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Assessment of Selected Heavy Metals in Water Samples from Vlora Bay, by using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

ValbonaTahiri[1], Astrit Denaj[2] & Fatjon Musli[3]

Abstract

In this study is presented an evaluation of Cr, Cu, Fe, Mn and Ni concentration levels in coastal waters ofVlora bay, Albania. Water samples were collected during spring-summer season in seven different sampling stations along three different depth levels: 10cm, 60cm and 120 cm respectively. Water samples were treated according to EPA3015A procedure (Microwave Assisted Acid Digestion of Aqueous Samples and Extracts). The measurements were carried out byOptima 2100™ DV, using ICP-OES technique. By the obtained results it is shown a heterogenicity distribution of heavy metal concentration values. Herein we noticed that Fe concentration level was above the allowed limit. Regarding the correlations, Fe shows: an uphill (positive) linear relationship with Cr, Ni and Mn and a downhill (negative) linear relationship with Cu. Although the coastline of Vlora does not represent a polluted environmental area regarding the concentration levels of heavy metals, it is needed to be monitored continuously since the area is subject to urban, industrial and touristic developments.

Keywords: water samples, heavy metals, ICP-OES, Vlora coastline,

1. Introduction

Vlora coastal environment is often environmentally burdened by port and traffic infrastructure, industrial areas, urban settlements, and tourism activities. Thus, the flux of various anthropogenic contaminants, especially heavy metals, are discharged and accumulated into marine coastal ecosystems (Adamo, P. et al, 2005, Baptista Neto, J.A. et al, 2000). Heavy metals are among the most persistent pollutants in the aquatic ecosystem, and they are not nullified from water by self-purification (Arnason, J.G. and Fletcher, B.A., 2003).

Due to a series of physical and biochemical processes (e.g., diagenetic, bioturbation, and resuspension processes, currents and waves, dredging, and shipping activities) the remobilization of heavy metals occurs at the sediment water interface, affecting overlying water, aquatic organisms, and threatening human health (Westerlund, S.F.G. et al, 1986). In short, all those specifics are expected to directly or indirectly affect the levels of concentration of metals and metalloids in the waters. In the Figure 1, is analyzed the dynamics of the sweaters on the study area, that represent an interesting system with inner flows circulating clockwise (Pano.N et al, 2014).

[1] Physics Department, Faculty of Technical Sciences, University "Ismail Qemali" of Vlora ,Vlora, Albania, vtahiri84@gmail.com
[2] Physics Department, Faculty of Technical Sciences, University "Ismail Qemali" of Vlora ,Vlora, Albania, astrit.denaj@yahoo.com
[3] Physics Department, Faculty of Technical Sciences, University "Ismail Qemali" of Vlora ,Vlora, Albania, fatjonmusli@gmail.com

Figure 1. Positions of sampling Stations

Referring to other similar studies (S.P.C Tankere, P.J.Statham, 1996; KljakovicGaspic.Z, et al., 2002) it is known that some heavy metals levels in the tissues of some maritime fish are low ,and generally the Adriatic Sea is not a contaminated environment regarding to dissolved elements that we are referring to. In this aspect, the study of the presence of such elements in Vlora coastal waters would exhibit twofold importance. The comparative analysis regarding to other country's measurement would be worthy as routine of environmental study. From the other side, it has the relevance regarding to the concrete estimation of the anthropogenic sources effect of such mettle presence in the sea. Bearing in mind that the tourism is very important part of the country's economy, many researchers have been involved independently recently in the study of pollution from industrial activities as Hg for example (Denaj, A. et al, 2015) and (Lazo P, Bushati S, 2008) the presence of metalloids in the rivers, atmosphere and in the sea water.

2. Materials and Methods

The analyzed samples were collected during spring and summer 2018 from seven sites from that part of Adriatic coastal area corresponds to Vlora Bay. From geographic point of view, we schematized the stations of measurement in areas with considerable natural waters discharges. It corresponds to the points between coordinates [40027.952' 19027.461', 40025.288', 19029.271] defined by a Garmin 72H, GPS. The first station is located nearby a small fishing port and the last one is the end point of the city coast. The stations were located at distance approximately 50 m from the coastline and samplers were taken in three vertical points: at surface and close under-surface straits at 10 cm, 60 cm, and 120 cm quote. Practically a good level of homogenization was reached by taking samplers with a horizontal Van Dorn Water Sample. After that, the samples were treated according to EPA3015A procedure (Microwave Assisted Acid Digestion of Aqueous Samples and Extracts) (EPA Method 200.7, 1994).The determination of the traces of metals is carried out by atomic emission spectroscopy with plasma coupled by induction (ICP-OES) according to standard NF EN ISO 11885(EPA Method 200.7, 1994). The analyses were performed in triplicate, the standard deviation (SD)was found in the analyzes of traces in triplicate elements. We used Optima 2100™ DV, ICP Optical Emission Spectrometry, with a ppb accuracy.

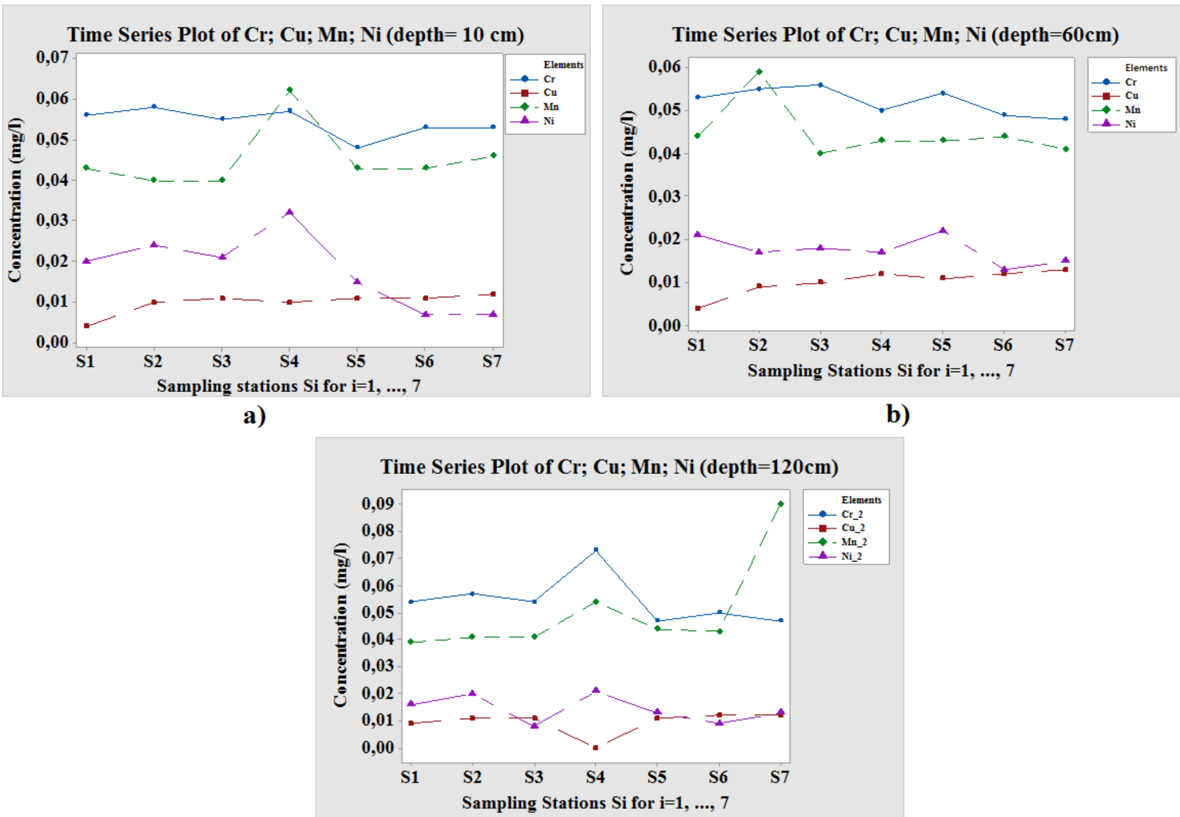
3. Results and Discussion

In order to better interpret the results, we have performed the statistical analyses of all the data. In figure 2 it is shown the time series plot of Cr, Cu, Mn, Ni concentrations, in three different depth levels a) 10cm, b) 60cm, c) 120cm.

Based on graphical data regarding the concentration values of Cr, Cu, Mn and Ni, evaluated through ICP-OES techniques, we notice that: In the quote of 10 cm under the sea surface, the concentration values of Cr and Cu are quasi homogeneous, while for the concentration values of Mn and Ni it is noticed a peak in S4 sampling station compared with other stations.

In the quote of 60 cm under the surface, the concentration values of Ni and Cu are quasi homogeneous, while regarding Mn concentration values it is noticed a peak in S2 sampling station compared with other stations. In the quote of 120 cm under the surface, the concentrations values of Cu and Ni are quasi homogeneous. Regarding the Mn concentration values it is noticed a peak in S7 sampling station compared to other stations. For Cr this peak is in S4.

By analyzing all the data in three different depth we notice that the maximum of concentration values is in S4 sampling station.



c)

Figure 2. Time Series Plot of Cr, Cu, Mn, Ni concentrations, depth a) 10cm, b) 60cm, c) 120cm.

In figure 3 it is shown the boxplot of Cr, Cu, Mn, Ni concentrations, in three different depth levels a) 10cm, b) 60cm, c) 120cm. In 10 cm quote from the sea surface it is noticed an outlier for Mn at the value 0.062mg/l, which correspond to the S4 sampling station. Regarding Ni, the mean value is higher than the median one, which shows that the most of the values are over the mean.

In 60 cm quote from the sea surface it is noticed an outlier for Mn at the value 0.059mg/l, which corresponds to the S2 sampling station. The median values of Cr, Cu and Mn are higher than the mean values, which shows again also for this distribution, the most of the values are over the mean value. In 120 cm quote from the sea surface, we notice two outliers both for Cr and Mn, with values 0.073mg/l (S4) and 0.090mg/l (S7) respectively.

These identified outlier in our statistical analysis led to a high heterogenicity of areas related the concentrations values of these metals.

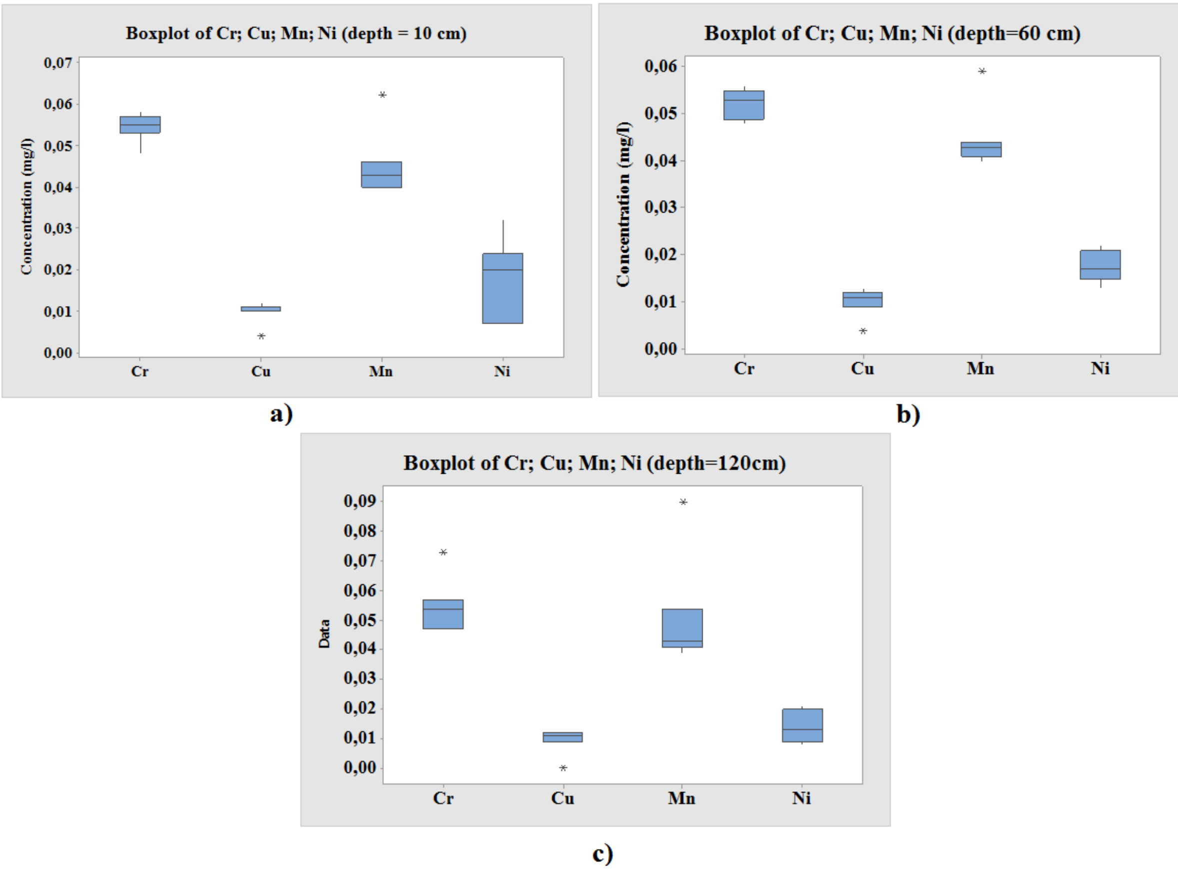


Figure 3. Boxplot of Cr, Cu, Mn, Ni concentrations, depth a) 10cm, b) 60cm, c) 120cm.

In figure 4 it is shown the time series plot of Fe concentrations, in three different depth levels a) 10cm, b) 60cm, c) 120cm.Since Fe concentration values were higher than other heavy metals, we decided to give the data in a detailed graphical plot: In 10cm quote from the sea surface, in S2 sampling station, there is a maximum concentration value of 0.848mg/l. In 60 cm quote from the sea surface, the concentration values begin to decrease in a quasi linear way starting from S1 to S7. In 120 cm quote from the sea surface, Fe concentration values have a quasi-homogenous distribution, except the value at S4 sampling stations. Where the concentration value is too far from the other analyzed stations.

In figure 5 it is shown the boxplot of Fe concentrations, in three different depth levels a) 10cm, b) 60cm, c) 120cm. In 10 cm quote from the sea surface, the median values are lower than the mean values, which shows that in this distribution most of the values are over the mean. In 60 cm quote from sea surface the median values and the means ones are approximately the same. This indicates that for this distribution the number of samples with the higher concentration values than the mean is the same with those that have lower concentrations values than the mean.

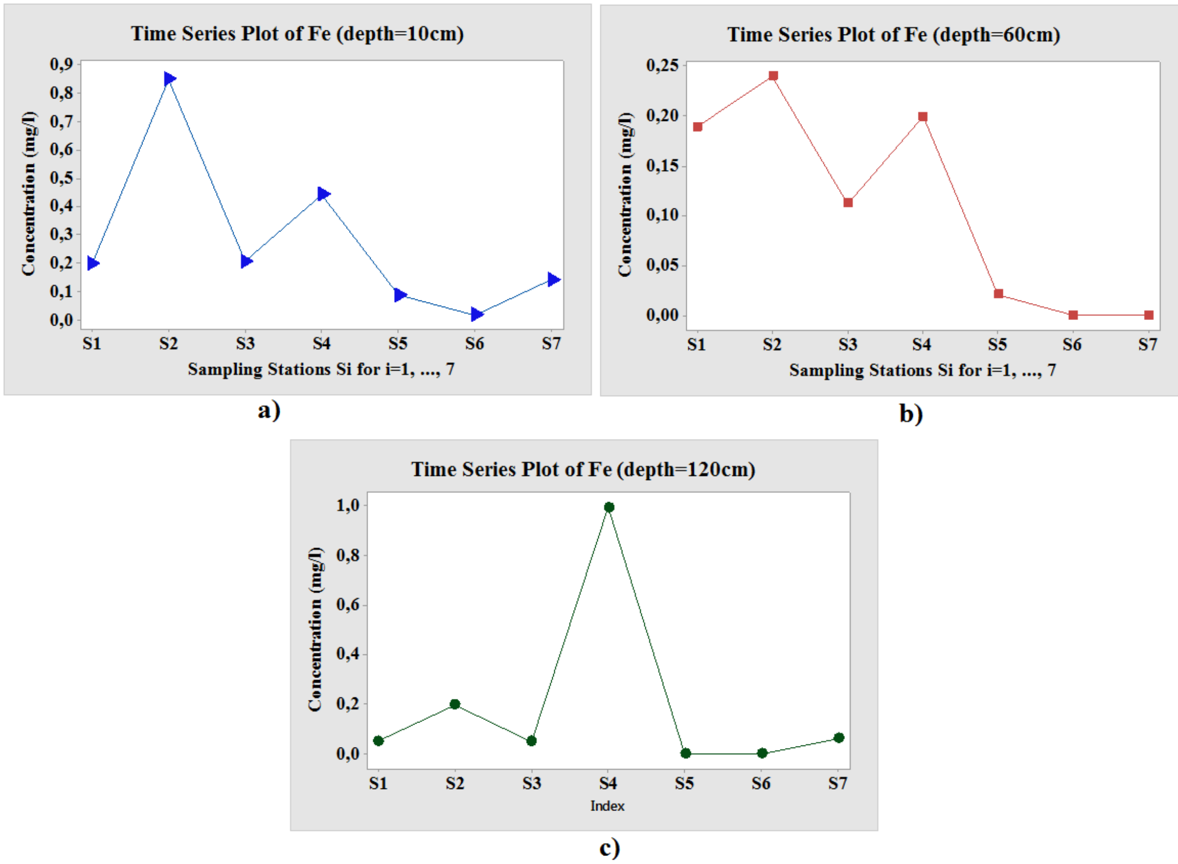


Figure 4. Time Series Plot of Fe concentrations, depth a) 10cm, b) 60cm, c) 120cm.

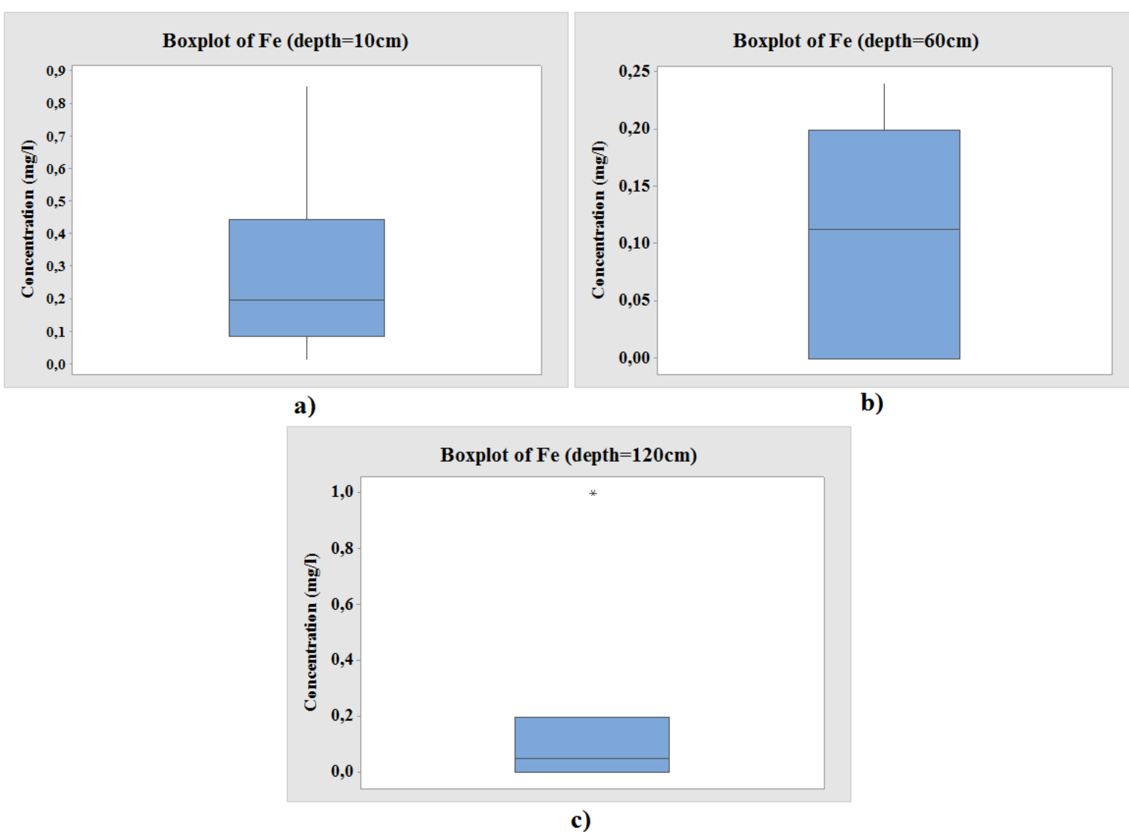


Figure 5. Boxplot of Fe concentrations, depth a) 10cm, b) 60cm, c) 120cm.

In 120 cm quote from the sea surface the median value is lower than the mean value. This indicates that in this distribution the most of values are above the mean value. Although, we notice an outlier of 0.996mg/l which corresponds to S4 sampling station. If we remove this value from our data,then we will have a quasinormal distribution of Fe concentration values.

In figure 6 it is shown a correlation of heavy metalsanalyzed at the three depth levels.

	Cr	*Cu*	*Fe*	*Mn*	*Ni*
Cr	1				
Cu	-0,36673	1			
Fe	0,712964	-0,06834	1		
Mn	0,223655	0,04307	0,09385	1	
Ni	0,617896	-0,30865	0,661726	0,49341	1

a)

	Cr	*Cu*	*Fe*	*Mn*	*Ni*
Cr	1				
Cu	-0,51288	1			
Fe	0,462209	-0,57196	1		
Mn	0,333032	-0,23939	0,574887	1	
Ni	0,631342	-0,58656	0,277937	-0,05295	1

b)

	Cr	*Cu*	*Fe*	*Mn*	*Ni*
Cr	1				
Cu	-0,92962	1			
Fe	0,946427	-0,96015	1		
Mn	-0,16588	0,030318	0,083358	1	
Ni	0,680741	-0,65059	0,692801	0,01173	1

c)

Figure 6. Correlations between heavy metalsanalyzed in a) depth 10cm, b) depth 60cm, c) depth 120cm

In 10cm quote from the sea surface, in S2 sampling station, there is a maximum concentration value of 0.848mg/l.

In 10cm quote from the sea surface, Fe shows a strong uphill (positive) linear relationship with Cr and Ni (0.66 – 0.71) and a weak uphill (positive) linear relationship with Mn of (0.09). While in correlation with Cu, it shows a weak downhill (negative) linear relationship of (-0.06).

In 60 cm quote from the sea surface Fe shows a moderate uphill (positive), linear relationship with Cr and Mn (0.4 – 0.5) and a weak uphill (positive) linear relationship with Ni (0.2). While in correlation with Cu, it shows a moderate downhill (negative) linear relationship (-0.5).

In 120 cm quote from the sea surface Fe shows a strong uphill (positive) linear relationship with Cr and Ni (0.69 – 0.9) and a weak uphill (positive) linear relationship with Mn (0.08While in correlation with Cu, it shows strong downhill (negative) linear relationship (-0.9).

4. Conclusion

Marine pollution is a serious problem, especially in countries in the process of industrialization like Albania. With the absence of stations and sewage treatment systems in these countries, wastewater is discharged into the sea without any prior treatment, leading to degradation of the sanitary quality of coastal waters and misleading of marine ecosystems.

The assessment of heavy metals in Vlora bay indicates the presence of slight pollution by Cr, Cu, Ni, and Mn, while the concentrations of Fe values were very close to allowed limit. According to different stations and different depth of water column we noticed a heterogenic distribution, this might be due to atmosphere pollution as well as anthropogenic sources and water current flows.

From the descriptive statistical analyses (showed by boxplots) of all the data we can conclude that:

In all the three different depth levels there is one specific outlier for Mn, which led to a heterogenicity in the distribution of its concentration values according to sampling stations.To understand and define this situation are needed further analyses in the future at this specific sampling stations.

For all the analyzed elements it is noticed that in 60 cm quote under the sea surface the most part of the sampling stations is with higher concentration values than the mean value. (The median values are higher than the mean values). We think that the main sources of these heavy metals in this quote are mostly from bottom sediment, which are not subject of this study.

Regarding the correlations, Fe shows: an uphill (positive) linear relationship with Cr, Ni and Mn and a downhill (negative) linear relationship with Cu.

Mainly, for all the depth levels, all the analyzed elements have a downhill (negative) linear relationship with Cu.

It is recommended a constant monitoring of heavy metals concentration in Vlora bay, since sea serves as a source of swimming and fisheries for the local inhabitants. The values reported in this study can serve as baseline data tomonitor future anthropogenic activities along the coast. The study showed a need for continuous pollution assessmentstudy of aquatic organisms in the marine environment.

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