher concentrations, compared to the season of maximum rainfall (rainy season). These results coincide with studies of trophic transfer and biomagnification of trace metals in coastal lagoons, where it has been observed that in the juvenile state of the swimming crab *C. arcuatus*, and in general, in primary, secondary, and tertiary consumers, Cd concentrations are significantly higher during the summer season, compared to the rainy season (Jara-Marini et al. 2020). At the spatial level, contrary to what was observed in this study, where individuals captured in the inner zone of the estuary were characterized by significantly lower Cd concentrations, other research indicates that high concentrations of Cd in organisms occur in zones dominated by mangroves, macrophytes, fluvial inputs and high loads of organic matter, as these are factors that predispose the presence of pollutants, including heavy metals (Aguilar-Ucán et al. 2014). These characteristics coincide with the inner zone of the Buenaventura Bay estuary.

The spatiotemporal differences observed for *C. arcuatus* can be explained basically for two reasons: the first is due to the fact that this species, like other decapitate crustaceans, undergo ontogenetic migrations that guarantee their development and reproduction. In this case, mature *Callinectes* females migrate to oceanic waters to spawn; larval individuals remain in the ocean for some time; and then juveniles or megalopae migrate to estuaries for development and maturation (Sastre et al., 1999). In other words, there is a circulation of individuals of this species during different climatic periods and between different areas of the bay according to their stage of development, as was verified in this study, when significant spatiotemporal differences were found in the LT of individuals. This implies that the uptake and accumulation capacity of Cd and other metals, including Pb, is affected by the circulation of these individuals, since the availability of the metal depends on the specific environmental conditions of the climatic season and zone of the bay; as well as by the metabolic conditions of the organism when they become established for some time (Pourang et al. 2004).

The carabali shrimp (*R. byrdi*) and the mantis shrimp (*S. aculeata*) only presented temporal statistical differences, even so, both temporally and spatially, the same pattern of results obtained in *C. arcuatus* was observed: higher Cd averages in individuals captured during the climatic seasons with less precipitation (dry season and transition season). Temporally, similar results have been found for penaeid shrimp (*Litopenaeus setiferus*), *a* family to which *R. byrdi* belongs, reporting that, in tropical estuaries, Cd levels in the tissue of these organisms are significantly higher in summer, the dry season in this study (Vázquez-Sauceda 2020). Spatially, for both species, individuals captured in the inner zone of the estuary presented lower Cd concentrations compared to individuals in the outer zone. However, the literature reports that the highest Cd levels in coastal ecosystems are associated with areas close to sources of anthropogenic pollution, such as river systems (Frías-Espericueta et al. 2010; Páez-Osuna 2005), which carry waste containing cadmium impurities (Vázquez-Sauceda 2020). This zone referred to corresponds to the inner zone of this study. And at the biological level, it is worth considering that Peneid shrimp spend the first part of their life cycle (when their size is small) in estuarine environments, where they are more likely to be exposed to higher levels of trace metals (Páez-Osuna and Ruiz-Fernández, 1995).

Influence of environmental parameters on Cd content in macroinvertebrate muscle tissue.

The environmental parameters in Buenaventura Bay that influenced the variation of Cd content in the muscle of the swimming crab *C. arcuatus* were temperature and mean sand. Cd concentrations in the tissue of this species tended to be higher when water temperature was higher and when the percentage of medium sand in the sediments was lower. About the positive effect of temperature on Cd accumulation, it can be said that temperature can affect the amounts of metal uptake by an organism, because the rates of biological processes are normally doubled, i.e., metal uptake could be accelerated (Pourang et al. 2004). Contrary to the positive relationship found with mean sand, other studies have found that high Cd concentrations in organisms, such as crabs, are associated with high concentrations of organic matter (Aguilar-Ucán et al. 2014).

For the mantis shrimp *S. aculeata*, the variation in Cd content was mainly influenced by salinity and transparency, where the lower the salinity, the higher the concentration of Cd in tissue. This inverse relationship between salinity and Cd content in muscle was also found for the squid *L. panamensis*. It is worth mentioning that salinity is a factor that regulates physicochemical processes of desorption, solubility, and bioavailability of the contaminant in the medium; it can affect the metabolic rate, alter physiological processes such as osmoregulation and membrane permeability (Barros et al. 2014). In this regard, it has been reported that a decrease in salinity favors an increase in the concentration of cadmium in free form, in the form of chloride, increasing its bioavailability in the medium (Mendoza-Díaz 2010).

The species *C. arcuatus, R. S. acuelata* and *L. panamensis*, had a higher concentration of Cd in the tissue during the dry and transition periods, which can be explained by the low precipitation during these periods, which represents a lower contribution of fluvial waters, less cold waters and higher salinity in the estuary; and due to the high temperatures that occurred during these seasons, since water temperature has a positive effect on the accumulation of Cd, finding that higher temperatures double the rates of biological processes and therefore accelerate the metal absorption capacity of an organism (Pourang et al. 2004); and in the case of salinity, the higher the salinity, the lower the toxic effect of metals, because the solubility of the metal decreases (Barros et al. 2014).

Conclusions

Buenaventura Bay exhibited high temporal and spatial variability. This means that both the seasons and the particularities of the different zones of the estuary and their interaction influenced the dynamics of the physicochemical variables of the water and sediments. The environmental water parameters that contributed most to this variation were temperature, salinity, pH, and dissolved oxygen. The dry season was characterized by significantly higher temperature, salinity, and pH, as opposed to the season of higher precipitation. Spatially, salinity and pH differentiated the outer zone from the inner zone of the estuary, with higher values. The composition of sediments in Buenaventura Bay was homogeneous between climatic seasons and in the estuarine gradient. However, it was evident that the sediments of the bay are mainly composed of fine sand; while the silt-clay fraction and the percentage of organic matter in the sediment were low, showing a negative correlation with fine sands. Conditions that did not favor the accumulation of Cd and Pb in the sediments. In addition, the concentrations obtained did not exceed the maximum permissible for marine sediment quality. Therefore, the Cd and Pb content in this matrix does not represent an environmental risk for the estuary. On the contrary, the Cd and Pb levels in this study indicate that they have decreased over the years, compared to the concentrations reported decades ago by other authors. On the other hand, the four species of macroinvertebrates presented Cd in muscle tissue, finding that the species with the highest accumulation corresponds to *S. aculeata > C. arcuatus > L. panamensis > R. byrdi.* However, the concentrations of this metal for the four species were below the permissible limit for organisms for human consumption, according to national and international standards. The environmental conditions during the climatic periods of lower rainfall and higher water salinity in the external zone favored a greater accumulation of Cd in the muscle tissue of the crustacean species, contrary to what was found for the squid *L. panamensis*. Among the environmental variables that best explained the Cd concentrations in the muscle of the species were salinity and water temperature, parameters that alter the rates of biological processes, the absorption capacity of Cd by an organism, the bioavailability of Cd in the environment and its toxicity.

Declarations

Ethical Approval

The methods used were approved by the ethics committee of the Institute of Environmental Studies (Spanish acronym: IDEA) of the Universidad Nacional de Colombia, following international, national, and institutional standards for the care and use of animals. The collection of invertebrates was carried out with the authorization of the Ministerio de Medio Ambiente y Desarrollo Sostenible de Colombia, Resolución 0255 de marzo de 12, 2014, issued by the Autoridad Nacional de Licencias Ambientales.

Consent to Participate

Not aplicable

Consent to Publish

Not aplicable

Author Contributions

Karen Erazo-Enríquez and Guillermo Duque conceptualized and designed the research. Karen Erazo-Enríquez and Guillermo Duque conducted the fieldwork. Karen Erazo-Enríquez and Pilar Cogua coordinated the laboratory work. The data were analyzed by Karen Erazo-Enríquez, Guillermo Duque, and Pilar Cogua. Karen Erazo-Enríquez wrote the article. All authors read and approved the final manuscript.

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Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

Data availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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Figures

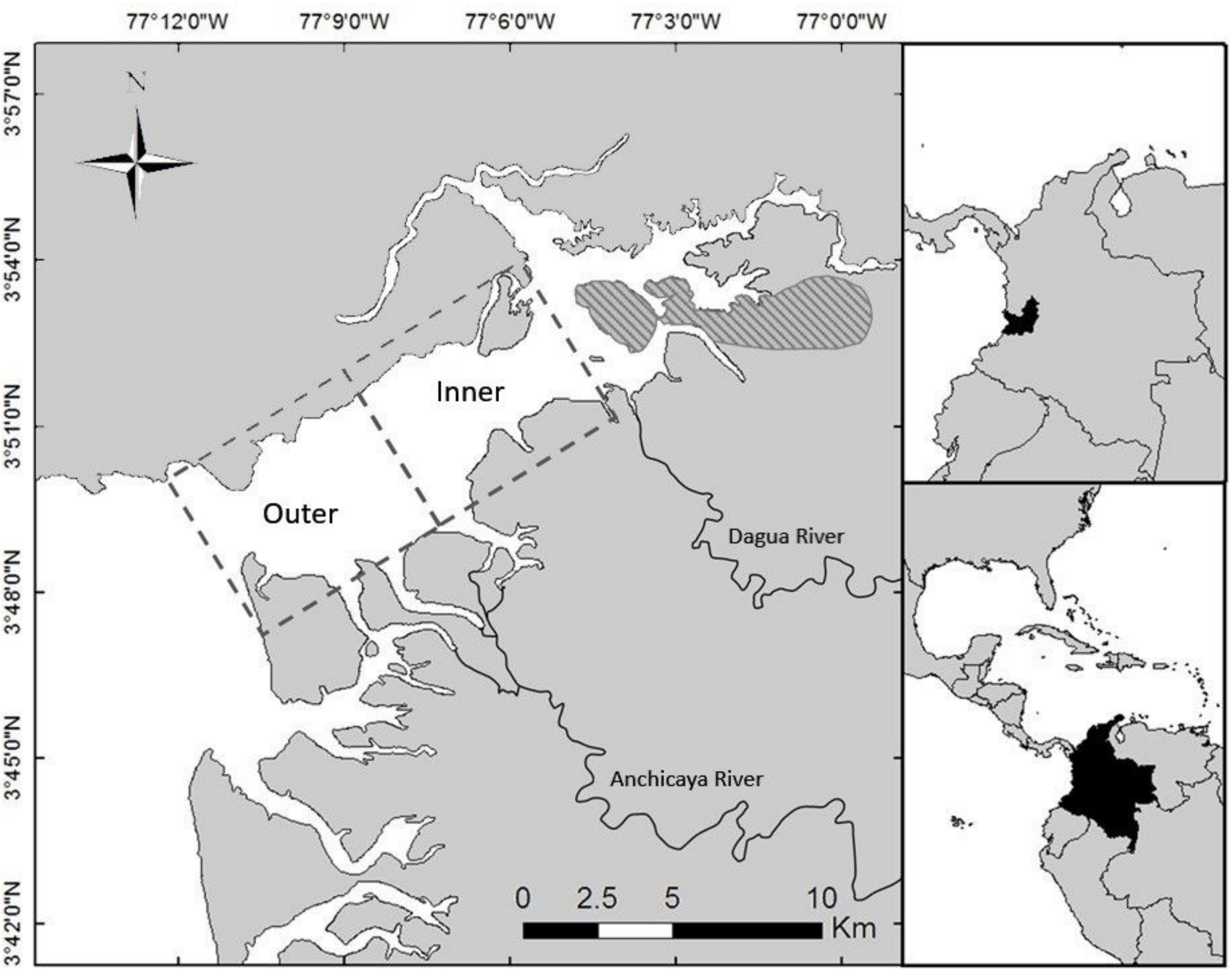

Figure 1

Buenaventura Bay, Colombian Pacific Ocean. Sampling zones distributed along an environmental gradient. Inner zone: greater influence of fluvial discharges (Dagua and Anchicayá rivers). Outer zone: greater influence of marine waters. (ECONACUA)

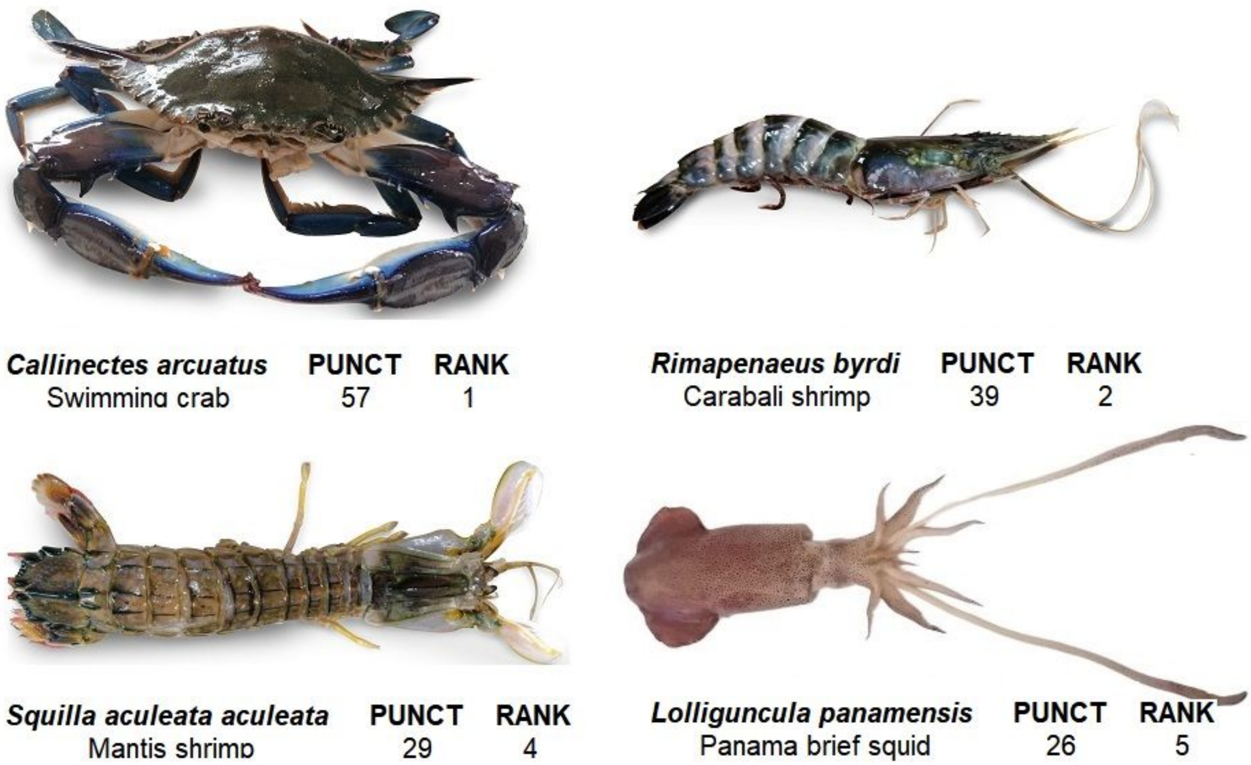

Figure 2

Invertebrate species used for Cd and Pb quantification in muscle. For each species, the results of the biological value index-BIVB are indicated. PUNT: Punctuation; RANK: ranking

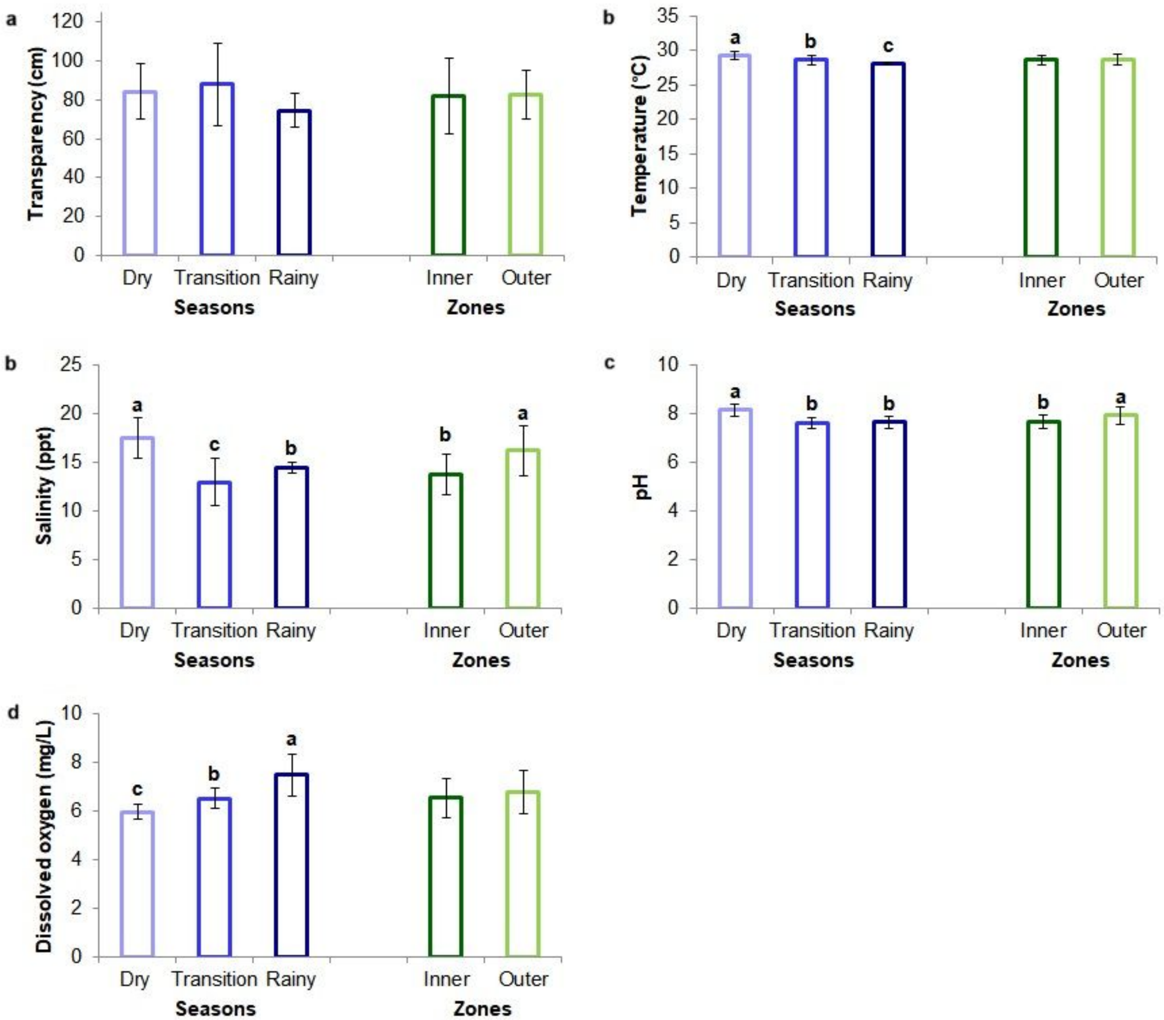

Figure 3

Temporal and spatial variation of physicochemical water variables in Buenaventura Bay. Seasons: Dry, lower precipitation; Transition, intermediate precipitation; Rainy, higher precipitation. Zones: Inner, greater influence of river discharges; Outer, greater influence of seawater. Letters indicate significant differences (Tukey, p <0.05)

Figure 4

Sediment grain size composition corresponding to two zones of Buenaventura Bay during three different Seasons. Seasons: Dry, lower precipitation; Transition, intermediate precipitation; Rainy, higher precipitation. Zones: Inner, greater influence by fluvial discharges; Outer, greater influence by seawater