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Hg, Cd, As, and Pb in surface sediments from the tropical coastal lagoon Estero Salado, Gulf of Guayaquil-Ecuador

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The Gulf of Guayaquil (GG) is the most important tropical estuarine system of the eastern coast of South America, receiving an average water flow of about 1 650 m^3 s^{-1} from a river basin of approximately 33 700 km^2. The city of Guayaquil surrounds the inner coastal lagoon of the Estero Salado (ES) that empties into the GG. This coastal lagoon is of high social, food production, and environmental importance for the city and the GG. However, there is limited high quality data on metal pollution in this zone, no recent information on Hg, and the extent to which sediment metal pollution extends into the GG is presently unknown. As, Cd, Pb, and Hg were analysed in surface sediments from the urban zone and gave average concentrations of 32.3, 2.08, 41.9, and 0.12 mg kg^{-1} (dry weight), respectively. Additionally, data were obtained for the first time for the El Morro Channel, south of the ES in the GG, which is expected to be a relatively pristine zone; average As, Cd, Pb and Hg concentrations were 6.6, 0.22, 7.9 and 0.02 mg kg^{-1} (dry weight), well below concentrations seen in the urban ES zone. Estimates of the geo-accumulation index for metal pollution, using the El Morro data as background values, were 1.7 (As), 2.7 (Cd), 1.8 (Pb) and 2.0 (Hg), making the ES class II and a moderately polluted estuary for As, Hg and Pb, but class III and "moderately to heavily polluted" for Cd. If the lowest concentrations of the EM samples are taken the ES is class III for As, IV for Hg and Pb, and V for Cd; id est, the ES would classify as a heavily to extremely polluted estuary regarding these metals. These data show the metal concentrations increase significantly as the main conurbation of Guayaquil is approached from offshore, indicating a strong anthropogenic source of metals from the city, with anticipated negative environmental impacts.

KEYWORDS

Pb, Cd, As, Hg, sediments, coastal lagoon, Estero Salado, Gulf of Guayaquil

Introduction

There is an extensive scientific literature that shows the importance of estuaries and near-shore waters in providing natural resources, with associated significant impacts on local economies, and ecosystems (e.g., Barbier et al., 2011; Birch, 2017). Estuarine environments nurture large numbers of species at all life stages, and help to sustain and protect them from predators (Dantas et al., 2016). Additionally, estuaries sustain environmental conditions in adjacent coastal waters (Thrush et al., 2013). Nonetheless, these ecosystem services have generally been undetermined (Pinto et al., 2010), and their benefits are not understood or used properly. Lack of planning and infrastructure investment can also lead to pollution and ecosystem damage (Chapman and Wang, 2001; Wang et al., 2014; Yi et al., 2021). Estuaries also sustain a variety of industries, ranging from aquaculture, fisheries, commerce and recreation to port infrastructure (e.g., Niemi et al., 2004; Oi et al., 2011; Yi et al., 2021). Wang et al. (2014) reported that Chinese estuaries had been damaged by both direct and indirect inputs of untreated or partially treated industrial and domestic waste water. Such pollution inputs can negatively impact flora and fauna in pelagic systems as well as migratory species (Birch and Hutson, 2009; Birch et al., 2013). It is well known that the health of residents adjacent to urbanized estuaries and water bodies can be impacted by metal pollution, e.g., Meneses et al. (2022) has reported impacts from Hg contamination.

Particles that form sediments are transported into estuarine and near shore waters through erosion of upstream deposits (Birch et al., 2013; Burton, 2013), surface run off from cities, agriculture, and aquaculture activities. The sediments in either completely or partially urbanized estuaries are effectively a filtering ecosystem for waters going into coastal areas (Larrose et al., 2010; Martin et al., 2012), and may be both sinks and sources of metals from land activities (Barletta et al., 2019; Yi et al., 2021). The inputs of a wide range of anthropogenic chemical elements and compounds have been increasing over recent decades in estuaries (Fan et al., 2020), and their biogeochemistry will change in response to variations in, e.g., dissolved oxygen, redox potential, and pH.

Heavy metals such as Hg, Pb, Cd and the metalloid As, are not required for metabolic processes and so the risk of toxicity is higher than those used in life processes (US EPA, 1999). All these metals are toxic to organisms at elevated concentrations, and are characterized by long residence times, and being bioaccumulated through the food chain (Zhang et al., 2009; Zhao et al., 2019; Ormaza-González et al., 2020). The As is inherent part of agricultural (pesticides), metallurgy, medicine, electronics, etc. industries (e.g., Cheng et al., 2019; Liu et al., 2022) and it is becoming a concern for human health (Zheng et al., 2020) since few years; chronic exposure could lead to risky hearth, ling, kidney ailments as it goes through the food trophic chain (see, Rehman et al., 2021). Because of this potential toxicity they are often studied in estuarine sediments (e.g. Wang et al., 2022), and are under constant scrutiny due to the well-known potentially toxic impact on fauna and flora, as well as on the health of people consuming these organisms (Järup, 2003; Worakhunpiset, 2018; Kolarova and Napiórkowski, 2021). Navarrete-Forero et al. (2019) have reported Hg concentrations in black clams (*Anadara* spp) and red crabs (*Ucides occidentalis*) from the Gulf of Guayaquil, that are >1000 times the safe limit for human consumption. Sites included near-shore environments close to or within urban catchments (Martínez and Poleto, 2014), and artisanal gold mining sites (Acquavita et al., 2021).

The Estero Salado (ES) is part of the tropical estuarine system of the Gulf of Guayaquil, which is the largest estuary in the eastern Pacific (Stevenson, 1981; Jiménez, 1983; Montaño-Armijos and Montolío, 2008; Delgado, 2013; Navarrete-Forero et al., 2019; Ormaza-González and Martillo-Bustamante, 2021). It extends over 13 701 km^2, of which 11 711 km^2 is water and the rest are islands and islets (Stevenson, 1981; CAAM, 1996), and nestled within it is the City of Guayaquil. Over the last 60 years, the ES has accumulated sediments and become heavily contaminated (pesticides, heavy metals, hydrocarbons, oils, fats, pharmaceuticals, etc.), resulting in local fisheries within the urbanized zone disappearing. Ayarza et al. (1993) reported that as early as 1985 most of the commercial species had declined. Recently, Ormaza-González et al. (2022, 2024) have reported the ES is in perennial anoxia, overloaded with fecal coliforms, and is hyper eutrophic, due mainly to unregulated urbanization (Arroyo et al., 2015) and unplanned and unmonitored industrial development (Chalén-Medina et al., 2017) with more than 190 industries discharging their liquid and solid residues (Ministerio del Ambiente, 2012) into the ES. Understanding the impact of metals on mangroves is also required (Kulkarni et al., 2018) as the ES is basically a mangrove system on which important local fisheries have depended in the past, including the red crab (*Ucides occidentalis*), black-shell clams (*Anadara tuberculosa, Anadara similis*), black mussel (*Mytella strigata*), cat fish (*Ariopsis guatemalensis*), and chame (Dormitator latifrons). Amongst the pollutants present, an improved knowledge of heavy metals in sediments is required.

To assess what sediment metal data may already be available for the ES, an extensive on line and *in situ* (institutional libraries) literature research was carried out which resulted in 6 820 results. However, there is no peer-reviewed work reported before 2010, although works reviewed within parent Institutes from Arriaga (1976), and Solórzano and Viteri (1993) exist, and Ayarza et al. (1993), gave information from a survey carried out in 1985 and can be considered the first work to provide some data on metals. Ayarza et al. (1993) reported Cd and Hg concentrations at sampling stations close to those used the present work, of up to 0.01 mg kg^{-1} for Cd and 1.13 to 2.98 mg kg^{-1} for Hg and these values can be considered the first reported in sediments and fauna for the ES. Post 2010 reports and BSc theses, e.g., Alcívar-Tenorio et al. (2011); Jiménez (2012); Chalén-Medina et al. (2017); Pernía et al. (2018) and Navarrete-Forero et al. (2019), do show high metal concentrations, but varied techniques were applied with very limited quality control and so their accuracy remains unclear. Careful work by Fernández-Cadena et al. (2014), indicated that the surface sediments of the central city part of the Estero Salado are polluted with potentially toxic metals.

Here we provide new high-quality data on the metals Pb, Cd, As, and Hg (not measured by Fernández-Cadena et al., 2014), in sediments from a wider range of sites around the city, as well as in the most southern zone of the ES, the El Morro (EM) Channel. This latter zone includes a wildlife refuge and is expected to be much less polluted than within the city, and the metal data given here are the first for this area. These new data are used to help assess the level of pollution in the city zone and thus provide the evidential background needed to stimulate improved environmental management of this major coastal population centre of the eastern tropical Pacific Ocean.

Materials and methods

Study area

The geographical limits of the ES have not officially been defined, but many authors (e.g., Stevenson (1981); Cruz (1992); Peñafiel et al. (2017)) have proposed, that its boundaries are from the core of the city (Figure 1A) to the southwest as far as the Canal del Morro (hereafter El Morro (EM), Figure 1B). In the present work the ES water body is considered to extend from 2°8.97' S, 79° 54.33'W in the north, to the El Morro channel in the south (2° 39.5'S, 80°10.5'W); i.e., about 49km. The Estero Salado has no important natural input of fresh water, and for that reason it is a salty ecosystem (hence the name: "Salado" which in Spanish means "salty"). Rain and legal/illegal discharges of industrial and domestic waters are the only source of freshwater. Average annual rainfall (1961-2017) in Guayaquil is 1755 mm (http://hikersbay.com/climate-conditions/ecuador/guayaquil/), whilst Morales-Estupiñan et al. (2020), reported around 1000 mm. Whatever the average, 60-70% of this rain occurs in January to April. It is possible that groundwater inputs may add to freshwater inflow but no information on this potential input could be found. The water within the ES is primarily replenished by large semidiurnal tidal cycles of up to 4 m in height (Ormaza-González et al., 2022); the ES and Gulf of Guayaquil has the largest tidal regime in the eastern south Pacific (Reynaud et al., 2018). The estimated residence time of water in the Gulf of Guayaquil is over 21 days (Stevenson, 1981), but for the ES this should be much longer. Here we consider the ES as a coastal lagoon (Pérez-Ruzafa et al., 2011; Marques-Figueiredo and Rockwell, 2022) as its natural fresh water input is only that from the city, and water turnover is primarily tidally driven.

Major factors leading to the general pollution of the ES are 1) Guayaquil is the economic center of Ecuador (Delgado, 2013) with

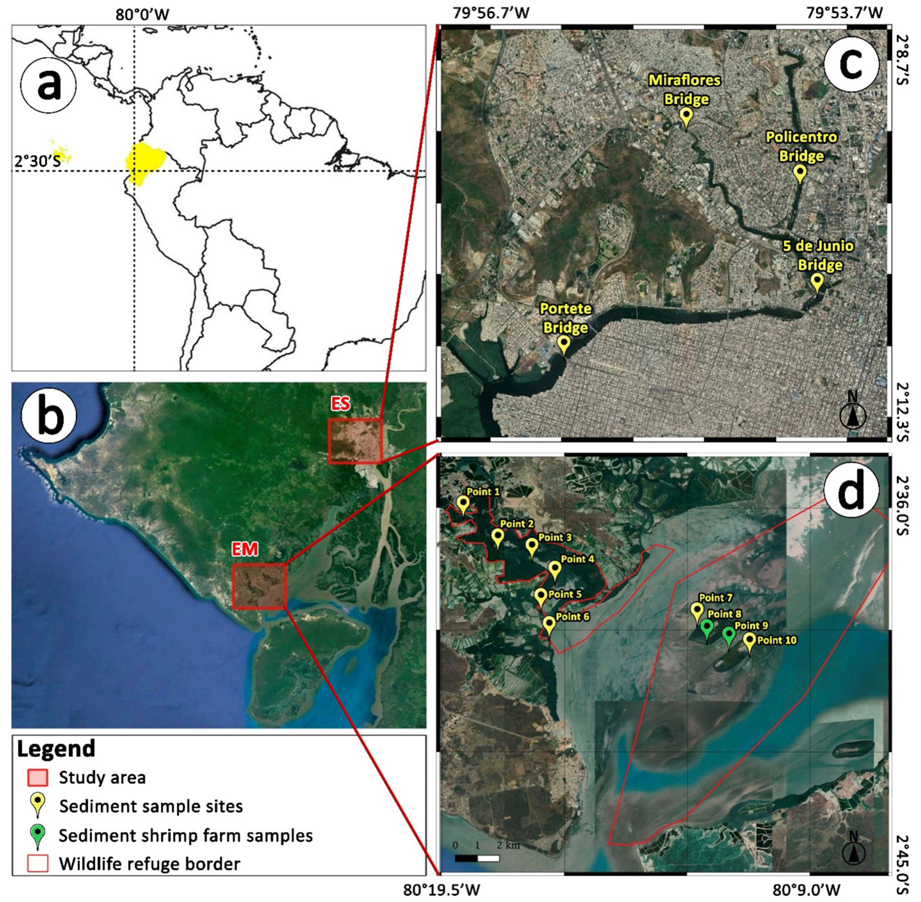

FIGURE 1
Ecuador **(A)**. The Gulf of Guayaquil, the Estero Salado (ES) and El Morro (EM) shown in panel **(B)**. Sampling sites in the urbanized Estero Salado (yellow dots panel **(C)**) and El Morro sites **(D)**. Exact locations of sampling sites for the current work are given in Table 1. Figure modified from Google Earth maps.

major growth of a wide range of industries and a large population (2.7 million inhabitants, INEC, 2022). 2) the southern part of the Estero Salado is the navigation channel to the port of Guayaquil (Figure 1), which is the largest in the country and the second busiest container port in the west coast of South America (Wilmsmeier et al., 2021). 3) The generally unplanned growth in population settlements (legal or illegal) has led to overload and collapse of sewage systems, wastewater treatment and disposal of solid waste. Cimentaciones (2000) found that 60% of the discharges to the estuary were domestic and the remaining 40% of industrial origin, and all types of wastewaters have been dumped into the ES without any or only minimal treatment. The city of Guayaquil has >190 registered industries (beverages, food, glass, car batteries, workshops, metallurgy, plastic, textile production, agriculture, etc., MAE, 2023) of which many are sources of polluting agents (Fernández-Cadena et al., 2014). According to the Ministry of Environment (MAE, 2023) only 54 comply with Ecuadorian environmental norms.

Sampling

Figure 1 shows the sampling sites used here, where the four sites within the narrow and urbanized ES (Figure 1C) give a good coverage of the city. Ten sediments samples were taken from the Canal El Morro to the south (Table 1; Figure 1D), including two from active shrimp ponds and mangrove banks. Samples from El Morro are generally considered reference points because of their distance from known contamination sources and they are within a protected wildlife refuge zone. No metal analyses have been reported for sediments from this area.

TABLE 1 Geographical positions of the stations in Figure 1.

Station	Latitude (S)	Longitude (W)
Miraflores Bridge	2° 09.7′	79° 55.1′
Portete Bridge	2° 10.3′	79° 54.8′
5 de Junio Bridge	2° 10.9′	79° 53.9′
Policentro Bridge	2° 10.1′	79° 54.1’
1	2° 36.0′	80° 17.5’
2	2° 37.0′	80° 16.6’
3	2° 37.2′	80° 15.8’
4	2° 37.8′	80° 15.3’
5	2° 38.4′	80° 15.6’
6	2° 39.1′	80° 15.3’
7	2° 38.8′	80° 11.7’
8	2° 39.5′	80° 10.5’
9	2° 39.2′	80° 11.5’
10	2° 39.5′	80° 10.9’

The stations at the bridges were sampled in February 2020 and the rest from El Morro Chanel, in October 2021. The extended sampling time gap was due to the Covid-19 pandemic.

Surface sediments (depth 10-15 cm) were collected using a hand-operated portable stainless-steel grab (Van Veen, 250 cm^2). These surface sediments were kept in clear low-density polyethylene bags (zipper-top). Then, samples were dried at ~35°C for 72 hours and finely ground (see, Skilbeck et al., 2017).

Metal analysis

For the determination of total Hg concentrations, around 0.25 (± 0.0001) g dry sediment was microwave digested in 10 ml of 65% nitric acid using a Mars Xpress^{TM} system (CEM). After that, samples were diluted into 100 ml with acid solution (HNO_3 and H_2SO_4, 65% and 95-97% strength respectively. Stannous chloride solution was used as the reductant. Cold vapor atomic absorption spectroscopy, with a Varian SpectrAA (model 220FS) coupled to a VGA 77 vapor generation was used. The laboratory is ISO/IEC 17025 certified.

Sample analysis for total Pb, Cd and As in sediment consisted of weighing accurately about 0.30 g dry sample into Teflon vessels, 6 ml of 65% nitric acid were added and samples digested in a microwave system (Mars Xpress^{TM}, CEM), samples were diluted to a final volume of 25 ml with ultrapure water. The final solutions were filtered through cellulose filter (Macherey Nagel, 4-12 µm pore size) pre-washed with 1% nitric acid solution. Atomic absorption spectrophotometry by graphite furnace (GFAAS) Varian (model SpectrAA 220Z) and Agilent (model 280Z) with Zeeman background correction were used. Analytical grade reagents were employed throughout analytical procedures.

Calibrations were run for each set of analyses. Hg calibration plot (0.2, 1, 2, 3, 5 and 7 µg [Hg] dm^{-3}), Cd calibration plot (0.2, 0.4, 0.8, 1.6 and 3.2 µg [Cd]. dm^{-3}), Pb calibration plot (1, 5, 9, 14 and 18 µg [Pb] dm^{-3}) and the As calibration plot (10, 20, 30, 40, 50 µg [As] dm^{-3}). Analyte range using cold vapor for Hg is 0.069 to 2.85 mg kg^{-1}, and using GFAAS for Pb, 0.035 to 1.50 mg kg^{-1}: As, 0.20 to 2.80 mg kg^{-1} and Cd, 0.014 to 2.12 mg kg^{-1}.

Manufacturer's recommended wavelengths and calibration ranges were used. Reagent blanks and certified reference materials BCR-277R estuarine sediment (CRM-JRC) for Cd, Hg, As and fresh water sediment 016 (Sigma-Aldrich) for Pb were used. Limits of quantification and detection limits are shown in Table 2, and recoveries for CRMs are shown in Table 3. Blanks were run for all sets of analyses.

The enrichment factor and the geo-accumulation index

An indication of relative contamination can be obtained from the Enrichment Factor (EF, Li et al., 2014, Equation 1) and Geo-Accumulation Index (Igeo, Zhang et al., 2017, Equation 2) which are amply used since the 60s by European metal studies in urban sediments (Martínez and Poleto, 2014; Barbieri, 2016). Here the average of these metal concentration from the EM is used as the Reference metal.

TABLE 2 Analytical parameters, calibration conditions of the analysis.

Metal	LOQ (mg kg^{-1})	DL (mg kg^{-1})
Hg	0.069	0.047
Cd	0.014	0.009
Pb	0.035	0.011
As	0.200	0.059

LOQ: Limit of quantification (the minimum concentration of an analyte that can be measured within specified limits of precision and accuracy; typically, 3 x standard deviation of the blank). DL: Detection Limit (minimum concentration of an analyte that can be detected in a sample; typically, 2 x standard deviation of the blank). Reference: The European Commission Regulation No 333/2007 ((https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX%3A32007R0333).

$$\mathbf{EF} = (\mathbf{Metal\ concentration})/(\mathbf{Reference\ Metal}) \tag{1}$$

$$\mathbf{Igeo} = \mathbf{log_2 C_i (1.5 \times B_i)^{-1}} \tag{2}$$

Where C_i is the actual concentration of the heavy metal i, and B_i is the geological background or the lowest concentration of the heavy metal i. The constant factor of 1.5 is used to account for variation in background values for metals (Muller, 1969: Zhang et al., 2017). For Geo-accumulation Igeo index, class, and classification for metal in estuarine sediments. see Barbieri (2016) and Zhang et al. (2017).

Metal bioavailability

The Reference index ISQG (see, Sediment Quality Guidelines (SQGs): A Review and Their Use in Practice | Geoengineer.org) were used. The concentration is normalized against the empirical threshold level; <1 the adverse effect is very low, whilst >1 would mean metal bioavailability (Krampah et al., 2019). Values for Threshold Effect Levels are: 0.6, 35, 0.17 and 7.3 for Cd, Pb, Hg and As mg kg^{-1} respectively.

Environmental quality standard – Ecuador

Ecuador has an Environmental quality standard (see TULAS, 2022 or MAE, 2023), which gives upper accepted concentrations of a healthy estuarine sediment.

Sediment grain size

Sediment grain size was measured because of its reported correspondence with trace metal concentrations (e.g. Martincic et al., 1990, Özşeker et al., 2022). Here, size ranges were determined using analytical certified sieves ASTM- E11 (ISO 3310/BS 410), and following recommendations in Blott and Pye (2012).

Results and discussion

Metals in surface sediments

Estero Salado

The present work (Table 4) found averages of 32.3, 0.12, 2.08, and 41.9 mg kg^{-1} for As, Hg, Cd and Pb respectively. The Canadian International Sediment Quality Guidelines (ISQG) use a strong acid/peroxide leach to determine metal concentrations, and thus their values provide a useful comparator for ES samples here. Average ratios of ES metal concentrations to ISQG values were 4.4, 0.7, 3.5 and 1.2 for As, Hg, Cd and Pb respectively, indicating elevated metal concentrations at the ES bridge sites in the order As>Cd>Pb>Hg. Of particular note is the extremely high concentration of Cd (6.08 mg kg^{-1}) and ISQG ratio of 10 at the Miraflores Bridge station, and a high concentration of As (36.7 mg kg^{-1}), also at this site suggesting a nearby source. Hg and Pb are similar to the ISQG reference values.

The Miraflores and 5 de Junio bridges have highest metal concentrations, with the Policentro and Portete Bridges being lower. Even though the four sampling sites are relatively close, the Miraflores and 5 Junio bridges are closest to an industrial and urban area of Guayaquil city, where waste inputs since the 1960s have had minimal treatment. Around these two bridges water circulation is restricted, and water volumes small, and so higher levels of metals in sediments might be expected, and water quality generally to be poorer. Recently Ormaza-González et al. (2024) found hyper-eutrophicated and anoxic conditions here. The Portete and Kennedy bridges have a stronger water circulation and greater volume.

The metal measurements reported here generally agree with the careful measurements of Fernández-Cadena et al. (2014) in showing high concentrations of As, Cd and Pb (no Hg measurements reported) around the Miraflores and 5 Junio bridges part of the ES.

TABLE 3 Trace elements concentration determined in certified reference materials (estuarine sediment BCR – 277R (https://crm.irmm.jrc.ec.europa.eu/p/40455/40459/By-material-matrix/Soils-sludges-sediment-dust/BCR-277R-ESTUARINE-SEDIMENT/BCR-277R) and fresh water sediment 3 CRM016 [Trace Metals - Fresh Water Sediment 3 certified reference material, pkg of 50 gSigma-Aldrich (sigmaaldrich.com)].

Certified material	Element	Certified concentration (mg kg^{-1})	Concentration obtained (mg kg^{-1})	Variation coefficient (%)	Recovery ranges (%)
BCR - 277R	As	18.3	16.0 ± 0.91	6	83-97
	Cd	0.61	0.57 ± 0.041	7	85-102
	Hg	0.128	0.138 ± 0.017	13	90-123
3 CRM016-50G	Pb	14.1 ± 0.657	16.6 ± 1.07	6	107-129

n=7.

TABLE 4 Sediment metal measurements at the ES bridges (see Figure 1).

Bridges	As	Ratio ISQG	Hg	Ratio ISQG	Cd	Ratio ISQG	Pb	Ratio ISQG
Portete	30.3	4.2	0.08	0.5	1.07	1.8	29.7	0.8
Miraflores	36.7	5.0	0.16	0.9	6.08	10	53.2	1.5
5 de Junio	35.5	4.9	0.16	0.9	0.9	1.5	56.4	1.6
Policentro	26.6	3.7	0.08	0.5	0.28	0.5	28.4	0.8
Range	26.6-36.7		0.08-0.16		0.28-6.08		28.4-56.4	
Average	32.3	4.4	0.12	0.7	2.08	3.5	41.9	1.2

Sampling Feb/2020. Concentrations in mg kg^{-1}. Reference ISQG (Sediment Quality Guidelines (SQGs): A Review and Their Use in Practice | Geoengineer.org) values for Threshold Effect Level are: 0.6, 35, 0.17 and 7.3 for Cd, Pb, Hg and As mg kg^{-1} respectively. The coefficients of variation in Table 3 can be applied to the data here.

In a more regional context, at a pristine estuary (north of Ecuador), which is within a mangrove natural reserve, the Cd sediment concentrations were very high (2.14 mg kg^{-1}) whilst Pb was a low 12.4 mg kg^{-1} (Romero-Estévez et al., 2020). The high and low concentrations of Cd and Pb respectively are difficult to explain in terms of evident anthropogenic inputs as there is no important population settlement, or any industrial activity close by, as is the case of the ES, and details of the drainage basin are not given. Additional natural and anthropogenic non-point or diffuse inputs (Abessa et al., 2018; Spencer, 2017) including from the atmosphere (e.g., Muñoz and Salamanca, 2003) and groundwater (Li et al., 2024) may have impacted these values, as well as analytical procedures.

The earliest measurements of metals in surface sediments of the ES were in 1985 in the same areas (Figure 1) as examined here by Ayarza et al. (1993). Using similar techniques to those used here, they found Cd and Hg concentration ranges of 0.01-0.03 and 0.1-2.98 mg kg^{-1} respectively. Cd concentrations were 20-250 times lower than those reported at that time in some other estuaries and coasts (e.g., Katz and Kaplan, 1981) whilst Hg was higher. In relation to 1985 data, Cd has notably increased (138 times), while Hg shows an important decrease (24 times).The most likely reasons for differences in Cd between then and now is the substantial industrial development in Guayaquil with associated discharges. The lower mercury values may reflect a reduction in alluvial gold extraction (Mestanza-Ramón et al., 2021), and the lower quality gasoline and diesel (Won et al., 2007; Jiang et al., 2014) used at that time. Differences in analytical procedures and sampling could also play a role in the variations found, but the data suggests substantial changes in concentrations of Cd and Hg.

El Morro

The sampling sites included two active aquaculture shrimp ponds and the surrounding banks which are fully covered by mangrove. El Morro and part of the surrounding area is a mangrove reserve (Figure 1). Table 5 gives concentration data for all El Morro samples with ISQG ratios, and Figure 2 shows the geographical pattern of metal distributions. There is no previous work in the El Morro channel with which to compare the data shown here.

The average values of ratios against ISQG limits are for As, Hg, Cd and Pb respectively, 0.91, 0.12, 0.37 and 0.23. The shrimp ponds ratios were similar or even lower (0.9, 0.16, 0.34 and 0.28 in the same order), and the samples from the mangrove area ISQG ratios were correspondingly even lower, 0.71, 0.0, 0.14 and 0.11. These low values support the view of the EM zone being a relatively metal uncontaminated area.

Grain size and organic carbon content of sediments

The sediments from the ES are mainly sandy silts (see data and curves in SM). The silt fraction is highest at the Miraflores site, whilst the silt is less significant in the other sites. Ayarza et al. (1993) reported that sediments from the ES are mainly fine sand, silt-clay. whilst in the data reported here, they are slightly coarser. Miraflores has more fine fractions than the other sites. Overall, the grain size distribution is quite similar between the ES and EM sites, which is not surprising given the similar Guayas drainage basin source.

The Organic Carbon (OC) content of the ES sediments at the Bridge stations 5 de Junio, Miraflores, Portete (Ayarza et al., 1993); and at the EM stations (Bobadilla-Cordova, 2024) are given in Table 6. Stations closest to the town of El Morro (1-3, Figure 1), have the highest OC content (5.1-6.3%) of the EM stations, which is anticipated as the town has no sewage treatment prior to discharge. Towards the mouth of EM, concentrations were down to 0.7-1.8%, and even lower in the mangrove (<0.3%). At the shrimp farm OC was 0.9-2.0%. Waters at the ES Miraflores bridge site have recently been reported as hyper-eutrophication, frequently anoxic and with low pH (Ormaza-González et al., 2024), and therefore high OC in sediments here is expected. This site also has elevated Cd, Hg and Pb as well as finer sediments, associations that have been found in earlier studies (e.g. Özşeker et al., 2022).

Estimates of metal pollution

Obtaining a measure of pollutant metal content of a sediment relative to background values is very important in assessing potential biological impact (Barbieri, 2016), and assigning a level of pollution to a site. An indication of the magnitude of metal contamination can be obtained using Enrichment Factors (EF) relative to a reference element (RE), but this cannot be applied

TABLE 5 Concentration (mg kg^{-1}) of metals in surface sediment of El Morro channel (1-7), shrimp (9-10) pond and mangrove sites (7-8).

Sampling site	As	Ratio ISQG	Hg	Ratio ISQG	Cd	Ratio ISQG	Pb	Ratio ISQG
1	6.69	0.92	0.07	0.392	0.22	0.37	7.94	0.23
2	5.46	0.75	<DL	0.000	0.44	0.73	8.96	0.26
3	7.34	1.01	0.04	0.206	0.62	1.03	7.37	0.21
4	7.52	1.04	0.04	0.204	0.04	0.07	9.92	0.28
5	8.16	1.13	0.04	0.206	0.26	0.43	8.84	0.25
6	6.99	0.96	<DL	0.000	0.12	0.20	6.03	0.17
7	5.88	0.81	<DL	0.000	0.08	0.14	4.71	0.13
8	4.35	0.60	<DL	0.000	0.09	0.15	3.19	0.09
9	6.55	0.90	<DL	0.000	0.15	0.25	10.3	0.29
10	7.23	0.99	0.03	0.201	0.19	0.32	11.9	0.34
Range	4.34-8.16		<DL-0.07		0.04-0.62		3.19-11.9	
Average	6.62	0.91	0.02	0.12	0.22	0.37	7.92	0.23

Samples taken September 2021, and sites are shown in Figure 2. <DL means below detection limit. Sampling sites in brackets equate to sites in Figure 1. The coefficients of variation in Table 3 can be applied to the data here.

here as no RE measurements were made. However, if the average values from EM are assumed to be the original concentrations of ES, the average EF for As, Hg, Cd and Pb would be 4.88, 6.00, 9.45, and 5.18 respectively. The four elements are in general enriched at least 5 times, which categorize the EM as extremely enriched according to Li et al. (2014).

Geo-accumulation index

This index is frequently used (Birch, 2017; Barbieri, 2016) and provides a classification of sediment pollution, where the index varies from 0 to >5 with level of pollution increasing with value.

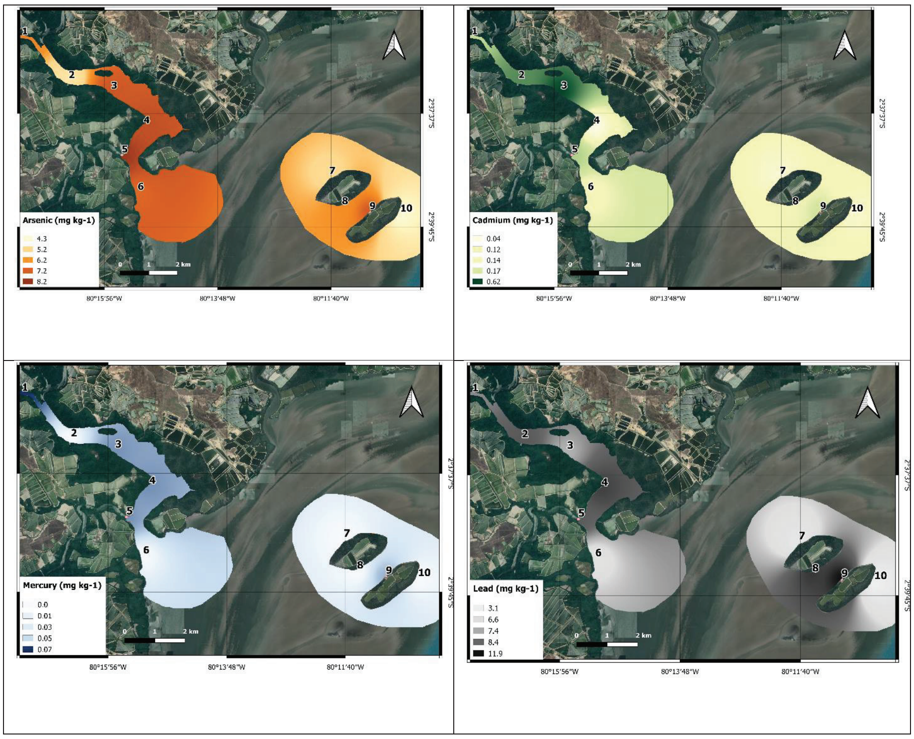

FIGURE 2
Total As, Cd, Hg and Pb surface distribution in the El Morro Channel. Sampling Oct 2021. Concentration in mg kg^{-1}. Exact positions for the Stations are given in Table 1.

TABLE 6 Organic carbon content of sediment samples from ES bridge stations (Ayarza et al., 1993) and EM (Bobadilla-Cordova, 2024) sites.

EM Stations	OC (%)	ES Stations	OC (%)
1	6.35	5 de Junio	4.54
2	6.07	Miraflores	10.5
3	5.08	Portete	4.60
4	1.75		
5	0.72		
6	1.81		
7 Mangrove	0.3		
8 Mangrove	0.17		
9	0.87		
10	2.05		

Data for stations 1-3 and bridges are expected to be influenced by local pollution.

In the original work of Muller (1969) it is reported (Barbieri, 2016; Birch, 2017) that sieved sediment (<2µm) was used and a total measure of metal obtained, and compared to global shale values. Since this pioneering work there have been a multitude of variations used in determining Igeo (Birch, 2017; Barbieri, 2016). Here we do have metal data from a polluted zone (ES surrounded by City), and background sites (El Morro), and thus an estimate of Igeo can be obtained using the ratio-to-reference (RTR) approach (Birch, 2017), or the so-called direct method (Yan et al., 2020), using metal concentrations from a nearby pristine area.

For this Igeo approach to be used, it is important to show that the two sites are not biased by particle size differences. It has been long established that generally finer grained components in sediments contain higher concentrations of metals than coarser fractions as a result of increased surface to volume ratio, and the presence of more adsorptive and absorptive phases (e.g. Martincic et al., 1990; Özşeker et al., 2022). Results of grain-size analysis of samples are shown in Supplementary Material. The sediment grain sizes are similar in both sites, thus making general comparisons between sites in terms of metal concentrations valid and allowing identification of polluted zones easier. Also, it can be assumed that the geological origin of the sediments in the El Morro channel are the same as the urbanized ES, as the whole ES is within the same geological basin of the Gulf of Guayaquil (Ormaza-González and Martillo-Bustamante, 2021), and the origin of the sediments in this coastal lagoon includes the outer Gulf of Guayaquil (Benites, 1975; Barrera Crespo et al., 2019). Therefore, the El Morro Channel and its vicinity can be considered as a suitable site for reference values for sediments closer to anthropogenic sources. Simple ratios of metal concentrations in the urbanized ES to those in El Morro show significant positive values of 4.88 (As), 5.84 (Hg), 9.42 (Cd) and 5.30 (Pb), indicating the ES is highly polluted by these metals.

The geological background B_i used in Igeo calculations was the average values of the 10 samples of the El Morro channel (Table 5), from which the Igeo indexes obtained were 1.7, 1.96, 2.65, and 1.82 for As, Hg, Cd and Pb respectively. Using these values and the categorization in Zhang et al. (2017) the urban ES is class II and moderately polluted zone for As, Hg and Pb, but class III and "moderately to heavily polluted" regarding Cd. However, if we take the lowest B_i of the EM samples (excluding the first 3 values close to the town and its pollution source), the ES is class III for As, IV for Hg and Pb, and V for Cd. These indexes would mainly classify the ES as a heavily to extremely polluted estuary regarding these metals.

Conclusions

The concentrations of As, Hg, Cd and Pb in sediments of the urban ES are high, and when compared to the Canadian interim sediment quality guidelines (ISQG), all except Hg have values greater than 1 indicating contamination and potential for impacts on the environment and its biota. Of particular note is Cd at Miraflores Bridge with an ISQG value of 10. The EF results classify the ES as extremely enriched and above upper limits of National standards. Using the Igeo index approach as applied here, the ES is class II and a moderately polluted estuary for As, Hg and Pb, but class III and "moderately to heavily polluted" for Cd. These approaches therefore overall classify the urbanized ES as a polluted lagoon system for these metals, in agreement for As, Cd and Pb with Fernández-Cadena et al. (2014). The work here shows the ES system is also contaminated with Hg.

High As, Hg, Cd and Pb concentrations lead to concerns over bioaccumulation of metals in benthic organisms with associated reduction in biodiversity and possible toxicity to humans where such species are consumed. In particular demersal and benthic seafood species such as the clam (*Anadara* spp.) and red crab (*Ucides occidentalis*) appear to bioaccumulate these metals. The fauna in the upper ES has practically disappeared.

The limited past sediment metal data for the ES from Ayarza et al. (1993), indicate an increase in Cd and decrease in Hg contamination over the past 3 decades in this zone because of changes in industrial activity and, e.g., alluvial gold extraction and gasoline contamination, respectively.

To the south of the ES in the El Morro channel region, the concentrations of the above sediment metals decrease relative to the polluted ES and give ISQG values below 1.0. Even lower ISQG values are found for the mangrove areas. The EM region can therefore be regarded as an overall non-polluted zone for the studied sediment metals.

Whilst the present and some other work indicate significant metal contamination in the ES, further research is needed on their sources, impacts on biota and the local population. Work is also needed on potential remediation methods that have been applied to temperate but not yet tropical estuaries (Oliveira et al., 2024; Patmont and Healy, 2024). The Estero Salado and the less contaminated El Morro zones fall under objectives in the UN initiative launched in 2019 ("Decade on Ecosystem Restoration") that provides a framework for Sustainable Development.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding author.

Author contributions

FO: Conceptualization, Formal analysis, Investigation, Validation, Writing – original draft, Writing – review & editing. RC: Formal analysis, Methodology, Validation, Writing – review & editing. AM: Data curation, Methodology, Software, Writing – review & editing. NB: Data curation, Investigation, Methodology, Resources, Writing – review & editing. IR: Investigation, Resources, Supervision, Writing – review & editing. PS: Investigation, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

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Conflict of interest

Publisher's note

Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmars.2024.1457548/full#supplementary-material

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