# Heavy metal pollution and toxicity assessment in Mallorquin swamp: a natural protected heritage in the Caribbean Sea, Colombia

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## Highlights

- 1. Sources and levels of metals in a protected coastal lagoon were studied in Colombia
- 2. Several contamination indexes shown a strong pollution by Cd and Pb in sediments
- 3. Cu & Hg exceeded the TEL and ERL values, indicating an ecotoxicological risk
- 4. Pollution mainly originates from anthropogenic industrial & agricultural activities

#### Abstract

This work reports the level and ecological impact of metals in the sediments of the Mallorquín swamp, a protected coastal lagoon in the Caribbean coast of Colombia. The distribution of metals was in the following decreasing order: Zn > Cu > Pb > Cd > Hg, showing statistically significant differences among sites. The average Pb and Cd concentrations in sediments were about 17 and 5 times higher, respectively, compared to those in background values. Several contamination indices suggested moderate contamination of Hg, Cu, and Zn, and strong pollution due to Cd and Pb. Multivariate analysis revealed spatial variations for metals and its anthropogenic origin, such as municipal and industrial wastewater discharges (Pb, Zn, and Hg) and agricultural activities (Cd and Cu). These findings showed the negative impact of human activities and the need to apply protective management strategies.

Caribbean

### Keywords

metals; sediment quality;

Coast; Colombia;

anthropogenic pollution

Coastal areas are often urbanized and industrialized, so they become subject to the release of trace metals in significant quantities (Bodin et al., 2013). This situation has caused the contamination of marine sediments becoming a widespread problem in the coastal waters of many countries, and constitutes a threat to marine resources and human health. Sediments show a high capacity to accumulate metals, even at low concentrations in the aquatic environment (El Nemr et al., 2007; Christophoridis et al., 2009). Metal contamination in aquatic environments has become a significant concern due to its toxicity, abundance, and persistence in the environment, and its subsequent accumulation in aquatic habitats (Fu et al., 2014; Islam et al., 2017; Wu et al., 2017). The pollution of coastal areas by metals is a global problem, and the Colombian Caribbean coastal area is not an exception (Fernandez et al., 2018). The Mallorquín swamp or Ciénaga de Mallorquín (Ramsar site, Decree 3888, Ministry of Environment, Housing and Territorial Development, 2009) is a unique estuarine coastal lagoon located in the state of Atlántico on the Colombian Caribbean coast, considered today as a marine ecosystem of great importance for the sustainable development of the region. Unfortunately, this lagoon suffers several pollution problems, just like other similar coastal areas around the world. Until the 1940s, it had an estuarine regime with a great variety of micro-systems and fishing resources as it belonged to the flood-prone delta of the Magdalena River. However, in 1935, with the construction of the buttresses, it functions as a coastal lagoon after modifying the estuarine regime given its connection and permanent dependence on the Magdalena River. Due to these circumstances, the problems for the ecosystem began when the exchange of the waters necessary for the natural balance was interrupted, causing serious consequences to the aquatic life that it houses, accumulation of contaminants, and considerable sedimentation processes. Associated with this problem, the phenomenon of expanding the urban or productive border, or both, is also typical of some companies in the industrial sector to gain land that they subsequently enable for their activities, generating further contamination. This is even more critical considering that invaded areas do not have public service coverage, especially those defined for sanitation, generating higher pressure on the system and its resources. In addition to the environmental problems that affluent ecosystems and their watershed suffer due to agricultural activities, there is also the pollution produced by an old garbage dump located in the District of Barranquilla, Las Flores sector. This activity has been improperly disposing of the solid waste of the city indiscriminately for 32 years, functioning as an open-air dump and promoting the progressive pollution of the waters. Therefore, the contamination state of marine sediments has often been used as an essential criterion to assess the quality condition of the coastal environment and to understand the possible environmental changes caused by anthropogenic activities (Chapman et al., 2013; Wang et al., 2014).

Accordingly, the aim of this study was to reveal the spatial variation of metals in surface sediments to evaluate its toxicity considering the sediment quality guidelines (SQGs) and Mean ERM Quotient (M-ERMQ). Furthermore, perform an evaluation and identification of potential sources of contamination and assess the extent of metal pollution in the environment using relevant indices.

The swamp Ciénaga de Mallorquin is a coastal lagoon that has estuarine characteristics and is considered an ecosystem of great importance for the sustainable development of the Caribbean region. It is located in the coastal area of the Colombian Caribbean, in the state of Atlántico between coordinates  $11^{\circ}$  05' 00" N and 74° 51' 00" W (Fuentes et al., 2018). It limits naturally to the north with the Caribbean Sea and to the south with the highway bypass that connects the village of La Playa with Las Flores, a neighborhood of the city of Barranquilla. It is connected to the east with the Magdalena River and to the west with the Arroyo León, a shallow stream (between 0.3 - 1.5 m), irregular in shape, and has an approximate area of 650 ha (Castro et al., 2018). Figure 1 shows the seven sampling sites in the Mallorquín swamp (E1 to E7) assessed in two dry season campaigns, February and August 2017. In each station, four sediment subsamples were collected from each cardinal point with a radius of 3 m. With these subsamples, a single composite sample representative of each site was obtained. Sediment samples were taken from the first 5 cm of topsoil with a Van Veen dredge type sampler thrown from a boat. The

 samples were transported to the laboratory in polyethylene bags, where they were dried in plastic trays at 40°C for 48 h until their analysis.

The metals considered in this study were total mercury (Hg), copper (Cu), zinc (Zn), cadmium (Cd), and lead (Pb) Total mercury was analyzed by taking 0.5 g of sediment sample and digesting it with mercury-free H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> (7: 3 v/v) and 5% KMnO<sub>4</sub> w/v at 100°C for 1 h, using method 7471B (USEPA, 2007a). Cu, Zn, Cd, and Pb were analyzed through sediment digestion with HNO<sub>3</sub>/HCI (8:2 v/v) in a microwave oven employing method 3051 A (USEPA, 2007b). The analyses were performed using a Thermo Elemental Solaar S4 spectrometer coupled with cold-vapor for Hg, flame for Cu and Zn, and graphite furnace for Cd and Pb. Validation was achieved with IAEA 405 (certified value; Hg 0.81 µg/g, Cu 47.7 µg/g, Pb 74.8 µg/g, Cd 0.73 µg/g, and Zn 279 µg/g) and recovery percentages for metals averaged at 97.6% (n=3). The relative standard deviation for a triplicate sample analysis was less than 10% for metals. The detection limits for the different metals were 0.001 µg/g for Hg, 0.008 µg/g for Cd, 0.011 µg/g for Pb, 0.05 µg/g for Zn, and 0.05 µg/g for Cu.

The degree of pollution was calculated as a function of the index of geoaccumulation (Igeo), enrichment factor (EF), contamination factor (CF), sediment quality guidelines (SQG), mean effect range median (ERM) quotient (M-ERM-Q), and pollution load index (PLI), as previously described by Islam et al. (2017) and Marrugo-Negrete et al. (2017). The different equations, interpretation details and categories of each index utilized could be found in Supplementary Table S1. The baseline or background values for the different metals were: Hg 0.045 ± 0.012 µg/g, Cu 11.8 ± 0.24 µg/g, Pb 0.087 ± 0.018 µg/g, Cd 0.055 ± 0.014 µg/g, and Zn 20.2 ± 2.2 µg/g. These values correspond to average concentrations of each metal analyzed from sediments collected at three stations in another important swamp, Ciénaga Grande de Santa Marta, a larger coastal lagoon with no noticeable anthropogenic pollution inputs.

The results per sample were calculated as the mean ± standard deviation per triplicate. A Student t-test was used to evaluate if there were significant differences between the average concentrations from two different sampling sites or expeditions. Pearson's correlation and principal component analyses were used to check for significant relationships among metals in the sediment samples and common origin among these. A multivariate cluster analysis (MCA) and the PCA were employed to identify associations and a common origin among metals. MCA was applied to identify different geochemical groups, clustering the samples with similar metal contents; whereas, for further evaluation of the extent of metal contamination in the study area and source identification, a PCA was used with Varimax rotation to minimize the number of variables with high loading on each component. A hierarchical MCA was performed according to the average linkage (between groups) method and Pearson's correlation as a similarity measure. The results are reported as a dendrogram, thus, providing a visual summary of the cluster. The criterion of significance was set at < 0.05. Statistical analyses were performed with the software SPSS v23.0.0.

Table 1 summarizes the basic statistics related to the metal concentrations in sediment from the protected area of Ciénaga de Mallorquín, as well as the background values and sediment quality guidelines (SQGs) used in this study. The concentration of metals in sediment follow a decreasing order: Zn > Cu > Pb > Cd > Hg, and showed statistically significant differences among sampling sites (p > 0.05). This indicates that the exposure to different degrees of contamination with metals in the sediments shows spatial variations. The highest concentrations of metals are shown at sites E2 (Las Flores), E5 (La Playa), and E6 (Arroyo León), associated with dumping of solid and liquid waste of industrial and domestic type, produced by the industry, residential areas, and agriculture activities near its tributaries. In the case of E2, high concentrations come from an old garbage dump located in the District of Barranquilla, which for 32 years, improperly disposed of the solid waste of the city indiscriminately, functioning as an open-air dump and promoting the progressive pollution of the swamp waters. Regarding E5, the volume of domestic wastewater (80,000 m<sup>3</sup>/month) associated with the lack of a sewage system is possibly the

main source of contamination (UNINORTE, 2005). Finally, E6 is affected by the discharge of wastewaters from the southwest of the city of Barranquilla, coming from Arroyo Leon, a tributary of Ciénaga de Mallorquín. Moreover, the Magdalena River receives drainage from industrial and domestic wastewaters, contributing to the further metal enrichment of Ciénaga de Mallorquín (UNEP, 2006; Franco and León, 2012; Tejeda-Benitez et al., 2016). By comparing the average values of metals found in the study site with background values, the results indicated that sediments are contaminated. In particular, Pb and Cd were 17 and 5 times higher than their background values, respectively. All of the previously mentioned indicates that anthropogenic activities directly affect the high values of metal concentration in sediments of Ciénaga de Mallorquín.

The sediment quality guidelines (SQGs) provided a simple, comparative mean for assessing the risk of contamination in an aquatic ecosystem (Macdonald et al., 2000). Table 1 shows that Cu levels were higher than the values corresponding to the threshold effect level (TEL) for all the sampling sites and 43% of the sediments exceeded the effect range low (ERL). Also, Hg is present in 57% of the sediments in higher values than the reference TEL and ERL levels (Table 1). This suggests that Cu and Hg are probably the only elements in the sediments that produce adverse biological effects in the ecosystem (Long and Morgan, 1991; Long et al., 2000; SEPA, 2002). Considering M-ERM-Q, forty-three percent of the sediments have a probability of toxicity of 21% (0.11 = M-ERM-Q < 0.5), according to the sites with the highest concentrations of metals.

According to the PLI values, surface sediments in all the sampling sites indicate an environmental deterioration (PLI > 1), with higher impact for the following sites: E2 (very, PLI >= 6), and E5 and E6 (considerable, 3 < PLI < 6) depending on the functions of the metals in the sediments Zn > Cu > Pb > Cd > Hg. This implies that most sediment samples are highly contaminated with metals, demonstrating an obvious anthropogenic contribution (Sun et al., 2010)

When comparing the results with previous studies in Ciénaga de Mallorquín, metal concentrations are similar to those reported by INVEMAR (2005) and Franco and León

(2012) (Table 2). However, compared to other studies around the world, concentrations were within the range or even lower compared to those regions. This discrepancy may arise due to the sampling sites, the levels of contamination, geographic characteristics of the regions, and anthropogenic factors (Turk et al., 2016). It is also remarkable that several studies (García et al. 2008), Rumisha et al. 2012), Ra et al. 2013), Youssef et al. 2015), El-Sorogy et al. 2016) demonstrated that anthropogenic activities such as urbanization, industrialization, and wastewater disposal largely influence the metals concentrations in sediments, indicating pollution problems in Ciénaga Mallorquin. In comparison with these regions, the sediments of this swamp showed higher (average) Cu concentrations ( $30.4 \pm 9.4 \mu g/g$ ) and lower concentrations for Pb ( $1.55 \pm 0.22 \mu g/g$ ), and Zn ( $65.5 \pm 15.4 \mu g/g$ ).

The CF, EF, and Igeo values in sediments are summarized in Fig. 2. The range of CF for the different metals was 1.4-3.4 (Cu), 14.7-21 (Pb), 6.0-13.4 (Cd), 2.3-3.8 (Hg), and 2.3-4.2 (Zn). The CF average for all metals are indicated in a decreasing order: Pb (17.2) > Cd (8.6) > Hg (3.2) > Zn (2.9) > Cu (2.3). The CF average based on background values for all metals indicates contamination by human sources (CF > 1), with metals such as Cu and Zn generating a moderate degree of contamination (1 > CF < 3), whereas Hg showed a strong level of pollution (3 > CF < 6), and Pb and Cd recorded a very strong degree of contamination (CF > 6). The average EF values for Cu, Pb, Cd, Hg, and Zn in sediments were 0.72, 5.5, 2.7, 1.0, and 0.9, respectively (Fig 2b). The mean EF values suggest moderately severe enrichment with Pb (EF= 5 - < 10), moderate enrichment with Cd (EF = 3- < 5), and minor enrichment with Hg (EF=1 - < 3), unlike the EF values < 1.0 for Zn and Cu that indicate no enrichment. Cd, Pb, and Hg are anthropogenic metals usually generated by human activities. This is possibly associated with the direct contribution of industrial, agricultural, and domestic discharges from surrounding population centers and the Magdalena River, receiving in its route discharge from different anthropogenic sources (INVEMAR, 2005), as well as the leachates from the old sanitary landfill in the city of Barranquilla. The calculated Igeo values for each of the metals in the sediment samples are presented in Fig. 2c. The average Igeo values were found in the following decreasing order:

Pb > Cd > Hg > Zn > Cu. This order agrees with the results of the CF and EF values, indicating that the human activity has a severe effect on the quality of the environment of Ciénaga de Mallorquín.

The Igeo values range from -0.10 to 1.19 with an average value of 0.54 for Cu; 3.29 to 3.81 with an average value of 3.51 for Pb; 2.0 to 3.16 with an average value of 2.46 for Cd; 0.61 to 1.80 with an average value of 1.06 for Hg, and 0.58 to 1.50 with an average value of 0.93 for Zn. Therefore, the Igeo values indicate moderate to heavy pollution of metals in the study area, depending on each metal and sampling site. Then, Cu, Zn and Hg present a moderate contamination (1 < lgeo < 2), while Cd shows moderate to heavy contamination (2 < Igeo < 3), and Pb exhibits heavy pollution (4 < Igeo < 5). In comparison with recently reported studies on sediments (Gutiérrez-Mosquera et al., 2018) in other areas of Colombia (i.e., Bahia Solano and Nuquí along the Pacific coast of Chocó), Igeo values are similar compared to those reported in the current study for Pb, Cu, and Zn. However, these are lower for EF in all metals assessed. In comparison with other countries, CF, EF, and Igeo values are similar to those reported in surface sediments of the Yangtze River estuary in China (Wang et al., 2015), in sediments from coastal regions of West Bengal, the eastern part of India (Antizar-Ladislao et al., 2015), as well as surface sediments of coastal regions of the Sundarban mangrove wetland and the adjacent Hugli river estuary, in India (Watts et al., 2017).

The PCA biplot in Figure 3a shows the relationship between the trace elements and stations in the Mallorquin swamp. The first two principal components (PC) are able to account for 96.59% of the variance of all variables. PC1 shows the highest loadings for Cu and Cd and explains 94.01% of the variance, exhibiting an eigenvalue of 4.70. Cd shows the highest loading in PC1 (Supplementary Table S2). Moreover, the highest EF and CF values are observed for this toxic trace element. The Cd contamination of the Mallorquín swamp sediments has also been reported in other studies (INVEMAR, 2005; Franco and León, 2012). Metals such as Cu and Cd are possibly associated with wastewater discharges from domestic and industrial activities. However, these elements are so well known from

agricultural activities related to the use of phosphate-based (Acosta et al., 2011) and phosphate fertilizers (Nziguheba and Smolders, 2008; Atafar et al., 2010) applied in areas surrounding Ciénaga de Mallorquin, contaminating the sediments thought the tributaries of Arroyo León (E2). PC2 shows the loading of Hg, Pb, and Zn, and explains 2.58% of the total variance. Hg shows the highest loading in PC2 (0.417). Pb and Zn were the elements that did not demonstrate a clear association with either the first or the second component and had similar moderate loading plots for PC1 (Pb: 0.195; Zn: 0.198) compared to PC2 (Pb: 0.255; Zn: 0.221), indicating a quasi-independent behavior.

This could be explained as a source of compound pollution related to the rapid urban expansion, the large-scale integral development of industrial areas, and contribution of metals by the Magdalena River, where high concentrations of these have been reported in sediments (Tejeda- Benitez et al., 2016; Fernandez et al., 2018). These can directly influence the content of these metals in the sediments of Ciénaga de Mallorquín. Pb results can also be attributed to petrogenic sources due to nearby maritime ports and tourist activities with gasoline engines. However, to corroborate this hypothesis, hydrocarbon studies must be conducted and correlated with this metal. It should be noted that Hg is moderately shared by both PCs, suggesting that its probable source may be of a diverse nature. Hg concentrations are probably significantly related to the leachate discharge from the sanitary landfill in Ciénaga de Mallorquín, particularly at the E2 site through residues such as fluorescent lamps, liquid crystal displays, and batteries, among others (da Cunha et al., 2016). Besides, there is a contribution of the Magdalena River in the increase of Hg concentration in sediments in urban center areas of Barranguilla (Tejeda-Benitez et al., 2016). To better identify and decode the source of metals, the PCA was combined with Pearson's correlation analysis. According to the latter (Supplementary Table S3), the metals are all positively and significantly correlated and reflect the origin and migration of these elements, agreeing with previous studies (Suresh et al. 2011; Wang et al. 2012).

The sampling points were analyzed by grouping methods (Fig. 3a) and organized in a dendrogram to identify similar groups (Fig. 3b). The sampling sites were grouped in three

clusters: the first group with four sites (E1, E3, E4, and E7) represents 57%, and are mostly located towards the interior of the swamp. A second group with two stations (E5 and E6), represents 28%, located in the western part of the swamp, opposite the Magdalena River. Finally, a third group that represents only one site (E2), placed in front of the Las Flores sector, where an old dumpster operates. This distribution is also observed in the biplot of Figure 3a.

The spatial distribution of metal concentrations can be used to identify possible sources and some pollution hotspots (Fig. 4). The strongest tones indicate the stations that presented the highest concentrations of the metals analyzed. Results show that the concentrations of Cu, Zn, Pb, Cd, and Hg have similar spatial distribution patterns in sediments. In general, the highest concentrations of metals were found in the northeastern and southeastern regions of the study area, mainly located nearby sectors with anthropogenic sources of contamination (sanitary landfill, domestic wastewaters, and the tributaries of Arroyo León). These findings suggest that anthropic sources have an important impact on the contamination of the swamp. There is clearly a pattern in the spatial distribution for all metals in the sediments, where the highest concentration occurs toward the sector of Las Flores (east) associated with the contamination by the discharge of leachates from the old landfill of the City of Barranquilla and the area of influence of the Magdalena River. However, Cu and Pb have areas of high concentration towards the sector of La Playa (southeast) associated with the problem of expansion of the "urban" border and wastewater contamination. The distribution towards the central zone, where concentrations decreased from the internal part of the swamp, can result from the dilution effect caused by tidal cycles in the Caribbean Sea and flows from the Magdalena River. Finally, Zn values were the highest among all the metals. At low concentrations, Zn is beneficial for aquatic life, but becomes toxic at concentrations above the threshold value of 124 µg/g (Li et al., 2013).

Metal concentrations in the sediments showed spatial variability, higher in those areas that receive loads of pollutants from anthropogenic sources. In addition, it indicates that metal sources were quite complex and included different anthropogenic activities. The Igeo, CF, and EF indexes, suggested that the sediments are low to moderately contaminated by Hg, Cu, and Zn, while the contamination by Cd and Pb is moderate to strong. The pollution load index results indicate the progressive deterioration of sediment quality due to different anthropogenic activities. Concentrations of Cu and Hg exceeded the TEL and ERL values, indicating an ecotoxicological risk for the organisms living in the sediments of Ciénaga de Mallorquín. The multivariate statistical analyses suggest a mixed origin of metals by the influence of anthropogenic contributions. Therefore, Cd and Cu were originated mainly from agricultural and industrial sources, whereas Pb and Zn were derived mainly from industrial sources, discharge of domestic wastewater, and metal inputs from the Magdalena River. Hg was originated mainly from leachate discharges and inputs of the sediments must be implemented to reduce the discharge of pollutants by anthropogenic sources as well as provide a basis to effectively focus policies to protect and manage future ecological risks of the swamp Ciénaga de Mallorquín.

#### References

Acosta, J.A., Faz, A., Martínez-Martínez, S., Arocena, J.M., 2011. Enrichment of metals in soils subjected to different land uses in a typical Mediterranean environment (Murcia city, southeast Spain). Appl. Geochem. 26, 405–414.

Agah, H., Hashtroudi, M.S., Baeyens, W., 2012. Trace metals and major elements in sediments of the northern Persian Gulf. J. Persian Gulf. 3, 45–58.

Alonso-Hernández, C.M., Conte, F., Misic, C., Barsanti, M., Goméz Batista, M., Díaz-Asencio, M., Covazzi-Harriague, A., Pannacciulli, G., 2011. An overview of the Gulf of Batabano (Cuba): environmental features as revealed by surface sediment characterisation. Cont. Shelf. Res. 31,749–775.

- Antizar-Ladislao, B., Mondal, P., Mitra, S., Kumar, S. S., 2015. Assessment of trace metal contamination level and toxicity in sediments from coastal regions of West Bengal, eastern part of India. Mar. Pollut. Bull. 101, 886–894.
- Atafar, Z., Mesdaghinia, A., Nouri, J., Homaee, M., Yunesian, M., Ahmadimoghaddam, M.,
  Mahvi, A.H., 2010. Effect of fertilizer application on soil heavy metal contamination.
  Environ. Monit. Assess. 160, 83–89.
- Bastami, K.D., Afkhami, M., Mohammadizadeh, M., Ehsanpour, M., Chambari, S., Aghaei, S., Esmaeilzadeh, M., Neyestani, M.R., Lagzaee, F., Baniamam, M., 2015.
  Bioaccumulation and ecological risk assessment of heavy metals in the sediments and mullet Liza klunzingeri in the northern part of the Persian Gulf. Mar. Pollut. Bull. 94, 329–334.
- Bodin, N., N'Gom-Ka, R., Ka, S., Thiaw, O.T., Tito de Morais, L., Le Loc'h, F., Rozuel-Chartier, E., Auger, D., Chiffoleau, J.F., 2013. Assessment of trace metal contamination in mangrove ecosystems from Senegal, West Africa. Chemosphere 90, 150–157.
- Burgos-Núñez, S., Navarro-Frómeta, A., Marrugo-Negrete, J., Enamorado-Montes, H., Urango-Cárdenas, I., 2017. Polycyclic aromatic hydrocarbons and heavy metals in the Cispata Bay, Colombia: a marine tropical ecosystem. Mar. Pollut. Bull. 120, 379–386.
- Bramha, S.N., Mohanty, A.K., Satpathy, K.K., Kanagasabapathy, K.V., Panigrahi, S., Samantara, M.K., PrasadHeavy, M.V.R., 2014. Metal content in the beach sediment with respect to contamination levels and sediment quality guidelines: a study at Kalpakkam coast, southeast coast of India. Environ. Earth Sci. 72, 4463–4472.
- Canário, J., Branco, V., Vale, C., 2007. Seasonal variation of monomethylmercury concentrations in surface sediments of the Tagus Estuary (Portugal). Environ. Pollut. 148 (1), 380–383.
- Cormagdalena-Cra-Uninorte., 1998. Feasibility study for the recovery of the Mallorquín swamp. Executive report, Corporación Autónoma Regional del Atlántico, Barranquilla, p. 254.

- Chapman, P.M., Wang, F., Caeiro, S.S., 2013. Assessing and managing sediment contamination in transitional waters. Environ. Int. 55, 71–91.
- Christophoridis, C., Dedepsidis, D., Fytianos, K., 2009. Occurrence and distribution of selected heavy metals in the surface sediments of Thermaikos Gulf, N. Greece. Assessment using pollution indicators. J. Hazard. Mater. 168, 1082–1091.
- Chowdhury, R., Favas, P.J.C., Pratas, J., Jonathan, M.P., Ganesh, P.S., Sarkar, S.K., 2015. Accumulation of trace elements by mangrove plants in Indian Sundarban Wetland: prospects for phytoremediation. Int. J. Phytoremediation. 17, 885–894.
- da Cunha, R.C., Patrício, P.R., Vargas, S.J.R., da Silva, L.H.M., da Silva, M.C.H., 2016. Green recovery of mercury from domestic and industrial waste. J. Hazard. Mater. 304,417-424.
- Decree Number 3888., 2009. Wetlands of international interest: Ministry of Environment, Housing and Territorial Development. Republic of Colombia, p. 8.
- El Nemr, A.M., El Sikaily, A., Khaled, A., 2007. Total and leachable heavy metals in muddy and sandy sediments of Egyptian coast along Mediterranean Sea. Environ. Monit. Assess. 129, 151–168.
- El-Sorogy, A.S., Tawfik, M., Almadani, S.A., Attiah, A., 2016. Assessment of toxic metals in coastal sediments of the Rosetta area, Mediterranean Sea, Egypt. Environ. Earth Sci. 75, 398.
- El-Sorogy, A.S., Youssef, M., Al-Kahtand, K., Saleh, M.M., 2020. Distribution, source, contamination, and ecological risk status of heavy metals in the Red Sea-Gulf of Aqaba coastal sediments, Saudi Arabia. Mar. Pollut. Bull. 158, 111411.
- Espinosa, L.F., Parra, J.P., Villamil, C., 2011. Determinacion del contenido de metales pesados en las fracciones geoquímicas del sedimento superficial asociado a los manglares de la Cienaga Grande de Santa Marta, Colombia. Bol Invest Mar Cost 40,7–23.
- Franco, A. J., Leon-Luna, I. M., 2010. Geoquímica y concentraciones de metales pesados en un organismo de interés comercial (Corbula caribaea. D'orbigny, 1842) en la zona

submareal superficial de la Ciénaga de Mallorquín Atlántico. Boletín Científico CIOH. 28, 69-83.

- Fernandez-Maestre, R., Restrepo, B.J., Olivero-Verbel, J., 2018. Heavy Metals in Sediments and Fish in the Caribbean Coast of Colombia: Assessing the Environmental Risk. Int. J. Environ. Res. 25 (3), 289-301.
- Franco, A., León, I., 2012. Bioacumulación de metales traza en mugil incilis (hancoc k, 1830); Una herramienta útil para el biomonitoreo de la contaminación metálica en el litoral costero del departamento del Atlántico Colombia mugil incilis bioindicador de la contaminación metálica del litoral costero. Costas. 1 (1), 98–106.
- Fu, J., Zhao, C., Luo, Y., Liu, C., Kyzas, G.Z., Luo, Y., Zhao, D., An, S., Zhu, H., 2014. Heavy metals in surface sediments of the Jialu River, China: Their relations to environmental factors. J. Hazard. Mater. 270, 102–109.
- Fuentes-Gandara, F., Pinedo-Hernández, J., Marrugo-Negrete, J., Díez, S., 2018. Human health impacts of exposure to metals through extreme consumption of fish from the Colombian Caribbean Sea. Environ. Geochem. Health. 40, 229–242.
- Galvis, O., Téllez. S., Lora, A., 1992. Contribution to the knowledge of the environmental characteristics of the Mallorquín swamp. VIII Semin. Nac. Cien. Tecnol. Mar BCC, Bogotá, vol. 1, pp. 483–489.
- García, E.M., Cruz-Motta, J.J., Farina, O., Bastidas, C., 2008. Anthropogenic influences on heavy metals across marine habitats in the western coast of Venezuela. Cont. Shelf Res. 28, 2757–2766.
- González, R.M., Moguel, C.Z., Bolio, M.C., Canul, R.P., 2004 Concentración de Cd, Cr, Cu y Pb en sedimentos y en tres especies de pepino de mar (clase holothuroidea) de las costas del Estado de Yucatán, México. Ingeniería 8 (2),:7–19.
- Gutiérrez-Mosquera, H., Shruti, V.C., Jonathan, M.P., Roy, Priyadarse D., Rivera-Rivera, D.M., 2018. Metal concentrations in the beach sediments of Bahia Solano and Nuquí along the Pacific coast of Chocó, Colombia: A baseline study. Mar. Pollut. Bull. 135, 1–8.

- INVEMAR., 2005. Technical Report: First Monitoring of Heavy Metals in water, sediments and organisms of the Mallorquín marsh, Department of the Atlántico.
- Islam, M.A., Al-mamun, A., Hossain, F., Quraishi, S.B., Naher, K., Khan, R., Das, S., Hossain, S.M., Nahid, F., Tamim, U., 2017. Contamination and ecological risk assessment of trace elements in sediments of the rivers of Sundarban mangrove forest, Bangladesh. Mar. Pollut. Bull. 124, 356–366.
- Jiang, R., Huang, S., Wang, W., Liu, Y., Pan, Y., Sun, X. Lin, C., 2020. Heavy metal pollution and ecological risk assessment in the Maowei sea mangrove, China. Mar. Pollut. Bull. 161, 111816.
- Kamidis, N.I., Stamatis, N. Sylaios, G., 2004. Trace elements concentrations in the surface sediments and the water column of Kavala Gulf (northern Greece). Rapp Comm Int Mer Médit. 37:210.
- Li, F., Huang, J., Zeng, G., Yuan, X., Li, X., Liang, J., Wang, X., Tang, X., Bai, B., 2013. Spatial risk assessment and sources identification of heavy metals in surface sediments from the Dongting Lake, Middle China. J. Geochem. Explor. 132, 75–83.
- Long, E.R., Morgan, L.G., 1991. The potential for biological effects of sediment-sorbed contaminants tested in the national status and trends program. In: NOAA Technical Memorandum NOS OMA 52. US National Oceanic and Atmospheric Administration, Seattle, Washington.
- Long, E.R., MacDonald, D.D., Severn, C.G., Hong, B.C., 2000. Classifying probabilities of acute toxicity in marine sediments with empirically derived sediment quality guidelines. Environ. Toxicol. 19, 2598–2601.
- Ilgar, R., 2011. Determination of heavy metal concentrations in seabed sediments of the Dardanelles-cities area, Turkey. Am Eur J Txicological Sci. 3(1),23–27.
- Macdonald, D.D., Ingersoll, C.G., Berger, T.A., 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch. Environ. Contam. Toxicol. 39 (1), 20-31.

Marrugo-Negrete, J., Pinedo-Hernández, J., Díez, S., 2017. Assessment of heavy metal pollution, spatial distribution and origin in agricultural soils along the Sinú River Basin, Colombia. Environ. Res. 154, 380-388.

- Mendoza-Carranza, M., Sepulveda-Lozada, A., Dias-Ferreira, C., Geissen, V., 2016. Distribution and bioconcentration of heavy metals in a tropical aquatic food web: a case study of a tropical estuarine lagoon in SE Mexico. Environ. Pollut. 210,155–165.
- Mohammadizadeh, M., Bastami, K.D., Ehsanpour, M., Afkhami, M., Mohammadizadeh, F.,
  Esmaeilzadeh, M., 2015. Heavy metal accumulation in tissues of two sea cucumbers,
  Holothuria leucospilota and Holothuria scabra in the northern part of Qeshm Island,
  Persian Gulf. Mar. Pollut. Bull. 103, 354–359.
- Nziguheba, G., Smolders, E., 2008. Inputs of trace elements in agricultural soils via phosphate fertilizers in European countries. Sci. Total Environ. 390, 53–57.
- Ra, K., Kim, E.S., Kim, K.T., Kim, J.K., Lee, J.M., Choi, J.Y., 2013. Assessment of heavy metal contamination and its ecological risk in the surface sediments along the coast of Korea. J. Coastal. Res. 65, 105–110.
- Rumisha, C., Elskens, M., Leermakers, M., Kochzius, M., 2012. Trace metal pollution and its influence on the community structure of soft bottom molluscs in intertidal areas of the Dar es Salaam coast, Tanzania. Mar. Pollut. Bull. 64, 521–531.
- SEPA (State Environmental Protection Administration of China)., 2002. Marine Sediment Quality (GB 18668-2002). Standards Press of China, Beijing.
- Sun, Y., Zhou, Q., Xie, X., Liu, R., 2010. Spatial, sources and risk assessment of heavy metal contamination of urban soils in typical regions of Shenyang, China. J Hazard Mater. 174(1-3), 455-462.
- Suresh, G., Ramasamy, V., Sundarrajan, M., Paramasivam, K., 2015. Spatial and vertical distributions of heavy metals and their potential toxicity levels in various beach sediments from high-background-radiation area, Kerala. India. Mar. Pollut. Bull. 91 (1), 389-400.

- Tejeda-Benitez, L., Flegal, R., Odigie, K., Olivero-Verbel, J., 2016. Pollution by metals and toxicity assessment using *Caenorhabditis elegans* in sediments from the Magdalena River, Colombia. Environ. Pollut. 212, 238–250
- TurkCulha, S., Dereli, H., Karaduman, F.R., Culha, M., 2016. Assessment of trace metal contamination in the sea cucumber (*Holothuria tubulosa*) and sediments from the Dardanelles Strait (Turkey). Environ Sci Pollut Res. 23,11584–11597
- UNEP., 2006. Isaza, A., Sierra-Correa, C., Bernal- Velasquez, M., Londoño, L. M., & Troncoso, W. Caribbean Sea/Colombia and Venezuela, Caribbean Sea/ Central America and Mexico, GIWA Regional assessment 3b, 3c. University of Kalmar, Kalmar
- UNINORTE., 2005. Análisis sobre el Manejo Integrado del Recurso Hídrico en la Ciénaga de Mallorquín. Grupo de Investigación en Tecnologías del Agua de la Universidad del Norte. Convenio No. 79 de 20094, celebrado entre Universidad del Norte (UNINORTE) y la Corporación Autónoma Regional del Atlántico (CRA).Barranquilla, Colombia.
- USEPA., 2007a. SW-846 Test Method 7471B: Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique). p. 11.
- USEPA., 2007b. SW-846 Test Method 3051A: Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils. p. 30.
- Vallejo Toro, P.P., Vásquez Bedoya, L.F., Darío Correa, I., Bernal Franco, G.R., AlcántaraCarrió, J., Palacio Baena, J.A., 2016. Impact of terrestrial mining and intensive agriculture in pollution of estuarine surface sediments: spatial distribution of trace metals in the Gulf of Urabá, Colombia. Mar. Pollut. Bull. 111, 311–320.
- Vetrimurugana, E., Shruti, V.C., Jonathan, M.P., Roy, Priyadarsi D., Rawlins, B.K., RiveraRivera, D.M., 2018. Metals and their ecological impact on beach sediments near the Marine protected sites of Sodwana Bay and St. Lucia, South Africa. Mar. Pollut. Bull. 127, 568–575.
- Violintzis, C., Arditsoglou, A., Voutsa, D., 2009. Elemental composition of suspended particulate matter and sediments in the coastal environment of Thermaikos Bay,

Greece: delineating the impact of inland waters and wastewaters. J Hazard. Mater. 166,1250–1260

- Wang, Y., Hu, J.W., Xiong, K.N., Huang, X.F., Duan, S.M., 2012. Distribution of heavy metals in core sediments from Baihua lake. Proced. Environ. Sci. 16 (4), 51-58.
- Wang, J.W., Liu, R.M., Zhang, P.P., Yu, W.W., Shen, Z.Y., Feng, C.H., 2014. Spatial variation, environmental assessment and source identification of heavy metals in sediments of the Yangtze River Estuary. Mar. Pollut. Bull. 87, 364–373.
- Wang, H., Wang, J., Liu, R., Yu, W., Shen, Z., 2015. Spatial variation, environmental risk and biological hazard assessment of heavy metals in surface sediments of the Yangtze River estuary. Mar. Pollut. Bull. 93, 250–258.
- Watts, M.J., Mitra, S., Marriott, A.L., Sarkar, S.K., 2017. Source, distribution and ecotoxicological assessment of multielements in superficial sediments of a tropical turbid estuarine environment: A multivariate approach. Mar. Pollut. Bull. 115, 130–140.
- Wu, H., Liu, J., Bi, X., Lin, G., Feng, C.C., Li, Z., Qi, F., Zheng, T., Xie, L., 2017. Trace elements in sediments and benthic animals from aquaculture ponds near a mangrove wetland in southern China. Mar. Pollut. Bull. 117, 486–491.
- Youssef, M., El-Sorogy, A.S., Al-Kahtany, K.H., Al-Otaibi, N., 2015. Environmental assessment of coastal surface sediments Tarut Island, Arabian Gulf (Saudi Arabia). Mar. Pollut. Bull. 96, 424–433.

Station							
	Cu	Zn Pb Cd		Hg	M-ERM-Q	PLI	
E1	25.8±3.2	64.4±5.7	1.43±0.08	0.30±0.07	0.11±0.04	0.09	4.1
E2	45.9±2.9	95.0±6.2	1.89±0.13	0.67±0.05	0.25±0.08	0.17	7.3
E3	28.7±5.2	57.0±8.1	1.35±0.15	0.37±0.02	0.13±0.06	0.09	4.4
E4	18.9±6.1	51.6±4.3	1.44±0.09	0.33±0.03	0.11±0.09	0.08	3.8
E5	38.7±3.1	72.5±3.6	1.75±0.12	0.52±0.05	0.18±0.05	0.13	5.9
E6	32.6±2.9	67.9±1.9	1.67±0.15	0.48±0.08	0.17±0.02	0.12	5.4
E7	22.6±3.7	50.3±2.2	1.32±0.22	0.33±0.04	0.14±0.08	0.09	4.0
Mean	30.4±9.4	65.5±15.4	1.55±0.22	0.43±0.13	0.16±0.05	0.11	5.0
Background	13.4	22.4	0.23	0.22	0.048		
	Cu	Zn	Pb	Cd	Hg		
TEL <sup>a</sup>	18.7	124	30.24	0.68	0.13		
PEL <sup>a</sup>	108.2	271	112.18	4.21	0.7		
ERL <sup>b</sup>	34	150	46.7	1.2	0.15		
<b>ERM</b> <sup>b</sup>	270	410	218	9.6	0.71		

**Table 1.** Values of metal concentrations ( $\mu$ g/g), mean ERM Quotient (M-ERM-Q), pollution load index (PLI) and sediments quality guideline (SQGs) in surface sediments of the Mallorquin swamp

<sup>a</sup>CMEE: Canadian sediment quality guidelines for the protection of aquatic life; <sup>b</sup>NOAA: National Oceanic and Atmospheric Administration, USA.

TEL = Threshold Effects Level; PEL =Probable Effects Level; ERL = Effect Range Low; ERM = Effect Range Medium.

Region	Cu	Cd	Pb	Zn	Hg	References
Peninsula de Yucatán, México	1.84	2.22	19.37			González et al. (2004)
Kavala Gulf	21.3	0.3	40.1	258		Kamidis et al. (2004)
Mallorquin swamp, Colombia		1.1		41		Invemar (2005)
Western coast of Venezuela	3.79	0.31–1.3	9–29	26–242		García et al. (2008)
Thermaikos Gulf	32–130	0.3–8.4	38–190	84–537		Violintzis et al. (2009)
Dardanelles Strait	9–22		8–20	34–76		llgar (2011)
Santa Marta swamp, Colombia		1–3	29–82	28–65		Espinosa et al. (2011)
Cuba, Gulf of Batabano		0.1–1	3.1–18.2	7.9–457		Alonso-Hernández et al. (2011)
Mallorquin swamp & Pto Velero, Colombia		0.1–0.9		45–81		Franco and León (2012)
Salaam coast, Tanzania	0.3–2.1		0.8–2.2	2.6–9.3		Rumisha et al. (2012)
Persian Gulf	26 ± 1	0.16 ± 0.04	10 ± 0.2	64 ± 8		Agah et al. (2012)
Korea coast	36.5		35	122		Ra et al. (2013)
Kalpakkam coast - coast of India	52.47 ± 3.26	0.45 ± 0.18	21.49 ± 4.08	25.84 ± 31.45		Bramha et al. (2014)
Arabian Gulf, Saudi Arabia	5.78		58.68	17.57		Youssef et al. (2015)
Sundarban Wetland, Indian	38.31	0.21	15.8	34.4	0.070	Chowdhury et al. (2015)
Northern Persian Gulf	32.47 ± 4.37	4.29 ± 0.61	31.38 ± 12.61	62.08 ± 12.58		Bastami et al. (2015)
San Pedrito Lagoon, Mexico		4 ± 2	21 ± 6	37 ± 33		Mendoza et al. (2016)
Gulf of Urabá, Colombia	25.08–102.94		0.17–6.93	75.15–161.53		Vallejo Toro et al. (2016)
northern Qeshm Island, Persian Gulf	17.56-53.25	0.51-1.2	10.09-29.66	27.4-56.02		Mohammadizadeh et al. (2016)
Magdalena River, Colombia	26.9	2.02	16.8	99	0.12	Tejeda-Benitez et al. (2016)
Rosetta coast, Egypt	24.57		384.68	183.23		El-Sorogy et al. (2016)
Cispata Bahía, Colombia	1.63-15.36	0.009-0.014	0.49-1.39		0.016-0.135	Burgos et al. (2017)
Caribbean coast, Colombia		0.01–0.42	0.4–7.0	9–199		Fernandez et al. (2018)
Bahia Solano Beaches, Colombia	53.93		409.67	125.8		Gutiérrez-Mosquera et al. (2018)
Sodwana Bay, South Africa	4.53		1.27	2.81		Vetrimurugana et al., 2018
Maowei Sea, China	61.9	0.790	48.9	166		Jiang et al., 2020
Red Sea-Gulf of Aqaba, Saudi Arabia	30	0.91	6.6	24	0.84	El-Sorogy, et al., 2020
Mallorquin swamp, Colombia	30.4 ± 9.4	0.43 ± 0.13	1.55 ± 0.22	65.5 ± 15.4	0.16 ± 0.05	This study

## **Table 2.** Metals concentrations in sediments and comparison with other similar studies



**Figure 1.** Location of sampling stations at the Mallorquín swamp. E1: Vía La Playa, E2: Las Flores, E3: Connection Magdalena River - Swamp, E4: Central area, E5: La playa, E6: Mouth Arroyo León, E7: Connection Caribbean Sea – Swamp.



**Figure 2.** Box and whisker plots display the distributions of the different contamination indexes: (a) Contamination Factor, (b) Enrichment Factor, and (c) Geoaccumulation index



**Figure 3.** (a) PCA biplot of the sediments from Mallorquín swamp sampling sites indicating vectors of the variables considered with high loadings, and ordination of study sites; b) Dendrogram using Average Linkage (between groups) obtained by hierarchical clustering analysis for the sampling sites.

(a)





















**Figure 4.** Spatial distribution trends for metals in surface sediments at Mallorquín swamp. At a general level, the strongest tones indicate the stations that presented the highest concentrations of the metals analyzed.

Supplementary Data

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