Environmental risk of trace elements in mangrove ecosystems: An assessment of natural vs oil and urban inputs

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Highlights

- **City sewages and boatyards act as point sources for Zn, Cu and Pb.**
- **Ni and V contents show that oil industry has a low impact in mangroves.**
- **Zn, Cu, and Pb contents exceed adverse effect index (AEI) in two urban point sources.**

Abstract

The petrochemical industry and urban activities are widely recognized worldwide as a source of pollution to mangrove environments. They can supply pollutants such as trace elements that can modify the ecosystem structure and associated services, as well as human populations. Through geochemical data, multivariate statistical analysis and pollution indices such as the enrichment factor (EF), geo-accumulation index (Igeo), adverse effect index (AEI) and the pollution load index (PLI), we evaluated the factors that control trace element distribution, punctual sources and determined the pollution level of sediments and their potential biological impact in the mangrove ecosystem of Isla del Carmen, Mexico. The factor and cluster analysis highlighted that the distribution of trace elements is influenced by the mineralogy, texture as well as urban derived sources. The pollution indices showed values in the punctual sources from the urban area of EF > 10, Igeo > 3, AEI >3, PLI > 1 by Cu, Zn and Pb. Finally, the results revealed that mangroves from Isla del Carmen has a major influence from urban activities and natural sources rather than oil industry and also indicate a degraded environment as a result of anthropogenic activities that could have knock-on effect for human health if polluted marine organisms derived from the urban mangroves are consumed.

Capsule abstract: Surface sediments show the influence of point sources on selected trace element concentrations correlated with human activities within the mangroves of Isla del Carmen, Mexico.

Keywords: Trace Elements, Sediment, Oil Industry, Mangroves, Gulf of Mexico, Isla del Carmen

1. Introduction

Mangroves are vegetated intertidal coastal environments located in tropical and subtropical areas. They are characterized by the presence of plants adapted to frequent inundation by saline water imposed by a tidal regime (NOAA, 2014). To support and sustain the well-being of human being, mangroves provide a range of ecosystem services such as: nursery and breeding habitats for commercial shrimp, crabs and fish species; coastal protection against erosion processes, cyclones, storms, floods and carbon sequestration (Brander et al., 2012; Lovelock et al., 2015; Mehaur et al., 2018; Shi et al., 2019).

Like many other ecosystems, mangroves have been subjected to anthropogenic pressures resulting in decreases in mangrove area, particularly conversion to agriculture, aquaculture and salt ponds, urban expansion as well as alterations to sediment supply, sea level rise, drought and storms as a result of climate change (Ward et al., 2016; Veetil et al., 2018; Mafi-Gholami et al., 2019). Due to their location in coastal and estuarine settings they are also often exposed to a range of pollutants particularly those located proximal to industry or urban settings. Many of these pollutants are harmful to mangrove associate organisms and humans when transferred through the trophic chain (Senthilkumar et al., 2013; Kulkarni et al., 2018; Chai et al., 2019). Trace elements are common pollutants found in mangroves and are considered as a serious threat to human health and other living organisms due to their persistence, potential for bioaccumulation, and toxicity (Arrivabene et al., 2016; Celis et al., 2017; Singh and Kumar, 2017). However, it is important to note that trace elements can be derived from anthropogenic and natural sources that complicate analysis concerning their environmental impact (Anaya-Gregorio et al., 2018; Armstrong-Altrin et al., 2019). To resolve this issue geochemical indices such as the enrichment factor (EF), geoaccumulation Index (Igeo), pollution load index (PLI), adverse effect index (AEI), as well as statistical tools have been developed to provide a better understanding about the environmental risks that these substances pose to mangrove ecosystems and humans (Goher et al., 2014; Duodu et al., 2017; Benson et al., 2018).

Mangroves from Isla del Carmen are likely to be influenced by point source pollution from urban, industrial and petrochemical derived sources as a result of the proximity to an industrial port city and petrochemical source. Therefore, Isla del Carmen is an important area to study how oil industry and urban activities impact mangrove environments.

The aim of this study is to determine the agents that influence trace element distribution in mangroves with pollution sources including the oil industry and urban activities. Additionally, we aimed to evaluate the contamination level of sediments and their potential biological impact in the mangroves of Isla del Carmen, Mexico.

2. Study area

Isla del Carmen is located in the southeastern Gulf of Mexico in Campeche, Mexico (Figure 1). Twenty three percent of its surface corresponds to the urban area of Ciudad del Carmen, while the remaining 77% is covered by mangroves (INEGI, 2018). Ciudad del Carmen is the second most populated urban center (248,303 inhabitants) in Campeche state (INEGI, 2018). Isla del Carmen belongs to a natural protected area known as Wildlife Protection Area Laguna de Terminos, which includes the largest coastal lagoon environment in Mexico (about 7050.16 Km^2) (INEGI, 2018). In the north coast of the island the marine environment dominates and houses the Canterell oil field, which is the largest gas (38%) and offshore oil (56.5%) producer in Mexico (Nava et al., 2018; PEMEX, 2018) while, in the south coast it receives fluvial discharges of the Palizada, Chumpan and Candelaria rivers, which supply nutrients, sediments, as well as pollutants generated by agricultural, cattle feeding and other human activities (Carvalho et al., 2009). The weather is mostly humid warm with summer rainfall. The average annual temperature ranges from 26 to 28 °C, while the average annual rainfall ranges from 1500 to 2000 mm (INEGI, 2018). Seasonally, three different regimes are recognizable, the dry season (Feb-May), rainy season (Jun-Sep), and stormy season (Oct-Jan).

3. Materials and methods

Sediment samples were collected from thirty-six mangrove sites on Isla de Carmen, Mexico in August 2019 that corresponded to the rainy season; this season was chosen because the rivers' influence is higher in the area rather than other seasons (Figure 1). Samples were collected from creek edges directly adjacent to the mangroves using a Van Veen dredge from a boat at a water column depth from 0.5 to 2.5 m at mid-high tide to avoid running aground. In order to avoid contamination during sampling sediment samples were removed with a plastic spatula from the middle part of the dredge in such a way that sediments had no contact with the metallic parts of the equipment and to get the most recently deposited sediment, we collected the samples in first centimetre. Each sample was stored in sample bags at 4°C until chemical analysis. Samples were divided in two halves with one half used for geochemical analysis and the other for granulometry.

Samples were dried at 50 °C for 5 days and homogenized in an agate mortar by hand. All concentrations in this work were expressed with reference to dry weight. Major and trace element concentrations were determined using a RIGAKU ZSX Primus II X-ray fluorescence spectrometer system and analyzed in pressed powder briquettes. The accuracy of major elements was evaluated using the rock standard Argillite whose values ranged from 102.6 to 93%, with the exception of Na_2O (70.0%), P_2O_5 (73.1%) and K_2O (89.3%). The accuracy of trace elements was estimated using the standard CH-1 marine sediment, values ranged from 102.6 to 90.8% with the exception of V (111.8%) and Co (113.8%). Sediment particle size distribution was determined by sieving with a RX-29 Ro-Tap Sieve Shaker and a standard ASTM sieve set from -2.0, -1.0, 0.0, 1.0, 2.0, 3.0, and 4.0 Φ. Sediments were classified as mud, sand, and gravel based on the methodology proposed by Folk (1980). Organic matter and carbonates were estimated using a loss on ignition method: 1 g of sediment samples were weighed before and after incineration in a muffle furnace at 550 °C and again at 950 °C for 24 hrs in order to eliminate the organic matter and carbonates (Ahmed et al., 2018). Total organic matter and carbonates are reported as percentage of dry weight.

The results were interpreted using descriptive and multivariate statistical tools including correlation analysis to evaluate the strength of relationship among geochemical parameters. A cluster analysis was used to identify impacted locations in mangroves from Isla del Carmen, and factor analysis was performed to determine the variables that better explain the system variability (Statistical analyses were performed using the software STATISTIC 8). Geochemical indices such as EF, Igeo, PLI, and AEI were employed to evaluate the natural or anthropogenic origin for each trace element: to compare and contrast environmental quality with other locations inside the island, and to infer any possible adverse effect on benthic biota (Celis et al., 2018).

Enrichment Factor

This proxy is evaluated using equation (1)

$$EF = \frac{\left(\frac{X_{sample}}{Y_{sample}}\right)}{\left(\frac{X_{background}}{Y_{background}}\right)} \dots\dots\dots\dots\dots\dots\dots\dots\dots..(1)$$

Where X_{sample} and $X_{background}$ are the concentrations of any trace element analysed in the sample and Y_{sample} and $Y_{background}$ are the concentrations of a conservative element that is used to normalize the data. In this work, we used Al_2O_3 as a conservative element because it represents the clay fraction in the sediment and it is not affected by anthropogenic sources or geochemical changes such as redox processes (Celis et al., 2013). As background we employed the least contaminated station (Feng et al., 2010) rather than the Upper Continental Crust (UCC) (McLennan, 2001) to avoid any overestimation in the data interpretation. The enrichment factor results were divided into ranks to establish the degree of enrichment (Birth, 2003) (Table S2).

Geo-accumulation index

This proxy is evaluated using equation 2 (Müller, 1969).

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5B_n} \right) \quad \text{......} \quad (2)$$

Where "C_n" represents the concentration of any trace element in the sediment sample and "B_n" represents the background concentration of the same element; the value of 1.5 is a factor that considers possible variability generated by lithological changes. Geo-accumulation index results were divided into ranks to establish the degree of pollution (Birth, 2003) (Table S2).

Adverse Effect Index

The adverse effect index (AEI) can be applied to evaluate how many times the metal concentration in the sediment has exceeded the Threshold Effect Level (TEL) developed by Long et al., (1995); as well as inferring whether trace element concentrations in the sediment could adverse impact benthic biota (Muños et al., 2012; Hamdoun et al., 2015; Baptista et al., 2017). An AEI lower than 1 means that the trace element concentration in the samples is not high enough to produce adverse effects from sediment contamination to organisms where no toxicity studies are undertaken or available.

This proxy is calculated using equation (3)

$$AEI = \frac{[MC]}{[SQG_s]}$$

Where MC is the trace element concentration in the sample and SQGs is any sediment quality guideline such as Effect Range Low (ERL), Threshold Effect Level (TEL) and others. SQGs are based on the collection, revision and the integration of a range of studies performed in North

America using laboratory bioassays, equilibrium-partitioning modelling and field studies on the toxicity of metals in sediment on benthic composition (Long et al., 1995). In this work, we used the Threshold Effect Level (TEL) and the Analogous Effect Threshold (AET). Both were obtained via the Screening Quick Reference Tables (SQuirRts) supplied by NOAA, 2016.

Pollution Load Index

The pollution load index is calculated using equations 4 and 5 (Tomlinson et al., 1980).

$$\mathrm{PLI_{sample}} = \sqrt[n]{\mathrm{CF_{metal\ 1}} * \mathrm{CF_{metal\ 2}} * \ldots \mathrm{CF_{metal\ n}}} \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

$$\mathrm{CF} = \left[\frac{\mathrm{C_{mS}}}{\mathrm{C_{mB}}}\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

In general; the PLI is calculated with the n^{th} root of the variable called contamination factor (CF) which is evaluated using the equation (4). The super index “n” in the root represents the total number of samples. While the CF is defined as the ratio between the element concentration analyzed in the sample “C_{ms}” and the background concentration of the same element that is identified in the equation (5) as “C_{mB}". The background was derived using the least contaminated station (Feng et al., 2010). According to Tomlinson et al., (1980), PLI values of zero suggest the absence of pollutants, while PLI values of one or greater denotes the presence of pollutants or progressive deterioration of sediment quality.

4. Results

4.1. Textural analysis

Mud (silt and clay) content in the samples varied from 26.5 to 92.1%; while sand and gravel varied from 6.0 to 67.0% and 0.05 to 40.3%, respectively (Table 1). The mud, sand and gravel ternary diagram (Figure 2) showed that 75.1% of the samples were classified as mud, 13.8% were classified as muddy-sand and 11.1% were not well classified because they had similar values for each of these parameters.

4.2. Geochemical composition

The *average* organic matter (OM) content in the study area was 18.1% and varied between 6.8 and 36.4%. The highest concentration was found at station 6, which was located within the urban area of Ciudad del Carmen (Figure 1). The lowest concentration was found at station 31, approximately 35 km from station 6, such a contrast suggests that organic carbon could be associated to the local drainage piping of Ciudad del Carmen. The *average* carbonate concentration was 21.2%. The highest carbonate values were found in the middle of the island at stations 25 (32.4%), 26 (37.5%) and 27 (33.9%), which are characterized by the presence of shell banks and higher energy conditions. The lowest values where found at station 11 (8.3%) and 21 (6.5%). Major element concentrations varied within the following ranges: 11.4 – 35.3% for CaO, 11.2 – 34.5% for SiO_2, 2.23 – 9.53% for Al_2O_3 and 1.49 – 4.52% for Fe_2O_3 (Table 1). The *range* and *average* of trace elements are shown in Table 1. Stations 7 and 1 that are located close to the city sewages exhibited the highest values for Zn (794 mg kg^{-1}, 365 mg kg^{-1}), Cu (311 mg kg^{-1}, 81mg kg^{-1}) and Pb (111 mg kg^{-1}, 48 mg kg^{-1}) (Figure 3, Figure S2). Station 10 situated close to a boat yard, where there is limited water flux because of mangroves exhibited high values of Zn (471 mg kg^{-1}), Cu (35 mg kg^{-1}) and Pb (34 mg kg^{-1}) (Figure 3, Figure S2).

4.3. Pollution indices

4.3.1. Enrichment Factor

All the trace elements showed variations in their enrichment level degrees (Figure 4). All samples exhibited levels from no enrichment to minor enrichment for V, Cr, Rb, Sr, Ba and Zr. Moderate to severe EFs were found for Co and Ni at station 30 (5.1) and 30 (5.3) respectively. Values of EFs > 10 (severe and very severe enrichment) were found for Cu at stations 1 (24.5) and 7 (63.1), for Zn at stations 1 (27.6), 7 (40.3) and 10 (12.2), and for Pb at stations 1 (14.5) and 7 (22.5).

4.3.2. Geo-accumulation Index

The geo-accumulation Index shows (Figure 4) that none of the samples were moderately polluted with Sr, Ba and V. Between 4 and 14 of the samples were moderately polluted with Cr, Zr, Zn, Ni, Rb, Cu, Pb and Co (Figure 4). The highest values of Igeo were found at stations 1 (4.2, 6.3, 3.4), 7 (6.1, 7.5, 4.6), 10 (3, 6.7, 2.9), 29 (3.4, 4.7, 1.7) and 30 (1.6, 3.7, 1.2), being moderately to extremely polluted with Cu, Zn and Pb, respectively.

4.3.3. Adverse Effects Index

The estimated AEI values for the mangroves of Isla del Carmen showed that the samples could be associated with adverse effects on organisms caused by Cr (100%), Ba (100%), Ni (47.2%), Co (25%), Cu (11.1%), V (8.3%) and Zn (8.3%), (Figure 4). The *maximum* AEI values were found at station 7 for Cu (16.6), Zn (6.4), Pb (3.7) and Ba (3.2). While the *maximum* values of AEI at station 11 corresponded to V (1.2), and Ni (5.1), at station 9 the highest AEI corresponds to Co (1.9) and they are the at stations located within a small boat channel next to the urban mangroves.

4.3.4. Pollution Load Index

Calculated PLI values of > 1 were recorded at every site (Figure 5), which means that 100% of the samples had a significant deterioration of sediment quality due to trace element concentrations. However, for this index, there was an evident tendency of samples collected inside the tidal channels, and around Ciudad del Carmen, to exhibit PLI values > 2 (except station 13). Meanwhile, samples collected at places far away from human activity showed PLI values < 2 (except stations 29 and 30).

4.4. Factor and cluster analysis of sediment samples

A factor analysis was performed to identify the causes of variation between the geochemical and textural data from the mangroves. Four factors were identified that explained 81% of the system's *variance*. All factors were associated with the mineralogy, texture, anthropogenic and natural sources (Table 2). The first factor explained 29% of the total *variance* and was related with sediment mineralogy due to its interactions between major elements, carbonates and gravel. The second factor explained 20% of the total *variance*, and it was related to sediment texture because this factor grouped parameters such as sand, mud, OM, CaO, Na_2O, and S, which are widely associated to a specific sediment grain size. The third factor explained 17% of the total *variance* and they grouped P_2O_5, Cu, Zn, and Pb. It was linked to anthropogenic sources because the pollution indices noted that these elements are supplied by anthropogenic and point sources. Finally, the fourth factor explained 15% of the total *variance*; it grouped V, Co, Ni and Rb, which was linked to natural sources because according to the pollution indices these elements were likely to be supplied by the Palizada, Chumpan and Candelaria river catchments lithology.

In order to identify associations between 36 sediment samples, a cluster analysis was performed. The cluster diagram showed three main groups (A, B and C) (Figure 6). Group A was characterized by a higher content of gravel, sand, OM and CO_3. Group B was characterised by higher concentrations of SiO_2, Al_2O_3, K_2O, MgO, V, Cr, Ni, Rb, Zr. Group C was characterised by high mud content, OM, Fe_2O_3, P_2O_3, S, Co, Cu, Zn, Pb, and Ba. Group C also showed the highest PLI values and highest EF, Igeo and AEI of Co, Cu, Zn, Pb and Ba.

5. Discussion

5.1. Major and trace elements source

The geochemical composition and the ternary diagram (Figure S1) showed that mangrove sediments in the area are richer in CaO (Carbonates) than Al_2O_3 (aluminosilicates) and Fe_2O_3 (heavy minerals). Carbonates are supplied by shell fragments of organisms that live in the mangrove such as snails, oysters and other mollusks and bivalves. The negative *correlation* between CaO and CO_3 (0.48, $p < 0.05$) suggests that although the study area is characterized by biogenic sediment rich in carbonates, there are other calcium sources such as plagioclases, otherwise this *correlation* would be high. The negative *correlation* between CaO and MgO (-0.74, $p < 0.05$) noted that Mg substitutes Ca from carbonate minerals due to its similar radio atomic size. The positive *correlation* between Fe_2O_3 and TiO_2 (0.95, $p < 0.05$) is related to heavy minerals. Positive *correlation* between Al_2O_3 with SiO_2 (0.90, $p < 0.05$), and K_2O (0.93, $p < 0.05$), highlighted the presence of aluminosilicates such as plagioclases and the positive *correlation* between Al_2O_3 with SiO_2 (0.90, $p < 0.05$), Fe_2O_3 (0.92, $p < 0.05$), TiO_2 (0.89, $p < 0.05$), and K_2O (0.93, $p < 0.05$) suggests that all of these minerals are in fine particles such as mud rather than sand and gravel. On the other hand, negative *correlations* were recorded between CO_3 and SiO_2 (-0.88, $p < 0.05$), Al_2O_3 (-0.82, $p < 0.05$), Fe_2O_3 (-0.75, $p < 0.05$), TiO_2 (-0.75, $p < 0.05$), K_2O (-0.88, $p < 0.05$), indicating that biogenic sourced sediments were diluted by terrigenous sediment from the Palizada, Chumpan and Candelaria rivers and it is supported by the ternary diagram (Figure S1) where it is clear how CaO concentration decreases when sediment is getting rich in Al_2O_3.

The trace element data and the cluster analysis (Figure 6) highlighted stations 7, 10 and 1 as punctual sources, in these stations the highest trace elements concentration and pollution indices of Zn, Cu and Pb are identified. The lack of positive *correlation* for these elements with almost all the studied parameters and their spatial distribution support the idea that the city sewages and boat yards act as anthropogenic sources for these elements (Table S1). In contrast, the positive *correlations* for V (0.59, 0.61, 0.57, 0.87, $p<0.05$), Ni (0.65, 0.60, 0.56, 0.86, $p<0.05$), with Al_2O_3, Fe_2O_3, TiO_2 and Co suggest a terrestrial natural origin probably supplied by Palizada, Chumpan and Candelaria rivers, where their lithology are linked to mafic rocks (Ortiz et al., 2006). Relatively low *correlations* between Ba and Zr with almost all major and trace elements (Table S1) suggest an oil industry origin; as these elements are likely to be related to crude oil, residual fuel oils, accidental oil spills and oil drilling (Fieldler et al., 2009; Zhang et al., 2015). On the other hand, the cluster analysis showed that the association between stations were divided by three geochemical groupings according to their mineralogy, texture and anthropogenic/natural influence. This is supported by the factor analysis results where the mineralogy, texture, anthropogenic and natural sources were identified as factors that explained the geochemical variations from the mangrove sediments of Isla del Carmen.

5.2. Evidence of oil influence in the Carmen Island Mangroves

V and Ni are elements that are related to oil industry because they are abundant in crude oil. Generally, the ratio Ni/V is used to identify oil families such as Brent, West Texas, Maya, etc (Barwaise, 1990). However, this ratio also has been used as an oil pollution index in places with presence of an important oil industry such as the Gulf of Mexico (Cuevas et al., 2018; Ruiz et al., 2019). We used this ratio to identify the oil industry influence on the mangroves of Isla del Carmen. According to Barwaise (1990) the content of Ni and V in crude oil is about 340 mg kg^{-1} and 1580 mg kg^{-1} respectively. Also, according to the IIE (1998), the chemical composition of the Mexican fuel oil could have up to 20-60 and 200-350 mg L^{-1} of Ni and V respectively, giving two interval ratios from 0.3 to 0.17 and 0.1 to 0.05 evidencing geochemical markers that Ni and V come from Mexican oil industry activities. The ratios found in the mangroves of Isla del Carmen *ranged* from 0.5 to 1.5. Such values are higher than the values reported average in Veracruz (0.28) and Tamaulipas (0.17 – 0.23), states with high oil industry activity (Ruiz et al., 2012; Celis et al., 2018). These results suggest a low impact from oil industry sources and confirm the predominantly natural source of these trace elements. Recent studies on coastal sediments near to the Isla del Carmen also reported that the Ni and V contents are due to the natural sources and were derived by the contribution of intermediate and mafic source rocks like andesite and basalt (Armstrong-Altrin et al., 2018; Ramos-Vázquez and Armstrong-Altrin, 2019).

5.3. Ecological status of the area

The pollution indices such as the PLI reported in this study suggest that the Isla del Carmen mangroves are considered a degraded environment as a result of the trace elements present in the sediments. The EF, Igeo and AEI highlighted specific sites close to point sources that caused severe enrichment, very severe enrichment and those sites were classified as strongly polluted and extremely polluted mangrove environments for Zn, Cu and Pb.

The adverse effects that are likely to be evident in the mangrove ecosystem as a result of these trace element concentrations would be bioaccumulation and biomagnification in species at all the trophic levels (Baki et al., 2018; Karar et al., 2019). In addition, because of their toxicity, mangrove organisms would show a reduction in their growth development, as well as sexual and genetic anomalies (Souza et al., 2015), and even there would be a decrease in the number of benthic species (crabs, clams), fish and birds (Souza et al., 2018; Garriz et al., 2019) that coexist in the mangrove environment. Also, it could affect other proximal coastal environments such as the Terminos Lagoon, and the estuarine environment that exists in this natural system. Finally, it could affect human health if polluted marine organisms derived from the mangroves are consumed by the human population; as these levels of the trace elements are likely to cause serious damage to the kidney, central nervous system, liver, intestinal tract and reproductive system (Siddique et al., 2012; Abdel-Khalek et al., 2016). However, it is necessary to conduct further investigation to assess the impacts of these pollutants on local ecological diversity and biodiversity to fully assess the ecological status in the area.

6. Conclusion

The bulk geochemical data noted that almost all the trace element concentrations in the mangroves from Isla del Carmen are close to background levels; except for Zn, Cu and Pb where the spatial distribution suggests that the city sewages and boatyards act as point sources for these elements. The trace element distributions in the mangroves from Carmen Island are driven by natural and anthropogenic factors such as the mineralogy, texture and urban activities or urban sources. Finally, the mangroves from the Carmen Island can be considered impacted by the wastes generated within the urban area rather than by the extraction of oil activities that take place close to the Carmen Island, which suggests that there is limited impact from oil activities in the local area. However, levels are such that these areas can be considered as heavily polluted by some of the trace elements investigated and this is likely to cause adverse effects on benthic organisms associated with the mangroves.

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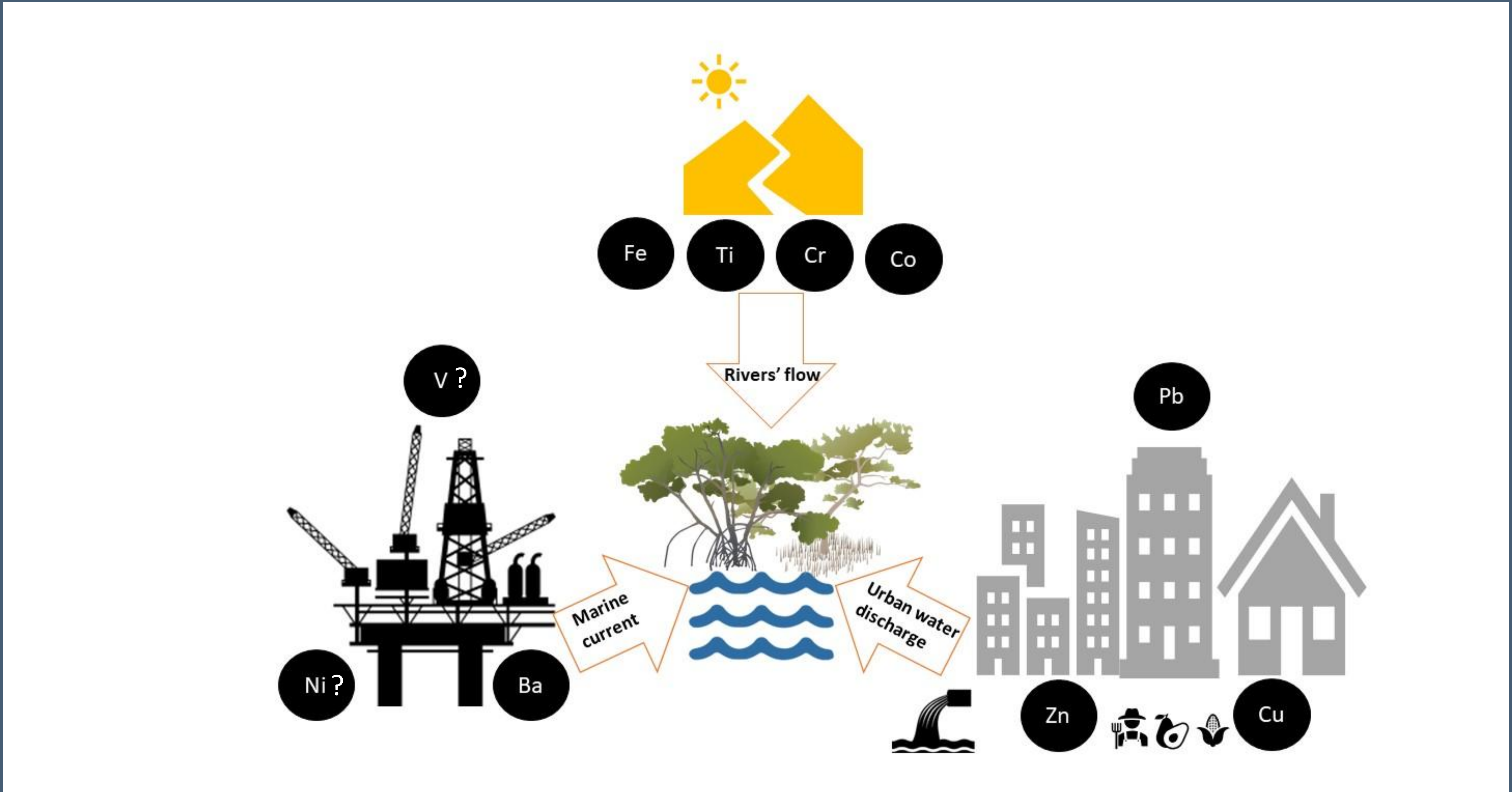
*Graphical Abstract



***Highlights (for review : 3 to 5 bullet points (maximum 85 characters including spaces per bullet point)**

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- **City sewages and boatyards act as point sources for Zn, Cu and Pb.**
- **Ni and V contents show that oil industry has a low impact in mangroves.**
- **Zn, Cu, and Pb contents exceed adverse effect index (AEI) in two urban point sources.**

Environmental risk of trace elements in mangrove ecosystems: An assessment of natural vs oil and urban inputs

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Highlights

- **City sewages and boatyards act as point sources for Zn, Cu and Pb.**
- **Ni and V contents show that oil industry has a low impact in mangroves.**
- **Zn, Cu, and Pb contents exceed adverse effect index (AEI) in two urban point sources.**

Abstract

The petrochemical industry and urban activities are widely recognized worldwide as a source of pollution to mangrove environments. They can supply pollutants such as trace elements that can modify the ecosystem structure and associated services, as well as human populations. Through geochemical data, multivariate statistical analysis and pollution indices such as the enrichment factor (EF), geo-accumulation index (Igeo), adverse effect index (AEI) and the pollution load index (PLI), we evaluated the factors that control trace element distribution, punctual sources and determined the pollution level of sediments and their potential biological impact in the mangrove ecosystem of Isla del Carmen, Mexico. The factor and cluster analysis highlighted that the distribution of trace elements is influenced by the mineralogy, texture as well as urban derived sources. The pollution indices showed values in the punctual sources from the urban area of EF > 10, Igeo > 3, AEI >3, PLI > 1 by Cu, Zn and Pb. Finally, the results revealed that mangroves from Isla del Carmen has a major influence from urban activities and natural sources rather than oil industry and also indicate a degraded environment as a result of anthropogenic activities that could have knock-on effect for human health if polluted marine organisms derived from the urban mangroves are consumed.

Capsule abstract: Surface sediments show the influence of point sources on selected trace element concentrations correlated with human activities within the mangroves of Isla del Carmen, Mexico.

Keywords: Trace Elements, Sediment, Oil Industry, Mangroves, Gulf of Mexico, Isla del Carmen

1. Introduction

Mangroves are vegetated intertidal coastal environments located in tropical and subtropical areas. They are characterized by the presence of plants adapted to frequent inundation by saline water imposed by a tidal regime (NOAA, 2014). To support and sustain the well-being of human being, mangroves provide a range of ecosystem services such as: nursery and breeding habitats for commercial shrimp, crabs and fish species; coastal protection against erosion processes, cyclones, storms, floods and carbon sequestration (Brander et al., 2012; Lovelock et al., 2015; Mehaur et al., 2018; Shi et al., 2019).

Like many other ecosystems, mangroves have been subjected to anthropogenic pressures resulting in decreases in mangrove area, particularly conversion to agriculture, aquaculture and salt ponds, urban expansion as well as alterations to sediment supply, sea level rise, drought and storms as a result of climate change (Ward et al., 2016; Veetil et al., 2018; Mafi-Gholami et al., 2019). Due to their location in coastal and estuarine settings they are also often exposed to a range of pollutants particularly those located proximal to industry or urban settings. Many of these pollutants are harmful to mangrove associate organisms and humans when transferred through the trophic chain (Senthilkumar et al., 2013; Kulkarni et al., 2018; Chai et al., 2019). Trace elements are common pollutants found in mangroves and are considered as a serious threat to human health and other living organisms due to their persistence, potential for bioaccumulation, and toxicity (Arrivabene et al., 2016; Celis et al., 2017; Singh and Kumar, 2017). However, it is important to note that trace elements can be derived from anthropogenic and natural sources that complicate analysis concerning their environmental impact (Anaya-Gregorio et al., 2018; Armstrong-Altrin et al., 2019). To resolve this issue geochemical indices such as the enrichment factor (EF), geoaccumulation Index (Igeo), pollution load index (PLI), adverse effect index (AEI), as well as statistical tools have been developed to provide a better understanding about the environmental risks that these substances pose to mangrove ecosystems and humans (Goher et al., 2014; Duodu et al., 2017; Benson et al., 2018).

Mangroves from Isla del Carmen are likely to be influenced by point source pollution from urban, industrial and petrochemical derived sources as a result of the proximity to an industrial port city and petrochemical source. Therefore, Isla del Carmen is an important area to study how oil industry and urban activities impact mangrove environments.

The aim of this study is to determine the agents that influence trace element distribution in mangroves with pollution sources including the oil industry and urban activities. Additionally, we aimed to evaluate the contamination level of sediments and their potential biological impact in the mangroves of Isla del Carmen, Mexico.

2. Study area

Isla del Carmen is located in the southeastern Gulf of Mexico in Campeche, Mexico (Figure 1). Twenty three percent of its surface corresponds to the urban area of Ciudad del Carmen, while the remaining 77% is covered by mangroves (INEGI, 2018). Ciudad del Carmen is the second most populated urban center (248,303 inhabitants) in Campeche state (INEGI, 2018). Isla del Carmen belongs to a natural protected area known as Wildlife Protection Area Laguna de Terminos, which includes the largest coastal lagoon environment in Mexico (about 7050.16 Km^2) (INEGI, 2018). In the north coast of the island the marine environment dominates and houses the Canterell oil field, which is the largest gas (38%) and offshore oil (56.5%) producer in Mexico (Nava et al., 2018; PEMEX, 2018) while, in the south coast it receives fluvial discharges of the Palizada, Chumpan and Candelaria rivers, which supply nutrients, sediments, as well as pollutants generated by agricultural, cattle feeding and other human activities (Carvalho et al., 2009). The weather is mostly humid warm with summer rainfall. The average annual temperature ranges from 26 to 28 °C, while the average annual rainfall ranges from 1500 to 2000 mm (INEGI, 2018). Seasonally, three different regimes are recognizable, the dry season (Feb-May), rainy season (Jun-Sep), and stormy season (Oct-Jan).

3. Materials and methods

Sediment samples were collected from thirty-six mangrove sites on Isla de Carmen, Mexico in August 2019 that corresponded to the rainy season; this season was chosen because the rivers' influence is higher in the area rather than other seasons (Figure 1). Samples were collected from creek edges directly adjacent to the mangroves using a Van Veen dredge from a boat at a water column depth from 0.5 to 2.5 m at mid-high tide to avoid running aground. In order to avoid contamination during sampling sediment samples were removed with a plastic spatula from the middle part of the dredge in such a way that sediments had no contact with the metallic parts of the equipment and to get the most recently deposited sediment, we collected the samples in first centimetre. Each sample was stored in sample bags at 4°C until chemical analysis. Samples were divided in two halves with one half used for geochemical analysis and the other for granulometry.

Samples were dried at 50 °C for 5 days and homogenized in an agate mortar by hand. All concentrations in this work were expressed with reference to dry weight. Major and trace element concentrations were determined using a RIGAKU ZSX Primus II X-ray fluorescence spectrometer system and analyzed in pressed powder briquettes. The accuracy of major elements was evaluated using the rock standard Argillite whose values ranged from 102.6 to 93%, with the exception of Na_2O (70.0%), P_2O_5 (73.1%) and K_2O (89.3%). The accuracy of trace elements was estimated using the standard CH-1 marine sediment, values ranged from 102.6 to 90.8% with the exception of V (111.8%) and Co (113.8%). Sediment particle size distribution was determined by sieving with a RX-29 Ro-Tap Sieve Shaker and a standard ASTM sieve set from -2.0, -1.0, 0.0, 1.0, 2.0, 3.0, and 4.0 Φ. Sediments were classified as mud, sand, and gravel based on the methodology proposed by Folk (1980). Organic matter and carbonates were estimated using a loss on ignition method: 1 g of sediment samples were weighed before and after incineration in a muffle furnace at 550 °C and again at 950 °C for 24 hrs in order to eliminate the organic matter and carbonates (Ahmed et al., 2018). Total organic matter and carbonates are reported as percentage of dry weight.

The results were interpreted using descriptive and multivariate statistical tools including correlation analysis to evaluate the strength of relationship among geochemical parameters. A cluster analysis was used to identify impacted locations in mangroves from Isla del Carmen, and factor analysis was performed to determine the variables that better explain the system variability (Statistical analyses were performed using the software STATISTIC 8). Geochemical indices such as EF, Igeo, PLI, and AEI were employed to evaluate the natural or anthropogenic origin for each trace element: to compare and contrast environmental quality with other locations inside the island, and to infer any possible adverse effect on benthic biota (Celis et al., 2018).

Enrichment Factor

This proxy is evaluated using equation (1)

$$EF=\frac{\left(\frac{X_{sample}}{Y_{sample}}\right)}{\left(\frac{X_{background}}{Y_{background}}\right)} \dots\dots\dots\dots\dots\dots\dots\dots\dots . . (1)$$

Where X_{sample} and $X_{background}$ are the concentrations of any trace element analysed in the sample and Y_{sample} and $Y_{background}$ are the concentrations of a conservative element that is used to normalize the data. In this work, we used Al_2O_3 as a conservative element because it represents the clay fraction in the sediment and it is not affected by anthropogenic sources or geochemical changes such as redox processes (Celis et al., 2013). As background we employed the least contaminated station (Feng et al., 2010) rather than the Upper Continental Crust (UCC) (McLennan, 2001) to avoid any overestimation in the data interpretation. The enrichment factor results were divided into ranks to establish the degree of enrichment (Birth, 2003) (Table S2).

Geo-accumulation index

This proxy is evaluated using equation 2 (Müller, 1969).

$$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right) \quad (2)$$

Where "C_n" represents the concentration of any trace element in the sediment sample and "B_n" represents the background concentration of the same element; the value of 1.5 is a factor that considers possible variability generated by lithological changes. Geo-accumulation index results were divided into ranks to establish the degree of pollution (Birth, 2003) (Table S2).

Adverse Effect Index

The adverse effect index (AEI) can be applied to evaluate how many times the metal concentration in the sediment has exceeded the Threshold Effect Level (TEL) developed by Long et al., (1995); as well as inferring whether trace element concentrations in the sediment could adverse impact benthic biota (Muños et al., 2012; Hamdoun et al., 2015; Baptista et al., 2017). An AEI lower than 1 means that the trace element concentration in the samples is not high enough to produce adverse effects from sediment contamination to organisms where no toxicity studies are undertaken or available.

This proxy is calculated using equation (3)

$$AEI = \frac{[MC]}{[SQG_S]}$$

Where MC is the trace element concentration in the sample and SQGs is any sediment quality guideline such as Effect Range Low (ERL), Threshold Effect Level (TEL) and others. SQGs are based on the collection, revision and the integration of a range of studies performed in North

America using laboratory bioassays, equilibrium-partitioning modelling and field studies on the toxicity of metals in sediment on benthic composition (Long et al., 1995). In this work, we used the Threshold Effect Level (TEL) and the Analogous Effect Threshold (AET). Both were obtained via the Screening Quick Reference Tables (SQuirRts) supplied by NOAA, 2016.

Pollution Load Index

The pollution load index is calculated using equations 4 and 5 (Tomlinson et al., 1980).

$$\mathrm{PLI_{sample}} = \sqrt[n]{\mathrm{CF_{metal\ 1}} * \mathrm{CF_{metal\ 2}} * \ldots \mathrm{CF_{metal\ n}}} \ldots \ldots \ldots \ldots \ldots \ldots (4)$$

$$\mathrm{CF} = \left[\frac{\mathrm{C_{mS}}}{\mathrm{C_{mB}}}\right] \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (5)$$

In general; the PLI is calculated with the n^{th} root of the variable called contamination factor (CF) which is evaluated using the equation (4). The super index "n" in the root represents the total number of samples. While the CF is defined as the ratio between the element concentration analyzed in the sample "C_{ms}" and the background concentration of the same element that is identified in the equation (5) as "C_{mB}". The background was derived using the least contaminated station (Feng et al., 2010). According to Tomlinson et al., (1980), PLI values of zero suggest the absence of pollutants, while PLI values of one or greater denotes the presence of pollutants or progressive deterioration of sediment quality.

4. Results

4.1. Textural analysis

Mud (silt and clay) content in the samples varied from 26.5 to 92.1%; while sand and gravel varied from 6.0 to 67.0% and 0.05 to 40.3%, respectively (Table 1). The mud, sand and gravel ternary diagram (Figure 2) showed that 75.1% of the samples were classified as mud, 13.8% were classified as muddy-sand and 11.1% were not well classified because they had similar values for each of these parameters.

4.2. Geochemical composition

The *average* organic matter (OM) content in the study area was 18.1% and varied between 6.8 and 36.4%. The highest concentration was found at station 6, which was located within the urban area of Ciudad del Carmen (Figure 1). The lowest concentration was found at station 31, approximately 35 km from station 6, such a contrast suggests that organic carbon could be associated to the local drainage piping of Ciudad del Carmen. The *average* carbonate concentration was 21.2%. The highest carbonate values were found in the middle of the island at stations 25 (32.4%), 26 (37.5%) and 27 (33.9%), which are characterized by the presence of shell banks and higher energy conditions. The lowest values where found at station 11 (8.3%) and 21 (6.5%). Major element concentrations varied within the following ranges: 11.4 – 35.3% for CaO, 11.2 – 34.5% for SiO_2, 2.23 – 9.53% for Al_2O_3 and 1.49 – 4.52% for Fe_2O_3 (Table 1). The *range* and *average* of trace elements are shown in Table 1. Stations 7 and 1 that are located close to the city sewages exhibited the highest values for Zn (794 mg kg^{-1}, 365 mg kg^{-1}), Cu (311 mg kg^{-1}, 81mg kg^{-1}) and Pb (111 mg kg^{-1}, 48 mg kg^{-1}) (Figure 3, Figure S2). Station 10 situated close to a boat yard, where there is limited water flux because of mangroves exhibited high values of Zn (471 mg kg^{-1}), Cu (35 mg kg^{-1}) and Pb (34 mg kg^{-1}) (Figure 3, Figure S2).

4.3. Pollution indices

4.3.1. Enrichment Factor

All the trace elements showed variations in their enrichment level degrees (Figure 4). All samples exhibited levels from no enrichment to minor enrichment for V, Cr, Rb, Sr, Ba and Zr. Moderate to severe EFs were found for Co and Ni at station 30 (5.1) and 30 (5.3) respectively. Values of EFs > 10 (severe and very severe enrichment) were found for Cu at stations 1 (24.5) and 7 (63.1), for Zn at stations 1 (27.6), 7 (40.3) and 10 (12.2), and for Pb at stations 1 (14.5) and 7 (22.5).

4.3.2. Geo-accumulation Index

The geo-accumulation Index shows (Figure 4) that none of the samples were moderately polluted with Sr, Ba and V. Between 4 and 14 of the samples were moderately polluted with Cr, Zr, Zn, Ni, Rb, Cu, Pb and Co (Figure 4). The highest values of Igeo were found at stations 1 (4.2, 6.3, 3.4), 7 (6.1, 7.5, 4.6), 10 (3, 6.7, 2.9), 29 (3.4, 4.7, 1.7) and 30 (1.6, 3.7, 1.2), being moderately to extremely polluted with Cu, Zn and Pb, respectively.

4.3.3. Adverse Effects Index

The estimated AEI values for the mangroves of Isla del Carmen showed that the samples could be associated with adverse effects on organisms caused by Cr (100%), Ba (100%), Ni (47.2%), Co (25%), Cu (11.1%), V (8.3%) and Zn (8.3%), (Figure 4). The *maximum* AEI values were found at station 7 for Cu (16.6), Zn (6.4), Pb (3.7) and Ba (3.2). While the *maximum* values of AEI at station 11 corresponded to V (1.2), and Ni (5.1), at station 9 the highest AEI corresponds to Co (1.9) and they are the at stations located within a small boat channel next to the urban mangroves.

4.3.4. Pollution Load Index

Calculated PLI values of > 1 were recorded at every site (Figure 5), which means that 100% of the samples had a significant deterioration of sediment quality due to trace element concentrations. However, for this index, there was an evident tendency of samples collected inside the tidal channels, and around Ciudad del Carmen, to exhibit PLI values > 2 (except station 13). Meanwhile, samples collected at places far away from human activity showed PLI values < 2 (except stations 29 and 30).

4.4. Factor and cluster analysis of sediment samples

A factor analysis was performed to identify the causes of variation between the geochemical and textural data from the mangroves. Four factors were identified that explained 81% of the system's *variance*. All factors were associated with the mineralogy, texture, anthropogenic and natural sources (Table 2). The first factor explained 29% of the total *variance* and was related with sediment mineralogy due to its interactions between major elements, carbonates and gravel. The second factor explained 20% of the total *variance*, and it was related to sediment texture because this factor grouped parameters such as sand, mud, OM, CaO, Na_2O, and S, which are widely associated to a specific sediment grain size. The third factor explained 17% of the total *variance* and they grouped P_2O_5, Cu, Zn, and Pb. It was linked to anthropogenic sources because the pollution indices noted that these elements are supplied by anthropogenic and point sources. Finally, the fourth factor explained 15% of the total *variance*; it grouped V, Co, Ni and Rb, which was linked to natural sources because according to the pollution indices these elements were likely to be supplied by the Palizada, Chumpan and Candelaria river catchments lithology.

In order to identify associations between 36 sediment samples, a cluster analysis was performed. The cluster diagram showed three main groups (A, B and C) (Figure 6). Group A was characterized by a higher content of gravel, sand, OM and CO_3. Group B was characterised by higher concentrations of SiO_2, Al_2O_3, K_2O, MgO, V, Cr, Ni, Rb, Zr. Group C was characterised by high mud content, OM, Fe_2O_3, P_2O_3, S, Co, Cu, Zn, Pb, and Ba. Group C also showed the highest PLI values and highest EF, Igeo and AEI of Co, Cu, Zn, Pb and Ba.

5. Discussion

5.1. Major and trace elements source

The geochemical composition and the ternary diagram (Figure S1) showed that mangrove sediments in the area are richer in CaO (Carbonates) than Al_2O_3 (aluminosilicates) and Fe_2O_3 (heavy minerals). Carbonates are supplied by shell fragments of organisms that live in the mangrove such as snails, oysters and other mollusks and bivalves. The negative *correlation* between CaO and CO_3 (0.48, $p < 0.05$) suggests that although the study area is characterized by biogenic sediment rich in carbonates, there are other calcium sources such as plagioclases, otherwise this *correlation* would be high. The negative *correlation* between CaO and MgO (-0.74, $p < 0.05$) noted that Mg substitutes Ca from carbonate minerals due to its similar radio atomic size. The positive *correlation* between Fe_2O_3 and TiO_2 (0.95, $p < 0.05$) is related to heavy minerals. Positive *correlation* between Al_2O_3 with SiO_2 (0.90, $p < 0.05$), and K_2O (0.93, $p < 0.05$), highlighted the presence of aluminosilicates such as plagioclases and the positive *correlation* between Al_2O_3 with SiO_2 (0.90, $p < 0.05$), Fe_2O_3 (0.92, $p < 0.05$), TiO_2 (0.89, $p < 0.05$), and K_2O (0.93, $p < 0.05$) suggests that all of these minerals are in fine particles such as mud rather than sand and gravel. On the other hand, negative *correlations* were recorded between CO_3 and SiO_2 (-0.88, $p < 0.05$), Al_2O_3 (-0.82, $p < 0.05$), Fe_2O_3 (-0.75, $p < 0.05$), TiO_2 (-0.75, $p < 0.05$), K_2O (-0.88, $p < 0.05$), indicating that biogenic sourced sediments were diluted by terrigenous sediment from the Palizada, Chumpan and Candelaria rivers and it is supported by the ternary diagram (Figure S1) where it is clear how CaO concentration decreases when sediment is getting rich in Al_2O_3.

The trace element data and the cluster analysis (Figure 6) highlighted stations 7, 10 and 1 as punctual sources, in these stations the highest trace elements concentration and pollution indices of Zn, Cu and Pb are identified. The lack of positive *correlation* for these elements with almost all the studied parameters and their spatial distribution support the idea that the city sewages and boat yards act as anthropogenic sources for these elements (Table S1). In contrast, the positive *correlations* for V (0.59, 0.61, 0.57, 0.87, $p<0.05$), Ni (0.65, 0.60, 0.56, 0.86, $p<0.05$), with Al_2O_3, Fe_2O_3, TiO_2 and Co suggest a terrestrial natural origin probably supplied by Palizada, Chumpan and Candelaria rivers, where their lithology are linked to mafic rocks (Ortiz et al., 2006). Relatively low *correlations* between Ba and Zr with almost all major and trace elements (Table S1) suggest an oil industry origin; as these elements are likely to be related to crude oil, residual fuel oils, accidental oil spills and oil drilling (Fieldler et al., 2009; Zhang et al., 2015). On the other hand, the cluster analysis showed that the association between stations were divided by three geochemical groupings according to their mineralogy, texture and anthropogenic/natural influence. This is supported by the factor analysis results where the mineralogy, texture, anthropogenic and natural sources were identified as factors that explained the geochemical variations from the mangrove sediments of Isla del Carmen.

5.2. Evidence of oil influence in the Carmen Island Mangroves

V and Ni are elements that are related to oil industry because they are abundant in crude oil. Generally, the ratio Ni/V is used to identify oil families such as Brent, West Texas, Maya, etc (Barwaise, 1990). However, this ratio also has been used as an oil pollution index in places with presence of an important oil industry such as the Gulf of Mexico (Cuevas et al., 2018; Ruiz et al., 2019). We used this ratio to identify the oil industry influence on the mangroves of Isla del Carmen. According to Barwaise (1990) the content of Ni and V in crude oil is about 340 mg kg^{-1} and 1580 mg kg^{-1} respectively. Also, according to the IIE (1998), the chemical composition of the Mexican fuel oil could have up to 20-60 and 200-350 mg L^{-1} of Ni and V respectively, giving two interval ratios from 0.3 to 0.17 and 0.1 to 0.05 evidencing geochemical markers that Ni and V come from Mexican oil industry activities. The ratios found in the mangroves of Isla del Carmen *ranged* from 0.5 to 1.5. Such values are higher than the values reported average in Veracruz (0.28) and Tamaulipas (0.17 – 0.23), states with high oil industry activity (Ruiz et al., 2012; Celis et al., 2018). These results suggest a low impact from oil industry sources and confirm the predominantly natural source of these trace elements. Recent studies on coastal sediments near to the Isla del Carmen also reported that the Ni and V contents are due to the natural sources and were derived by the contribution of intermediate and mafic source rocks like andesite and basalt (Armstrong-Altrin et al., 2018; Ramos-Vázquez and Armstrong-Altrin, 2019).

5.3. Ecological status of the area

The pollution indices such as the PLI reported in this study suggest that the Isla del Carmen mangroves are considered a degraded environment as a result of the trace elements present in the sediments. The EF, Igeo and AEI highlighted specific sites close to point sources that caused severe enrichment, very severe enrichment and those sites were classified as strongly polluted and extremely polluted mangrove environments for Zn, Cu and Pb.

The adverse effects that are likely to be evident in the mangrove ecosystem as a result of these trace element concentrations would be bioaccumulation and biomagnification in species at all the trophic levels (Baki et al., 2018; Karar et al., 2019). In addition, because of their toxicity, mangrove organisms would show a reduction in their growth development, as well as sexual and genetic anomalies (Souza et al., 2015), and even there would be a decrease in the number of benthic species (crabs, clams), fish and birds (Souza et al., 2018; Garriz et al., 2019) that coexist in the mangrove environment. Also, it could affect other proximal coastal environments such as the Terminos Lagoon, and the estuarine environment that exists in this natural system. Finally, it could affect human health if polluted marine organisms derived from the mangroves are consumed by the human population; as these levels of the trace elements are likely to cause serious damage to the kidney, central nervous system, liver, intestinal tract and reproductive system (Siddique et al., 2012; Abdel-Khalek et al., 2016). However, it is necessary to conduct further investigation to assess the impacts of these pollutants on local ecological diversity and biodiversity to fully assess the ecological status in the area.

6. Conclusion

The bulk geochemical data noted that almost all the trace element concentrations in the mangroves from Isla del Carmen are close to background levels; except for Zn, Cu and Pb where the spatial distribution suggests that the city sewages and boatyards act as point sources for these elements. The trace element distributions in the mangroves from Carmen Island are driven by natural and anthropogenic factors such as the mineralogy, texture and urban activities or urban sources. Finally, the mangroves from the Carmen Island can be considered impacted by the wastes generated within the urban area rather than by the extraction of oil activities that take place close to the Carmen Island, which suggests that there is limited impact from oil activities in the local area. However, levels are such that these areas can be considered as heavily polluted by some of the trace elements investigated and this is likely to cause adverse effects on benthic organisms associated with the mangroves.

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Table
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Tables and Figures

Table 1 Range and average concentration of textural and chemical parameters in the surface sediment samples.

	Surface sediment				
	Average	Range		Average	Range
Gravel (%)	6.80	0.05-40.3	**Sr (mg kg^{-1})**	897.8	451.0-1397.0
Sand (%)	26.2	6.00-67.0	**Ba (mg kg^{-1})**	299.3	222.0-413.0
Mud (%)	67.0	26.5-92.1	**Cr (mg kg^{-1})**	152.9	57.0-289.0
CO_3 (%)	21.2	6.50-37.5	**Zr (mg kg^{-1})**	95.6	43.0-156.0
OM (%)	18.1	6.80-36.4	**Zn (mg kg^{-1})**	88.6	12.0-794.0
S (%)	0.98	0.4-1.8	**Ni (mg kg^{-1})**	47.5	15.0-96.0
CaO (%)	23.3	11.4-35.3	**V (mg kg^{-1})**	44.1	26.0-68.0
SiO_2 (%)	22.4	11.2-34.5	**Rb (mg kg^{-1})**	34.3	15.0-55.0
Al_2O_3 (%)	5.26	2.23-9.53	**Cu (mg kg^{-1})**	22.6	3.00-311.0
Na_2O (%)	3.64	1.34-7.45	**Pb (mg kg^{-1})**	13.8	3.00-111.0
Fe_2O_3 (%)	2.90	1.49-4.52	**Co (mg kg^{-1})**	11.1	4.00-22.0
MgO (%)	2.44	1.41-3.44			
K_2O (%)	0.98	0.49-1.54			
TiO_2 (%)	0.27	0.11-0.47			
MnO (%)	0.06	0.04-0.11			
P_2O_5 (%)	0.17	0.05-0.73			

Note: n=36, OM=Organic Matter.

Table 2 Factor Analysis for Mangrove Carmen Island

	Factor 1		Factor 2		Factor 3		Factor 4
Gravel	**-0.72**	**Sand**	**0.66**	**P_2O_5**	**-0.94**	**V**	**0.87**
CO_3	**-0.84**	**Mud**	**-0.60**	**Cu**	**-0.97**	**Co**	**0.89**
SiO_2	**0.89**	**OM**	**-0.92**	**Zn**	**-0.93**	**Ni**	**0.86**
Al_2O_3	**0.91**	**CaO**	**0.86**	**Pb**	**-0.98**	**Rb**	**0.85**
Fe_2O_3	**0.88**	**Na_2O**	**-0.79**				
TiO_2	**0.89**	**S**	**-0.76**				
K_2O	**0.88**						
MgO	**0.82**						
MnO	**0.70**						
Expl.Var	**7.96**		**5.45**		**4.61**		**4.05**
Prp.Totl	**0.29**		**0.20**		**0.17**		**0.15**

Note: n=36, Varimax raw and $p<0.05$, OM=Organic Matter.

Figure 1 Study area and sampling location

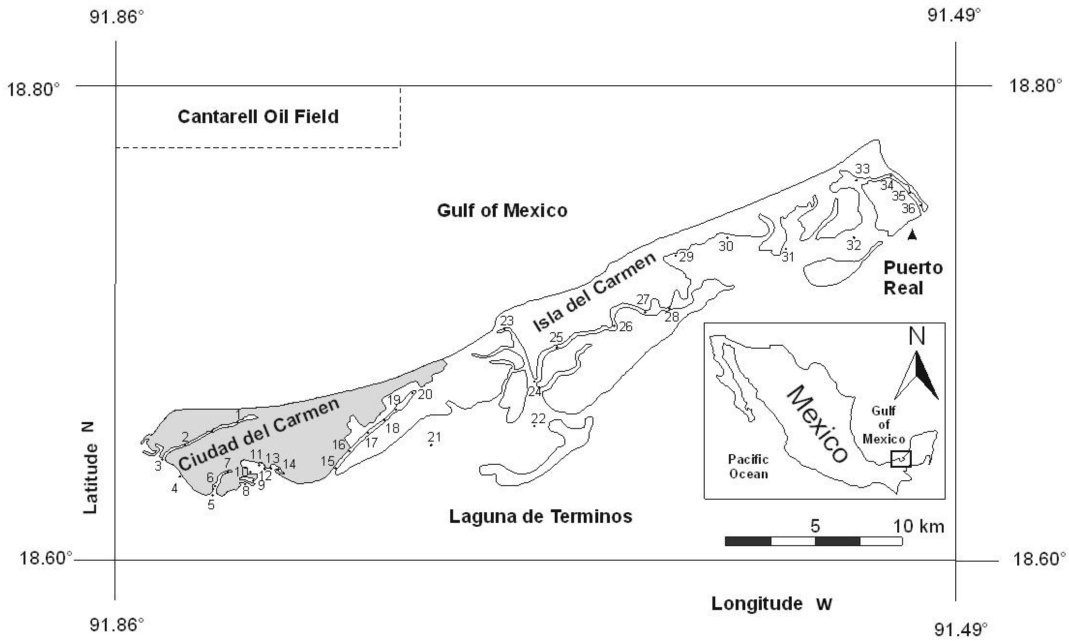


Figure 2 Textural classification of surface sediments after Shepard (1954).

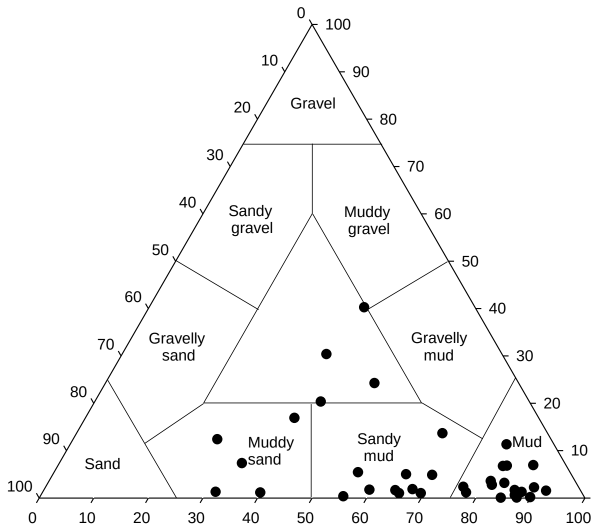


Figure 3 Variation of Ba, Co, Cr, Cu, Ni, Pb, Rb, Sr, V, Zn and Zr. Horizontal lines show the median values over every station.

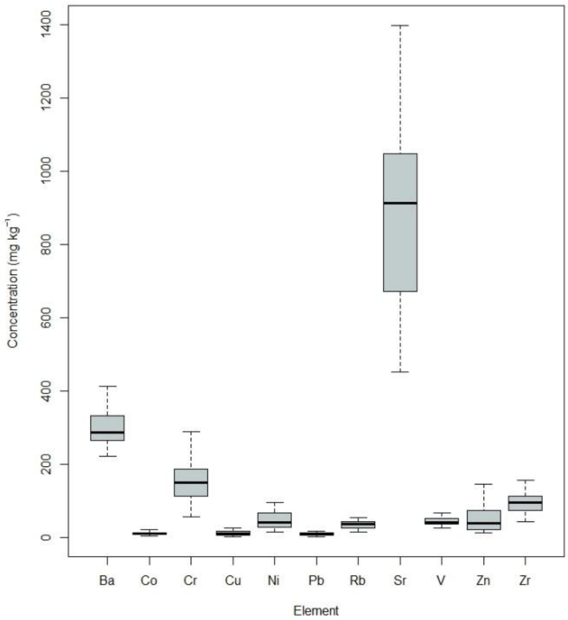


Figure 4 Variations of Enrichment Factors (EFs), Geo-accumulation Index and Adverse Effects Index for Ba, Co, Cr, Cu, Ni, Pb, Rb, Sr, V, Zn and Zr. The colored zones within the plots are gradients of pollutants enrichment: green (0-1) no enrichment, yellow (1-3) minor enrichment, orange (3-5) moderate enrichment, pink (> 5) moderate to severe enrichment.

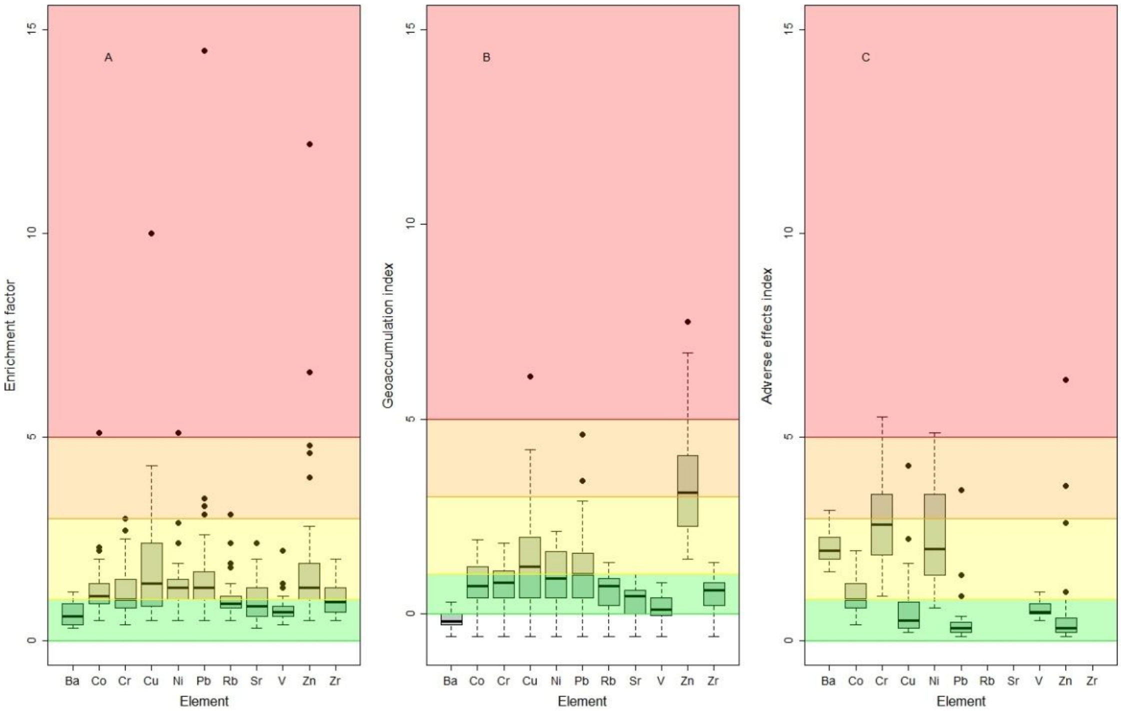
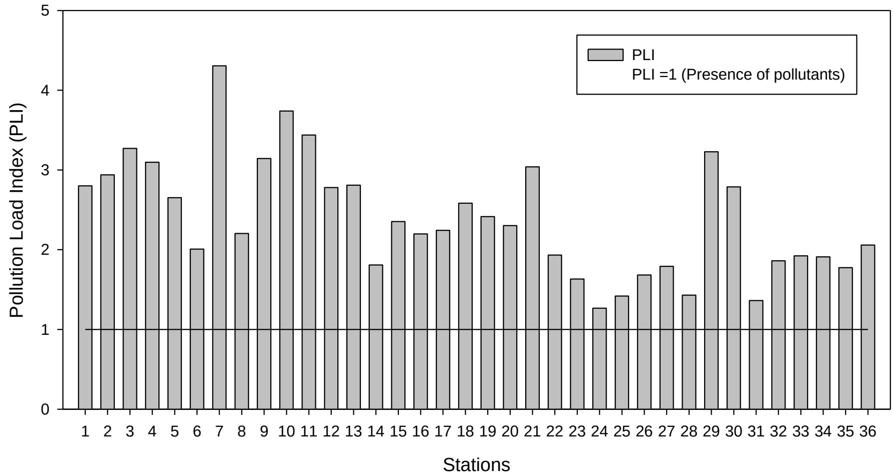
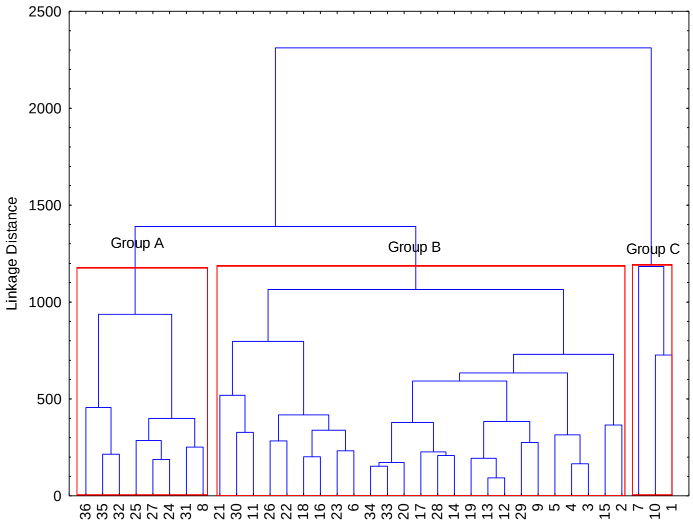


Figure 5 Variation of Pollution Load Index (PLI) for all the stations.



Note: As background the minimum value of the surface sediment sample of each trace element analyzed were used.

Figure 6 Tree diagram from cluster analysis.



Note: n=36 cases, Complete linkage (Manhattan) distances.

***conflict of Interest Statement**

We have no competing interests to declare.

Credit Author Statement.

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