Discrimination of Heavy Metal Sources in the Sefidrud Delta Coastal Lagoons, Caspian Sea, N Iran: A Statistical Approach

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Discrimination of heavy metal sources in the Sefidrud Delta coastal lagoons, Caspian Sea, N Iran: a statistical approach

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Abstract

Amirkola (more than 500 years in age), Kiashahr and Zibakenar (a few decades in age) lagoons are located on the Sefidrud Delta, the southern coast of the Caspian Sea. Evaluating the pollution degree caused by heavy metals (including Cu, Cr, Co, Ni, Pb, Zn and V), 106 sediment samples and three sediment cores were taken from studied lagoons. Three indices, including geo-accumulation index ($I_{\text{geo}}$), contamination factor (CF), and pollution load index (PLI), were employed to determine the contamination degree in the lagoons. Based on contamination indices, the Kiashahr and Zibakenar lagoons show significant to moderate contamination with Co, Cu, Pb, Zn and V. Nonparametric statistical analysis (Two-step cluster analysis, analysis of variance, and T-test technique) was used to discriminate the pollution sources. Statistical methods indicated the unique interpretation of contaminants sources. There is a significant difference in metal concentrations between Amirkola and two younger lagoons. Despite the same geogenic origin of sediments in the Sefidrud Delta and lagoons deposits, Co, Zn, and Pb show anthropogenic sources in the newly-formed Kiashahr and Zibakenar lagoons.

Keywords: Metal contamination, statistical analysis, anthropogenic source, Sefidrud Delta, Coastal lagoon, Caspian Sea

1. Introduction

River deltas and their related coastal lagoons are influenced mainly by human activities (e.g. urbanization, industries, agriculture, river damming, fisheries, navigation and harbour activities) in the catchment areas and coasts. The continuous changes in morphology and increasing sediment pollution cause deltaic regions to be frequently evaluated in order to protect these areas. Coastal lagoons are shallow back-barrier water bodies, usually extended along the coastline, detached by a barrier from the sea (Kjerfve, 1994). Coastal lagoons play an important role in flood control and coastline stability, aquaculture and tourism activities.
These areas act as sediment traps and contain sediments and other materials derived from source area lithology, agricultural, urban and industrial activities (Etemadi Deilami et al., 2010; Kazancı et al., 2004). Heavy metals, as one of the environmental pollutants, can accumulate in lagoon bed sediments. Several studies have been conducted on the accumulation of these metals in coastal lagoons in different regions of the world (e.g., Chen et al., 2010; Uluturhan et al., 2011; Wang et al., 2015; García and Muñoz-Vera, 2015; Beraldi et al., 2019; Ontiveros-Cuadras et al., 2019; Zonta et al., 2019; Romano et al., 2021).

The Sefidrud River, with a length of more than 820 km, originates from the Zagros Mountains and enters the Caspian Sea after joining small rivers originated from the Alborz Mountains. The largest delta of the southern coast of the Caspian Sea has been formed by this river over the past 2 million years. The Sefidrud Delta was formed during Pleistocene (Annels et al., 1975) and developed based on tectonic, sea-level changes and gradual regression of the Caspian Sea (Kazancı et al., 2004; Jedari Eivazi et al., 2005; Kazancı and Gulbabazadeh, 2013). During the Caspian Sea regression, some lagoons were formed. Longshore currents (from northwest to southeast) have also significantly impacted coastal morphology and lagoons formation. These currents have driven sediments almost parallel to the coast and gradually create coastal sand spits. These sand spits, along with river and delta sediments, have entirely cut off the connection between the isolated part of the sea and created lagoons (Kousari, 1986; Lahijani et al., 2009; Leroy et al., 2011) such as Amirkola, Zibakenar and Kiashahr lagoons, which were formed during Quaternary.

Excessive discharge of urban, industrial and agricultural wastewaters and runoff, which contains various pollutants such as heavy metals, has resulted in the accumulation of this group of pollutants in delta’s coastal sediments and shoreface deposits (Rafiei et al., 2017), lagoons on the Sefidrud Delta and the Anzali Lagoon (Rafiei et al., 2012; Vesali Naseh et al., 2012; Rafiei et al., 2015).
The goals of this study were to investigate: 1) the concentration, degree of contamination, and spatial distribution of Cr, Cu, Co, Ni, Pb, Ti, V, Zn and Zr in the surface sediments of Amirkola, Zibakenar, and Kiashahr lagoons; 2) the temporal distribution of mentioned metals in the core samples taken from the three mentioned lagoons, 3) Comparison of heavy metal concentrations and their sources in studied lagoons.

2. Materials & Methods

2.1. Study Area

The Sefidrud Delta with an area of 1700 km$^2$ is located in the Gilan Province (37°00' - 37°27' N and 49°28' - 50°16' E) north of Iran. Strong longshore current and high sediment supply have created coastal lagoons on the Sefidrud Delta. The Amirkola, Kiashahr, and Zibakenar lagoons are the main existing coastal lagoons on this delta (Fig. 1).

Among them, the Amirkola Lagoon was created due to the activity of the old Sefidrud and separated from the Caspian Sea about 500 years ago (around 1600 AD) (Jedari Eivazi et al., 2005; Leroy et al., 2011; Kazancı and Gulbabazadeh, 2013; Haghani, 2015) and is the oldest. The Amirkola Lagoon, with 12.3 km$^2$, is located between Lahijan, Kiashahr and Langarud cities and has a maximum water depth of 2 meters (Naderi Beni et al., 2013).

The Zibakenar and Kiashahr lagoons, located on the new Sefidrud Delta (the currently active delta lobe), were formed due to the last few decades’ of displacements (avulsion) of the Sefidrud River on its delta (Sarvar, 2008; Kazancı and Gulbabazadeh, 2013; Haghani, 2015). The Kiashahr Lagoon is located in the eastern part of the delta and northeast of Kiashahr. The Zibakenar Lagoon is located in the western part of the delta and the north of Zibakenar city (Fig. 1). The water depth in these lagoons is generally less than 2 m and is controlled by freshwater entering through precipitation and irrigation.

2.2. Sampling
A total of 106 surface sediment samples (Amirkola: 56, Zibakenar: 22 and Kiashahr: 28 samples) and three core samples (one core sample for each lagoon) were collected from all three lagoons (Fig. 1). Surface samples were taken by Van Veen Grab in a regular network and packed in polyethylene bags. The core samples were taken by PVC pipe and hand auger. Two ends of the tubes were sealed after taking core samples so that their contents remain intact. Samples were sent to Bu-Ali Sina University and Geological Survey of Iran (GSI) laboratories for various physicochemical and chemical analyses.

2.3. Physicochemical Analysis

All samples were dried at room temperature then a part of each sample was used for physicochemical analyses. Particle size analysis was performed on the samples. Twenty percent hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) solution was added to 50 g of each sample to dissolve the organic matter; then, samples were washed with deionized water. After that, the coarse-grained and fine-grained fractions of samples were separated using the wet sieving method. For granulometry purposes, a column of sieves was used for the coarse- and medium-grained parts (Lewis & Macconchie, 1994). The fine-grained fraction (under 62.5 microns) was tested by Fritsch A22 Compact particle size analyzer in the sedimentology laboratory of Bu-Ali Sina University.

To determine the pH of samples, 2 g of dry samples were mixed with 10 ml of deionized water (1:5 sediment to water ratio) and stirred for 2 hours (Segura et al., 2006). The mixture was then let to settle, and the pH was measured from the clear liquid above the sediments. The titration method was carried out to determine the samples' calcium carbonate content (Carver, 1971). This process was repeated three times to ensure the results. The organic matter amount in sediments was determined by the burning method, for which 1 g of the air-dried sample was heated at 400°C (Heiri et al., 2001) for 4 hours in the oven. The weight difference was related to organic matter amount.
**2.4. Chemical Analysis**

Inductively coupled plasma-optical emission spectrometry (ICP-OES) method was used to determine Cr, Cu, Co, Ni, Pb, Ti, V, Zn and Zr concentrations in the samples. For this purpose, the < 0.0625 mm fraction of samples were entirely digested by a mixture of four acids: hydrochloric, nitric, fluoric and perchloric. The experiment was performed at the geochemical laboratory of GSI, Iran, using Varian 735.

**2.5. Contamination Assessment**

Both single and integrated pollution indices were used to evaluate the environmental assessment of Cr, Cu, Co, Ni, Pb, Ti, V, Zn and Zr in the studied lagoons. Geo-accumulation (I$_{geo}$) and contamination factor (CF) are single indices, and pollution load index (PLI) is an integrated Index. These approaches are the most common environmental risk assessment methods (Caeiro et al., 2005; Hou et al., 2013).

Geo-accumulation Index (I$_{geo}$) can determine the amount of metal pollution in sediments by comparing the concentration of specific metals in samples with the pre-industrial concentration of the same metal in the background (Zhao et al., 2012) and is calculated by the following equation (Müller, 1969):

$$I_{geo} = \log \frac{C_n}{1.5B_n}$$

where $C_n$ is the metal concentration (n) in the sediment sample, $B_n$ is the geochemical background of the studied metal (n), and coefficient 1.5 has been applied to minimize possible geogenic and anthropogenic effects (Qingjie and Jun, 2008). In this study, background values are the average concentration of metals in the Upper Continental Crust (UCC) (Rudnick and Gao, 2003). The geo-accumulation index is divided into seven categories (Müller, 1981), from 0 to 6 (Table 1), based on the level and degree of pollution. Class 0 specifies the lack of contamination, whereas class 6 indicates the upper limit of the contamination. The highest class
6 reflects 100-fold enrichment of the metals than their background values (Harikumar and Jisha, 2010).

Contamination factor (CF) is the ratio of the concentration of each metal (\(C_M\)) to the background values (\(C_B\)):

\[
CF = \frac{C_M}{C_B}
\]

The average concentration of metals in the UCC has been used as the background. The CF categories are presented in Table 1 (Håkanson, 1980). The CF is applied to find the contamination level of metals.

The pollution load index (PLI) was performed based on Suresh et al. (2012) to assess the environmental quality of sediments. This index is calculated by the \(n^{th}\) root resulting from the multiplication of \(n\) pollution index (CF) for a single sediment sample as follows:

\[
\text{PLI for a sample} = (CF_1 \times CF_2 \times \ldots \times CF_n)^{1/n}
\]

where \(n\) is the number of sediment samples in each lagoon. The PLI for a lagoon is the \(n^{th}\) root of the product of \(n\) PLI values.

\[
\text{PLI for a lagoon} = (\text{PLI}_1 \times \text{PLI}_2 \times \ldots \times \text{PLI}_n)^{1/n}
\]

where \(n\) is the number of lagoons. The PLI values greater than 1 indicate metal contamination, while values less than 1 indicate no contamination (Tomlinson et al., 1980).

2.6. Statistical Analysis

Statistical analysis methods are usually used in environmental studies to determine data distribution and correlation among the variables. In this study, SPSS for Windows version 21 was used for statistical analysis. Correlation analysis is used to describe the strength and direction of the linear relationship between the studied elements.

Cluster analysis (CA) was conducted to categorize samples of different lagoons based on their constituent elements' similarities. In this study, two-step cluster analysis was conducted to identify relatively homogeneous groups of variables, using an algorithm that starts with each
variable in a separate cluster and combines clusters until only one is left. As the variables have significant differences in scaling, standardization was performed before computing proximities, which can be achieved automatically by the hierarchical cluster analysis procedure.

One-way analysis of variance (ANOVA) and compare means analysis were used to investigate the differences or similarities between the studied elements in different lagoons. The nonparametric tests, including the Kruskal-Wallis and Mann-Whitney test with Bonferroni adjustment method, were used for pairwise comparison.

3. Results and Discussion

3.1. Physicochemical Analysis

The granulometric analysis results of Amirkola, Zibakenar, and Kiashahr lagoons are presented in Table 2. Based on granulometry results, the texture of most sediment samples in Amirkola Lagoon is fine to medium grain. The sediment samples were frequently classified as slightly sandy mud to slightly muddy sand (Fig. 2). Some gravelly samples in this lagoon were mostly close to the lagoon's barrier and sea-side. Most samples from Zibakenar and Kiashahr lagoons have fine grain texture, so more than 55% of samples were classified as mud, sandy mud, slightly gravelly mud, and slightly gravelly sandy mud based on Folk (1980). Currently, none of these lagoons have major water inlets.

The titration results (Table 2) showed that the carbonate contents of the sediment samples are relatively high (mean carbonate content in Amirkola: 54.49%; Zibakenar: 44.40%; and Kiashahr: 43.30%) and constitute about half of the sediments. The high carbonate content in the samples is mainly due to gastropod and pelecypod (bivalve) shell fragments. Organic matter content in the lagoons is variable. The mean amount of organic matter measured for Amirkola, Zibakenar, and Kiashahr lagoons were 21.01%, 11.52%, and 9.96%, respectively. The higher
amount of organic matter in Amirkola Lagoon might result from its age and plant growth around it. The mean pH values measured for Amirkola, Zibakenar and Kiashahr lagoons were 7.75, 7.53 and 7.58, respectively, indicating neutral to slightly alkaline conditions in all three lagoons.

3.2. Chemical Analysis

Descriptive statistics of some major and minor element concentrations in sediment samples of all three lagoons are displayed in Table 3. Out of 56 samples in the Amirkola Lagoon, the Pb, Ni, and Co concentrations were below the detection limit in 40, 33 and 52 samples, respectively. The concentration of Cu, Cr, Co, Ni, Pb, Zn and V was considered because of their potentially toxic natures. The order of mean metal concentration is Zn > Pb > Ni > V > Cu > Cr > Co for Amirkola Lagoon, V > Zn > Co > Cu > Ni > Pb > Cr for Zibakenar Lagoon, and Zn > V > Co > Cu > Ni > Pb > Cr for Kiashahr Lagoon (Table 3). The concentration order of metals in Amirkola Lagoon is different from the two other lagoons. Both Zibakenar and Kiashahr lagoons show almost the same order. Also, the variation of the heavy metals in the Amirkola, Zibakenar and Kiashahr lagoons are demonstrated in Fig. 3. Noticeable differences in metal concentrations and ranges are seen in three lagoons. Differences were studied by comparing the mean values of metals in sediment samples. The mean values of studied metals in the Amirkola Lagoon were considerably lower than the other two (Table 3). Also, major element contents in the Amirkola sediment samples were lower than the other lagoons except for Ca. The higher amount of Ca in the Amirkola Lagoon comparing to other lagoons is associated with higher CaCO$_3$ content (Table 2) in this lagoon. High Al content in the Zibakenar and Kiashahr lagoons samples is due to more mud and clay minerals in these lagoons.

The highest heavy metal concentrations are observed in Zibakenar and Kiashahr lagoons. The mean concentration values of Cu, Co, Cr, Ni, Pb, V and Zn in the Zibakenar and Kiashahr
lagoons are at least two times higher than that of Amirkola Lagoon. The ranges of Zn and Pb in the Kiashahr Lagoon are about 450 and 90 mg/kg, respectively, indicating the metals' heterogeneous dispersion in this lagoon. Cobalt (16.47-239.37 mg/kg) and V (19.90-306.27 mg/kg) also show a wide range in Zibakenar Lagoon. The distribution maps of some metals in the Zibakenar and Kiashahr lagoons are shown in Fig. 4. Metals distribution map for the Amirkola Lagoon is not displayed due to the lack of data and/or uniform dispersal of the elements in this lagoon.

Therefore, as can be seen, the concentration of potentially toxic metals is much lower in the Amirkola Lagoon comparing to the Zibakenar and Kiashahr lagoons. The last two lagoons have been formed over the past five decades on the new Sefidrud Delta (Sarvar, 2008; Yamani et al., 2013; Haghani, 2015). The Amirkola Lagoon was formed on the old Sefidrud Delta over 500 years ago (Jedari Eivazi et al., 2005; Leroy et al., 2011; Kazancı and Gulbabazadeh, 2013; Haghani, 2015).

A core sample has been taken from each lagoon to investigate the changes in metallic element concentration over time. Sedimentary facies changes and concentrations of heavy metals studied in each core sample are displayed in Fig. 5. The core sample of the Amirkola Lagoon with a depth of 180 cm is composed of muddy and sandy deposits. Lead, Co, and Zn increase slightly from the bottom to the top, indicating human activities around the lagoon during past decades. Chromium and V have a negative relationship with mud and a positive relationship with sand amounts. These elements have a geogenic origin. In the Zibakenar Lagoon core sample with a depth of 185 cm, metal elements directly correlate with the amount of mud and show a decrease toward the surface except for Pb and Zn, which may have an anthropogenic origin. The core sample taken from the Kiashahr Lagoon was about 155 cm, and the whole core is almost composed of mud deposits, so the elements do not show any remarkable changes along with the core depth. Only Pb and Zn have been increased at the surface sediments. This
lagoon has an outlet towards the Caspian Sea and Kiashahr harbour, therefore increasing Pb and Zn toward the port might be related to human activities.

### 3.3. Assessment of heavy metal pollution

Descriptive statistics results of the geo-accumulation index ($I_{geo}$) in the three lagoons sediment samples are presented in Table 4. According to the results, the mean $I_{geo}$ of Cr and Ni in all lagoons is almost similar and does not show any specific changes, so all samples are practically uncontaminated with Cr and Ni.

In general, mean $I_{geo}$ values of the Amirkola Lagoon samples are classified as practically uncontaminated for all studied metals. Only three samples out of 16 show $I_{geo}$ values between 0 and 1, representing these samples are uncontaminated to moderately contaminated with Pb in the Amirkola Lagoon.

The two other lagoons are moderately contaminated by Co and uncontaminated to moderately contaminated by Cu. The samples of Kiashahr Lagoon are also uncontaminated to moderately contaminated by Zn.

Table 5 shows descriptive statistics results of CF and PLI in sediment samples of all three lagoons. Based on the CF results, all samples are not contaminated with Cr and Ni. The samples taken from Amirkola Lagoon show CF values less than 1, indicating low contamination with metals except for Pb, whose mean CF value is 1.43. The samples are moderately contaminated with Pb for Amirkola Lagoon sediment samples.

Cobalt's mean CF values are 4.86 and 3.92 in Zibakenar and Kiashahr lagoons, respectively, indicating considerable contamination. Copper (CF = 1.53), Pb (CF = 1.46), V (CF = 1.10) and Zn (CF = 1.35) show moderate contamination in the Zibakenar lagoon. The Kiashahr lagoon sediments are moderately contaminated with Cu (CF = 1.63) and Pb (CF = 1.63), low contaminated with V (CF = 0.84), and considerably contaminated with Zn (CF = 3.83).
The order of mean CF values is Pb > Cu > Zn > Co > Ni > V > Cr for Amirkola Lagoon, Co > Cu > Pb > Zn > V > Ni > Cr for Zibakenar Lagoon, and Co > Zn > Cu = Pb > V > Ni > Cr for Kiashahr Lagoon.

According to the mean PLI values, the samples taken from all three lagoons are unpolluted with studied metals. As is evident in Table 5, the highest PLI value in the Amirkola Lagoon is less than 1 and indicates that all samples of this lagoon have no metal pollution. Since the Zibakenar and Kiashahr lagoons’ maximum PLI values are higher than 1, some samples in those lagoons show metal pollution. About 85.7% of the Zibakenar Lagoon and 67.8% of the Kiashahr Lagoon samples had PLI higher than 1 and showed different degrees of metal pollution (Fig. 6). The PLI value of the whole lagoon is 0.24 for Amirkola, 1.05 Zibakenar and 1.12 for Kiashahr lagoons, which confirmed that metal pollution had increased from the Amirkola Lagoon to the Zibakenar and Kiashahr lagoons.

### 3.4. Metal source

The Sefidrud delta is the largest in the southern Caspian Sea formed in the Pleistocene. This delta is wave-dominated during the sea-level rise and river-dominated when sea-level falls (Naderi Beni et al., 2013). The Sefidrud course has been frequently changed between the Anzali and Amirkola lagoons (Kousari, 1986). The last major avulsion had occurred in AD 1600 when the river course was shifted from the east, near the present Amirkola Lagoon, towards the west near the current Kiashahr Lagoon (Krasnozhon et al., 1999; Lahijani et al., 2009; Kazancı and Gulbabazadeh, 2013). The Sefidrud before the latest avulsion is known as Old Sefidrud and New Sefidrud (or Sefidrud) after avulsion. Old Sefidrud created the Amirkola Lagoon, and New Sefidrud formed the Zibakenar and Kiashahr lagoons.

Most of the sediments entered into the delta are transported to the coast by the Sefidrud River. Then the origin of sediments in all three lagoons is the same due to a common geological source. The total concentration of elements is expected to be approximately similar in the
lagoons. However, the chemical analysis results indicate differences in the amount of some heavy metals in the lagoons. Despite the common geological origin of sediments, toxic metals are not uniformly distributed in studied lagoons. Based on the metals distribution and pollution indices, no metal contamination is observed in Amirkola Lagoon, which is formed about 500 years ago. Lead has increased in surface sediments of this lagoon. Lead variation in the core taken from the Amirkola Lagoon shows an increase in Pb content in the uppermost portion of the core (Fig. 5).

As presented in Table 4, the similarity of I_{geo} values for Cr and Ni show the same origin for these metals in all studied lagoons. Considering the same geogenic origin of the sediments entering into all studied lagoons, the observed differences in I_{geo} values might be from the anthropogenic origin. In the newly-formed Zibakenar and Kiashahr lagoons, the distribution map of elements (Fig. 4) shows that the scattering pattern of some metals is different in the two lagoons. On the other hand, in Kiashahr Lagoon, Zn and Co had the highest pollution level, while in Zibakenar Lagoon, Co indicates the highest contamination level. Differences in the amount and type of heavy metals can indicate an anthropogenic source. The pattern of increasing element concentration towards some recreational and touristic facilities and particular areas also increases the role of anthropogenic-originated pollutants. Statistical analysis was performed to investigate the origin of metals in sediment samples and differences in element contents of the three studied lagoons.

### 3.4.1. Correlation Matrix

Pearson’s correlation coefficients of elements in studied lagoons are summarized in Table 6. Correlation matrix for the Amirkola Lagoon shows that Cr, Cu, Fe, K, Mg, Na, Ti, V, Zn and Zr have a strong positive correlation with Al, and Ba, Ca, Mn and Sr have a strong negative correlation with Al (Table 6). The first group belongs to silicate minerals, and the second one
belongs to carbonate minerals in sediment samples of this lagoon. Nickel, P and Pb show no positive nor negative correlation with Al. Lead only has a strong positive correlation with Ni, indicating the exact behaviour of these elements.

In the Zibakenar Lagoon, the relationship between elements changes (Table 6). Aluminum as a geogenic element has a strong positive relationship with Cu, K, Mg and Ni and does not show a clear relationship with other elements. Heavy metals such as Co, Cr, Fe, Pb, Ti, V, Zn and Zr have a strong positive relationship and have no significant relationship with other studied elements.

In the Kiashahr Lagoon, these relationships are entirely different from the other two lagoons (Table 6). Aluminum has a strong positive relationship with Co, Cr, Cu, Fe, Ni, Ti, V and Zr, and a very strong negative relationship with Ca and Sr. In this lagoon, unlike the Amirkola Lagoon, Zn has no relation with Al, and on the contrary, Ni has a strong relationship with Al. Lead and Zn do not show any correlation with other heavy metals.

Since the entrance sediments of all studied lagoons have the same geological source, the detected changes in metal correlations might be a cause of an anthropogenic source for some metals.

3.4.2. Analysis of variance

One-way analysis of variance (ANOVA) was achieved to compare the studied lagoons in terms of metal content and find the differences between them. At first, the residual values of the model were examined, and their normality was tested (Table 7). This test shows that the residual values are not normal except for Co, but it should be noted that Co can only be measured in 5 samples in the Amirkola Lagoon and was below the detection limit in 51 samples. The same thing goes for Pb and Ni were not detectable in all samples of the Amirkola Lagoon. The Pb and Ni concentrations were above the detection limit in 16 and 23 samples, respectively.
Therefore, due to the normality of the model's residual values, the nonparametric equivalent of the one-way analysis of variance (Kruskal-Wallis test) was used to compare the three lagoons. Based on the results presented in Table 8, all studied metals show significant differences in error level of one percent in all three lagoons ($P < \alpha = 0.01$) but Pb due to many missing samples in the Amirkola Lagoon. Therefore, the Mann-Whitney test with the Bonferroni method was used for pairwise comparison in studied lagoons.

### 3.4.3. Two-Step Cluster Analysis

As the nonparametric analysis of variance showed a difference between the three lagoons, a two-step cluster analysis was used to find the similarities and differences in the metal content of the studied lagoons. The Two-Step Cluster Analysis is used as an investigation tool to disclose natural groupings (or clusters) in a dataset that would otherwise not be clear. For this purpose, all samples taken from each lagoon were placed in the same group then were re-categorized using this method. Cobalt, Ni and Pb in the Amirkola Lagoon were put aside from the analysis due to a considerable amount of missing data.

Various measures are used to quantify the "goodness" of a cluster solution. In a good cluster solution, the elements within a cluster are similar to one (cohesive), while the clusters themselves are quite different (separated). A popular measure is the silhouette coefficient, which is a measure of both cohesion and separation. In a good solution, the within-cluster distances are small, and the between cluster distances are large, resulting in a silhouette measure close to the maximum value of 1 (Fig. 7a). The distribution of cases in the final cluster solution is seen in Fig. 7a. Out of 106 samples taken from all three lagoons, 50 samples were placed in cluster 1 and 56 samples in cluster 2. Cluster 2 consists of all the Amirkola Lagoon samples, and the first cluster consists of all samples from the Zibakenar and Kiashahr lagoons. As expected, the Amirkola Lagoon, formed on the old Sefidrud Delta, is entirely different from
the two newer lagoons in terms of metal content. Figure 7b also ranks the features from the
most to the least importance.

Aluminum and Zr had the highest, and Zn had the least importance on separating two clusters.
The differences in Al, Zr, Cu, Fe and Ti contents between the Amirkola Lagoon and the other
two lagoons caused the separation of these two groups from each other.
The Mann-Whitney test with the Bonferroni adjustment method is used to perform pairwise
comparisons. To apply the Bonferroni adjustment, the \( p \)-value obtained from the Mann-
Whitney test should multiply by the number of pairwise comparisons and then compare with
the error rate of the first type (\( \alpha \)) (Tabachnick and Fidell, 2012). In this study, considering that
the number of comparisons is 3, Bonferroni \( p \) is as follow:

\[
\text{Bonferroni } p = 3 \times (p - \text{value})
\]

If Bonferroni \( p \) is greater than one, the value of Bonferroni \( p \) is considered one.

3.4.4. Independent samples t-test

The results of the independent samples t-test are presented in Table 9. There are significant
differences between the Zibakenar and Kiashahr lagoons and the Amirkola Lagoon for all
studied metals except Pb because of the latter lagoon's missing data. The mean values of studied
metals in the Zibakenar and Kiashahr lagoons are higher than Amirkola Lagoon (Table 3). In
other words, the distributions of these metals in three lagoons are entirely different.
The result of comparing the two Zibakenar and Kiashahr lagoons reveals remarkable
information. The difference between the studied metals in these two lagoons is not significant.
In other words, these metals are similar in terms of distribution and value. Only two elements
of Zn and Ni have significant differences in these lagoons. The mean values of Pb in the
Zibakenar and Kiashahr lagoons were 90.41 and 247.02 mg/kg, and the mean values of Ni were
38.87 and 34.54 mg/kg, respectively. The significant difference in Zn values in two lagoons of
the same geogenic origin can only be justified with an anthropogenic source.
It seems high Zn pollution indices in the Kiashahr Lagoon are due to human impact on sediment pollution. The mean value of Ni in the Kiashahr Lagoon was lower than Zibakenar, while the highest concentration of this metal was observed in the Kiashahr Lagoon. Most samples of the Zibakenar Lagoon have higher Ni content than the Kiashahr Lagoon samples. Perhaps this significant difference in the concentration of Ni in the two lagoons is due to the local airport and touristic facilities next to the Zibakenar Lagoon.

4. Conclusion

The Sefidrud Delta is the largest in the south of the Caspian Sea, formed during the Holocene. Amirkola, Zibakenar and Kiashahr are the most important lagoons that are created during this delta formation. According to the previous studies (Jedari Eivazi et al., 2005; Leroy et al., 2011; Kazanci and Gulbabazadeh, 2013; Haghani, 2015), Amirkola Lagoon was created 500 years ago by Old Sefidrud. The other two young lagoons result from the current activity of the Sefidrud River created over the past few decades.

Physicochemical properties of sediment samples, heavy metals content and their distribution were investigated in all three lagoons. The physicochemical properties of sediment samples show that the average organic matter, carbonate content and sand percentage in Amirkola Lagoon sediments are more than the other two lagoons. In contrast, the Zibakenar and Kiashahr lagoons are mainly muddy and have a lower amount of sand. Comparing Cr, Cu, Co, Ni, Pb, Ti, V, Zn, and Zr contents in the lagoons shows that the average of these metals in Amirkola Lagoon is significantly less than the other lagoons. Kiashahr Lagoon's age and the most negligible anthropogenic impacts play an essential role in this difference. Through the past 500 years, the geological source of the Sefidrud River sediment has not changed. During recent years, the increase of human activities in the delta and its upstream areas, such as dam construction, various industries and factories, and agricultural activities (e.g. using fertilizers...
and pesticides), has considerably augmented heavy metals concentrations in the Zibakenar and Kiashahr lagoons.

Low CF and PLI values for metals and sediments in the Amirkola Lagoon reveal geogenic sources for studied metals. This fact was supported by $I_{geo} (< 0)$ index as well. The CF and $I_{geo}$ values for Cu, Cr, Co, Ni, Zn and V showed an unpolluted status. Lead shows moderate CF values (average CF 1.43), indicating anthropogenic sources. On the other hand, sediment samples of the Zibakenar and Kiashahr lagoons showed high CF values for Co, Zn, Cu and Pb, while $I_{geo}$ showed high values for Co and Zn. According to the PLI values, most of the Zibakenar and Kiashahr lagoons samples were polluted (PLI > 1), suggesting inputs from anthropogenic sources. The Amirkola Lagoon was found to be uncontaminated based on the lagoon PLI values, but the Zibakenar and Kiashahr lagoons were considered to be contaminated.

Statistical analyses showed significant differences in heavy metal contents between the Amirkola and two other studied lagoons. The sediment samples were taken from the Amirkola Lagoon display meaningful lower metal concentrations than the other two.

Also, two recently formed Zibakenar and Kiashahr lagoons show differences in Zn and Ni contents. The Kiashahr Lagoon is connected to the Caspian Sea through a canal linking Kiashahr harbour to the sea. The high amount of Zn in the sediments of this lagoon is related to the passing of fishing boats and yachts through this route. Zibakenar Lagoon is also located near a small local airport and recreational and touristic centre. The increasing Ni content in the sediments, especially in the southern part of the lagoon, can be related to these facilities. For centuries, the primary source of sediments and heavy metals of the Sefidrud Delta deposits has been the Sefidrud River sediments. A new source of sediment contaminants in this delta is human impacts and activities (domestic, industrial and agricultural) developed during the past few decades.
An increase in Zn and Pb contents was observed from the bottom to the top of the cores taken from all three lagoons, but it is much more dramatic in the Zibakenar and Kiashahr lagoons. Since the primary source of sediments stayed the same, human activities and anthropogenic sources are appeared to be the main source of heavy metals in the studied lagoons during the past decades.

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Declarations

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Author contribution:

1. Behrouz Rafiei: Supervisor of two MSc theses achieved at Bu-Ali Sina University, wrote the manuscript. Performed some statistical calculations.
2. Fatemeh Ahmadi-Ghomi: Developed the manuscript and performed the computations, drew some figures and translated the material, discussed the results and contributed to the final manuscript.

3. Asghar Seif: Introduced and performed the statistical method and calculations.

4. Ali Shakibaazad: Advisor of two MSc theses achieved at Bu-Ali Sina University and conducted some analytical procedures at Geological Survey of Iran.

5. Sonia Shamshiri: Her MSc. thesis is part of the manuscript

6. Zahra Sharifi Abzahli: Her MSc. thesis is part of the manuscript

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Figure captions

Fig. 1. Location map and sampling points of the studied lagoons. (ZKL: Zibakenar Lagoon; KSL: Kiashahr Lagoon; AKL: Amirkola Lagoon). Red squares indicate the core sample location in each lagoon.

Fig. 2. Textural classification of studied samples in three lagoons based on Folk (1980). (Black circles: Zibakenar samples; Red circles: Kiashahr samples; Yellow circles: Amirkola samples)

Fig. 3. Box plot diagram of metal concentrations in studied lagoons.

Fig. 4. Distribution map of some studied metals in the Zibakenar and Kiashahr lagoons.

Fig. 5. Sedimentary facies and heavy metals concentrations changes in core samples taken from studied lagoons. The Amirkola Lagoon sediments are temporally different from the others.

Fig. 6. Box Plot diagram of PLI values in all three lagoons.

Fig. 7. Results of two-step cluster analysis, a) Silhouette measure shows values close to the maximum amount, and cluster sizes including two distinct clusters; b) features from the most to the least predictor (variable) importance.

Table 1. Classification of pollution indices used in this study.

| Index                        | Class       | Description                                      |
|------------------------------|-------------|--------------------------------------------------|
| Geo-accumulation (Müller, 1969) | $I_{\text{geo}} \leq 0$ | Practically uncontaminated                        |
|                              | $0 < I_{\text{geo}} \geq 1$ | Uncontaminated to moderately contaminated         |
|                              | $1 < I_{\text{geo}} \geq 2$ | Moderately contaminated                           |
|                              | $2 < I_{\text{geo}} \geq 3$ | Moderately to heavily contaminated                |
|                              | $3 < I_{\text{geo}} \geq 4$ | Heavily contaminated                              |
|                              | $4 < I_{\text{geo}} \geq 5$ | Heavily to extremely contaminated                 |
|                              | $5 < I_{\text{geo}}$ | Extremely contaminated                            |
| Contamination factor (Häkanson, 1980) | $\text{CF} \geq 1$ | Low contamination                                 |
|                              | $1 < \text{CF} \geq 3$ | Moderate contamination                            |
|                              | $3 < \text{CF} \geq 6$ | Considerable contamination                        |
|                              | $\text{CF} < 6$ | Very high contamination                           |
Table 2. Summarized physicochemical properties of studied samples in three lagoons.

| Element         | Amirkoal Lagoon (56) | Kiashahr Lagoon (28) | Zibakenar Lagoon (22) |
|-----------------|-----------------------|-----------------------|------------------------|
|                 | Range | Mean | Range | Mean | Range | Mean |
| Gravel (%)      | 0.25-88.68 | 9.25 | 0.12-36.91 | 5.59 | 0.38-51.91 | 9.69 |
| Sand (%)        | 4.55-93.3 | 42.13 | 5.52-80.62 | 26.55 | 5.48-96.80 | 20.59 |
| Clay (%)        | 3.6-68.71 | 48.45 | 0.00-89.05 | 56.5 | 1.63-87.17 | 59.20 |
| Carbonate (%)   | 4.58-79.16 | 54.49 | 8.00-66.65 | 43.30 | 23.53-66.65 | 44.40 |
| Organic matter (%) | 9.25-65.78 | 21.01 | 1.00-15.00 | 9.96 | 2.00-28.00 | 11.52 |
| pH              | 7.09-8.24 | 7.75 | 7.10-7.97 | 7.58 | 6.90-7.88 | 7.53 |

Table 3. Descriptive statistics of some major and minor element concentrations in sediment samples of the studied lagoons

| Element          | Amirkola (n=56) | Zibakenar (n=22) | Kiashahr (n=28) |
|------------------|-----------------|------------------|-----------------|
|                  | Range | Mean | Median | SD   | Range | Mean | Median | SD   | Range | Mean | Median | SD   |
| Al (%)           | 0.32-3.86 | 0.99 | 0.61 | 0.7 | 0.91-9.27 | 7.91 | 8.24 | 1.68 | 4.17-9.41 | 6.97 | 7.31 | 1.6 |
| Fe (%)           | 0.30-4.81 | 1.01 | 0.75 | 0.8 | 0.84-8.20 | 4.25 | 4.10 | 1.35 | 2.24-5.66 | 3.97 | 4.24 | 0.9 |
| Ca (%)           | 3.59-40.00 | 24.2 | 25.4 | 5.8 | 5.01-11.65 | 8.77 | 8.78 | 1.87 | 6.53-12.2 | 10.9 | 3.8 |
| K (%)            | 0.07-0.98 | 0.24 | 0.15 | 0.1 | 0.36-2.27 | 1.95 | 2.00 | 0.38 | 1.02-2.36 | 1.69 | 1.77 | 0.4 |
| Mg (%)           | 0.54-1.08 | 0.74 | 0.72 | 0.0 | 0.53-1.56 | 1.41 | 1.45 | 0.21 | 1.25-1.67 | 1.47 | 1.45 | 0.1 |
| Na (%)           | 0.10-0.67 | 0.23 | 0.20 | 0.1 | 0.19-1.83 | 0.86 | 0.77 | 0.34 | 0.44-1.54 | 0.96 | 0.93 | 0.3 |
| Mn (mg/kg)       | 595.94-3506.05 | 151 | 143 | 619 | 484.30-1594.06 | 111 | 111 | 256. | 875.60-138 | 142 | 269 |
| Cr (mg/kg)       | 3.75-51.02 | 12.5 | 9 | 8.60 | 9.6 | 1.82-25.26 | 13.9 | 13.7 | 4.12 | 7.04-12.4 | 12.9 | 3.2 |
| Cu (mg/kg)       | 6.00-38.01 | 13.9 | 11.5 | 6.7 | 29.20-61.79 | 42.9 | 44.0 | 7.53 | 34.49-45.8 | 42.4 | 10.0 |
| Co (mg/kg)       | < 15.0 | 7.36 | 5.98 | 2.1 | 16.47-239.37 | 84.1 | 74.2 | 47.2 | 38.21-67.7 | 70.9 | 17.0 |
| Ba (mg/kg)       | 173.61-424.67 | 344. | 342. | 53. | 140.59-487.24 | 384. | 385. | 62.9 | 363.52-424. | 432. | 30. |
| Ni (mg/kg)       | < 10.00-32.13 | 15.0 | 12.7 | 5.2 | 14.42-47.64 | 38.8 | 40.4 | 6.97 | 24.69-34.5 | 32.1 | 7.6 |
| P (mg/kg)        | 405.81-1411.48 | 799. | 771. | 231 | 873.85-2497.65 | 107 | 982. | 337. | 1012.70-114 | 113 | 104 |

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Table 4. Descriptive statistics of $I_{geo}$ values in all studied lagoons.

|        | Cr      | Co      | Cu      | Ni      | Pb      | V       | Zn      |
|--------|---------|---------|---------|---------|---------|---------|---------|
| Amirkola (n=56) |         |         |         |         |         |         |         |
| Min    | -5.20   | -2.17   | -2.81   | -2.80   | -0.32   | -4.56   | -2.75   |
| Max    | -1.44   | -1.34   | -0.14   | -1.13   | 0.42    | -1.57   | -0.46   |
| Mean   | -3.75   | -1.86   | -1.72   | -2.29   | -0.08   | -3.56   | -1.88   |
| Median | -4.00   | -2.12   | -1.86   | -2.47   | -0.13   | -3.78   | -1.92   |
| SD     | 0.88    | 0.40    | 0.60    | 0.43    | 0.19    | 0.73    | 0.59    |
| Zibakenar (n=22) |         |         |         |         |         |         |         |
| Min    | -6.25   | -0.66   | -0.52   | -2.29   | -0.77   | -2.87   | -0.35   |
| Max    | -2.45   | 3.21    | 0.56    | -0.57   | 0.38    | 1.07    | 0.20    |
| Mean   | -3.41   | 1.54    | 0.01    | -0.89   | -0.05   | -0.60   | -0.15   |
| Median | -3.33   | 1.52    | 0.07    | -0.80   | -0.04   | -0.62   | -0.13   |
| SD     | 0.68    | 0.69    | 0.25    | 0.35    | 0.21    | 0.70    | 0.13    |
| Kiashahr (n=28)  |         |         |         |         |         |         |         |
| Min    | -4.29   | 0.56    | -0.28   | -1.51   | -0.77   | -1.81   | -0.70   |
| Max    | -3.01   | 1.93    | 0.84    | -0.46   | 2.07    | -0.33   | 2.35    |
| Mean   | -3.56   | 1.30    | 0.11    | -1.05   | -0.01   | -0.93   | 0.96    |
| Median | -3.46   | 1.33    | 0.09    | -1.12   | -0.06   | -0.82   | 0.99    |
| SD     | 0.43    | 0.43    | 0.31    | 0.33    | 0.62    | 0.47    | 0.96    |
Table 5. Descriptive statistics of CF and PLI values of studied metals in all three lagoons. PLI values of each lagoon are presented in this table.

|                | CF       |        |        |        | PLI | PLI (Lagoon) |
|----------------|----------|--------|--------|--------|-----|--------------|
|                | Cr       | Co     | Cu     | Ni     | Pb  | V            |
| Amirkola (n=56)| Min 0.04 | 0.33   | 0.21   | 0.22   | 1.20| 0.06         |
|                | Max 0.55 | 0.59   | 1.36   | 0.68   | 2.00| 0.50         |
|                | Mean 0.14| 0.43   | 0.50   | 0.32   | 1.43| 0.15         |
|                | Median 0.09| 0.35  | 0.51   | 0.27   | 1.37| 0.11         |
|                | SD 0.10  | 0.12   | 0.24   | 0.11   | 0.20| 0.09         |
|                |          |        |        |        |     | 0.24         |
| Zibakenar (n=22)| Min 0.02 | 0.95   | 1.04   | 0.31   | 0.88| 0.21         |
|                | Max 0.27 | 13.84  | 2.21   | 1.01   | 1.95| 3.16         |
|                | Mean 0.15| 4.86   | 1.53   | 0.83   | 1.46| 1.10         |
|                | Median 0.15| 4.29  | 1.57   | 0.86   | 1.45| 0.98         |
|                | SD 0.04  | 2.73   | 0.27   | 0.15   | 0.19| 0.62         |
|                |          |        |        |        |     | 1.05         |
| Kiashahr (n=28)| Min 0.08 | 2.21   | 1.23   | 0.53   | 0.88| 0.43         |
|                | Max 0.19 | 5.72   | 2.68   | 1.09   | 6.30| 1.19         |
|                | Mean 0.13| 3.92   | 1.63   | 0.74   | 1.63| 0.84         |
|                | Median 0.14| 4.10  | 1.58   | 0.69   | 1.49| 0.92         |
|                | SD 0.04  | 1.05   | 0.35   | 0.17   | 1.01| 0.24         |
Table 6. Pearson’s correlation coefficients of some studied elements in all three lagoons.

|       | Al  | Ba  | Ca  | Co  | Cr  | Cu  | Fe  | K   | Mg  | Mn  | Na  | Ni  | P   | Pb  | Sr  | Ti  | V   | Zn  | Zr  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|       |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Al    |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Ba    | -0.503** 1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Ca    | -0.596** .756** 1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Co    | 0.017  -0.949  -0.474 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Cr    | .889**  -0.562**  -0.694**  489  1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Cu    | .654**  -0.437**  -0.568**  854  .591**  1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Fe    | .695**  -0.390**  -0.660**  941  .711**  .729**  1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| K     | .959**  -0.508**  -0.584**  .071  .880**  635**  .645**  1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Mg    | .453**  -0.162  -0.055  -0.433  .530**  .017  .206  .452**  1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Mn    | -0.299*  .622**  .331*  .055  -0.245  -0.318**  -0.251  -0.299  .383**  1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Na    | .821**  -0.514**  -0.659**  .118  .790**  .621**  .717**  .825**  .209  -0.397**  1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Ni    | .250  .024  -0.191  0.004  .310  .153  .387  .206  .276  .176  .311  1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| P     | .251  -0.474**  -0.677**  .433  .276  .660**  .604**  .233  -0.302  -0.225  .439**  .098  1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Pb    | .164  .149  .078  -0.134  .248  .029  0.000  .173  .446  .345  .042  .693**  -1.95  1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Sr    | -0.656**  .829**  .869**  -0.452  -0.692**  -0.629**  -0.648**  -0.650**  .093  .407**  -0.733**  -0.196  -0.682**  .099  1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Ti    | .962**  -0.569**  -0.675**  208  .948**  .613**  .713**  .961**  .480**  -0.317  .862**  .258  .252  .166  -0.702**  1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| V     | .889**  -0.567**  -0.763**  750  .919**  .706**  .889**  .866**  .364**  -0.288  .847**  .356  .451**  .102  -0.773**  .933**  1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Zn    | .801**  -0.575**  -0.712**  222  .781**  .734**  .711**  .801**  .169  -0.321  .790**  .185  .520**  .052  -0.760**  .823**  .824**  1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Zr    | .972**  -0.588**  -0.584**  -126  .905**  .595**  .642**  .968**  .555**  -0.248  .748**  .216  .183  .222  -0.605**  .952**  .856**  .750**  1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
|       |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Al    | .031  1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Ba    | .190  -0.121  1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Ca    | -0.144  .701**  -0.439**  1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Co    | -0.361  .668**  -0.525**  .957**  1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Cr    | .533**  -0.506  -0.167  -0.431  -0.537**  1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Cu    | -0.301  .665**  -0.511**  .970**  .994**  -0.511**  1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Fe    | .972**  -0.588**  -0.584**  -126  .905**  .595**  .642**  .968**  .555**  -0.248  .748**  .216  .183  .222  -0.605**  .952**  .856**  .750**  1 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |

** Amirkola

** Zibakanar

** Kishahr

** 1
Table 7. Models’ residual values normality test.

| Metal | Lagoon | N  | Mean Rank | Test Statistic | Asymp. Sig. (2-tailed) |
|-------|--------|----|-----------|----------------|------------------------|
| Al    | 1      | 57 | 29.00     |                |                        |
| Co    | 2      | 22 | 87.95     | 79.697         | 0.000                  |
| Cr    | 3      | 28 | 77.54     |                |                        |
| Cu    | 1      | 5  | 6.10      |                |                        |
| Fe    | 2      | 22 | 33.07     | 11.904         | 0.003                  |
| Ni    | 3      | 28 | 27.14     |                |                        |
| Pb    | 1      | 4  | 29.32     |                |                        |
| Ti    | 2      | 22 | 88.46     | 77.395         | 0.000                  |
| V     | 3      | 28 | 79.66     |                |                        |
| Zn    | 1      | 17 | 29.00     | 1.409          | 0.494                  |
| Zr    | 2      | 22 | 36.29     | 1.409          | 0.494                  |

Table 8. Nonparametric equivalent analysis of variance (Kruskal-Wallis test) (1: Amirkola Lagoon; 2: Zibakenar Lagoon; 3: Kiashahr Lagoon).

| Metal | Lagoon | N  | Mean Rank | Chi-Square | Asymp. Sig. |
|-------|--------|----|-----------|------------|-------------|
| Al    | 1      | 5  | 29.19     | 77.395     | 0.000       |
| Co    | 2      | 22 | 84.60     | 77.395     | 0.000       |
| Cr    | 3      | 28 | 79.66     |            |             |
| Cu    | 1      | 57 | 29.32     |            |             |
| Fe    | 2      | 22 | 80.93     | 71.092     | 0.000       |
| Ni    | 3      | 28 | 43.96     |            |             |
| Pb    | 1      | 17 | 29.00     | 1.409      | 0.494       |
| Ti    | 2      | 22 | 82.43     | 78.320     | 0.000       |
| V     | 3      | 28 | 81.68     |            |             |
| Zn    | 1      | 57 | 29.09     |            |             |
| Zr    | 2      | 22 | 81.57     |            |             |
Table 9. Independent sample t-test results. (1: Amirkola Lagoon; 2: Zibakenar Lagoon; 3: Kiashahr Lagoon)

|       | Al  | Co  | Cr  | Cu  | Fe  | Ni  | Pb  | Ti  | V   | Zn  | Zr  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| **Z** | -6.743 | -3.418 | -6.743 | -6.630 | -6.517 | -5.711 | -1.542 | -6.743 | -6.742 | -6.742 | -6.742 |
| Asymp. Sig. (2-tailed) | .000 | .001 | .000 | .000 | .000 | .123 | .000 | .000 | .000 | .000 | .000 |
| Bonferroni p | 0.000 | 0.003 | .000 | .000 | .000 | .000 | .369 | .000 | .000 | .000 | .000 |

|       | Z   | -7.463 | -2.737 | -7.359 | -7.387 | -7.032 | -5.929 | -7.462 | -7.415 | -7.415 | -7.462 |
|-------|-----|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Asymp. Sig. (2-tailed) | .000 | .006 | .000 | .000 | .000 | .574 | .000 | .000 | .000 | .000 | .000 |
| Bonferroni p | .000 | 0.012 | .000 | .000 | .000 | 1.000 | .000 | .000 | .000 | .000 | .000 |

|       | Z   | -2.525 | -1.303 | -1.101 | -1.101 | -2.586 | -1.821 | -1.821 | -2.833 | -1.980 | -4.233 |
|-------|-----|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Asymp. Sig. (2-tailed) | .012 | .192 | .271 | .271 | .960 | .100 | .903 | .856 | .048 | .000 | .856 |
| Bonferroni p | **0.036** | 0.576 | 0.813 | 0.813 | 1.000 | **0.03** | 1.000 | 0.285 | 0.144 | **0.000** | 1.000 |
Figure 1

Location map and sampling points of the studied lagoons. (ZKL: Zibakenar Lagoon; KSL: Kiashahr Lagoon; AKL: Amirkola Lagoon). Red squares indicate the core sample location in each lagoon.
Figure 2
Textural classification of studied samples in three lagoons based on Folk (1980). (Black circles: Zibakenar samples; Red circles: Kiashahr samples; Yellow circles: Amirkola samples)
Figure 3

Box plot diagram of metal concentrations in studied lagoons.
Figure 4

Distribution map of some studied metals in the Zibakenar and Kiashahr lagoons.
Figure 5

Sedimentary facies and heavy metals concentrations changes in core samples taken from studied lagoons. The Amirkola Lagoon sediments are temporally different from the others.
Figure 6

Box Plot diagram of PLI values in all three lagoons.
Figure 7

Results of two-step cluster analysis, a) Silhouette measure shows values close to the maximum amount, and cluster sizes including two distinct clusters; b) features from the most to the least predictor (variable) importance.