Distribution pattern of heavy metals in the surficial sediment of Gorgan Bay (South Caspian Sea, Iran)

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Abstract

The Gorgan Bay is an important ecosystem receiving discharge from their tributaries. In this study, concentration of Pb, Zn, Ni, Fe, Al, Cu and As was seasonally determined at 22 sampling points during 2012-2013.Sediment samples were collected using a Van Veen grab. The levels of heavy metals were determined by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry) and AAS (Atomic Absorption Spectrophotometer). The percentages of sand, silt, clay and TOM (Total Organic Matter) in the sediment samples were determined (44.4± 15, 53.4 ± 14, and 2.2 ±2.2 and 7.2% ± 1.6, respectively). The results showed that range of Al, As, Cu, Fe, Ni, Pb and Zn in the sediment samples were 0.4-2%, 2.6- 8.6 ppm, 8.1-12.4 ppm, 0.9 – 1.2 % , 11.5-16.8 ppm, 5.9-13.6 ppm and 21.8-28.8 ppm, respectively. In spring, both Al and Ni were higher than the guideline level. In the event that arsenic was exceeds the guidelines in summer. In general, according to the results of EF (Enrichment Factor) and PLI (Pollution Load Index) can be concluded, Gorgan Bay is low risk and not contaminated. According to the results of the nmMDS (non-metric Multidimensional Scaling), PCA (Principal Components Analysis) and the map of distribution of heavy metals, it seems Gorgan Bay are divided into two separate zones (the eastern and the western parts).

Keywords: Distribution pattern, Heavy metals, Sediment, Gorgan Bay

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Introduction

Transitional coastal ecosystems, a term used for a variety of ecosystems such as lagoons, estuaries, semi-enclosed bays and saltmarshes, characterized by heterogeneity within ecosystem, constitute areas of special ecological and economical interest since they are located to the inter-surface of land and sea (Nixon, 1988).

In these coastal ecosystems, sediments play an important role in biogeochemical cycles (Pomeroy *et al.*, 1965). Much of allochtonous material is incorporated in the sediments, through assimilation, adsorption and direct sedimentation processes of suspended particulate, so they act as a trap of detritus material and mineral nutrients supply (Lijklema, 1986).

Heavy metals are the important source of hazardous pollutants in the aquatic ecosystems (Martin and Covghtry, 1982; Gibbs and Miskiewicz, 1995). They discharged into aquatic system during their transport are distributed between the aqueous phase and sediments. Because of adsorption, hydrolysis and co-precipitation of metal ions, a large quantity of them are deposited in the sediment while only a small portion of free metal ions stay dissolved in water column. The accumulation and mobility of heavy metals in sediments controlled by various factors such as nature of the sediment particles, properties of adsorbed compounds, metal characteristics, redox reactions and biodegradation of sorptive substance under specific conditions (Tam and Wong, 2000; Buccolieri *et al.*, 2006; ElNemr *et al.*, 2007; Bastami *et al.*, 2012). Hence, sediments are enumerated as sources of heavy metals in marine environments and play a key role in transmission and deposition of metals. Accumulated heavy metals in sediment can be chemically altered by organisms and converted into organic complexes, some of which may be more hazardous to animal and human life, via the food chain. Coastal ecosystems surrounded by industrialized communities continuously receive much more heavy metal loadings by river discharges, inlets and estuaries filled with run-off from adjacent grounds (Unnikrishnan and Nair, 2004). Up to now, heavy metal pollution in coastal ecosystems and estuary has been studied by many worldwide researchers (De Mora *et al.*, 2004; Maanan *et al.*, 2004; Zhang *et al.*, 2007; Bastami *et al.*, 2012). Arsenic is released into the environment through natural and anthropogenic sources (US EPA, 2006). The World Health Organization (WHO), the Environmental Protection Agency (EPA) and several studies (Wilson, 2005) have shown that inorganic arsenic can increase the risk of lung, skin, bladder, liver, kidney and prostate cancer in humans (WHO, 2004). Copper is an essential micronutrient and can readily be accumulated by aquatic organisms, but is not biomagnified in aquatic ecosystems (Jaagumagi, 1990). Lead is carcinogenic to human. Children absorb lead much more efficiently than adults (4 to 5 times more), which affects their IQ (Galvin, 1996; WHO, 2004). Nickel is not generally very toxic, but high ingestion of it can cause renal problems and skin allergies by contact (WHO, 1990, 1991). Zinc is also an essential micronutrient (WHO, 2001).

Southeastern Caspian Sea water shores are unique brackish water bodies and enclosed Gorgan shallow wetland bay with high ecological status is influenced by hydromorphological elements such as depth variation, freshwater flow and wave exposure. The Gorgan Bay (36°48'N, 53°35'E and 36°55'N, 54°03'E, 400 km^2, 60 km ×12 km, maximum depth of 6.5 m and average depth 1.5 m) is a semi-confined triangular-shaped bay, located at the south-east extremity of the Caspian Sea along Iranian coastline in the Golestan Province (Fig.1).

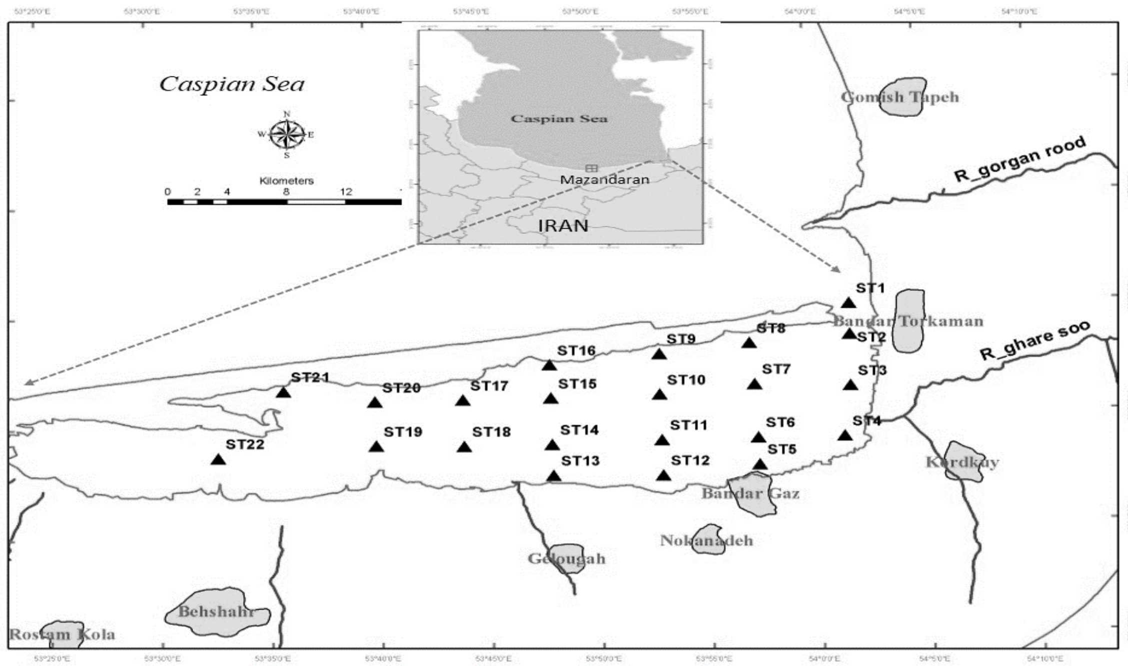


Figure 1: Map of the studied sites at Gorgan Bay, South Caspian Sea, Iran.

Gorgan Bay is formed during the Newcaspian /Holocene period by a sandy spit which is named Miankaleh coastal barrier system. The bay basin is bounded on the west, south and north by Mazandaran Province, Golestan Province and Miankaleh Peninsula, respectively. There are no tides in the Gorgan Bay. It is connected to the Caspian Sea through mouth of Ashoradeh-Bandartorkaman situated northeastern part of the bay (approximately; width of 400 m, 3 km long). There are strong currents in the Ashoradeh-Bandartorkaman mouth affected by storm surge and inter annual water level fluctuations in the Caspian Sea. This bay more influenced by its processes within the basin. Water balance in the Gorgan Bay is influenced by water intrusion from the Caspian Sea, precipitation, evaporation and a lesser extent by fresh river water. It receives freshwater inflow from a number of small rivers and streams, among them two rivers affect the bay, Gorgan-rood from the above of the inlet and Qaresoo enters from the east. These two rivers drainage runoffs from residential and agricultural areas into the bay.

Generally, there is a counter-clockwise flow pattern in the Gorgan Bay in four seasons. This current pattern is driven primarily by prominent wind stress and then is affected by bottom topography and domain geometry. In the northern and southern shores, currents are along the coastal areas and moving from west to east by effecting dominant winds (Sharbaty, 2011, 2012). The bay is surrounded by urban areas and agricultural lands. It is the marine part of a larger protected area including a peninsula called "Miankaleh Wildlife Refuge" and an international wetland (Ramsar Convention Site). *Ruppia maritima* is one seagrass species that dominates the eastern and shallow parts of the lagoon and in some places becomes so intensive that makes boating impossible. The remaining of this vegetation is very important for organic loads of bottom sediments.

Heavy metal concentrations were reported in the Gorgan Bay by Hasanzadeh (2000), Jahangiri (2001), Lahijani *et al* (2010), Bagheri *et al*. (2012), Bastami *et al* (2012), Saghali *et al*. 2013 and Bastami *et al*. (2014). These results showed that the eastern part of the Gorgan Bay has higher concentrations of heavy metals and that reveal no threatening influence of the metals in the bay. The main source of heavy metals was natural and sometimes caused by human activity. However, continuous monitoring is necessary to pursue the condition of the region.

The main objectives of this study were: 1) to evaluate heavy metals in sediment from Gorgan Bay; 2) to assess relationship between the elemental contents, grain size and organic matter and 3) to determine the zonation and pattern of distribution heavy metals (Al, Fe, Ni, Pb, As, Cu, and Zn) in the sediments of the Gorgan Bay.

Materials and methods

Four replicate samples of sediments (three samples for heavy metals and one for grain size analysis) were collected at four successive seasons including winter (March), spring (June), summer (November) and autumn (December) 2012-2013 at 22 stations to cover all parts and depths of the bay (Fig. 1).

Depth of stations was measured by The Hondex PS-7 Depth Sounder. The sediment samples were collected with a Van Veen grab (0.025 m^2; UNEP, 2006). After sampling, sediment samples were packed and carried to the laboratory in iced-boxes and stored at 4 °C until analysis. After drying in an oven, sediment samples were ground by using a hand mortar followed by screening with a 0.5 mm sieve to remove large particles. Sediment sample (1 g) was digested using HNO_3, $HClO_4$, HF and HCl (MOOPAM, 2010; ASTM-D4698-92, 2013). Samples were analyzed (Al, As, Cu, Fe, Ni, Pb and Zn) by using ICP- AES (Perkin Elmer Plasma 400). As contents were analyzed by hydride generation using an AAS (Varian). Standard samples were used to monitor the performance of the instrument and data quality. The analytical results of the quality control samples showed good agreement with the certified values (Table 1).

Grain size analysis was performed using laser particle size analyzer (LPS; HORIBA-LA950, France and Japan). Before analysis, about 4 g samples were combusted in an oven at 550 °C for 4 h and 950 for 2 h to remove organic matter and biogenic carbonate, respectively. These separate fractions were classified by the soil texture triangle (Folk *et al*., 1970; Flemming, 2000).

For determination of total organic matter, sediment samples were dried at 70 °C for 24 h and then combusted in an oven at 550 °C for 4 h. Total organic matter, as described by Abrantes *et al*. (1999).

EF determined as follows:

Enrichment Factor = $(H_s/Al_s)/(H_c/Al_c)$

Where H_s and H_c: are heavy metal concentrations in sample and background reference, respectively. Al_s and Al_c: are the aluminum contents in sample and background reference, respectively.

Table 1: Certified vs. measured concentrations of selected metals (in µg/g except Al and Fe which (a; Precision, b; Accuracy). are in mg/g) in the standard reference material.

Reference material		Metals						
		Al	**As**	**Cu**	**Fe**	**Ni**	**Pb**	**Zn**
IAEA-433	Amount	78.2	18.9	30.8	40.8	39.4	26	101
	Measured ±SD	73.4±4.2	21.5±1.8	27.5±2.6	36.8±1.9	34.5±3.1	29±2.7	89±8
	Recovery	94	114	89	90	88	112	88

(a)

sample code	Average error
1	1.0
2	2.0
3	3.0
4	11.4
5	4.6

(b)

In this study, we used background concentrations of metals in sediment (from a depth of 1 m) from Gorgan Bay which are5 ppm, 10 ppm,19 ppm, 6 ppm,31ppm ,1.09% and 1.48% for As, Cu, Ni, Pb, Zn, Al and Fe, respectively (Bagheri *et al*., 2012; Bastami *et al*.,2012).

To assess the sediment environmental quality, an integrated pollution load index of six metals was calculated as suggested by Suresh *et al*. (2011).

$PLI = (CF_1 * CF_2 * CF3 \; ... \; CF_{n)})^{1/n}$

Where CF metals is the ratio between the content of each metal to the background values, $CF_{metals} = CH_{metal}/CH_{back}$

Before the analysis, the normality and homoscedasticity assumptions were checked using the Shapiro–Wilk normality test and the Bartlett test and, when necessary, a log transformation of the data was utilized. SPSS18 software and primer5were used to analyze the results. The significant differences in the calculated parameters among different seasons and stations were determined by t-test or Mann-Whitney test analysis. Data are presented as mean ± SD. A Spearman correlation analysis was performed to test the relationship between sediment parameters (TOM, sand, silt and clay contents) and metals.

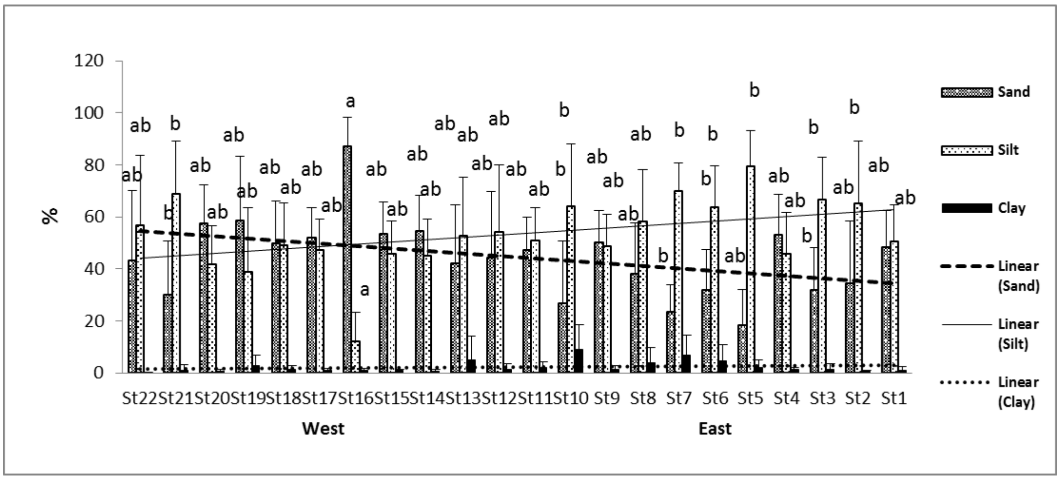
PCA was applied to investigate the similarity of metals in sediment. Similarity among sites was analyzed by ordination techniques (nmMDS) based on Bray–Curtis similarity matrix. The zoning map of the distribution of heavy metals using the software ArcGIS 9.2 prepared. Also for interpolation, the method of inverse distance weighting (IDW) is used.

Results

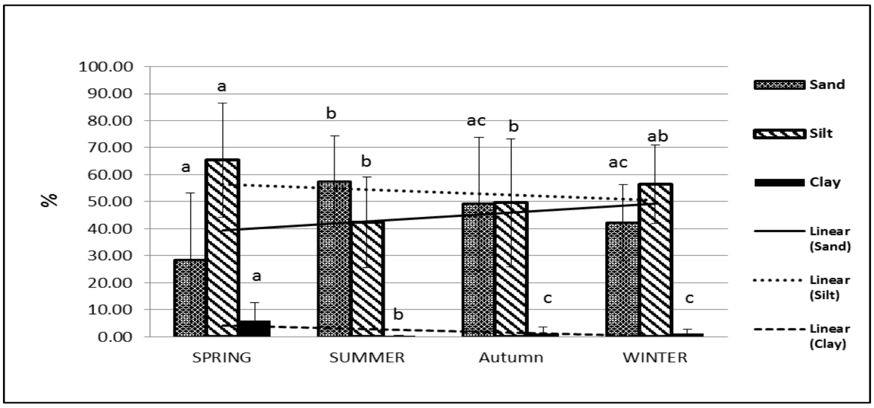
Sediment grain size analysis

In this study, the mean values of sand, silt, clay and TOM was measured 44.4±15, 53.4±14, and 2.2 ±2.2 and 7.2% ± 1.6, respectively. Meanwhile, the highest and lowest temporal mean for silt, clay and TOM was observed in spring (65.4, 6.1, and 8.1%) and summer (42.4, 0.15, and 6.3%), respectively. In contrast, the maximum and minimum amounts (28.5-57.4%) of sand were observed in the summer and spring, respectively. Generally, more than 90% of the bay sediment components were formed from the silt and sand. The USDA soil texture triangle showing a silty loam dominant texture of Gorgan Bay. Station10 and 22 had the highest (3.8m) and the lowest (0.6m) depth, respectively.The highest mean percentage of sand was recorded at station 16 (87.13%) and the lowest at station 5(18.31%; Fig. 2a).

The silt and clay percentages followed an opposite trend in respect to that of sand. The sediments of western and almost all northern shoreline stations had coarser composition, mostly composed of sand where current dynamics prevent the accumulation of fine particles and toward eastern, mouth and southern part of the bay, the textural gradient shows a shift towards lower sand content and it can be seen that the sediments are dominated sharply by silt component. The deferent textural properties of the sediments in the two parts of the bay indicate special hydrodynamic processes, and hence depositional conditions. There is also significant difference between the mean values for grain size at different seasons (Fig.2b), especially between spring and summer values.



(a)



(b)

Figure 2: Seasonal (b) and spatial (a) variation (mean± SD) of grain size in Gorgan Bay sediment samples. Different letters above the bars show significant difference (a; one way ANOVA and Test-Tukey; *p*<0.05 , b; Kruskal- Wallis and Mann-Whitney test; *p*<0.05); Dotted and Continuous lines show the trend of changes.

For TOM, in Gorgan Bay, the highest concentration was measured in the sample collected near to the western littoral zone covered with macrophytes (10.22%, station 21), and values relatively high were observed in the deeper area of the basin, while the mouth part and north-eastern area was characterized by the lowest values, with a minimum value (2.65 % and 4.69) measured at the stations of 16 and 2 (Fig. 3a). Based on one way ANOVA there is a significant difference between spring (%8.1) and summer (%6.3) (p =0.0192) and the trend is decreasing from spring to winter (Fig. 3b).

Heavy metals analysis

Our results showed that range of Al, As, Cu, Fe, Ni, Pb and Zn in the sediment samples of the different seasons were 0.4-2%, 2.6- 8.6 ppm, 8.1-12.4 ppm, 0.9 – 1.2 % , 11.5-16.8 ppm, 5.9-13.6ppm and 21.8-28.8 ppm, respectively (Table 2).

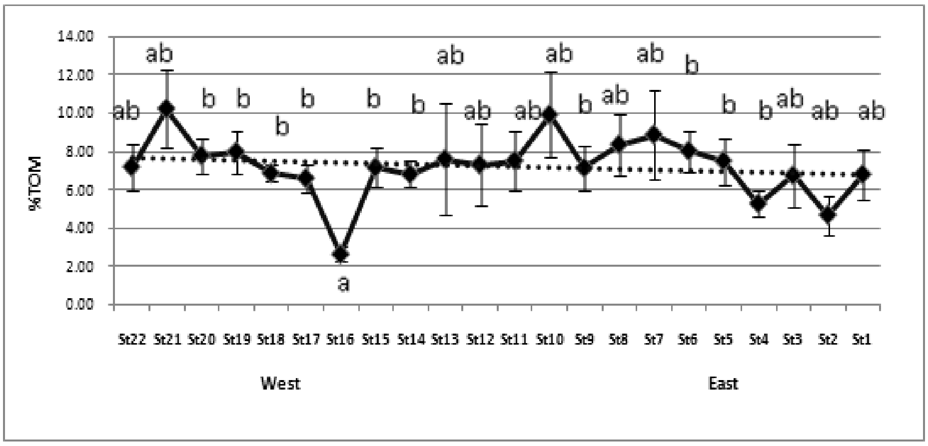
Table 4 shows the heavy metals concentrations (mean ±SD) reported in sediments from different regions of the world. As assessed in the present study, means of heavy metals concentrations (Al; 1.2%, As; 4.8ppm, Cu; 10.5ppm, Fe; 1%, Ni; 13.6 ppm, Pb; 9.1ppm and Zn; 23.9ppm) in surface sediments of the Gorgan Bay were markedly lower than those of other results and some of the sediment quality guidelines, including LEL (Lowest Effect Level), ERL (Effect Range Low), ERM (Effect Range Medium), PEL (Probable Effects Level), TEL (Threshold Effect Level), SEL (Severe Effect Level) and AET (Apparent Effects Threshold) levels (Smith *et al*. 1996; MacDonald *et al*. 2000; NOAA , 2009). On the whole, heavy metals concentration in the sediment of Gorgan Bay was in a descending order as:

Al >Fe>Zn>Ni>Cu>Pb>As

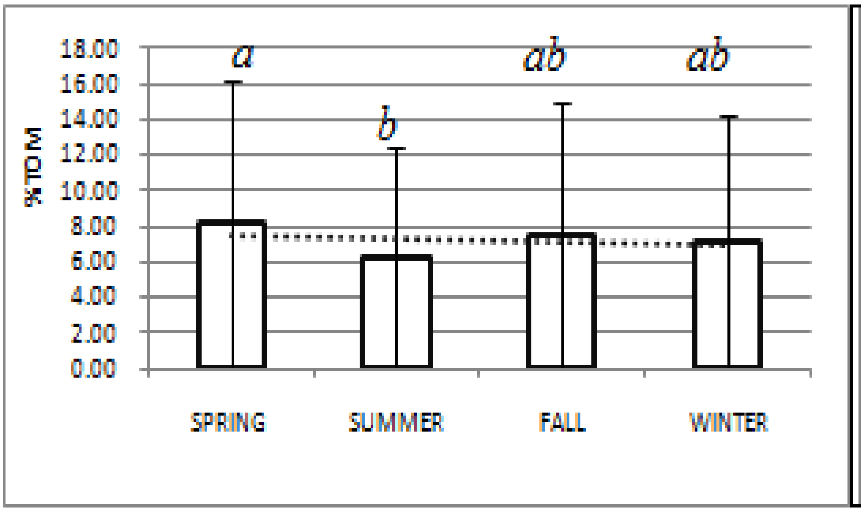
The trend of the metals is decreasing from spring to winter (Fig. 4).The highest concentration of Al, As, Cu, Fe, Ni, Pb and Zn was measured 2(spring), ٨.6 (summer), 12.4 (summer), 1.2 (spring), 16.8 (spring), 13.6 (spring) and 2٨.8 (spring), respectively (Table 2). In spring, both Al and Ni were higher than the guideline (AET and TEL, respectively). In the event that arsenic was exceeds the guidelines (TEL and ERL) in summer (Fig. 4).

The range of Al, As, Cu, Fe, Ni, Pb and Zn in the samples of the different stations were 0.4-2.1%, 2.5-10.3 ppm, 4.4-16.9 ppm, 0.4-1.6%, 6.2-21.5 ppm, 4.7-12.9 ppm and 10.7-39.4 ppm, respectively (Table 3).

The highest concentration of Al, As, Cu, Fe, Ni, Pb and Zn was measured in the sample collected near to the eastern port of the bay (2.1%; station3, 16.9ppm; station 5, 1.6%; station 3, 21.5 ppm; station 3, 12.9 ppm; station 5, 39.4 ppm; station 3, respectively), on the contrary, the highest arsenic concentration was measured in the western part (10.3 ppm; station 16).



(a)

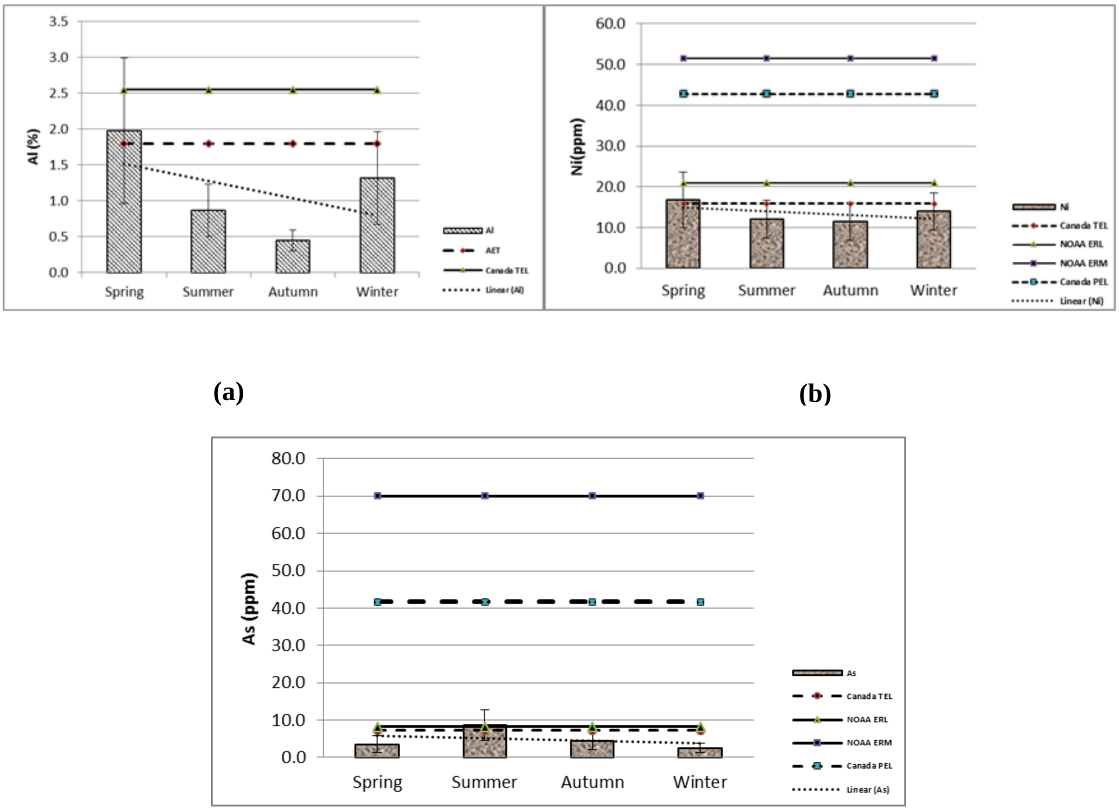


(b)

Figure 3 : Means (±SD) of spatial (a) and temporal (b) variations of TOM in the sediments from the Gorgan Bay. Different letters above the bars show significant difference (one way ANOVA and Test-Tukey; *p*<0.05); Dotted line shows the trend of changes.

Table 2: Seasonal content of heavy metals (mean ±SD; in ppm except Al and Fe which are in %) in the sediments of Gorgan Bay, n = 66.

Season	Element						
	Al	**As**	**Cu**	**Fe**	**Ni**	***Pb***	**Zn**
Spring	2 ± 1	3.6±2.2	11.6±4.7	1.2±0.5	16.8±6.7	5.1+13.6	28.8±14.3
Summer	0.40.9	8.6±4.1	12.4±5.4	0.9±0.3	12±4.6	5.9±2	22.8±9.5
Autumn	0.4±0.1	4.5±2.5	9.8±3.7	1±0.4	11.5±4.7	6.2±2.6	22.2±8
Winter	1.3±0.6	2.6±1.3	8.1±2.2	1±0.4	14±4.5	10.6±3.3	21.8±7.8



(a) (b)

(c)

Figure 4: Seasonal means (±SD) of Al (a) Ni (b) and As (c) in Gorgan Bay sediments Dotted line shows the trend of changes.

Values relatively high were observed in the deeper area of the basin, while the western part was characterized by the lowest values. The trend of the metals is increasing from shallow to the deeper stations (Fig. 5).

There is a significant difference between both the seasonal and spatial variations of Al, Cu, Fe, Ni, Pb, Zn (one way ANOVA; $p<0.05$) and As (Kruskal- Wallis; $p<0.05$). Also the Al concentration was higher of AET at stations 3 and 5.The Ni concentration was higher of TEL at stations 1, 2, 3, 4, 5, 6, 7 and 10. The amount of the station 3 was also higher than ERL. Arsenic level was higher of the ERL and the TEL only at station 16 (Tables 3 and 4).

In the present study, there was significantly a negative relationship between the sand and other parameters i.e. sedimentary metal contents (except As), Depth, sand, clay and TOM, while a positive correlation was found between silt and clay with metal contents (except As), TOM and depth. The As showed significantly a positive relationship with sand (0.370, $p<0.01$). In contrast showed significantly a negative relationship with silt (-0.34, $p<0.01$), clay (-0.47, $p<0.01$) and TOM (-0.236, $p< 0.05$).

Table 3: Spatial content of heavy metals (mean ±SD; in ppm except Al and Fe which are in %) in the sediments of Gorgan Bay, n = 12.

Station	Depth (m)	Element						
		Al	As	Cu	Fe	Ni	Pb	Zn
ST1	0.5±2.6	1 ± 1.7	5.3±2.5	13.2±3.8	1.3±0.3	18±4.2	10.7±4.2	31.7±5.3
ST2	0.5±2.6	1.7 ± 1.1	6.8±3.2	12.3±2.2	1.3±0.3	17±4.1	11.9±5.0	31.8±5.8
ST3	0.2±2.2	1.2 ±2.1	1.6±4.5	16.3±2.7	1.6±0.3	21.5±3.3	12.8±4.9	39.4±9.8
ST4	0.1±1.8	1.5±0.9	4.9±1.8	13.8±3.1	1.3±0.3	16.2±4.4	12.0±4.5	27.6±5.0
ST5	0.1±1.8	1.9±1.3	4.9±2.4	16.9±5.9	1.5±0.4	20.4±5.6	12.9±7.8	34.5±8.5
ST6	0.2±3.0	1.7±1.2	6.3±2.8	14.7±4.0	1.3±0.4	18.3±5.1	10.9±6.5	33.9±2.3
ST7	0.1±3.3	1.7±0.9	4.4±1.9	14.9±3.3	1.4±0.3	18.8±3.7	10.4±4.7	32.1±5.1
ST8	0.1±2.5	1.4±0.7	2.8±1.1	11.6±3.4	1.1±0.2	15.7±2.4	9.9±2.9	27.4±5.9
ST9	0.4±2.3	1.3±0.7	4.8±3.5	10.1±2.6	1.0±0.1	13.9±2.1	8.6±2.8	23.6±2.8
ST10	0.1±3.8	1.3±0.6	5.1±3.1	14.3±5.5	1.3±0.3	17.2±3.3	9.4±4.0	31.4±6.5
ST11	0.1±3.1	1.1±0.5	2.5±0.8	9.5±2.2	0.9±0.1	12.6±3.0	9.4±3.7	21.5±3.7
ST12	0.0±1.8	0.8±0.4	5.8±5.4	8.3±1.4	0.8±0.1	9.8±2.2	5.9±1.6	16.8±3.7
ST13	0.1±0.9	0.5±0.2	4.0±2.9	5.2±1.6	0.5±0.2	8.2±8.4	2.4±4.7	10.3±3.1
ST14	0.3±2.6	0.7±0.3	3.9±2.6	7.2±1.6	0.8±0.1	10.7±3.2	7.7±4.3	17.3±3.9
ST15	0.1±3.5	0.5±1	3.3±1.9	9.6±1.6	0.9±0.2	12.7±1.8	8.3±3.7	22.9±3.0
ST16	0.1±1.1	0.8±0.6	10.3±4.0	4.4±0.9	1.0±0.4	9.7±2.2	10.2±6.4	21.8±12.8
ST17	0.3±2.7	1.0±0.4	3.7±2.1	10.2±1.3	1.0±0.2	13.1±2.8	8.5±3.1	23.2±4.1
ST18	0.1±2.0	0.8±0.4	4.4±3.1	8.5±1.3	0.8±0.1	11.3±3.4	9.3±3.5	18.7±3.4
ST19	0.1±0.8	0.5±0.2	4.6±4.5	6.0±1.0	0.5±0.1	6.2±1.8	6.7±3.2	11.3±2.0
ST20	0.1±1.6	0.8±0.4	5.3±5.9	9.9±1.7	0.8±0.1	11.0±1.3	7.4±32.2	19.7±2.9
ST21	0.1±1.0	0.7±0.4	5.7±5.5	8.6±1.1	0.7±0.1	10.4±1.3	7.4±2.8	17.9±2.5
ST22	0.3±0.6	0.4±0.3	3.5±3.2	6.3±4.3	0.4±0.2	6.4±1.3	5.0±3.5	10.7±5.7
SD ±Mean	-	1.2±0.5	4.8±1.6	10.5±3.6	1.0±0.3	13.6±4.4	9.1±2.3	8.3±23.9

TOM had a positive correlation with Pb and a negative relationship with As (Table 5).

There was a positive correlation between most metals. But Arsenic had the significant positive and negative relationship with copper and lead, respectively (Table 5).

PCA (KMO=0.83, Eigenvalues≥1, p<0.001)analyses was run on transformed and normalized levels of heavy metals(Al, As, Cu, Fe, Ni, Pb and Zn) concentrations in sediment and principal components produced. By plotting all data together, the first two components (64% and 16%) accounted for 80% of the total variance (Fig. 6). The first axis PC1 was characterized by strong positive correlation with Ni, Fe, Zn, Al, Pb and Cu had weak correlations with the second axis PC2. But As had strong positive correlations with the second axis PC2. These results indicated that Ni, Fe, Zn, Al, Pb and Cu had a great significance in explaining the system variability, respectively. That represents the same input source (human or natural) for most these metals in the Gorgan Bay

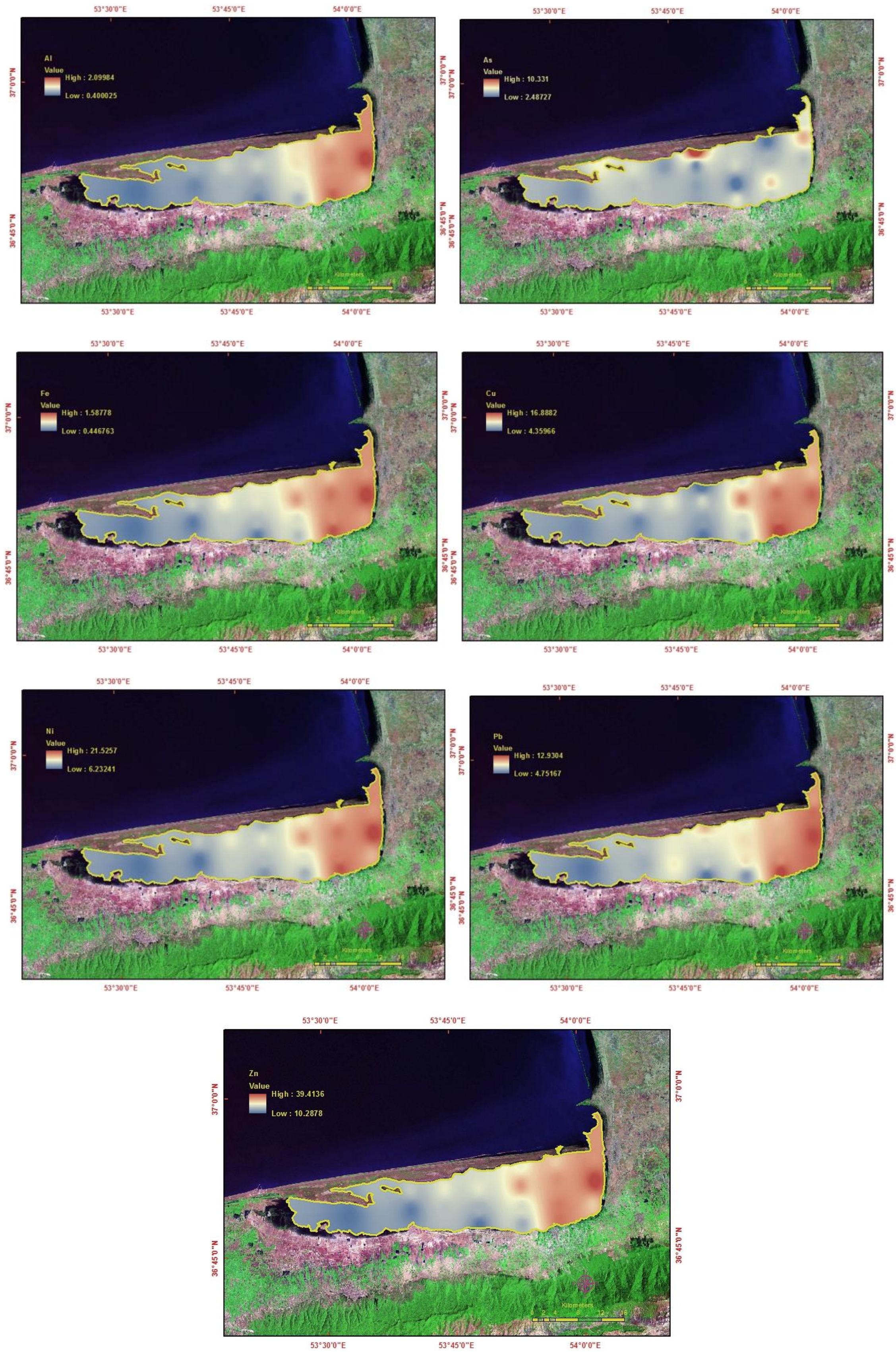


Figure 5: The zoning map of the distribution of Al (%), Fe (%), As (ppm), Ni (ppm), Pb (ppm), Zn (ppm) and Cu (ppm) in Gorgan Bay (IDW; inverse distance weighting).

Table 4: Comparison of mean (±SD) or range of heavy metal concentrations (in ppm except Al and Fe which are in %) in the surface sediments from Gorgan Bay and around the word.

Region/ guideline	Al	As	Cu	Fe	Ni	Pb	Zn	Reference
Gorgan Bay (Iran)	0.5±1.2 (0.4-2.1)	1.6±4.8 (2.5-10.3)	3.4±10.5 (4.4-16.9)	0.3±1.0 (0.4-1.6)	4.4±13.6 (6.2-21.5)	2.3±9.1 (4.7-12.9)	8.3±23.9 (10.7-39.4)	This study
Gorgan Bay (Iran)		2.12±7.77 (4.4-11.8)	8.8±18.0 (3.8-31.1)	--	14.7±29.2 (10.3-50.4)	4.9±11.5 (4.1-18.3)	22.15±42.1 (13-75)	Bastami *et al.*,2012
Gorgan Bay (Iran)	0.7±1.3 (0.3-2.4)	2.1±7.8 (4.4-11.8)	--	0.99±2.04 (0.81-3.81)	14.7±29.2 (10.3-50.4)	--	--	Bagheri *et al.*,2012
Caspian Sea (Iran)	1.1±6.05 (3.8-7.8)	3.04±12.5 (6.97-20.1)	11.9±34.7 (13.2-50.9)	0.59±3.6 (2.2-4.4)	11.8±51.6 (29.4-67.8)	4.17±4.17 (11.3-24.6)	17.9±85.3 (55.9-146)	De Mora *et al.*,2004
Mediterranean Sea		4.8±9.43 (5-24)	85.87±65.63 (10-208)	--	16.31±5.85 (8-29)	23.81±12.8 (8-54)	62.75±115.75 (38-227)	Moreno *et al.*, 2009
Canada TEL	--	7.24	18.7	--	15.9	30.2	124	Smith *et al.* 1996
ERL	2.5**	8.2	34	--	21	47	150	MacDonald *et al.* 2000
ERM	--	70	270	--	52	220	410	MacDonald *et al.* 2000
LEL	--	--	--	2**	--	--	--	NOAA , 2009
SEL	--	--	--	4**	--	--	--	NOAA, 2009
AET	1.8	--	--	--	--	--	--	SQuiRTs*
PEL	--	41.6	108	--	42.8	112	271	SQuiRTs*

*Sediment value from NOAA Screening Quick Reference Tables (SQuiRTs)
** for fresh water
LEL; lowest Effect Level, ERL; Effect Range Low, ERM ; Effect Range Medium, PEL; Probable Effects Level, TEL; Threshold Effect Level, SEL; Severe Effect Level, AET; Apparent Effects Threshold.

Table 5: Spearman's correlation coefficients for metals, sand, silt, clay, TOM and depth in surface sediments from the Gorgan Bay (N=88; *p*<0.05).

N=88		Al (%)	As (ppm)	Cu (ppm)	Fe (%)	Ni (ppm)	Pb (ppm)	Zn (ppm)	Depth (m)	TOM (%)	Sand (%)	Silt (%)
As(ppm)	r	-.435**	1									
Cu(ppm)	r	.331**	.394**	1								
Fe (%)	r	.560**	.103	.788**	1							
Ni(ppm)	r	.663**	-.083	.611**	.811**	1						
Pb(ppm)	r	.809**	-.524**	.270*	.589**	.773**	1					
Zn(ppm)	r	.570**	.106	.837**	.946**	.813**	.584**	1				
TOM (%)	r	.151	-.236*	.097	.165	.157	.307**	.196	.133	1		
Sand (%)	r	-.538**	.370**	-.304**	-.447**	-.530**	-.654**	-.489**	-.236*	-.437**	1	
Silt (%)	r	.513**	-.346**	.308**	.445**	.518**	.623**	.483**	.216*	.399**	-.993**	1
Clay (%)	r	.429**	-.473**	-.045	.197	.384**	.579**	.194	.297**	.422**	-.547**	.486**

** $p \leq 0.01$ *$p \leq 0.05$.

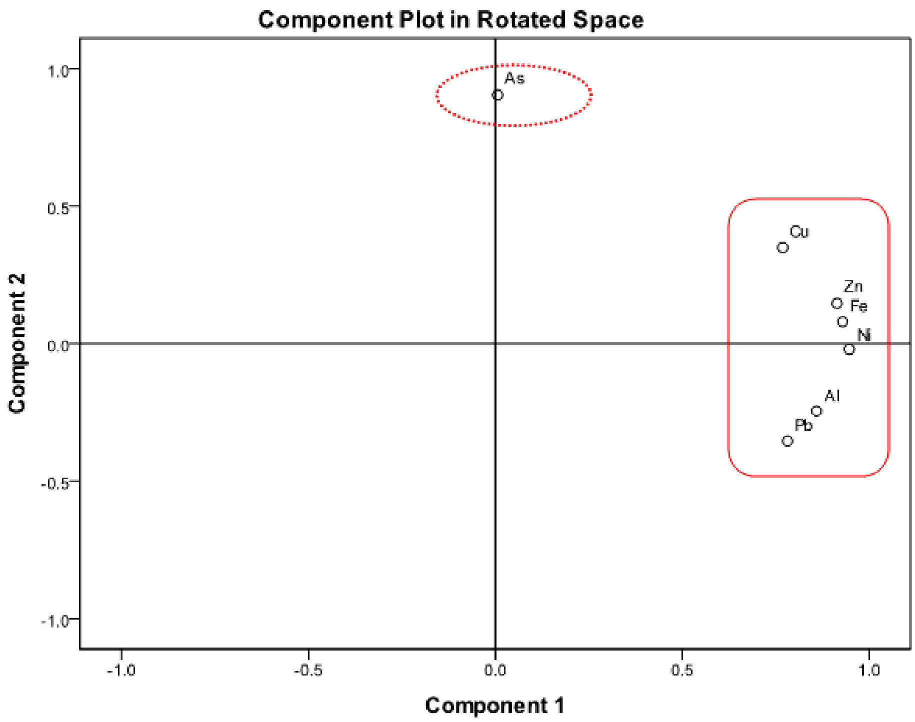


Figure 6 : PCA diagram of heavy metals (Al, As, Cu, Fe, Ni, Pb and Zn) in sediment of Gorgan Bay.

Also the presence of these metals in the same groups might reflect a similar behavior or suggest common bio-originated sources (Agah, *et al*., 2012).

To better explore dissimilarities among stations, nmMDS was performed (Fig. 7). Two-dimensional ordination diagrams confirmed the distinct grouping of some sites in Gorgan Bay and stations were clearly separated on the basis of heavy metals concentrations. Most stations in the eastern part of the bay (station1 to 6, 7 and 10) were separated from the other stations in the western part and station 16. This result suggested that the Gorgan Bay sediments affected by environmental conditions, separated into discrete zones. Based on the concentration of metal ions (except arsenic), the eastern part of the bay (from station 12) was separated from the western part (Fig. 7). Consequently, it appears that Gharasoo River and the bay mouth has increased concentration of these metals in the eastern part of the bay.

EF values were interpreted as; EF<1 (no enrichment), EF 1 to 3 (minor enrichment), EF 3 to 5 (moderate enrichment), EF 5 to 10(moderately severe enrichment), EF 10 to 25 (severe enrichment), EF 25 to 50 (very severe enrichment) and EF>50 (extremely severe enrichment) (Grant and Middleton, 1990; Abrahim and Parker, 2008). In this study, mean value of EF ranged from 0.3 to 1.5 over the year (Table 4b). All the metals had the highest and lowest EF value during autumn and spring, respectively (Table 6a). The range of this factor for Cu (except for stations 10 and 22), Fe, Zn and Ni (except for station 13) was lower than 1 almost at all sites (Table 6b), which represents no enrichment in sediment along Gorgan Bay.

The range of this factor for Ni was 1 to 3 at station 13. Therefore, this station was minor enrichment. The range of EF for As also were1 to 3 at most sites in the west and south west bay, which represents minorenrichment in the sediment. However, this factor for Asrepresents a moderate enrichment at station 12, 19 and 21. Almost atall stations (except 1, 3, 4, 8, 9 and 12) Pb had an enrichment factor of 1–3, indicating a low enrichment.

An area with PLI value>1 is polluted whereas PLI value<1 indicates no contamination (Seshan *et al.*, 2010). PLI value in the Gorgan Bay was<1. Also, the maximum and the minimum PLI were 0.54and 0.17, respectively (Table 7). Based on PLI value, Gorgan Bay should be classified as no metal pollution.

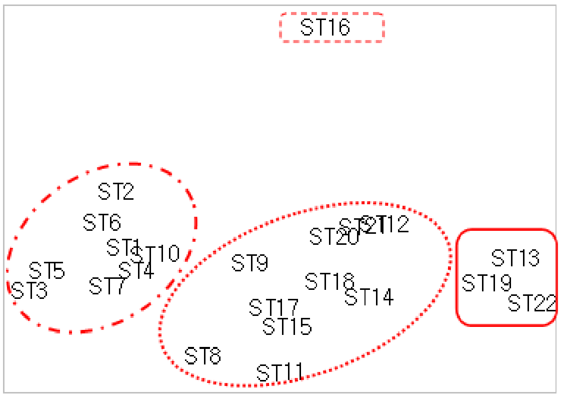


Figure 7: nm-MDS ordination diagram of heavy metals in sediment of Gorgan Bay (Distances, 2-d: stress: 0.1).

Table 6: Enrichment factor of six metals of different seasons (a) and stations (b) in the sediments of Gorgan Bay.

Season	As (ppm)	Cu(ppm)	Fe (%)	Ni(ppm)	Pb (ppm)	Zn(ppm)
Spring	0.4	0.6	0.4	0.5	1.2	0.5
Summer	2.2	1.6	0.8	0.8	1.2	0.9
Autumn	2.2	2.4	1.6	1.5	2.5	1.7
Winter	0.4	0.7	0.6	0.6	1.5	0.6

(a)

Station	As(ppm)	Cu(ppm)	Fe (%)	Ni(ppm)	Pb (ppm)	Zn (ppm)
ST1	0.5	0.4	0.2	0.2	0.8	0.2
ST2	0.6	0.2	0.2	0.2	1.0	0.2
ST3	0.3	0.2	0.2	0.2	0.7	0.3
ST4	0.4	0.4	0.2	0.3	0.9	0.2
ST5	0.4	0.5	0.2	0.3	1.1	0.2
ST6	0.5	0.4	0.2	0.2	1.0	0.6
ST7	0.5	0.4	0.3	0.2	1.0	0.2
ST8	0.3	0.5	0.2	0.2	0.7	0.3
ST9	1.1	0.4	0.1	0.2	0.7	0.1
ST10	1.1	1.0	0.4	0.3	1.2	0.4
ST11	0.4	0.5	0.2	0.4	1.4	0.3
ST12	3.4	0.4	0.3	0.3	0.8	0.3
ST13	2.9	0.8	0.6	2.2	2.0	0.5
ST14	1.8	0.6	0.3	0.6	2.5	0.4
ST15	0.8	0.3	0.2	0.2	1.3	0.2
ST16	1.5	0.2	0.5	0.2	2.0	0.8
ST17	1.1	0.3	0.3	0.4	1.3	0.3
ST18	1.5	0.3	0.2	0.5	1.5	0.3
ST19	4.6	0.5	0.4	0.5	2.6	0.3
ST20	3.0	0.4	0.2	0.2	1.0	0.2
ST21	3.1	0.3	0.2	0.2	1.3	0.2
ST22	2.2	1.4	0.5	0.6	1.9	0.6
mean(±SD)	1.5±1.2	0.5±0.3	0.3±0.1	0.4±0.4	1.3±0.6	0.3±0.2

(b)

Table 7: PLI of seven metals of different stations in the sediments from Gorgan bay.

Station	ST1	ST2	ST3	ST4	ST5	ST6	ST7	ST8	ST9	ST10	ST11
CF	0.36	0.39	0.36	0.33	0.52	0.54	0.34	0.26	0.24	0.37	0.20
Station	**ST12**	**ST13**	**ST14**	**ST15**	**ST16**	**ST17**	**ST18**	**ST19**	**ST20**	**ST21**	**ST22**
CF	0.21	0.24	0.23	0.21	0.34	0.22	0.23	0.17	0.20	0.18	0.30

Discussion

The major factors affecting spatial variation of heavy metals in the sediment are TOM and the grain size (Huang and Lin, 2003; Liaghati *et al*., 2004). The fine grains, representing the higher rate of surface to volume and ionic absorption power, are more capable in the absorption of contaminated organic and inorganic materials (Horowitz and Elrick, 1987). Generally, fine-grained sediments carrying lots of organic matter are more contaminated than coarse-grained sediments (De Mora and Sheikholeslami, 2002).

In present study, the silt and clay percentages followed an opposite trend in respect to that of sand (Fig. 2). The sediments of western stations had coarser composition, mostly composed of sand where current dynamics prevent the accumulation of fine particles and toward eastern, mouth and southern part of the bay, the textural gradient shows a shift towards lower sand content and it can be seen that the sediments are dominated sharply by silt component. The deferent textural properties of the sediments in the two parts of the bay indicate special hydrodynamic processes and hence depositional conditions (Sharbaty, 2011).

In this study, so organic matter content probably can be explained by (1) terrestrial inputs from Qaresoo River at some sites (sites 3 and 4) which were next to the river inlet, (2) organic productivity due to discharge of domestic and agricultural sewage from southern part of the bay at several sites (sites 5, 12, 13, 18, 19, and 22),(3) Macrophytes spreading in the western part of the bay, at station 21 especially and (3) the rate of sedimentation. In this study, the highest TOM values were observed at the station 10 (9.92%; with highest depth) and station 21 (10.22%; covered with macrophytes).The lowest value of TOM was measured at station 16 with the highest sand (87%). But that did not show strong and clear correlation with other parameters (Table 4).

The results of correlation (Table 5) indicating the prime important role of silt and clay in controlling spatial distribution of sedimentary metals in the Gorgan Bay than organic matters. These results might implicate either simultaneous entrance of heavy metals to aqueous environments by means of fine particles (silt and clay) and organic matters or their similar sources. Furthermore, the results approve the role of organic matters as carriers of sedimentary metals and their contribution in spatial distribution of heavy metals in the sediment. Positive correlation between heavy metals and PCA result (Table 5, Fig. 6) suggest that metals have common sources, mutual dependence and identical behavior during transport to the bay. The branch of Neka-rood River, Gharasoo River and other streams emptying into the southern and western shorelines of the Gorgan Bay mainly drain agricultural farms where the application of chemical fertilizers might enhance the nutrient loadings and subsequently plant growth (Lahijani *et al.*, 2010). Therefore, organic matter loadings in the Gorgan Bay may increase by the increase in river discharges, development of macrophytes communities (*R. maritima*) in shallow western part of the bay and phytoplankton growth in water column of the bay.

In this study, it seems that the seasonal variation of heavy metals in Gorgan Bay, is associated with the distribution of sediment particles. For this reason, most likely values of these metals, with increasing amounts of fine particles (silt and clay) is increased in spring. The maximum amount of arsenic and copper were observed in summer, which could be due to increased amounts of coarse particles. The positive correlation between the concentrations of copper and arsenic can confirm this issue. Similar results by Kaki *et al.* (2011) reported that the pattern of trace elements accumulation according to textures revealed that sandy mud and sand sediments recorded high concentrations of arsenic, mud registered high concentrations of cadmium and the sediment combining sand and mud registered high concentrations of copper.

Table 6 shows the heavy metals concentrations (mean±SD) reported in sediments from different regions of the world. As assessed in the present study, means of heavy metals concentrations in surface sediments of the Gorgan Bay were markedly lower than those of other results and LEL, ERL, ERM, PEL, TEL, SEL and AET levels. Our results revealed that the element concentrations in sediments of the Gorgan Bay did not exceed the sediment quality guidelines and posed no environmental concerns (with the exception of Ni, Al and As which were greater than some guidelines levels at some stations, especially in the eastern part of the bay). According to the results of the multivariate analysis (nmMDS, Fig. 7) and the map of distribution of heavy metals (Fig. 5), it seems Gorgan Bay is divided into two separate zones (the eastern and the western parts). The areas with the highest metal inputs were along the east regions toward the northeast part of the bay. Similar results have been reported by previous studies such Bagheri *et al*. (2012); Bastami *et al.* (2012) and Bastami *et al*. (2014).

EF which is an appropriate tool to determine sedimentary metals source produced by anthropogenic events or natural origin, normalizes metals concentrations according to the sediment texture properties (Morillo *et al*., 2004; Selvaraj *et al*., 2004; Adamo *et al*., 2005; Vald’es *et al*., 2005). In this index, aluminum is widely used, indicating aluminum silicate at coastal areas where this element is predominant. EF was also applied as a degree of sedimentation (Huang and Lin, 2003; Woitke *et al*., 2003). In general, according to the results of EF (Table 6) and PLI (Table 7) can be concluded that in terms of concentration of heavy metals, Gorgan Bay is low risk and not contaminated by heavy metals of Pb, Ni, Zn, Fe, AS, Al and Cu. There are many industries, agricultural and fish farms, dye and paper manufactures using herbicides, fungicides and chemical fertilizers around the Gorgan Bay through which metals such as Ni, As, Pb, and Cu can be released into the rivers and consequently the sediments of the Bay. In addition to pollutants, patterns of sediment contamination were affected by hydrological factors (specifically sedimentation patterns), and by the physical and chemical characteristics of the sediments. Fine-grained sediments with high surface area-to-volume ratios and/or high total organic maters contents, for example, acted as good absorbents for many pollutants. Given that Gorgan Bay is a sensitive ecosystem under development and environmental stress, so we recommend to the government to monitor and manage pollutants around Bay and also assess the ecological status of the bay.

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